R&D 6286-CH-01

(1)

CORROSION OF ALUMINIUM ALLOYS BY IRFNA

Final Technical Report

by

M.F.A.Dove, N.Logan and J.P.Mauger

September 1991

United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

London England

CONTRACT NUMBER DAJA 45-89-C-0022

University of Nottingham

Department of Chemistry

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188
Exp Date Jun 30, 1986

1a REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for Public Release; distribution unlimited
2b DECLASSIFICATION / DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION University of Nottingham Department of Chemistry 6b. OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) University Park Nottingham NG7 2RD, ENGLAND	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING / SPONSORING ORGANIZATION European Research Office 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAJA45 - 89 - C - 0022
8c. ADDRESS (City, State, and ZIP Code) 223/231 Old Marylebone Road London NW1 5TH ENGLAND	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)

Corrosion of Aluminium Alloys by IRFNA

12. PERSONAL AUTHOR(S)

Dove, Michael Frank Arthur, Logan, Norman and Mauger, Jeremy Peter

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Final Technical	FROM 89/8/24 TO 90/8/23	September 1991	92

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	See reverse side

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Corrosion rate and related data have been obtained for 2014(3L65) aluminium alloy, either untreated or subjected to certain surface pre-treatments, before contact with IRFNA, gelled IRFNA (IRFNA + SiO_2 + $LiNO_3$) and these media containing added P_2O_5. The temperature dependence of the corrosion reaction in gelled IRFNA has also been studied electrochemically, using a -20°C temperature cycle. Similar temperature cycling data involving IRFNA were presented in the First Interim Report.

continued on reverse....

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	
22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code) / 22c OFFICE SYMBOL

corrosion, corrosion rate, 2014 aluminium, gelled IRFNA, P_2O_5, surface pre-treatment, ClF_3, HF/F_2, electropolishing and anodising, electrochemistry, d.c. polarisation, corrosion potential, polarisation resistance, electrochemical impedance spectroscopy, temperature cycling, weight change, intergranular corrosion, XPS, AES, film thickness, activation energy.

19. (contd)

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(i) electrochemical: d.c. polarisation and electrochemical impedance spectroscopy
(ii) surface analytical: X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and optical microscopy
(iii) weight change experiments on metal coupons.

Corrosion potential (E_{corr}) and polarisation resistance (R_p) data have been obtained for the range of red fuming nitric acid media and metal surface pre-treatments employed. Most of the systems showed similar behaviour with time, R_p increasing (i.e. corrosion rate decreasing) and then levelling off after ca. 100 days. The highest R_p values (i.e. lowest instantaneous corrosion rates) were observed for the media containing P_2O_5.

For gelled IRFNA and gelled IRFNA containing 3wt. % P_2O_5 the corrosion rates after 60 days' contact, determined by weight change, were much larger than those determined electrochemically. This discrepancy has been attributed to non-uniform corrosion (e.g. intergranular corrosion).

The lowest corrosion rates determined by weight change occurred where the alloy had been pre-treated with gaseous ClF_3 before immersion in gelled IRFNA or gelled IRFNA containing 0.5wt.% P_2O_5. The latter medium gave a low corrosion rate even in the absence of the ClF_3 pre-treatment. Pre-treatment with a gaseous HF/F_2 mixture or by electropolishing and anodising, before immersion in gelled IRFNA, conferred no advantage as judged electrochemically but these pre-treatments were not evaluated by weight change.

XPS/AES indicated that some form of fluoride available to the metal surface remains in gelled IRFNA, despite the expected loss of HF by reaction with SiO_2, and that the thickness of the predominantly Al_2O_3 film on the alloy increases only marginally after 8 days in gelled IRFNA if the metal is not then water-washed before surface examination. For alloy which had not been subjected to any surface pre-treatment before immersion in gelled or ungelled IRFNA, E_{corr} and R_p values showed a cyclic variation with temperature and activation energies of the same order of magnitude were determined. The marked effect of temperature on corrosion rate highlights, as in the case of ungelled IRFNA, the desirability of keeping the 2014 aluminium alloy/gelled IRFNA system cool (e.g. at +5°C).

Stress is placed on the importance of further studies, which should involve the promising ClF_3 pre-treatment for 2014 Al and P_2O_5 addition to gelled IRFNA, together with extension to other Al alloys, metal pre-treatments and gel additives.

Abstract

Corrosion rate and related data have been obtained for 2014(3L65) aluminium alloy, either untreated or subjected to certain surface pre-treatments, before contact with IRFNA, gelled IRFNA (IRFNA + SiO_2 + $LiNO_3$) and these media containing added P_2O_5. The temperature dependence of the corrosion reaction in gelled IRFNA has also been studied electrochemically, using a ±20°C temperature cycle. Similar temperature cycling data involving IRFNA were presented in the First Interim Report.

The methods of investigation were
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For gelled IRFNA and gelled IRFNA containing 3wt.% P_2O_5 the corrosion rates after 60 days contact, determined by weight change, were much larger than those determined electrochemically. This discrepancy has been attributed to non-uniform corrosion (e.g intergranular corrosion).

The lowest corrosion rates determined by weight change occurred where the alloy had been pre-treated with gaseous ClF_3 before immersion in gelled IRFNA or gelled IRFNA containing 0.5wt.% P_2O_5. The latter medium gave a low corrosion rate even in the absence of the ClF_3 pre-treatment. Pre-treatment with a gaseous HF/F_2 mixture or by electropolishing and anodising, before immersion in gelled IRFNA, conferred no advantage as judged electrochemically but these pre-treatments were not evaluated by weight change.

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cyclic variation with temperature and activation energies of the same order of magnitude were determined. The marked effect of temperature on corrosion rate highlights, as in the case of ungelled IRFNA, the desirability of keeping the 2014 aluminium alloy/gelled IRFNA system cool (e.g. at +5°C).

Stress is placed on the importance of further studies, which should involve the promising ClF_3 pre-treatment for 2014 Al and P_2O_5 addition to gelled IRFNA, together with extension to other Al alloys, metal pre-treatments and gel additives.

Keywords

corrosion
corrosion rate
2014 aluminium
gelled IRFNA
P_2O_5
surface pretreatment
ClF_3
HF/F_2
electropolishing and anodising
electrochemistry
d.c. polarisation
corrosion potential
polarisation resistance
electrochemical impedance spectroscopy
temperature cycling
weight change
intergranular corrosion
XPS
AES
film thickness
activation energy

Participating scientific personnel

Dr. M.F.A. Dove
Dr. N. Logan
(Principal Investigators)

Mr J.P. Mauger

The work reported here constitutes part of the research to be submitted by Mr. J.P. Mauger to the University of Nottingham for the degree of Ph.D.

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1. INTRODUCTION

This Final Scientific Report presents the results of the work carried out under the revised agreement of April 1989. This agreement outlined four areas of research which may be summarised as follows:

A) The temperature dependence of the corrosion reaction of 2014 aluminium in Inhibited Red Fuming Nitric Acid (IRFNA).

B) The development of a new electrochemical cell for the rapid comparison of corrosion rates in various acid samples.

C) The corrosion rate of 2014 aluminium in gelled IRFNA (gelled acid) and related studies.

D) Long term corrosion studies on "as supplied" samples of gelled acid.

The work carried out under Part A was reported in the First Interim Report[1]. Work carried out under parts C and D was reported in the Second Interim Report[2]. Following technical discussions with Dr.B.D.Allan (Fax, 7th June 1990) it was decided not to proceed with Part B of the initial agreement. This Final Scientific Report contains the results obtained during the period March-October 1990, final conclusions drawn from the work, overall and recommendations for further studies.

Some of the work described in this Report has involved IRFNA or gelled IRFNA (gelled acid) containing 0.5 or 3.0wt.% P_2O_5 added as a potential corrosion inhibitor. Information on the range of phosphorus(V) acids generated when P_2O_5 is added to pure nitric acid, or to a blend of red fuming nitric acid containing 44wt.% of

dinitrogen tetraoxide (N_2O_4) and termed "high density acid" (HDA), and the variation in their relative proportions as a function of P_2O_5 concentration and time, has been obtained from ^{31}P nmr spectroscopy[3]. Similar chemistry is expected to operate in IRFNA or gelled IRFNA, modified somewhat by the presence of HF in these media.

At a relatively late stage in the project it was decided to undertake weight change studies of metal coupons in order to provide an alternative assessment of the corrosion rates of some of the 2014 aluminium alloy/gelled IRFNA systems for comparison with those determined electrochemically for these systems.

2. ELECTROCHEMISTRY

2.1. Experimental

Eleven bottom working electrode cells (Figure 1), constructed from 2014 aluminium, have been used in the present program. The cells were refurbished and the working electrodes were polished. The polishing procedure involved grinding the electrode with four grades of silicon carbide paper, polishing on 6μm and 1μm diamond wheels and finally washing in distilled water and methylated spirit. The first four cells (GA1-GA4) were set up in October 1989. The cell filling procedure was:

i) The metal components were degreased using 1,1,1-trichloroethane.

ii) The cell body and lid were assembled and weighed.

iii) The gelled acid (supplied by Dr.B.D.Allan, MICOM, Redstone Arsenal, Alabama) was "spooned" into the cell and packed down using a stainless steel spatula.

iv) The cell was assembled and reweighed, the charge of gelled acid being determined by difference.

Four cells (GA5,6,8,9) were set up in which the metal surfaces of the cell were pre-treated prior to the cell being filled with gelled acid. GA5 was pre-treated[4] with HF/F_2 (1atm., 24 hours, 25°C). GA6 was electropolished and anodised. The electropolishing solution was a mixture of Na_2CO_3 (150g/dm^{-3}) and Na_3PO_4 (50g/dm^{-3}) in deionised water. The conditions were 80°C, 6Adm^{-2}, 14V, 2 minutes. The anodising solution was 15wt.% H_2SO_4 and the conditions were 25°C, 1Adm^{-2}, 12V, 30 minutes. The anodic oxide

film produced was sealed in boiling deionised water (30 minutes). GA8 and GA9 were pre-treated[5] with ClF_3 (1atm., 25°C, 24 hours). Cells GA7 and GA11 were filled with a modified form of gelled acid, containing 3wt.% P_2O_5. Gelled acid (*ca.*200g) was accurately weighed into a FEP screw-capped bottle. P_2O_5 (3wt.%) was added to the gelled acid. The resultant mixture was stirred using a glass rod and left for 12 hours to equilibrate, before being loaded into the cells. Cell GA10 was filled with IRFNA in which 3wt.% P_2O_5 had been dissolved.

The details of the cells are listed in Table 1. E_{corr} and R_p data have been obtained[6] for all eleven cells.

2.2 Results and Discussion

2.2.1 Gelled Acid (Cells GA1-GA4)

The electrochemical results obtained for cells GA1-GA6 were discussed in the Second Interim Report[2]. A brief summmary of the conclusions is presented here.

2.2.1.1 E_{corr} vs Time (Figures 2-5)

The E_{corr} values showed a sharp fall during the 12 hours after each cell was set up. This was attributed to the breakdown of the air-formed oxide film on the aluminium surface. E_{corr} levelled off at *ca.* -650mV. After *ca.* 10 days, E_{corr} rose slowly levelling off at between -510mV and -540mV after 90 days. The steady increase in E_{corr} was assigned to the growth of a film of corrosion products on the metal surface.

2.2.1.2 R_p vs Time (Figures 2-5)

The R_p values for cells GA1-GA4 were steady at *ca.* 2000Ω during the 10 days after each cell was set up. R_p rose steadily during the next 80 days and levelled off in the range 80-150kΩ. The R_p vs time curves observed for cells GA1-GA4 were qualitatively similar to the E_{corr} vs time curves. A similar interpretation may be proposed. The R_p values recorded during the first 10 days were low indicating a high corrosion rate. The corrosion rate slowed as a film of corrosion products was deposited on the metal surface.

2.2.1.3 Electrochemical Impedance Spectroscopy

Bode plots obtained for cell GA1 after 1 and 92 days were compared (Figure 6).

Three main time constants were observed in the impedance spectra:

(i) A time constant at *ca.* 100Hz, attributed to the oxide film on the metal surface.

(ii) An inductive feature at low frequencies, assigned to the formation of an aluminosilicate complex at the gelled acid/oxide interface.

(iii) A time constant at *ca.* 5Hz, which appeared after 10 days immersion in gelled acid, assigned to the corrosion product film.

2.2.2 HF/F_2 Pre-treated Cell (GA5)

Cell GA5 was pre-treated with HF/F_2 (1atm., 25°C, 24 hours). The E_{corr} and R_p vs time curves (Figure 7) were similar to those recorded for the untreated cells (GA1-GA4). The fluorination

appeared to be protective during the first 10 days of the cell's lifetime (high R_p). However, no long term increase in R_p was observed. No electrochemical evidence was obtained to indicate that the pre-treatment would provide a long term decrease in the corrosion rate.

2.2.3 ClF_3 Pre-treated Cells (GA8 and GA9)

Cells GA8 and GA9 were pre-treated with ClF_3 (1atm., 25°C, 24 hours). The E_{corr} and R_p vs time curves (Figures 8 and 9) were similar to those recorded for the untreated cells (GA1- GA4). High values for E_{corr} and R_p were recorded for cell GA9 during the first day of its lifetime. However, no electrochemical evidence was obtained to indicate that the ClF_3 pre-treatment would lead to a lower corrosion rate.

2.2.4 Cells Containing Modified Gelled Acid (3wt.% P_2O_5 GA7 and GA11

Cells GA7 and GA11 contained gelled acid to which 3wt.% P_2O_5 had been added. The discussion mainly concerns cell GA7, since cell GA11 was only monitored for a relatively short time. However, the results obtained for cell GA11 up to *ca.* 25 days appear to confirm the conclusions drawn for cell GA7.

2.2.4.1 E_{corr} vs Time (Figures 10 and 11)

The E_{corr} values fell steadily during the first 13 days after cell GA7 was set up to reach a minimum of -764mV. After the first 13 days E_{corr} rose and had reached -485mV after 105 days.

2.2.4.2 R_p vs Time (Figures 10 and 11)

The R_p values measured for cell GA7 remained steady in the range 4-20kΩ during the first 13 days after the cell was set up. However, one anomalous R_p value of 76kΩ was measured after 7 days. R_p rose steadily after the first 13 days and an estimated R_p value of *ca.* 10^7Ω was obtained after 105 days.

The initial fall in potential has been attributed to a stripping of the air-formed oxide film present on the metal surface. The subsequent rise in potential may be attributed to the formation of a protective layer of corrosion products. The main difference between the cells containing gelled acid and modified gelled acid (3wt.% P_2O_5) was the substantially higher R_p values reached by the cells containing the latter.

The steady state R_p value for cell GA7 was about two orders of magnitude higher than those recorded for cells GA1-GA4. This implied that the equilibrium corrosion rate of 2014 aluminium in modified gelled acid (3wt.% P_2O_5) would be *ca.* 100 times lower than in gelled acid. This apparent decrease in the corrosion rate may be attributed to a change in the corrosion product layer which forms after the initial air-formed oxide film has been stripped. The corrosion product layer in gelled acid is assumed to be a mixture of aluminium oxide and aluminium nitrate species. In modified gelled acid (3wt.% P_2O_5) the layer is assumed to have incorporated some phosphate species leading to a more resistive (i.e. protective) film.

2.2.4.3 Electrochemical Impedance Spectroscopy

Cell GA7 has been monitored using EIS; the variation of the

impedance spectrum with time is shown in Figure 12.

The impedance spectrum recorded after 1 day showed one main time constant at *ca.* 1000Hz. This has been assigned to the air-formed oxide present on the metal prior to immersion.

The impedance spectrum recorded after 103 days showed one main time constant at *ca.* 0.1Hz. This has been assigned to the corrosion product layer. There appeared to be no contribution to the measured impedance from the original oxide film. This is in contrast to gelled acid where a time constant due to the original oxide film was observed after 92 days. The modified gelled acid (3wt.% P_2O_5) appeared to have totally stripped the oxide film and replaced it with a highly resistive corrosion product layer. No low frequency intercept was observed in the impedance spectrum measured after 103 days. Hence, the R_p value obtained after 103 days was estimated by extrapolating the impedance spectrum.

The inductive behaviour observed for cells containing gelled acid was evident after 1 day. Measurements obtained after 103 days imply that there is a very low frequency ($<10^{-2}$ Hz) inductive feature.

2.2.5 Cell Containing Modified IRFNA (3wt.% P_2O_5) (GA10)

Cell GA10 contained IRFNA to which 3wt.% P_2O_5 had been added. The E_{corr} and R_p (Figure 13) both rose rapidly during the 10 days after the cell was set up, thereafter the E_{corr} and R_p values levelled off at *ca.* -180mV and 6MΩ, respectively. The rise in E_{corr} was indicative of a film thickening process. The high values measured for E_{corr} and R_p implied that the film was highly

protective.

The corrosion behaviour of 2014 aluminium in modified IRFNA (3wt.% P_2O_5) appears similar to the corrosion behaviour in modified gelled acid (3wt.% P_2O_5). The protective film is assumed to contain phosphate. The main difference was that in the absence of silica, the main gelling agent, the protective film was established more rapidly.

2.2.6 Electropolished and Anodised Cell (GA6)

Cell GA6 was electropolished in a Na_2CO_3/Na_3PO_4 mixture (14V, 6Adm^{-2}, 80°C), anodised in H_2SO_4 (12V, 1Adm^{-2}, 25°C) and sealed in boiling, deionised water. The E_{corr} and R_p vs time curves (Figure 14) were very similar for the first *ca.* 70 days to those obtained for the untreated cells (GA1-GA4, Figures 2-5). It was concluded that the pre-treatment would not provide a long term decrease in the corrosion rate since the R_p value decreased, i.e. the corrosion rate increased, after *ca.* 70 days.

3. SURFACE STUDIES

3.1 Experimental.

Surface studies of 2014 aluminium before and after treatment with gelled acid have been undertaken. Six coupons were investigated by X-ray photoelectron spectroscopy (XPS) and another six coupons by Auger electron spectroscopy (AES). The twelve coupons (2 x 1cm) were cut from a 2mm thick sheet of 2014 aluminium and polished using the polishing procedure described in Section 2.1.

Details of the treatment of the coupons were as follows:

(i) Polished blanks (4 coupons).

(ii) Immersion in gelled acid for 8 days (30 days for XPS) and blown dry in a stream of nitrogen (4 coupons).

(iii) Immersion in gelled acid for 8 days (30 days for XPS) and washed in water (4 coupons).

The four coupons in (iii) above were water washed in order to remove traces of gelled acid on the metal surface. The water washing procedure consisted of five steps:

a) The metal coupon was immersed in deionised water for 30s.

b) The coupon was gently rubbed using a rubber teat in order to remove any loose surface deposits.

c) The coupon was immersed in fresh deionised water (30s) and again rubbed with a teat.

d) The coupon was rinsed in deionised water, placed in a weighing bottle and oven dried for 10 minutes at 110°C.

e) The coupon was allowed to cool to room temperature and sealed in the weighing bottle ready for analysis.

Three coupons, one each from (i), (ii) and (iii) above, were investigated using the AES facility by Loughborough Consultants Ltd.; three corresponding coupons were investigated using the XPS facility by Loughborough Consultants Ltd. The results of the surface studies are presented in Figures 15-17 and Tables 2-4. Subsequently two coupons which had been immersed in gelled acid containing 0.5wt.% P_2O_5 for 90 days were studied by AES; one coupon had been previously treated with ClF_3 prior to immersion. The depth profile data are presented in Figures 31 and 32.

3.2 Results and Discussion.

3.2.1 2014 Aluminium Blanks

The aluminium blanks were polished and degreased. One blank was investigated using AES and one blank was studied using XPS.

3.2.1.1 Auger Electron Spectroscopy (Figure 15).

The two major components of the film on the metal surface were Al and O. The other elements detected on the surface were Si, S, Cl, C, Ca and Cu. The S, Cl, Ca and C were largely confined to the surface of the film. These elements are presumably derived from surface contamination of the sample either during handling or the degreasing process.

Relatively low levels of Si and C persist throughout the film. These elements are assumed to be due to residual silicon carbide grains left over from the grinding process. Copper was also detected in the subsurface layers; this is expected since it is the main alloying component in 2014 aluminium.

The variation of the aluminium:oxygen ratio with depth is shown in Figure 18. The aluminium:oxygen ratio in the immediate subsurface layer (relatively free of contamination) was *ca.* 2:3. This indicated that the surface film was predominately composed of Al_2O_3. The ratio rose with depth as successive layers of the oxide film were etched away.

A measure of the oxide film thickness may be obtained from the depth at which the oxygen concentration falls to half of its maximum value. The thickness derived in this way for the blank sample was *ca.* 10nm.

3.2.1.2 X-Ray Photoelectron Spectroscopy (Table 2).

XPS spectra have been recorded for a blank sample of 2014 aluminium. Al, O, Si, C, F and Mg were detected on the surface of the sample. The sample was subjected to a 1 and a 4 minute etch. The concentrations of F, C, Mg and Si fell after etching confirming that these elements were present largely as a result of surface contamination. This confirms the observations from the AES spectra.

Peak binding energies were measured for the Al, Si, O, and F peaks on the unetched surface. Two binding energies were obtained for the Al doublet. The lower binding energy (71.9eV) is difficult to assign, however it may be due to aluminium metal. The higher binding energy (74.2eV) is probably due to Al_2O_3.

The binding energy measured for Si (99.8eV) was consistent with an organo-silicon complex. This indicated that the silicon was derived from contamination of the system with a silicon-containing oil or grease. The binding energy measured for O (531.8eV) was

consistent with Al_2O_3. The binding energy measured for F (684.9eV) indicated the presence of a metal fluoride on the surface (presumably AlF_3). However, the sample had not been exposed to any F-containing medium. The F-contamination of the surface was presumed to have occurred possibly by F removed from other samples in the system by ion-etching.

3.2.2 2014 Aluminium Coupons Immersed in Gelled Acid and Dried in a Stream of Nitrogen.

3.2.2.1 Auger Electron Spectroscopy - 8 Days in Gelled Acid (Figure 16)

The major components of the surface studied were Al and O. The other elements detected were N, Si, Cl, C, Ca, K, Cu and F. The elements Cl, Ca, C and K, which all occurred in very small concentrations, arise from contamination during handling.

Copper, which was first detected at a depth of 2.8nm, is the largest alloying component in the aluminium; silicon was detected at a depth of >19nm and is believed to be a residue of the polishing process. The surface Si, F and N are all believed to be derived from the gelled acid.

The presence of F on the surface indicates that not all the HF in IRFNA is destroyed in the gelation process. Presumably some of the HF is converted to SiF_6^{2-} which could remain in the gelled acid. Al is known to have a very high affinity for F and so the SiF_6^{2-} species may react with the Al to leave Si and F on the surface. The N was confined to the subsurface layers (1.1-2.8nm). If this

nitrogen is derived from gelled acid it is presumably due to nitrogen-oxygen species diffusing into the oxide film via cracks or flaws.

The aluminium:oxygen ratio (Figure 18) rose steadily with depth. At the immediate sub-surface layer (0.6nm) the ratio was *ca.* 2:3 indicating that the film was predominantly composed of Al_2O_3. The thickness of the oxide film was *ca.* 12.5nm which indicated that the film had been thickened slightly in contact with gelled acid.

3.2.2.2 X-Ray Photoelectron Spectroscopy - 30 Days in Gelled Acid (Table 3)

Al, O, C, Si, F and N were detected on the metal surface. The sample was subjected to a 1 min etch. No clear conclusions could be drawn from the results after etching. The C was assumed to be largely a surface contaminant derived from the handling of the sample or from the system.

Peak binding energies have been measured for the other elements. The peaks obtained for Al (75.6eV) and O (532.4eV) have been assigned to Al_2O_3. The F peak (687.6eV) may be due to either SiF_6^{2-} or alternatively an organo-fluorine species. The Si peak (102.1eV) appears largely to be an organo-silicon complex. The N peak (407.7eV) may be assigned to the NO_3^- ion.

3.2.3 2014 Aluminium Coupons Immersed in Gelled Acid and Water Washed

3.2.3.1 Auger Electron Spectroscopy - 8 Days in Gelled Acid (Figure 17)

The major components of the surface film were Al and O. The other

elements detected were N, F, Si and Cu. The N, F and Si are believed to be derived from the gelled acid.

The aluminium:oxygen ratio (Figure 18) rose more slowly than was observed for the other two samples. This indicated a thicker film. The film thickness was *ca.* 55nm which is over four times the thickness observed for either of the other two samples. This very substantial increase in film thickness is obviously attributable to the water washing procedure (Section 3.1). The aluminium:oxygen ratio once again confirmed that the surface film was predominantly composed of Al_2O_3.

3.2.3.2 X-Ray Photoelectron Spectroscopy - 30 Days in Gelled Acid (Table 4)

C, O, Al, Si, F and N were detected on the metal surface. The sample was ion-etched for 1 and 4 minutes. This confirmed that the N was confined only to the very surface layer of the film. The C was assumed to be a contaminant derived from the system or due to handling.

Peak binding energies have been measured for the other elements. The peaks due to Al (74.5eV) and O (532.3eV) were attributed to Al_2O_3. The Si peak (100.4eV) was assigned to an organo-silicon compound. The N peak (407.1eV) was assigned to NO_3^- and the F peak (685.4eV) is attributable to either AlF_3 or SiF_6^{2-}.

3.2.4. 2014 Aluminium Coupons Immersed in Gelled Acid Containing 0.5wt.% P2O5 and Dried in a Stream of Nitrogen

3.2.4.1. Auger Electron Spectroscopy - 90 Days Immersion Figure 31)

The sample surface was visibly coated with corrosion products, which were found to be distributed unevenly thus making it impossible to select a truly representative area with the narrow Auger electron beam. The principal cationic components of the surface were found to be Al(III) and significant amounts of the oxygen-binding elements, Si(10 atom%) and P(6.3 atom%), were observed. Oxygen (*ca.* 60 atom%) and fluorine (5.3 atom%) balanced the charges of these elements. The conclusions from the depth profile study were that silicon and fluorine were only significant in the surface whereas phosphorus was still present down to 6.5nm, the maximum depth examined. The thickness of the oxide layer, in the region selected for depth profiling, was in excess of 6.5nm, since the oxygen content (50 atom%) had not decreased to half of its maximum value at this depth.

3.2.4.2. Auger Electron Spectroscopy-ClF_3 Pre-treated - 90 Days Immersion (Figure 32)

The results for this sample were broadly similar to those described above for the coupon which had not been pre-treated: the surface was covered unevenly with corrosion products. The most significant differences were that the aluminium(III) content of the surface was unusually low (average value 5.3 atom% for the three sites examined), but this increased rapidly in the immediate subsurface, and also that unoxidised aluminium metal was detected

at and below 2.7nm. This sample was depth profiled in one position to 15nm, which approximates to the apparent oxide film thickness; fluorine and phosphorus were still evident down to 15nm and copper was also detected at levels below 5nm.

The role of the ClF_3 pre-treatment of these coupons is not readily apparent from these AES studies on account of the thick and non-uniform layer of corrosion products.

4. WEIGHT CHANGE STUDIES

4.1 Experimental

Weight change studies have been undertaken in order to provide an alternative assessment of some of the 2014 Al/gelled acid systems studied using electrochemistry. Two sets of weight change experiments have been undertaken, the details of which are listed in Tables 5 and 6. Half of the coupons used in the study involving gelled acid containing 0.5wt.% P_2O_5 (Set B) were pre-treated using ClF_3 (1atm., 25°C, 24 hours).

Each of the coupons was engraved with an identifying number. Prior to being placed in the relevant acid sample the coupons were degreased using 1,1,1-trichloroethane and weighed. Upon removal from the acid each coupon was water washed using the procedure described in Section 3.1 and reweighed. The results of the weight change studies are shown in Figures 19-24.

4.2 Results and Discussion.

4.2.1 Set A (Comparing Gelled Acid with Gelled Acid Containing 3wt.% P_2O_5) (Figures 19 and 20)

Figure 19 presents the actual weight loss data obtained from 8 coupons in gelled acid and 8 coupons in gelled acid containing 3wt.% P_2O_5. The striking difference between the two sets of data is that the weight losses of the coupons in gelled acid increase nearly monotonically whereas those in gelled acid containing 3wt.% P_2O_5 show a surprisingly large initial (after 2 days) weight loss,

but thereafter they lose weight more slowly.

Figure 20 shows the same data in the form of corrosion rates. The coupons in gelled acid undergo an initially high corrosion rate (*ca.* 0.15mgcm^{-2}day^{-1}) which decreases steadily to *ca.* 0.1mgcm^{-2}day^{-1}. On the other hand the coupons in gelled acid containing 3wt.% P_2O_5 undergo a much higher initial corrosion rate (*ca.* 1mgcm^{-2}day^{-1}) which decreases rapidly and after about 17 days is less than that in gelled acid. After 98 days the corrosion rate has fallen to *ca.* 0.06mgcm^{-2}day^{-1}.

The steady state corrosion rate of 2014 aluminium in gelled acid was found to be approximately double the steady state corrosion rate in modified gelled acid (3wt.% P_2O_5). This confirms the inhibiting effect of P_2O_5 in gelled acid. The P_2O_5 is expected to be solvolysed in gelled acid[3] and the inhibition is believed to be due to the formation of an aluminium phosphate film.

The formation of such a phosphate film could be preceded by the removal of the air-formed film; this is indeed consistent with the exceptionally high initial corrosion rate. The subsequent lower corrosion rates may then be seen as a consequence of the inhibiting effect of the phosphate film. This interpretation is consistent with the EIS study of cell GA7 (see Section 2.2.4.3).

4.2.2. Set B (Comparing Gelled Acid with Gelled Acid Containing 0.5wt.% P_2O_5) (Figures 21A-24)

4.2.2.1 Coupons with No Pre-treatment

The weight of the coupons which had been immersed in gelled acid decreased steadily during the first 29 days of immersion (Figure

21A). No results were obtained after 29 days because the numbers by which the coupons were identified had become obscured by corrosion. The corrosion rate also decreased from *ca.* 0.3mgcm^{-2}day^{-1} after 6 days to *ca.* 0.1mgcm^{-2}day^{-1} after 29 days (Figure 22A). The weights of the samples which had been immersed in modified gelled acid (0.5wt.% P_2O_5) decreased steadily during the 59 day immersion period (Figure 21A). The corrosion rate was steady at *ca.* 0.05mgcm^{-2}day^{-1} during the 59 days of immersion (Figure 22A).

The samples which had been immersed in IRFNA showed no clear pattern of weight changes. Some of the samples showed a small weight gain and some a small weight loss (Figure 21B). The average corrosion rate was *ca.* 0.005mgcm^{-2}day^{-1} (Figure 22B).

The inhibiting effect of P_2O_5 in gelled acid has been confirmed by these results. However, the average corrosion rate of 2014 aluminium in modified gelled acid (0.5wt.% P_2O_5, Figure 22A) is *ca.* 10 times higher than the corrosion rate in IRFNA (Figure 22B).

4.2.2.2 ClF_3 Pre-treated Coupons.

The weight changes of the coupons immersed in gelled acid and modified gelled acid (0.5wt.% P_2O_5) were of a generally similar pattern but the variation of the weight changes with time was more extreme for modified gelled acid (Figure 23). Eventually, after 58 days, a net weight increase was recorded for both gelled acid media . The weights of the coupons immersed in IRFNA showed little change during the 58 days of the study (Figure 23).

The corrosion rate of 2014 aluminium in gelled acid increased from *ca.* 0.01mgcm^{-2}day^{-1} after 6 days to a maximum of 0.04mgcm^{-2}day^{-1} after 13 days. The overall corrosion rate decreased during the remaining 45 days of the study to an estimated value of ca.0.001mgcm^{-2}day^{-1} (Figure 24): this has been attributed to the growth of a film of corrosion products. The corrosion rate of 2014 aluminium in modified gelled acid (0.5wt.% P_2O_5) showed a similar pattern. However, the maximum corrosion rate was higher (0.07mgcm^{-2}day^{-1}). The average corrosion rate of ClF_3 pre-treated aluminium in IRFNA was low (*ca.* 0.005mgcm^{-2}day^{-1}, Figure 24).

The ClF_3 pre-treatment appeared significantly to reduce the corrosion rate of 2014 aluminium in both gelled acid and modified gelled acid (0.5wt.% P_2O_5). A decrease in the corrosion rate of *ca.* 100-fold was observed for gelled acid after 58 days immersion of the coupons. The decrease was *ca.* 10-fold for modified gelled acid (0.5wt.% P_2O_5) after the same immersion period (cf. Figures 22A and 24). The decrease of the corrosion rate of ClF_3 pre-treated 2014 aluminium in gelled acid was not detected using electrochemical methods.

4.2.3 Microscopic Examination of the Coupons Used in the Weight Change Experiments

The coupons which had been used in the weight change study (Set B) were subsequently examined using an optical microscope at 200x magnification.

Both the untreated and ClF_3 pre-treated blanks appeared very similar. No obvious sign of corrosion could be detected on the

coupons. The rolling lines on the surface were still clearly visible. However, the ClF_3 pre-treatment appeared to leave a thin (presumably) fluoride film on the metal surface.

No difference could be detected between the untreated and ClF_3 pre-treated coupons which had been immersed in IRFNA. Both appeared to be covered with a thin film of corrosion products. The corrosion of the coupons appeared uniform.

The untreated coupons which had been immersed in gelled acid for about 60 days were extensively pitted. Grain structure could be detected in the bottom of the pits. Therefore it was concluded that the corrosion of the metal was mainly intergranular. The ClF_3 pre-treated sample after *ca.* 60 days immersion was markedly different in appearance: no sign of pitting or intergranular corrosion was detected on the coupons. A thin film of corrosion products was observed on the surface. The ClF_3 pre-treatment appeared to have changed the nature of the corrosion process from localised intergranular attack to uniform corrosion.

The untreated coupons which had been immersed in modified gelled acid (0.5wt% P_2O_5) for *ca.* 60 days were covered with a black film. The black film was only loosely adherent and most of it was removed by washing with water. Microscopic examination showed that the coupons were subject to localised intergranular attack. About 1/3 of the total surface area was badly pitted the remainder being covered with a thin film of corrosion products. The black film is probably a film of aluminium phosphate corrosion products. The ClF_3 pre-treated coupons, which had been immersed

in modified gelled acid (0.5wt.% P_2O_5) for the same length of time were also covered with a black film. About five small pits were observed on the surface. Therefore, the ClF_3 pre-treatment also changed the visible effects of the corrosion process in modified gelled acid (0.5wt.% P_2O_5), although the change was less striking than for unmodified gelled acid.

These results exemplify the difficulty in measuring accurate corrosion rates when the corrosion process is intergranular. The electrochemical study (Section 2) indicated that P_2O_5 was a better inhibitor than did the weight loss study.

Intergranular attack can bring about a large weight decrease for a relatively small amount of electrochemically measurable corrosion. A grain falling out of the surface is a mechanical process and hence cannot be detected electrochemically. Therefore, the weight loss technique in such situations will provide a more meaningful estimate of the corrosion rate. The evidence from the examination of coupons under a microscope thus correlates with the discrepant corrosion rates as determined by weight loss and electrochemical studies of both modified gelled acid (3wt.% P_2O_5) and gelled acid.

Hence, on the basis of these optical studies the ClF_3 pre-treatment appeared to change the nature of the corrosion process of 2014 aluminium in gelled acid from non-uniform (e.g. intergranular) to uniform corrosion. The amount of electrochemically determined corrosion was, however, unchanged by the pre-treatment. In the case of the modified gelled acid (0.5wt.% P_2O_5) the effect of the ClF_3 pre-treatment was visibly

favourable, although it was less marked than was observed for gelled acid: this is in keeping with the similar (low) corrosion rates as determined by the weight loss studies.

The mode of action of the ClF_3 pre-treatment was not apparent from these investigations.

5. TEMPERATURE CYCLING

5.1 Experimental.

Cells GA3 and GA4 were placed in a constant temperature bath at 25°C. E_{corr} and R_p (Figures 25 and 26) data were recorded, for each cell, at 72 minute intervals, during a 24 hour period. The same cells were then subjected to a +20°C temperature cycle. The structure of the cycle (Figure 27) consisted of a series of steps each comprising a heating period of 2 minutes at the rate of $1°Cmin^{-1}$ followed by a holding period of 34 minutes. The total length of time of each step was therefore 36 minutes. E_{corr} and R_p values were obtained at 72 minute intervals during the cycle (i.e. at 4°C intervals). The results are presented in Figures 28 and 29. Arrhenius plots (Figure 30) have been derived from the R_p data and used to calculate activation energies for the electrochemically measurable corrosion reaction of 2014 aluminium in gelled acid.

5.2 Results and Discussion

The E_{corr} and R_p values (Figures 28 and 29) showed a cyclic variation with temperature. The changes in E_{corr} comprised two parts, namely changes in the potential of the working electrode and changes in the potential of the reference electrode. The temperature dependence of the potential of the platinum reference electrode in gelled acid is not known and therefore it is difficult to draw any conclusions from the temperature dependence of the E_{corr}.

The R_p data showed an exponential variation with absolute temperature i.e. fitted the Arrhenius equation:

$$\text{Rate} \propto R_p^{-1} = A \exp(-E_a/RT)$$

A = Arrhenius constant R = Gas Constant = $8.31 JK^{-1}mol^{-1}$

E_a = Activation Energy/$kJmol^{-1}$ T = Temperature/K

Hence by plotting $\log R_p$ vs 1/T (Figure 30) and using linear regression analysis, values of the activation energies and Arrhenius constants for the cells have been obtained (Table 7). The activation energies reported in this Table are of the same order of magnitude as those obtained for the 2014 aluminium/IRFNA system [1,7].

The microscopic examination of the coupons used in the weight change experiments showed that those immersed in GA had undergone intergranular corrosion. The R_p measurements as a function of temperature were not, therefore, representative of the entire corrosion process and the scatter in the data points (Figure 30) may be, in some measure, a consequence of the interfering process(es) associated with intergranular corrosion. Nevertheless, for 2014 Al alloy in GA the electrochemical processes have similar temperature dependence and activation energy to those observed for this alloy in electrochemical cells of identical design containing IRFNA[1,7].

6. CONCLUSIONS

6.1. Electrochemistry.

Table 8A lists polarisation resistance (R_p) values (estimated from Figures 2-5, 7-11, 13 and 14) recorded for cells GA1-GA11 after the specified contact times of the 2014 aluminium alloy working electrode with each of the gelled acids or with modified IRFNA. R_p is inversely proportional to the corrosion current density, i_{corr}, and thus to the metal corrosion rate. It is recorded in Table 8A in preference to these latter parameters since they can only be calculated from R_p by making certain assumptions with regard to the magnitudes of b_a and b_c, the anodic and cathodic Tafel constants, which appear in the Stern-Geary relationship[6]. This point is elaborated further in the Appendix.

Table 8B has been generated from the data in Table 8A using the conversion factor for the polarisation resistances $205.2/R_p$, where R_p is in ohms; the resulting numbers have the same units, $mgcm^{-2}day^{-1}$, as those from the weight change/loss experiments. It must be noted that this conversion factor is one which was found appropriate for earlier electrochemical studies in RFNA, IRFNA and WFNA, as discussed in the Appendix. Until this conversion factor is further substantiated the ICR values in Table 8B should be used with caution.

For those cells monitored for times > 100 days, a steady state R_p value appeared to have been reached after this period. The R_p values in Table 8A indicate:-

(i) that MGA-3 gives very low electrochemically-determined corrosion rates ($mgcm^{-2}day^{-1}$) after 60 days (*ca.* 0.0002) or 100 days (*ca.*0.00002) and these rates are *ca.*10x lower after 60 days and *ca.*100x lower after 100 days than the corresponding rates in GA. These electrochemical corrosion rates are in conflict with those determined by weight loss for GA and MGA-3 after 60 days (Set A, Table 8A) which are large and differ from each other only by a factor of two.

(ii) that MIRFNA-3 gives an R_p value after 23 days of the same (high) order of magnitude as that given by MGA-3 after 60 or 100 days. This indicates that corrosion protection is established more rapidly in MIRFNA-3 compared to MGA-3.

(iii) that the cells giving rise to the largest R_p values (and thus the smallest electrochemical corrosion rates) i.e. GA10 after 23 days (MIRFNA-3) and GA7 after 60 and 100 days (MGA-3) contain P_2O_5 in the corrosive medium.

(iv) that no very obvious advantage accrues in gelled acid from the metal pre-treatments with HF/F_2, by electropolishing and anodising, or with ClF_3, compared to no metal pre-treatment. This conclusion for ClF_3 is, however, contrary to that arrived at from the weight change experiments on account of the inability of the electrochemical techniques used here to detect non-uniform (intergranular) corrosion (see Section 6.3 below).

Comparison of the Bode plots obtained from GA (Figure 13) and MGA-3 (Figure 14), before and after a *ca.*100-day time interval, indicates that after this time the MGA-3 appears to have totally

removed the original oxide film on the metal and replaced it with a highly resistive corrosion product layer, whereas the GA does not appear to have done this.

6.2. Surface Studies.

Both XPS and AES investigations were performed on coupons which had been subjected to no pre-treatment other than polishing before immersion in GA. After removal of the coupons from the gelled acid they were either dried in a stream of nitrogen, or water-washed, in preparation for XPS/AES examination.

The main conclusions are:-

(i) the Si, F and N, detected on the metal surface after immersion in the gel, are all believed to originate from the gel (although Si and F were also detected before immersion). Likely surface species are SiO_2 and NO_3^- and possibly SiF_6^{2-} and AlF_3. The presence of fluorine is taken to indicate that not all the HF in IRFNA is lost from the gel in the gelling process.

(ii) the thickness of the predominantly Al_2O_3 film (estimated from AES depth profile measurements) on the surface of the "blank" metal sample (*ca.* 10nm) increases only marginally (to *ca.* 12.5nm) after immersion in GA for 8 days followed by drying in a stream of nitrogen. In contrast, 8 days immersion in GA followed by water-washing resulted in a dramatic increase in thickness (to *ca.* 55nm). It is surmised that dilute nitric acid generated at the metal surface during the water-washing procedure is responsible for this.

Two coupons which had been immersed in modified gelled acid (0.5wt.% P_2O_5) for 90 days were subjected to Auger Electron Spectroscopy. They were both covered with a thick layer of corrosion products which were shown by AES to be non-uniform: this was also evident from their patchy appearance. Since AES samples a very small area (*ca.* $100\mu^2 = 10^{-4}mm^2$) this technique does not provide a meaningful average surface analysis; it is, however, the preferred technique to investigate variations in the composition under the surface. The results showed that:

(i) silicon appeared only at the surface whereas phosphorus and fluorine were apparent at greater depths,

(ii) the oxide layer was *ca.* 15nm thick, and

(iii) that unoxidised aluminium (0) was detected at 3nm, i.e. uncommonly near to the surface, for the coupon which was pre-treated with ClF_3.

The last feature (iii) was the only obvious difference between the coupons, and, thus, the only apparent effect of the ClF_3 pre-treatment with. It is unwise to speculate further on these spectra from samples which had been immersed for so long in this medium and which are known to have been corroded/pitted, using a technique which investigates such a small area of each specimen.

6.3. Weight Change Studies

Tables 8A and 8B also summarise steady state corrosion rates after *ca.* 60 days immersion, estimated from the weight change results depicted in Figures 20, 22A, 22B and 24, alongside the electrochemical results for the corresponding systems for purposes

of comparison.

The principal conclusions from the weight change studies are:

(i) GA corrosion is relatively rapid.

(ii) the GA(ClF_3) corrosion rate is at least 100x smaller than that for GA and is of similar magnitude to, or smaller than, those for IRFNA and IRFNA(ClF_3). The rate for MGA-0.5(ClF_3) appears to be identical to that for GA(ClF_3) but some experimental uncertainty arises from the very small magnitude of these rates. In both cases a small weight gain was measured after 58 days (Figure 23), which would translate into small negative(!) corrosion rates (Figure 24); these rates appear in Tables 8A and 8B as *ca.* 0.000mgcm^{-2}day^{-1}.

(iii) the MGA-0.5 corrosion rate is greater than the GA(ClF_3) corrosion rate but much smaller than the GA corrosion rate.

(iv) the MGA-0.5 corrosion rate is *ca.* 10 x smaller than the MGA-3 corrosion rate.

(v) the MGA-0.5 corrosion rate is larger than that for MGA-0.5(ClF_3).

The experimental error in these values of the steady state corrosion rate from weight change studies is considered to be ±0.003 on the basis of the results for a ClF_3 pre-treated coupon in IRFNA.

The weight change studies were supported by optical microscopic (200x magnification) examination of untreated and pre-treated pre- and post-immersion coupons (Set B only). The results of the optical microscopy are summarised briefly in Table 9. The observations recorded in this Table indicate that ClF_3

pre-treatment of 2014 Al prior to immersion in gelled acid, or modified gelled acid containing 0.5wt.% P_2O_5, stops intergranular corrosion at least up to the stated period of immersion. The HF in IRFNA also appears to prevent intergranular corrosion so that pre-treatment of the aluminium alloy with ClF_3 does not appear to increase substantially the protection already afforded by HF on immersion of the alloy in IRFNA (see also Tables 8A and 8B). Clearly, GA and MGA-0.5, both deficient in F^-, bring about intergranular corrosion, but the P_2O_5 in MGA-0.5 gives rise to a substantial decrease in corrosion rate compared to that for GA (Tables 8A and 8B).

6.4. Comparison of Corrosion Rates Determined by Electrochemistry and Weight Change

The greatest disparity between corrosion rates determined by electrochemistry and weight change after 60 days immersion occurs in the case of MGA-3 (0.0002 and 0.052mgcm^{-2}day^{-1}, respectively). The very slow corrosion rate indicated by electrochemistry could be reconciled to the moderately rapid rate measured by weight change (Set A) by the existence of intergranular corrosion, causing the detachment of whole grains of metal, a phenomenon undetectable electrochemically. This type of corrosion was observed for MGA-0.5 by optical microscopy (Table 9). A similar interpretation can be given for the discrepancy between the electrochemical and weight change corrosion rates for GA, e.g. 0.011 (cell GA3) and 0.100 (Set A) mgcm^{-2}day^{-1}, respectively (Tables 8A and 8B).

6.5. Temperature Cycling

The details of the temperature cycling process to which cells GA3 and GA4 were subjected were identical to those used in an earlier study involving four electrochemical cells of similar design containing IRFNA but unpolished working electrodes fabricated from sections of an oxidiser tank wall [7]. Two of the cells (BW1 and BW2B) contained working electrodes which had not been pre-treated and the other two (BW13 and BW14) contained working electrodes which had been washed with water.

In the present study involving cells GA3 and GA4 very similar results were obtained. E_{corr} and R_p values (i_{corr} rather than R_p was plotted in the earlier study) again showed a cyclic variation with temperature. Activation energies, of the same order of magnitude as those encountered in the IRFNA study, were obtained (Table 7).

The marked effect of temperature on corrosion rate highlights, as in the case of IRFNA, the desirability of keeping the Al alloy/gel system cool, at least over the temperature range studied.

For gelled acid, a temperature rise of between 20-40°C causes a 10x increase in corrosion rate. Therefore, in the absence of data at even lower temperatures, +5°C is clearly the best of the temperatures studied for the storage of gelled acid in 2014 aluminium alloy which has not been pre-treated with ClF_3.

7. RECOMMENDATIONS

The most promising gelled acid systems investigated in coupon weight change studies during the present programme proved to be GA(ClF_3) and MGA-0.5(ClF_3). These two systems gave very low corrosion rates, indistinguishable in the weight change study, after 58 days immersion of the 2014 aluminium alloy coupons. Since intergranular corrosion does not occur for either of these systems, electrochemical determination of corrosion rate for MGA-0.5(ClF_3) should provide a meaningful comparison with the GA(ClF_3) electrochemical results (Tables 8A and 8B). If ClF_3 pretreatment is not a viable proposition for practical reasons, then MGA-0.5 could be recommended. Since the effect of the ClF_3 pre-treatment cannot last indefinitely, the results of these relatively short term studies suggest that the addition of 0.5wt.% P_2O_5 would lead to lower corrosion rates in the long term.

Longer term (> 60 days) coupon studies are now warranted to ascertain for how long the added corrosion protection, afforded by the GA(ClF_3), MGA-0.5(ClF_3) and MGA-0.5 systems, compared to GA, survives.

It is also important that the type of coupon study reported here, involving measurement of weight changes augmented by Optical Microscopy (or SEM), XPS and AES investigations of metal surfaces, and based upon IRFNA as a standard oxidizer material, should be extended in a number of ways.

Furthermore, in order to remove some of the current uncertainties it is necessary to investigate the reaction between HF and SiO_2 in IRFNA and especially the nature, role and ultimate location of

any silicon fluoro-species (e.g. SiF_4, SiF_6^{2-}) generated.

Clearly, the variables to be addressed in an extended coupon study could be:-

(i) type of aluminium alloy

(ii) additive (corrosion inhibitor) to gel

(iii) metal surface pre-treatment

and the following candidates are suggested:-

Metals	Gel Additives	Metal Pre-treatments
1. Al 1100 (i.e. very pure Al)	P_2O_5	ClF_3
	H_3PO_4	H_3PO_4
2. Other Al alloys	$LiPF_6$	
3. Joined (welded) samples of Al types		

Additional variables are the concentration of gel additive and the conditions of metal pre-treatment.

Metals

So far as the welded samples are concerned, the intention would be to use surface analytical techniques to investigate areas of the individual alloys themselves and of the transition (weld) region.

Gel Additives

Some background nmr information relevant to the nature of the phosphorus species present in mixtures of P_2O_5 and GA, or H_3PO_4 and GA, is already available [3].

A topic of importance in the new research would be investigation of the fate of PF_6^- in GA with a view to considering it as a slow HF- and fluorophosphate-release agent. The main value of

such an agent would be to provide inhibitors to protect the Al_2O_3 surface on the Al alloy; clearly silica will also be competing for the HF. Possible systems for nmr studies would be:-

PF_6^- + RFNA + SiO_2 + $LiNO_3$ (not gelled)

or PF_6^- + GA + HNO_3 (diluent)

The HNO_3 to be employed here would be the analytically 100% material.

Other possible candidates as gel additives would be a silicate or a molybdate.

The concentration of any gel additive to be used would be 1wt.% or less.

Metal Pre-treatments

Concerning the use of H_3PO_4, the intention here would be to paint the syrupy acid on to the metal surface and allow it to remain there on immersion of the metal in the gelled acid medium.

New Research Proposal

The work accomplished to date is very positive and a detailed matrix of experiments, based on the suggestions set out above, should be submitted as a new research proposal.

FIGURE 1 THE BOTTOM WORKING ELECTRODE CELL

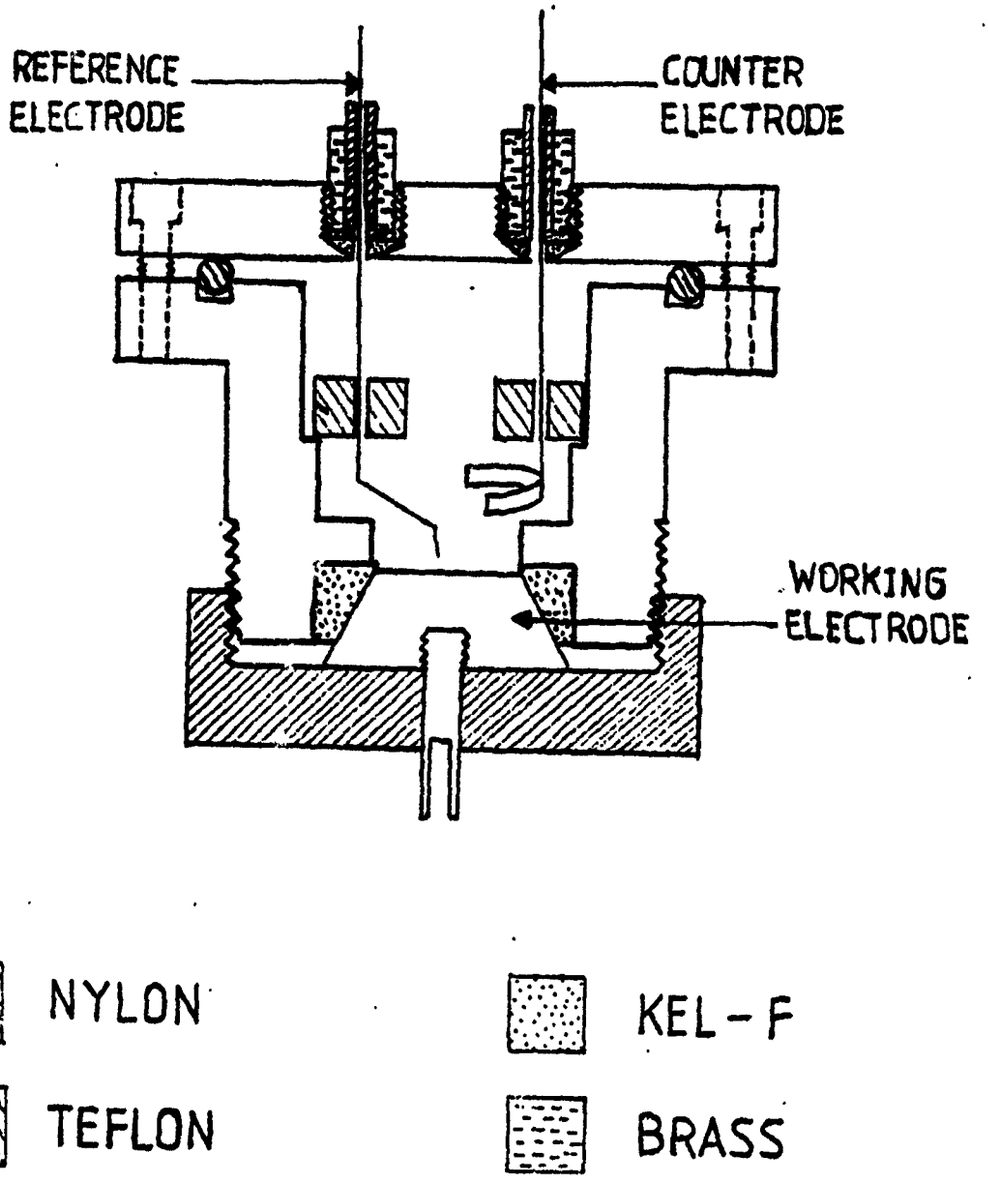

Figure 2 - Cell GA1

Ecorr and Rp vs Time

Gelled Acid - No Pretreatment

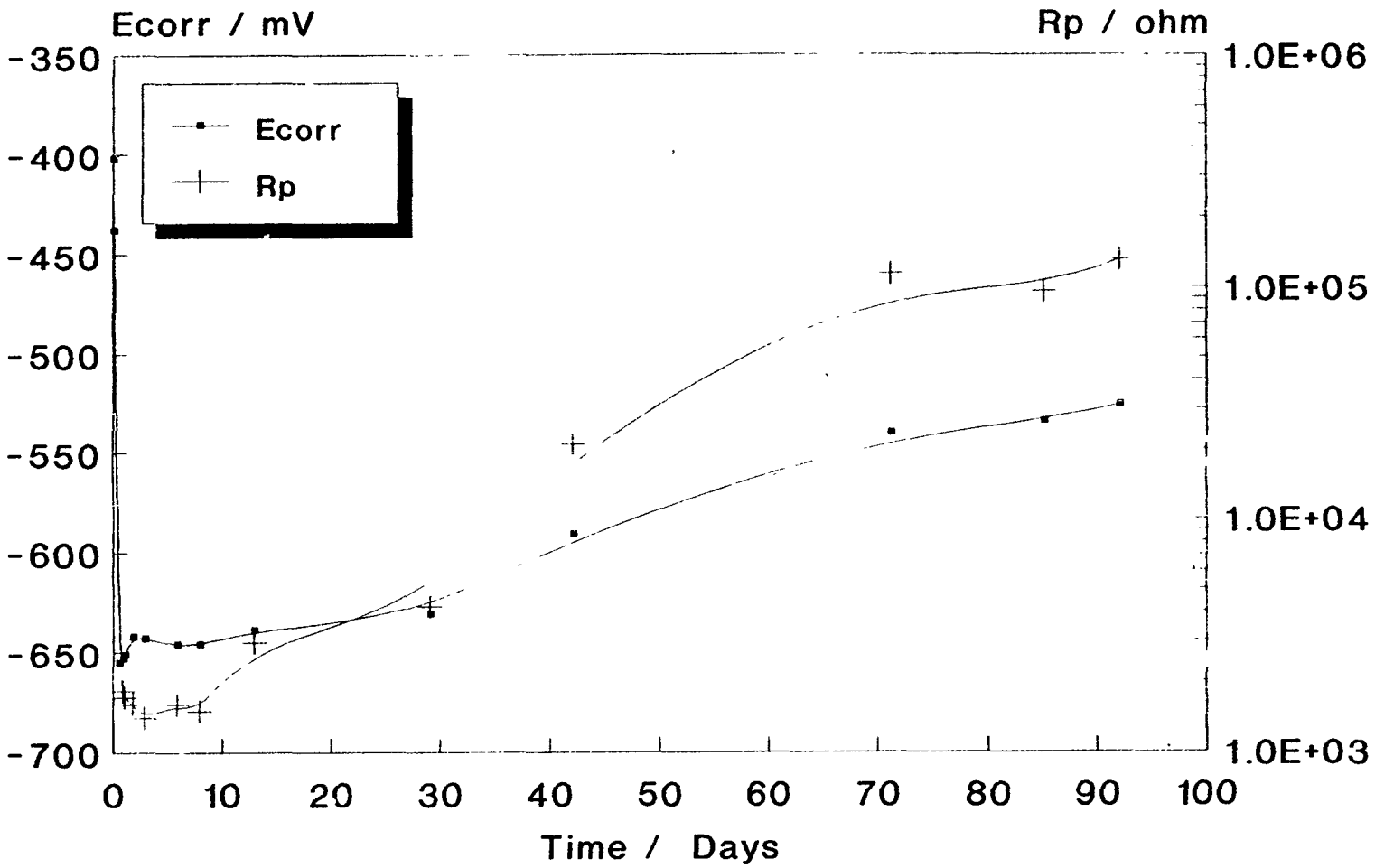

Figure 3 - Cell GA 2

Ecorr and Rp vs Time

Gelled Acid - No Pretreatment

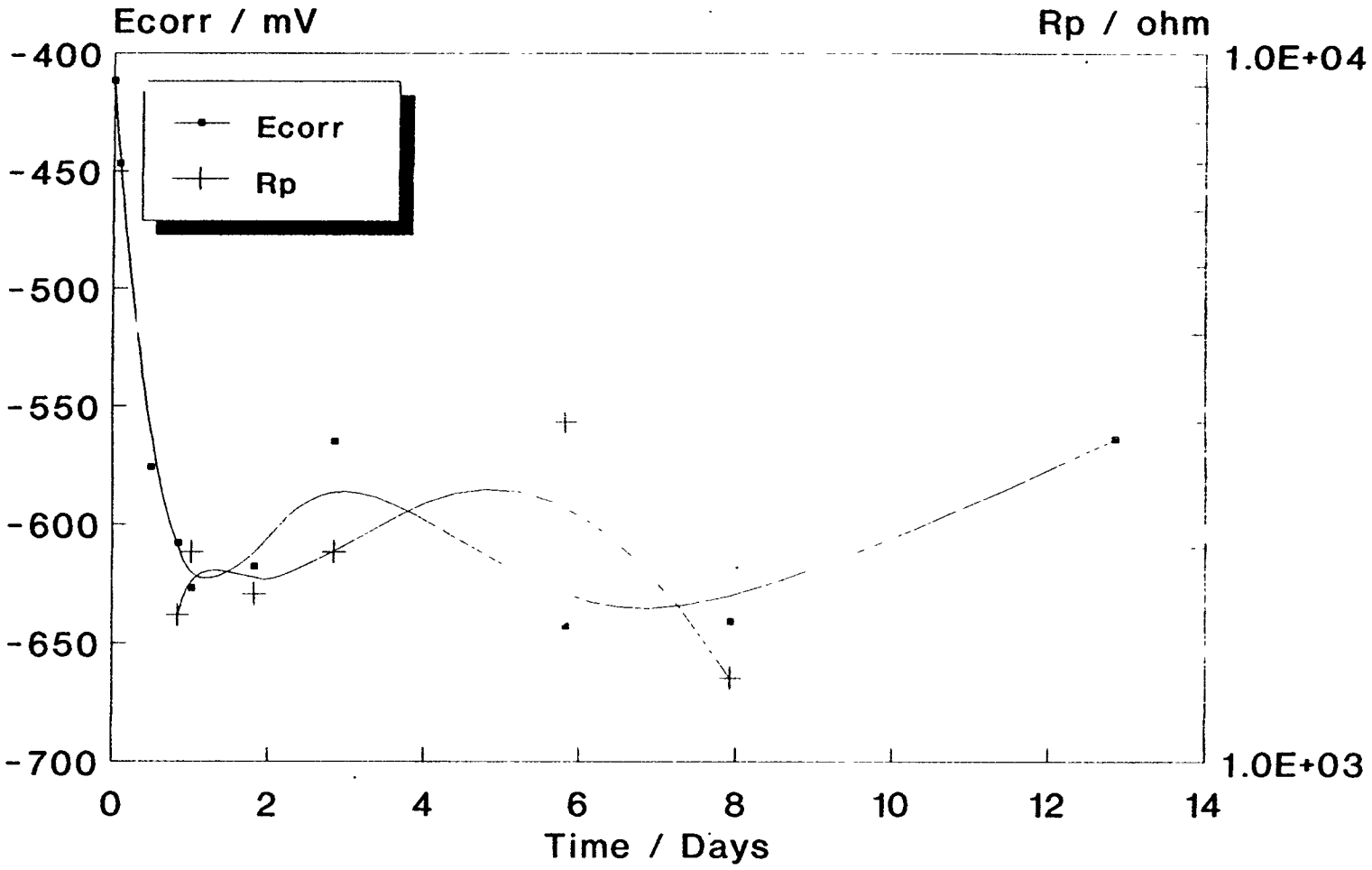

Figure 4 - Cell GA3

Ecorr and Rp vs Time

Gelled Acid - No Pretreatment

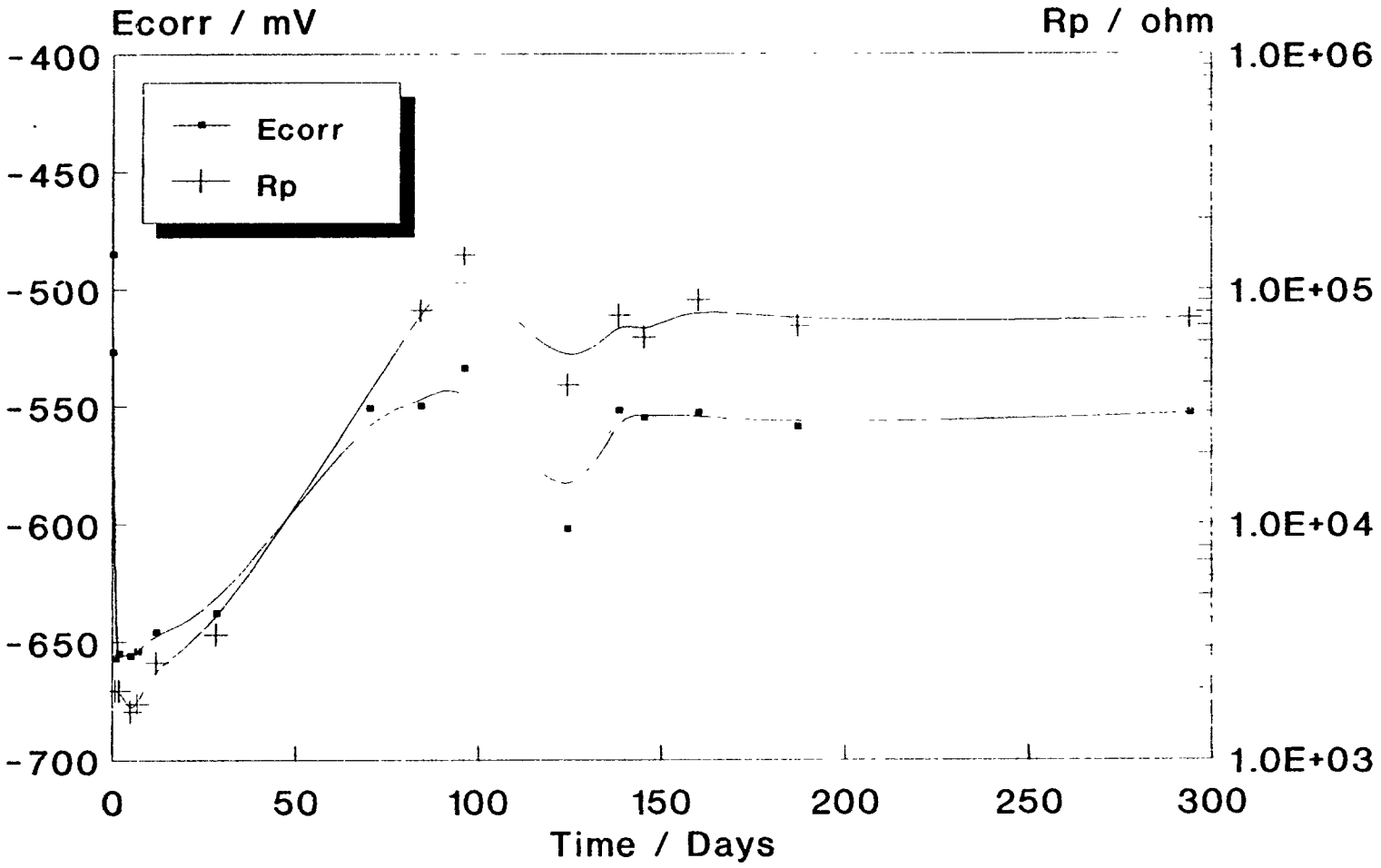

Figure 5 - Cell GA 4

Ecorr and Rp vs Time

Gelled Acid - No Pretreatment

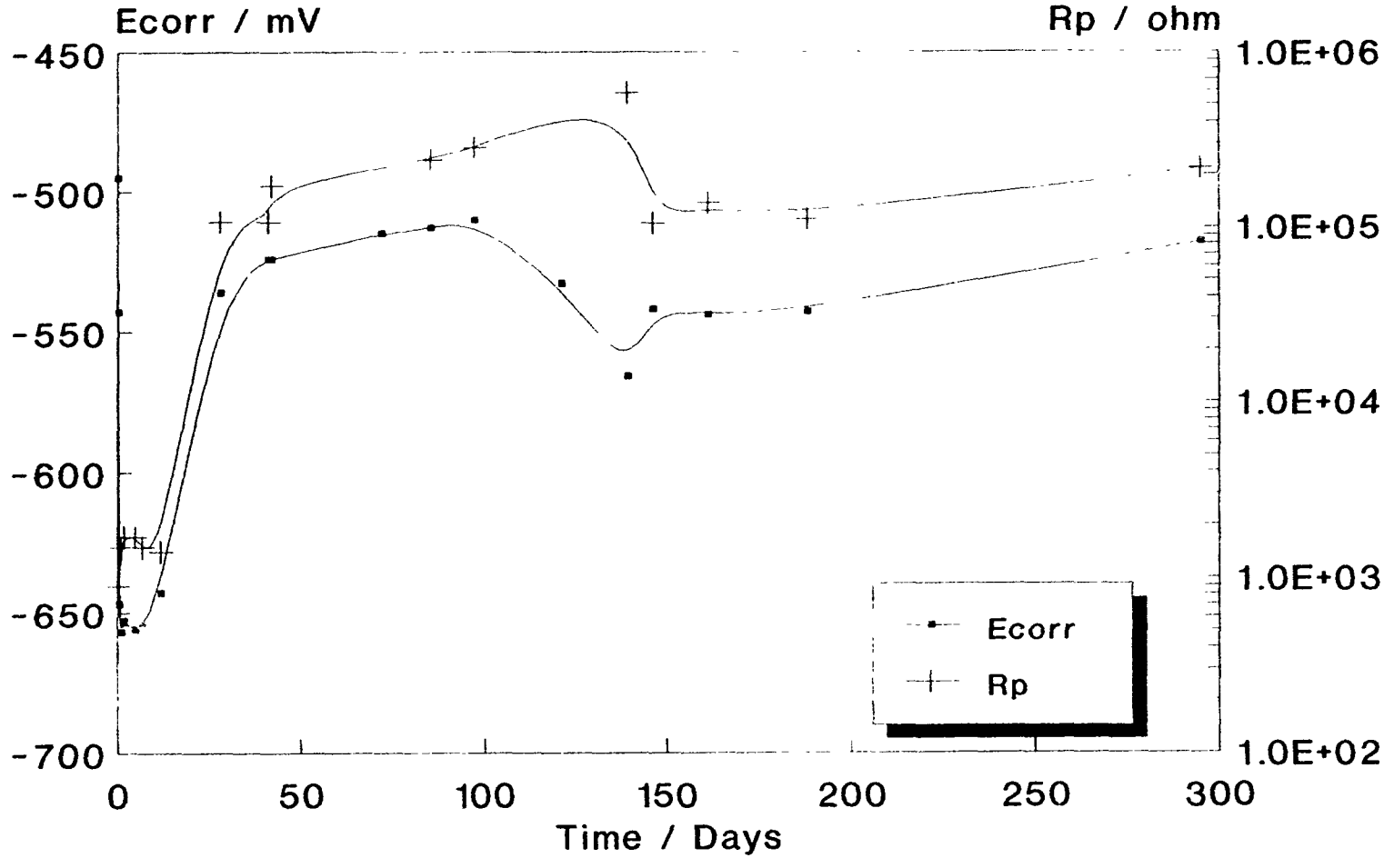

Figure 6 - Bode plots with Time

Cell GA1 - 2014 Al / Gelled Acid

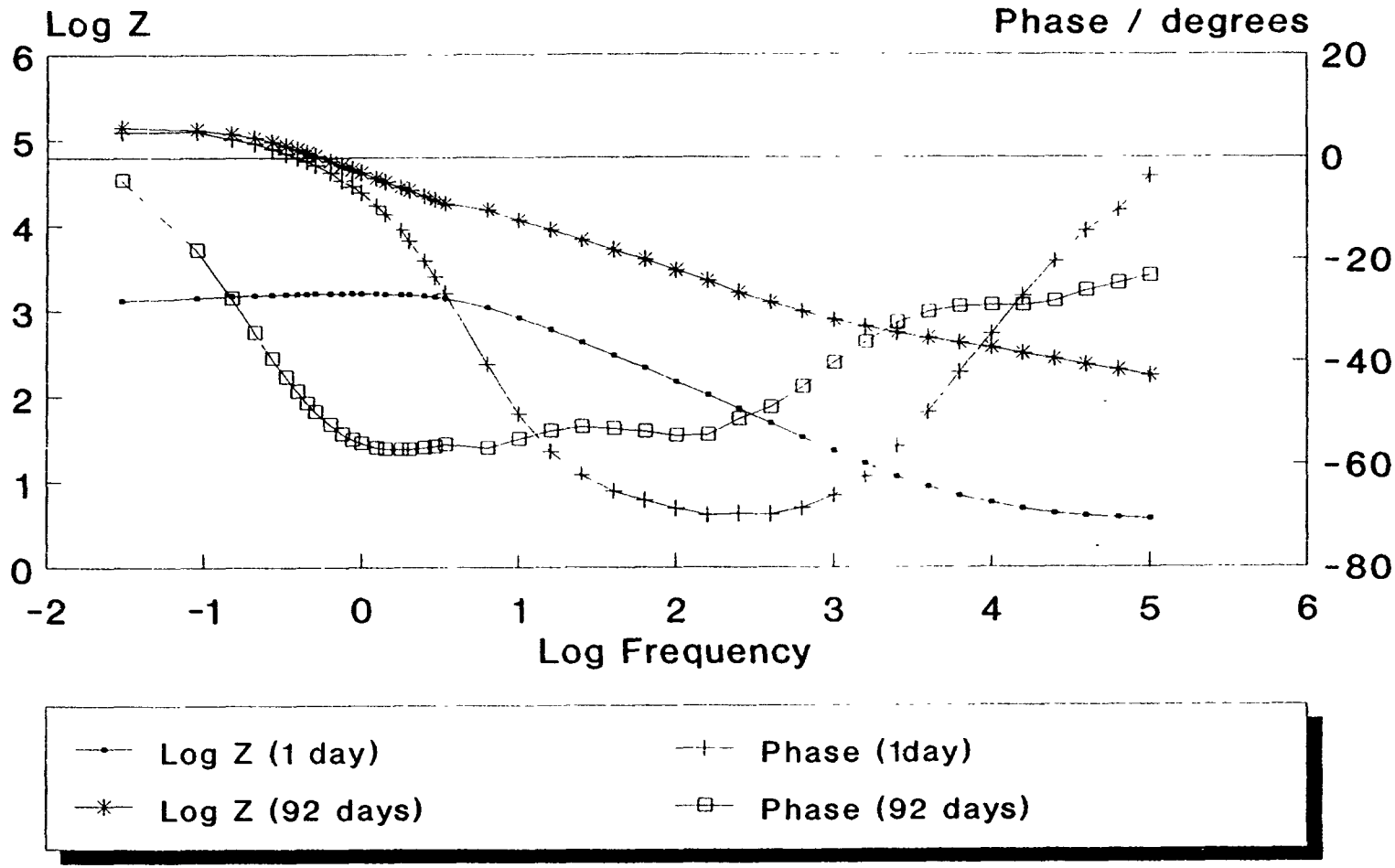

Figure 7 - Cell GA 5

Ecorr and Rp vs Time
HF / F2 Pretreatment

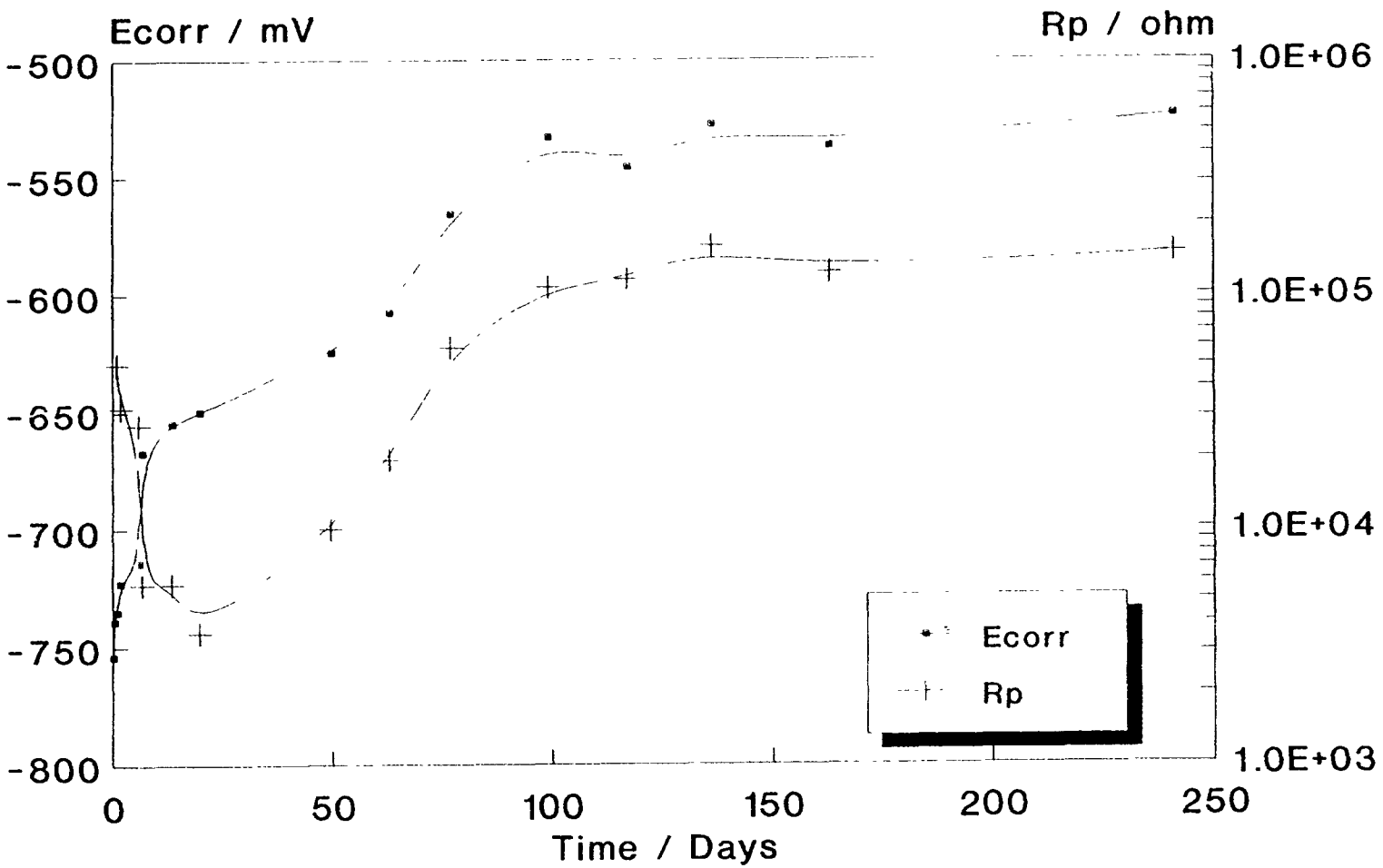

Figure 8 - Cell GA8

Ecorr and Rp vs Time

ClF3 Pretreatment

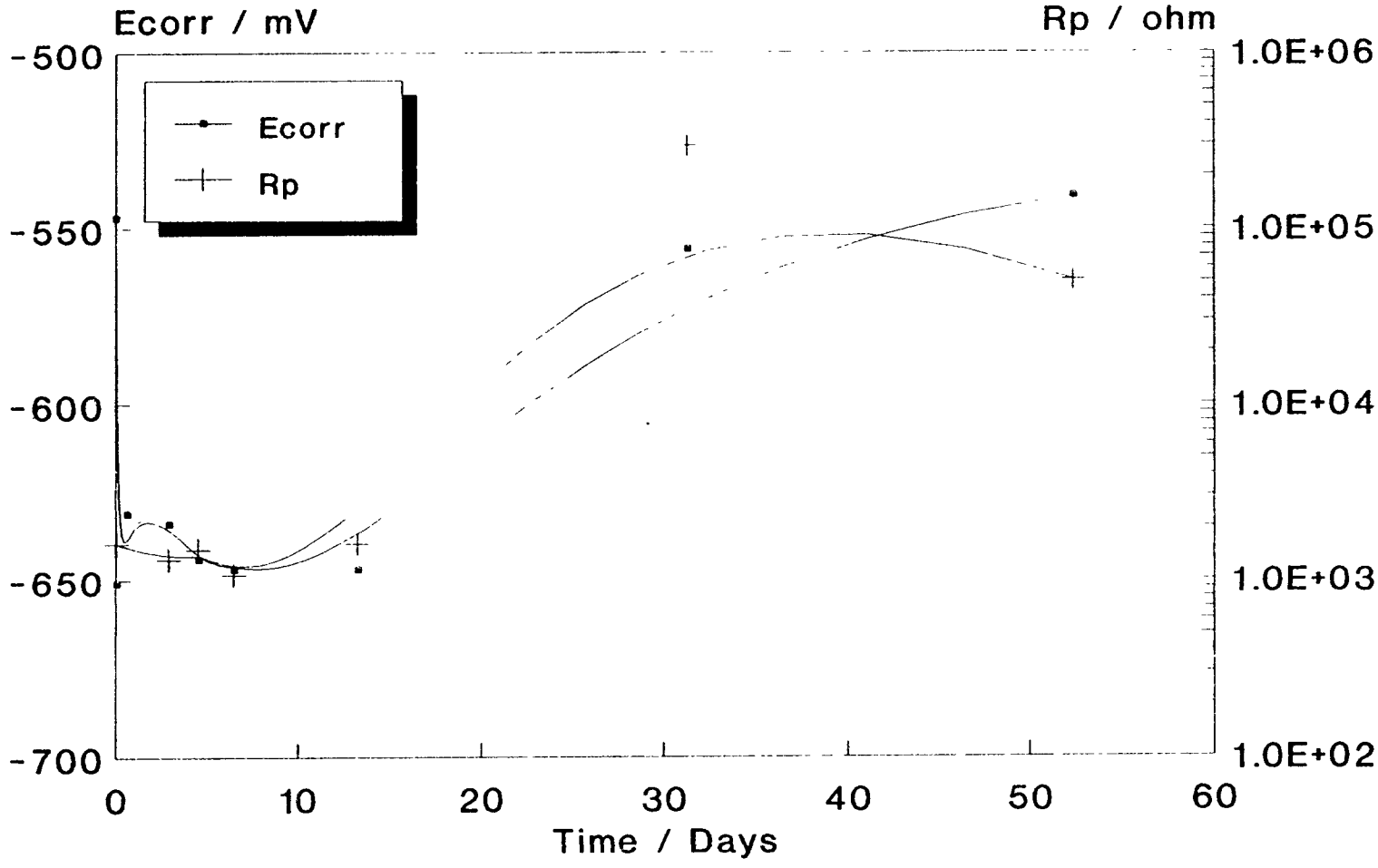

Figure 9 - Cell GA9

Ecorr and Rp vs Time

ClF3 Pretreatment

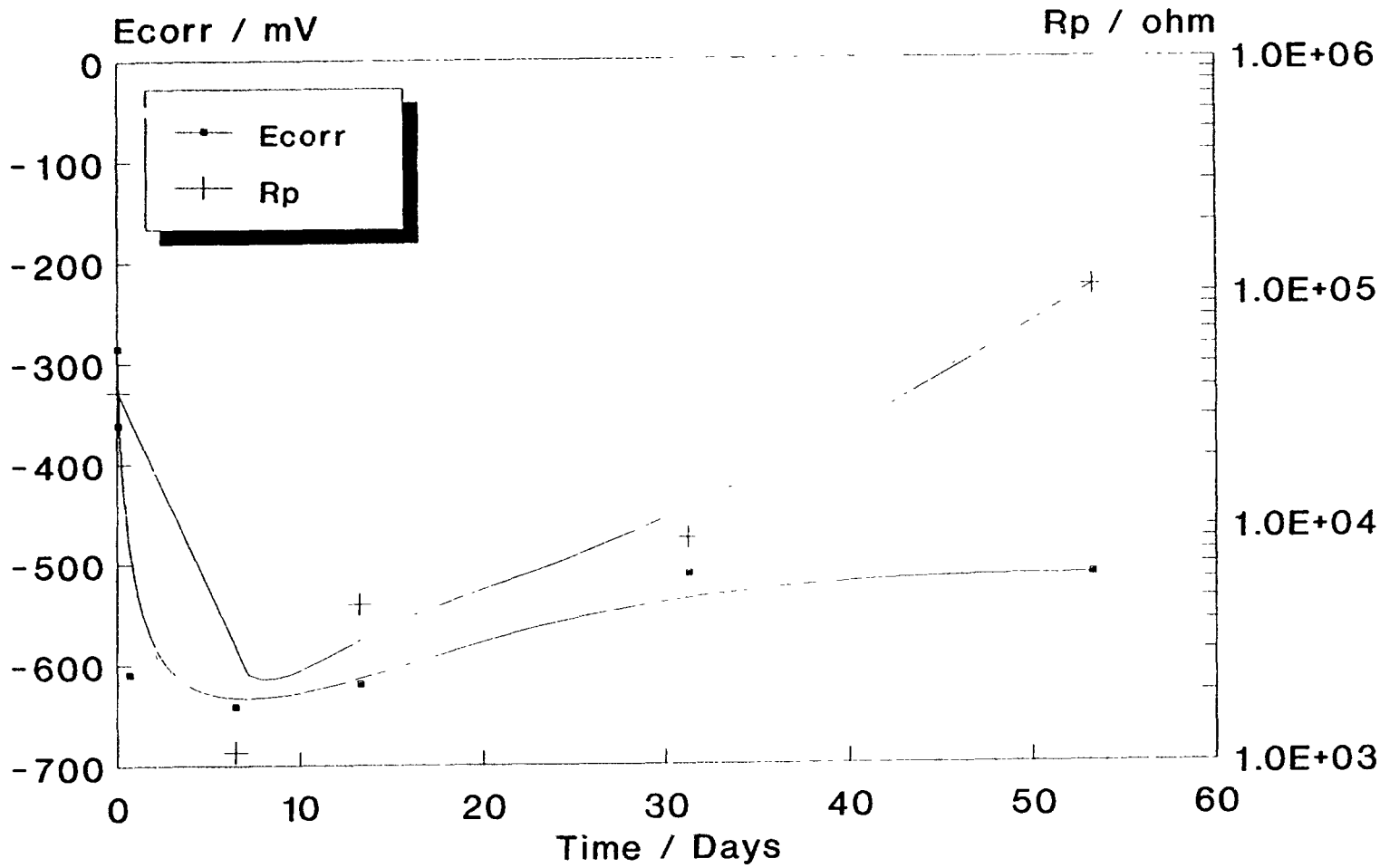

Figure 10 - Cell GA7

Ecorr and Rp vs Time

Modified Gelled Acid (3wt% P2O5)

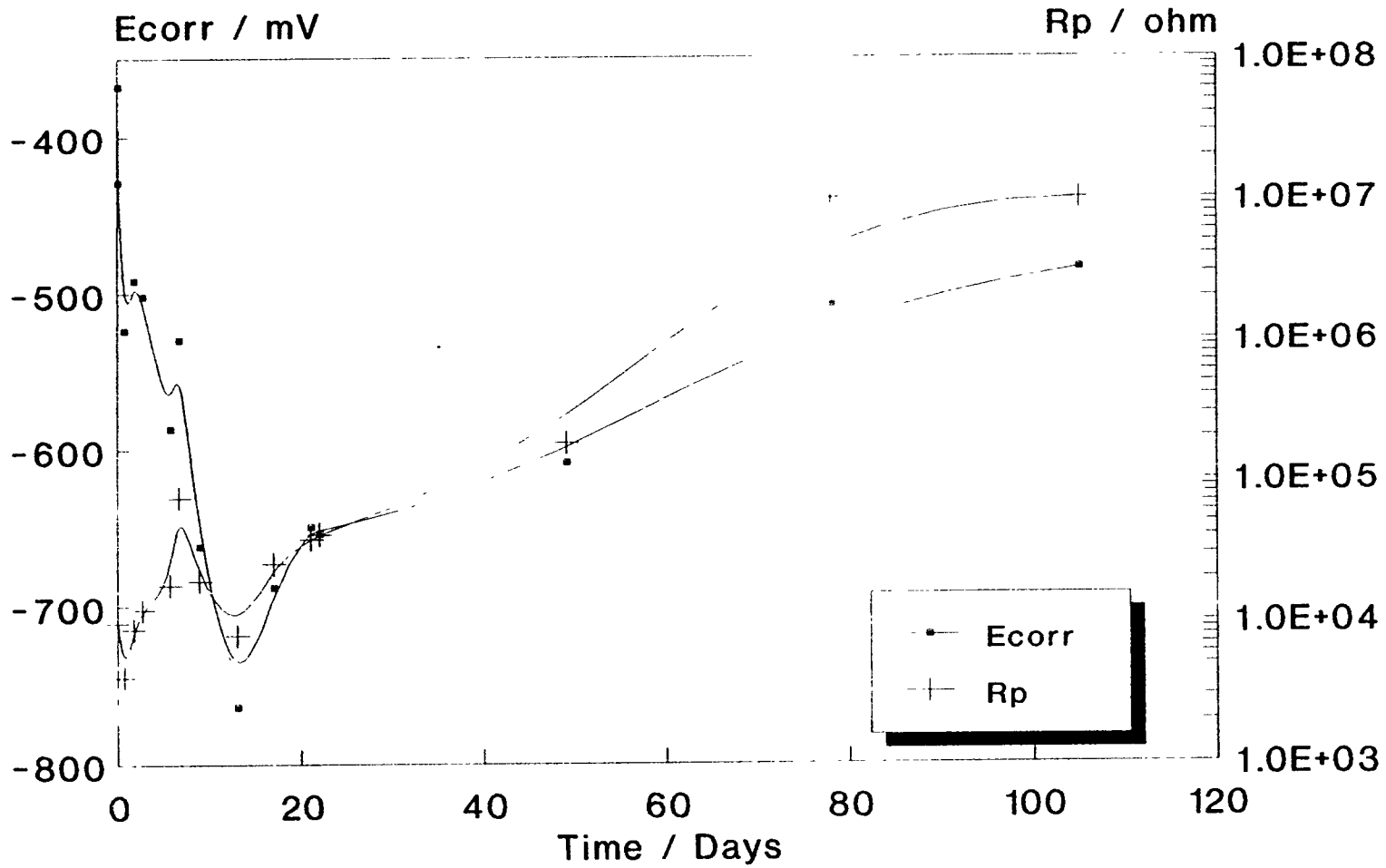

Figure 11 - Cell GA11

Ecorr and Rp vs Time

Modified Gelled Acid (3wt% P2O5)

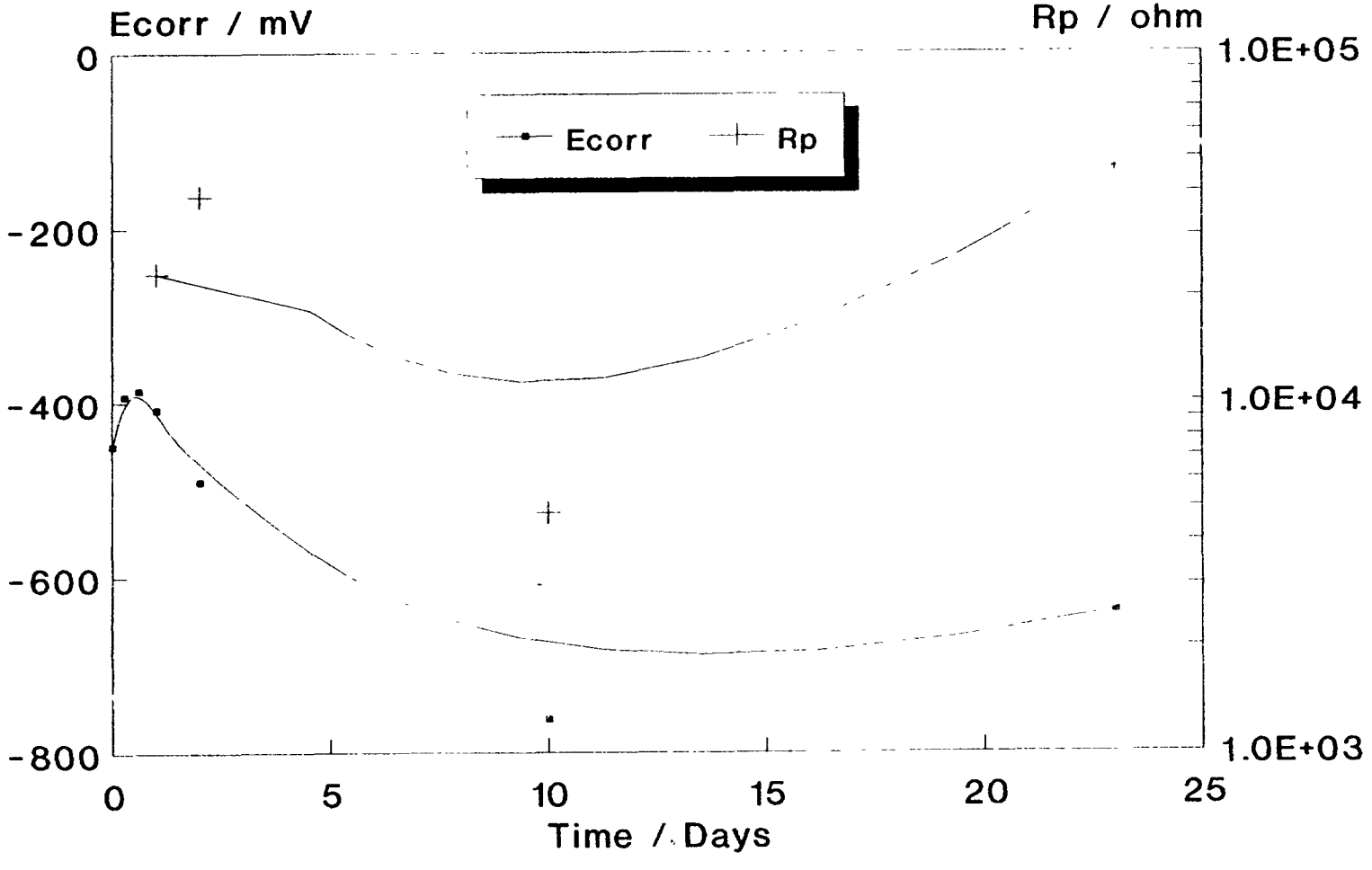

Figure 12 - Bode Plots with Time

Cell GA7 - 2014 Al

Modified Gelled Acid (3wt% P2O5)

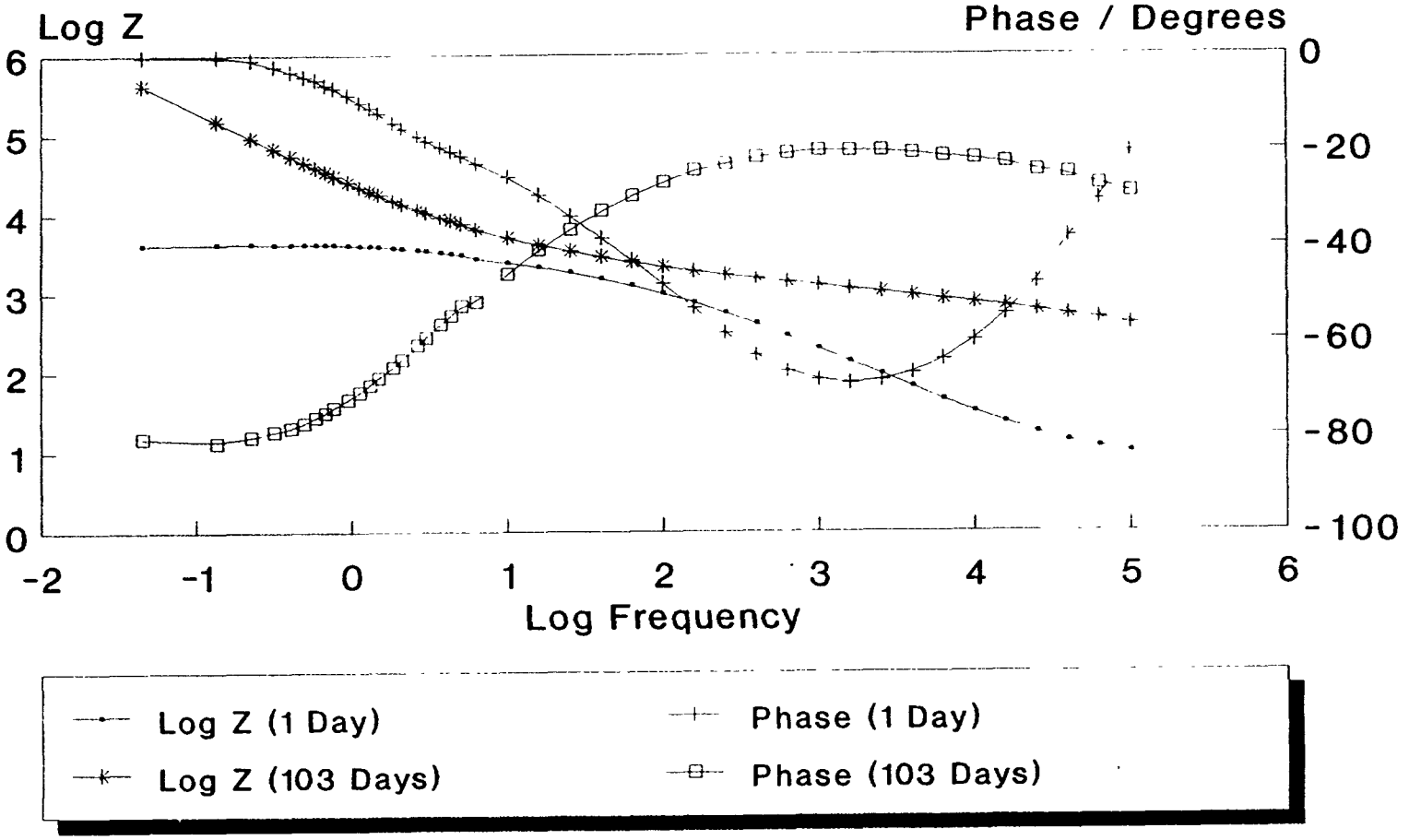

Figure 13 - Cell GA10

Ecorr and Rp vs Time

Modified IRFNA (3wt% P2O5)

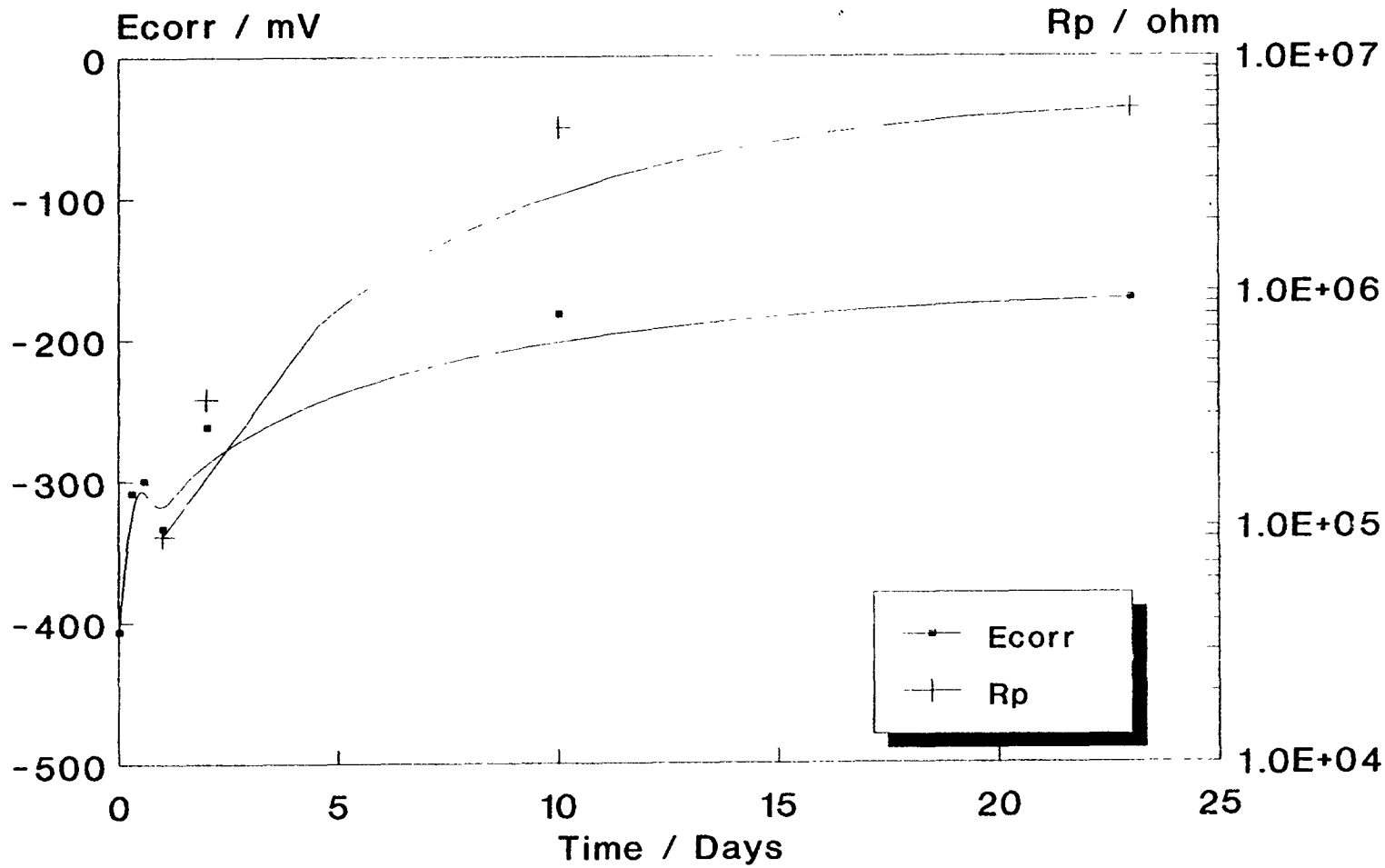

Figure 14 - Cell GA6

Ecorr and Rp vs Time
Electropolished and Anodised

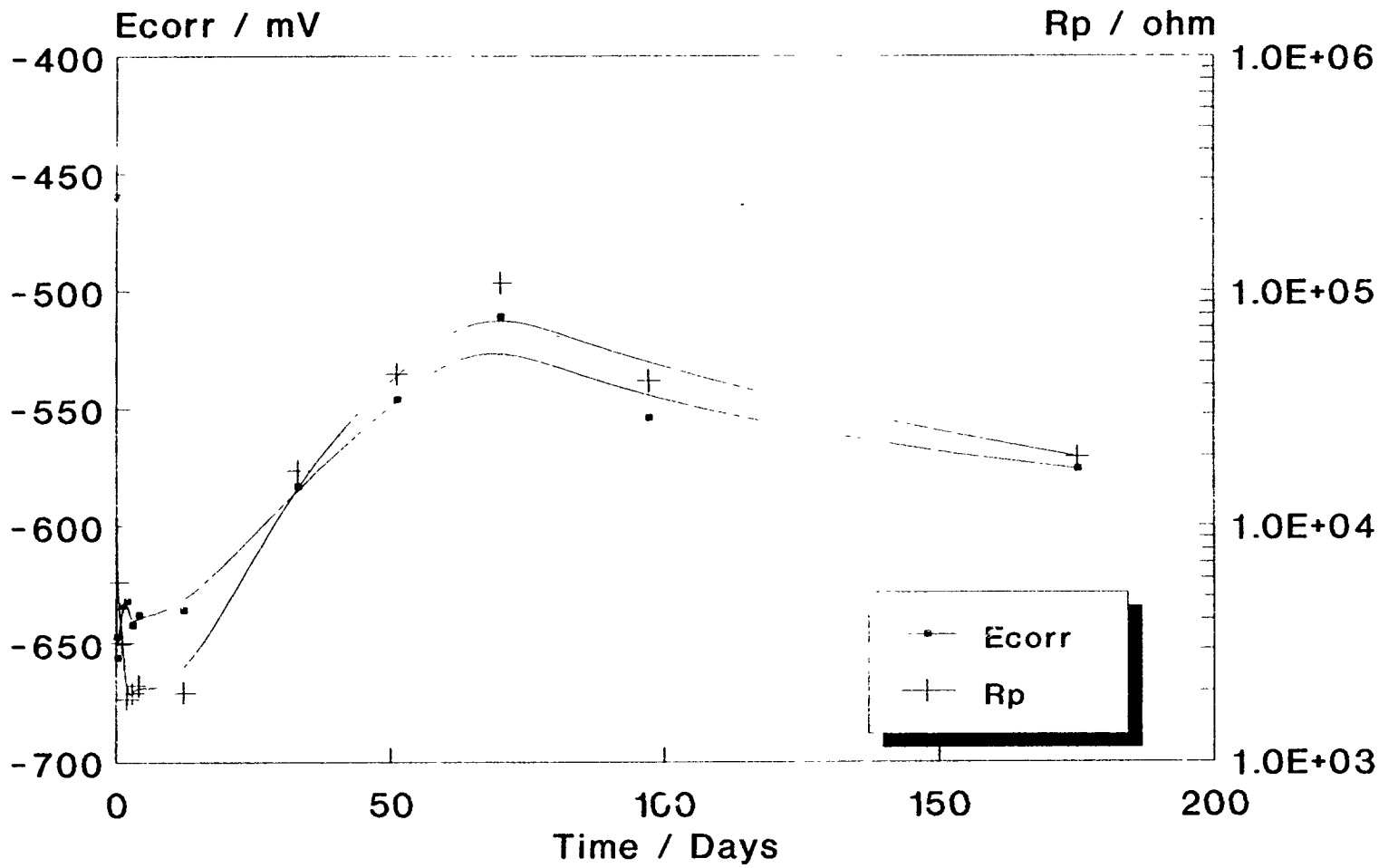

Figure 15 - Auger Depth Profile

2014 Al - Blank

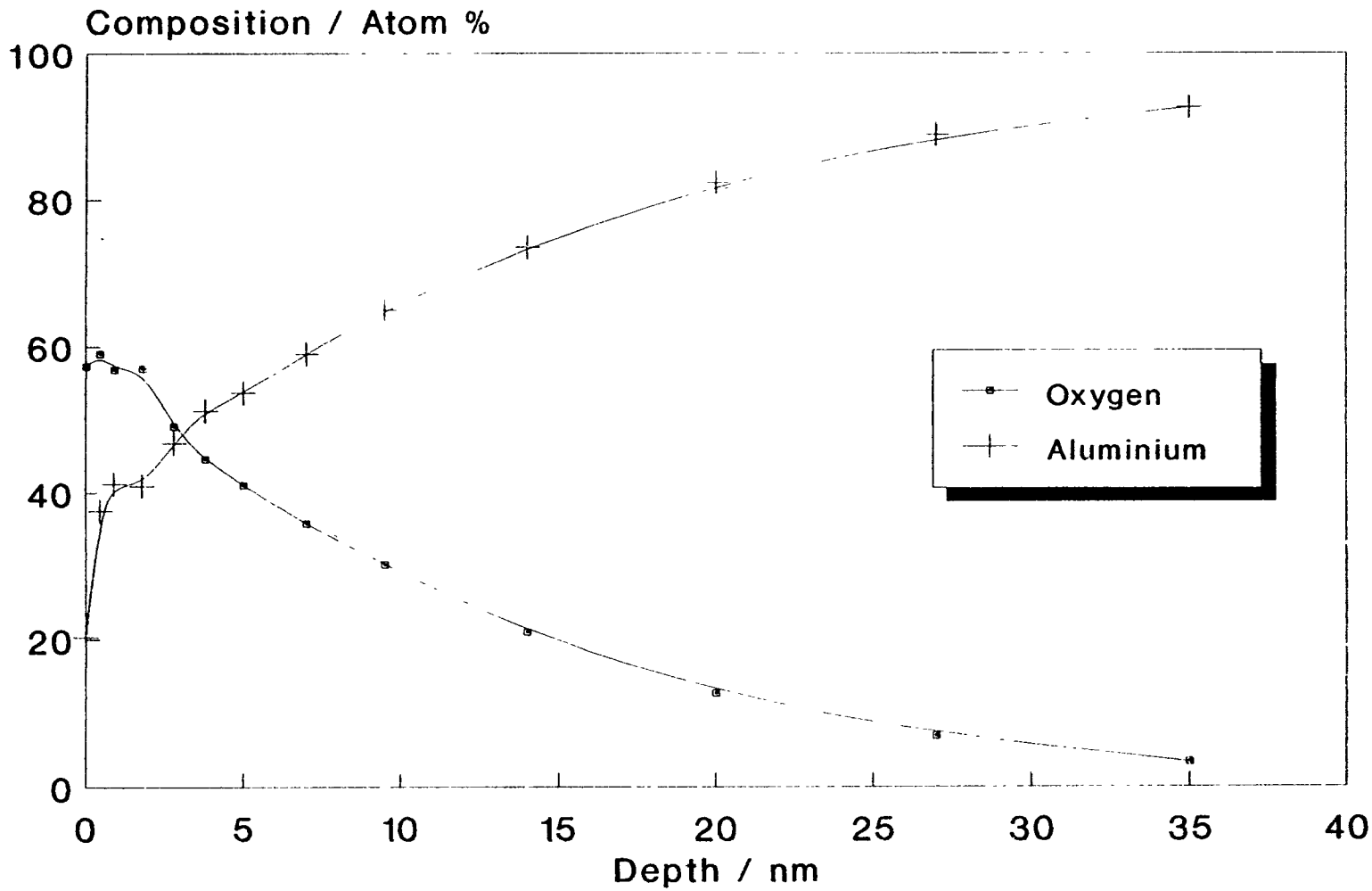

Figure 16 - Auger Depth Profile

8 Days in Gelled Acid
Blown Dry in Nitrogen

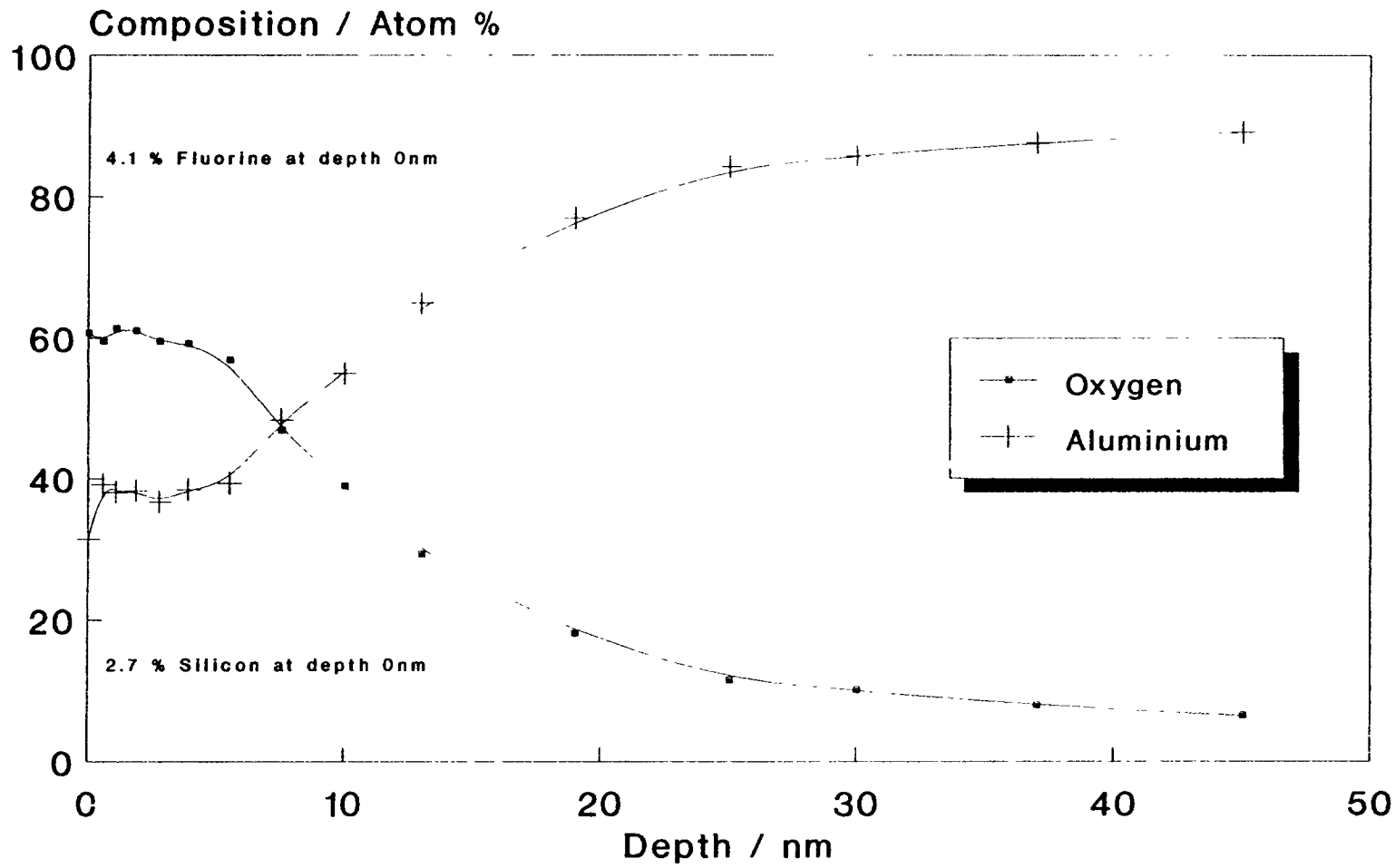

Figure 17 - Auger Depth Profile

8 days in Gelled Acid
Water washed

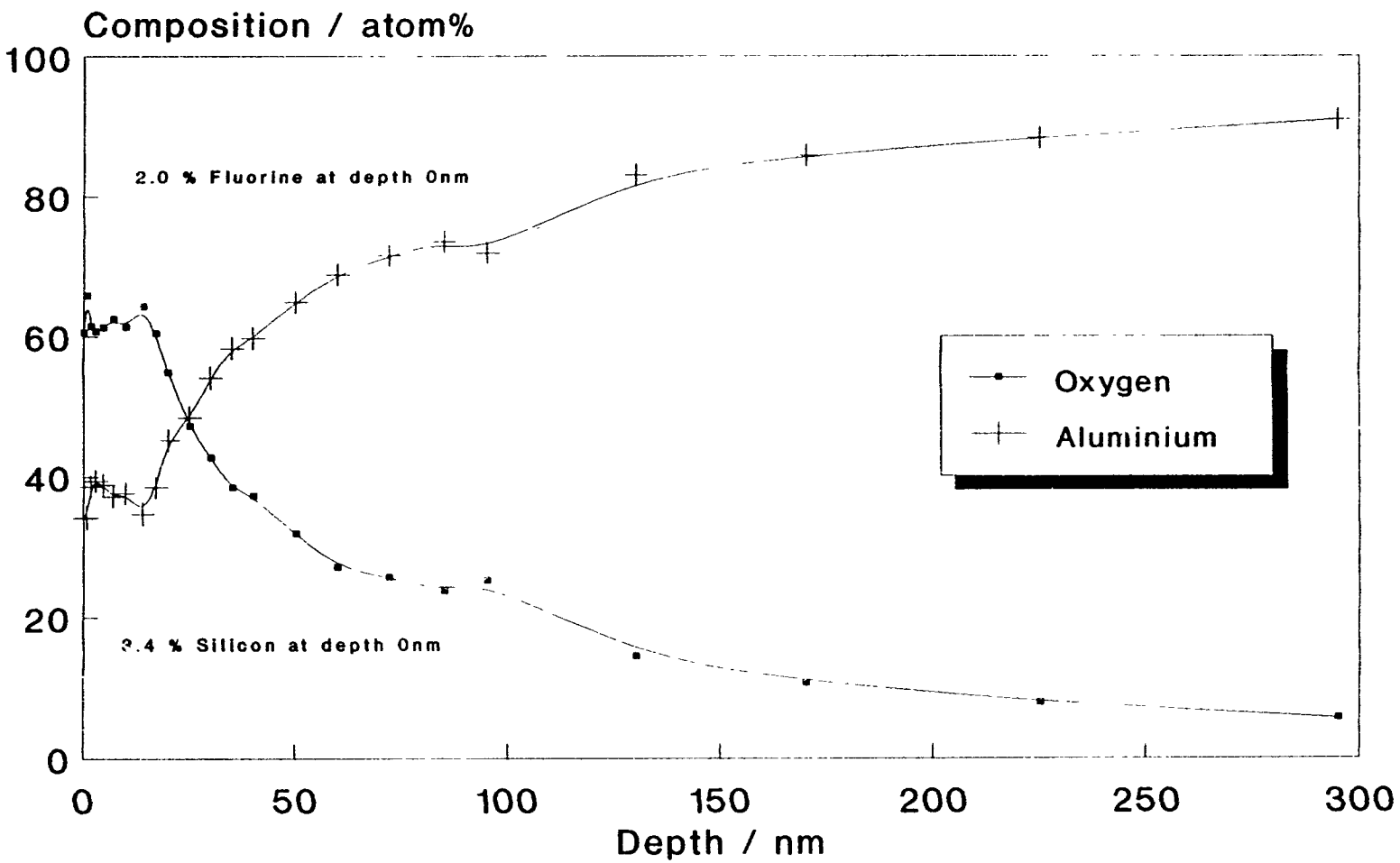

Figure 18 - Aluminium to Oxygen Ratios

From AES Spectra

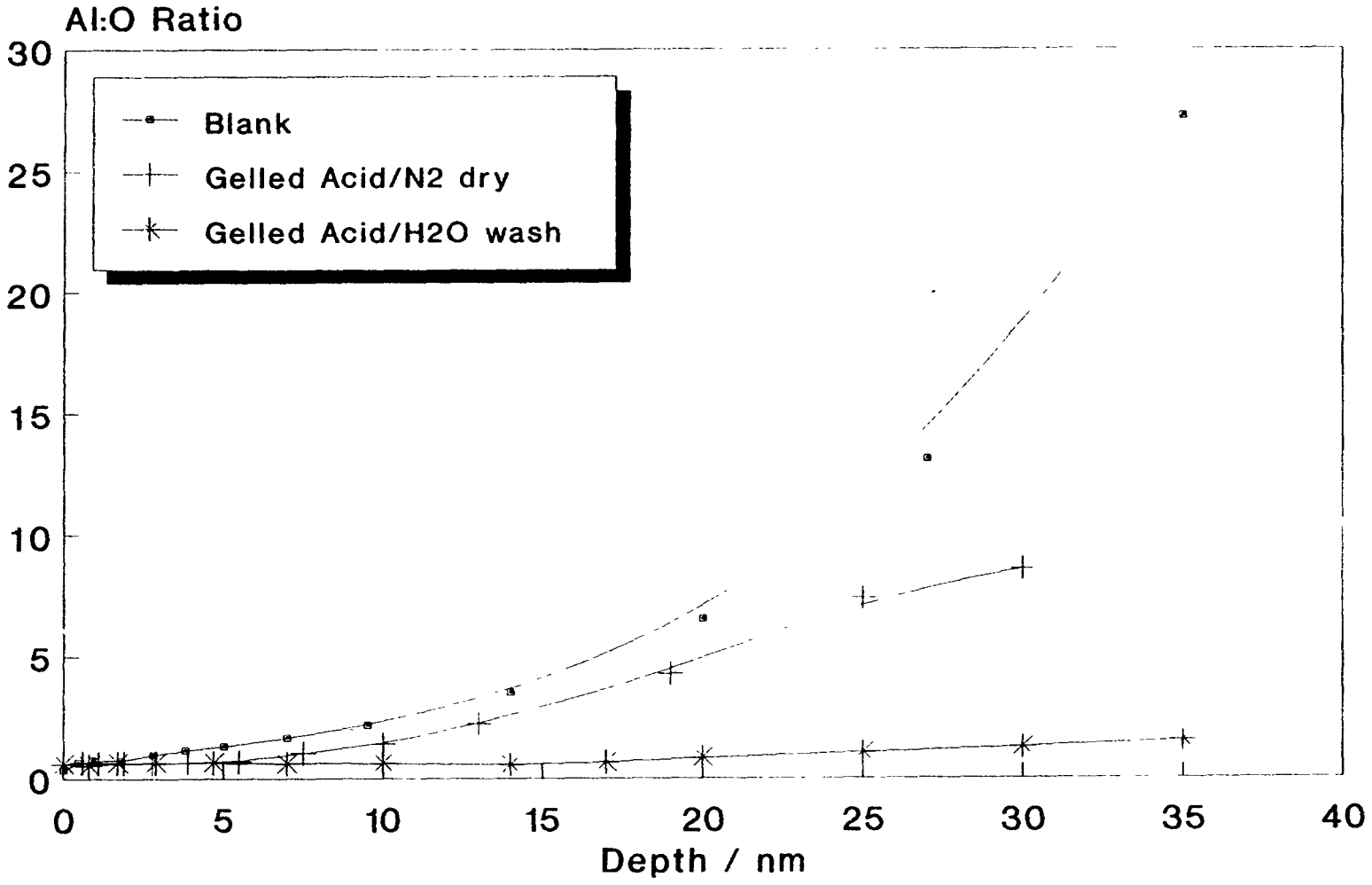

Figure 19 - Weight Loss Study

2014 Al / Set A

No Pre-treatment

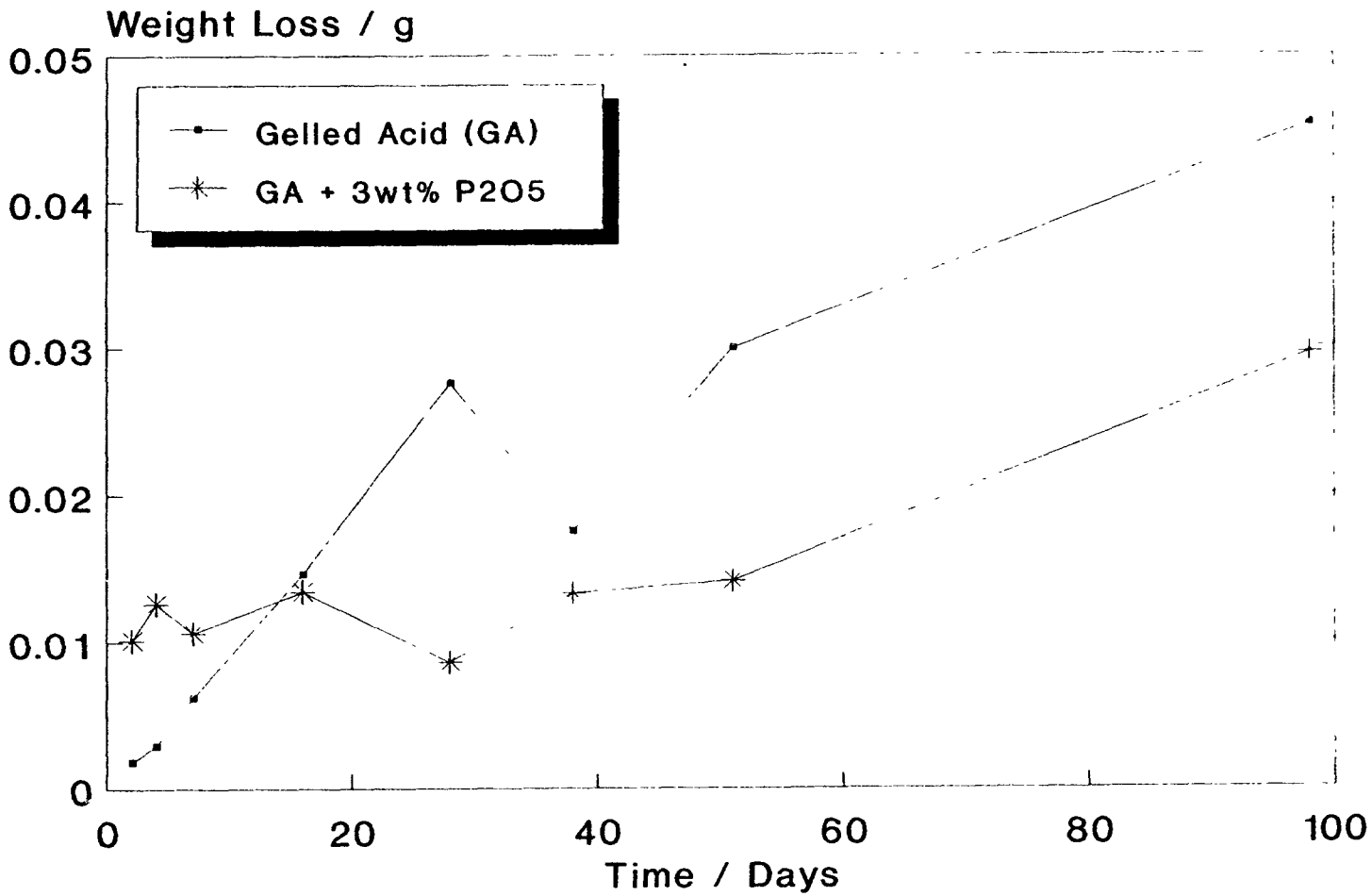

Figure 20 - Weight Loss Study

2014 Al / Set A

No Pre-treatment

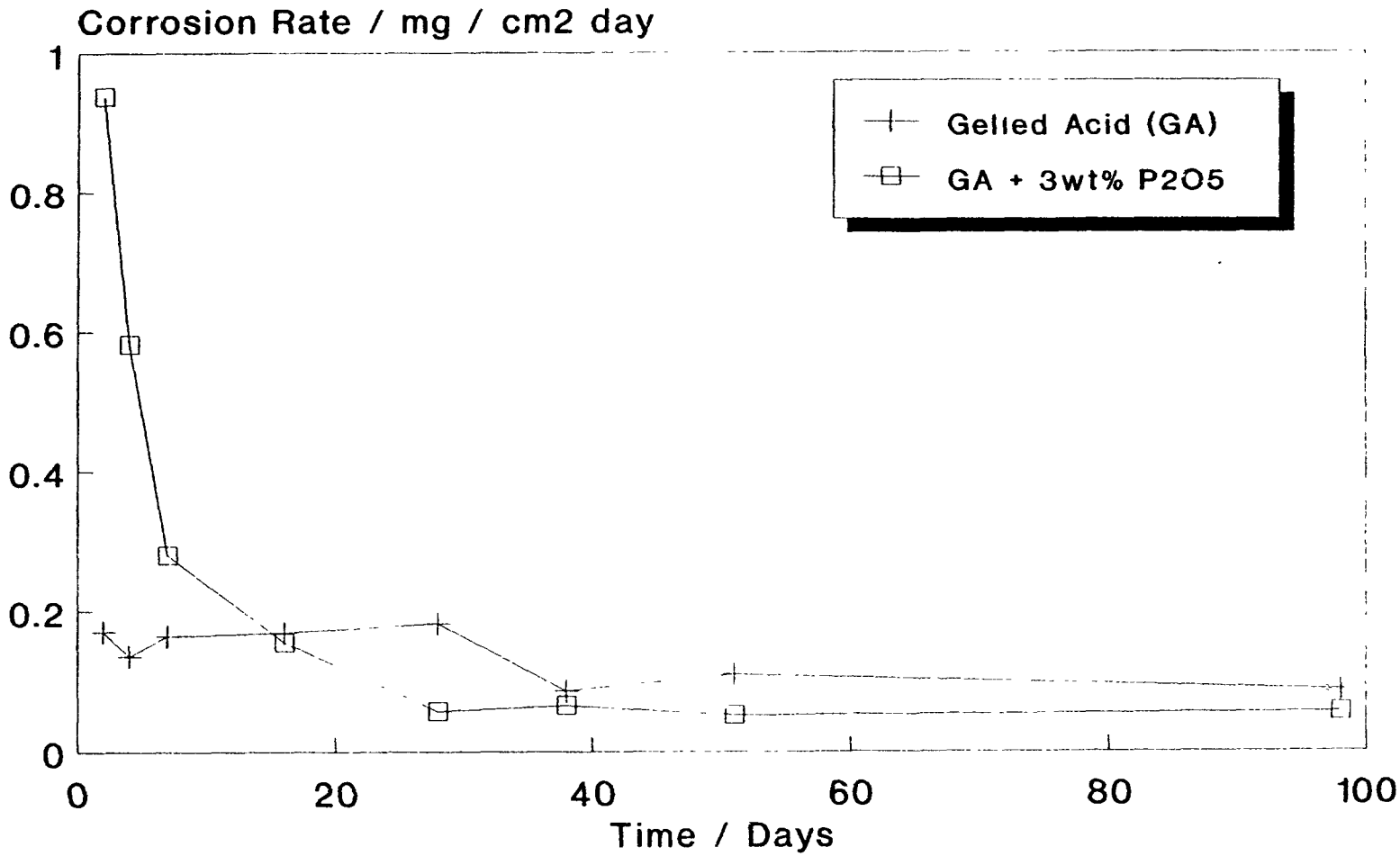

Figure 21A - Weight Change Study

Set B - No Pretreatment

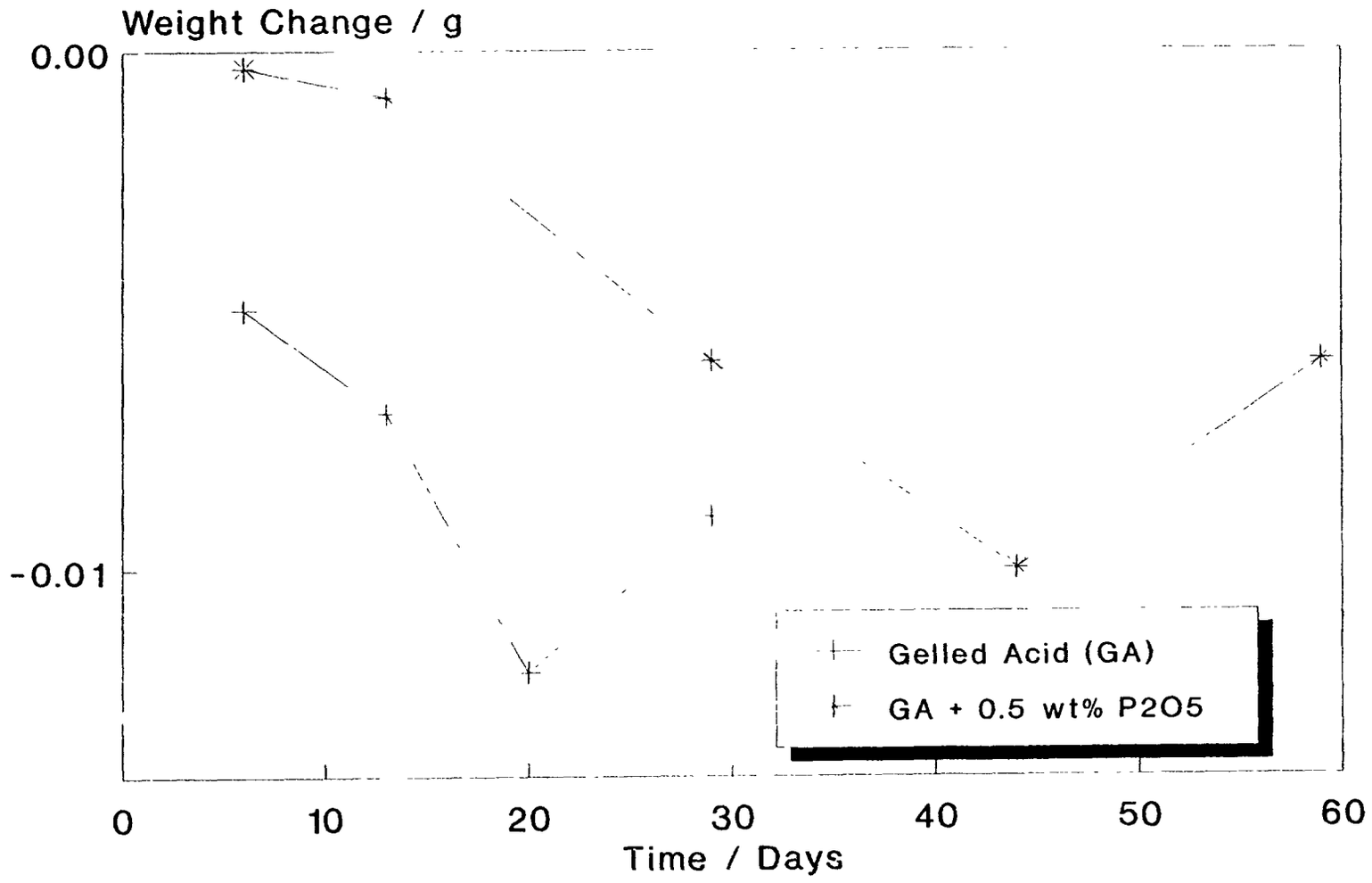

Figure 21B - Weight Change Study

Set B - No Pretreatment

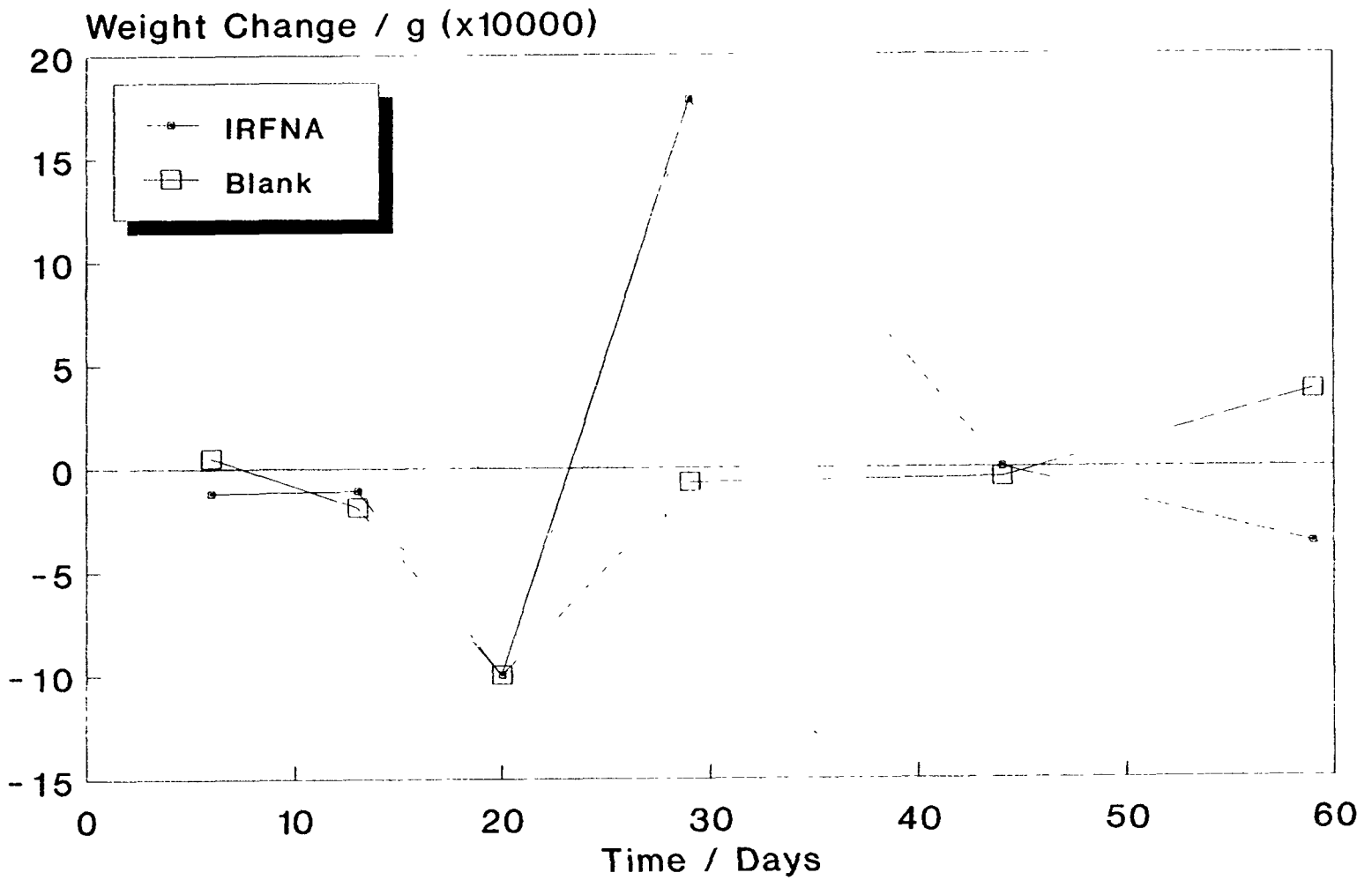

Figure 22A- Weight Change Study

Set B - No Pretreatment

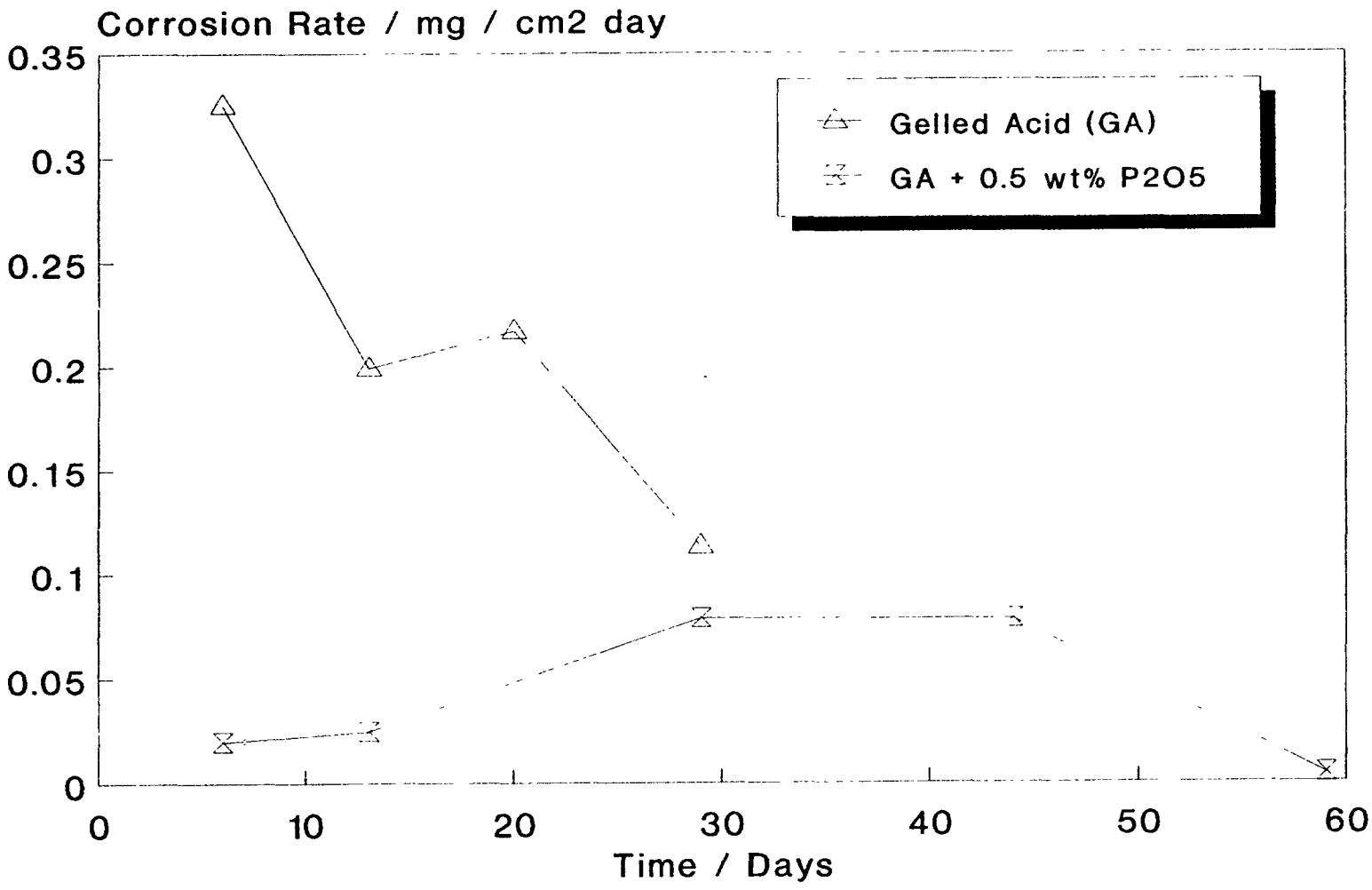

Figure 22B - Weight Change Study

Set B - No Pretreatment

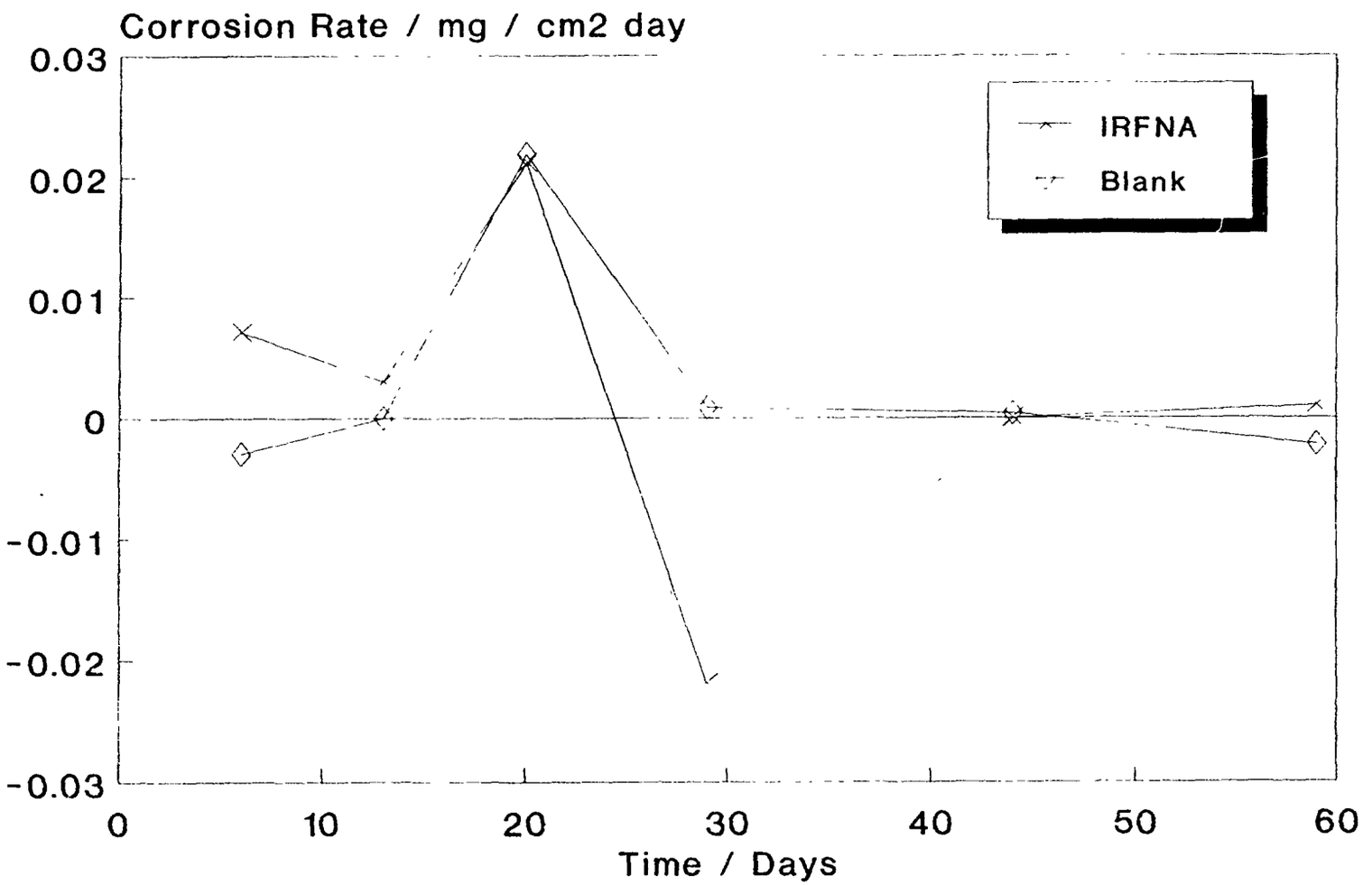

Figure 23 - Weight Change Study

Set B - ClF3 Pretreatment

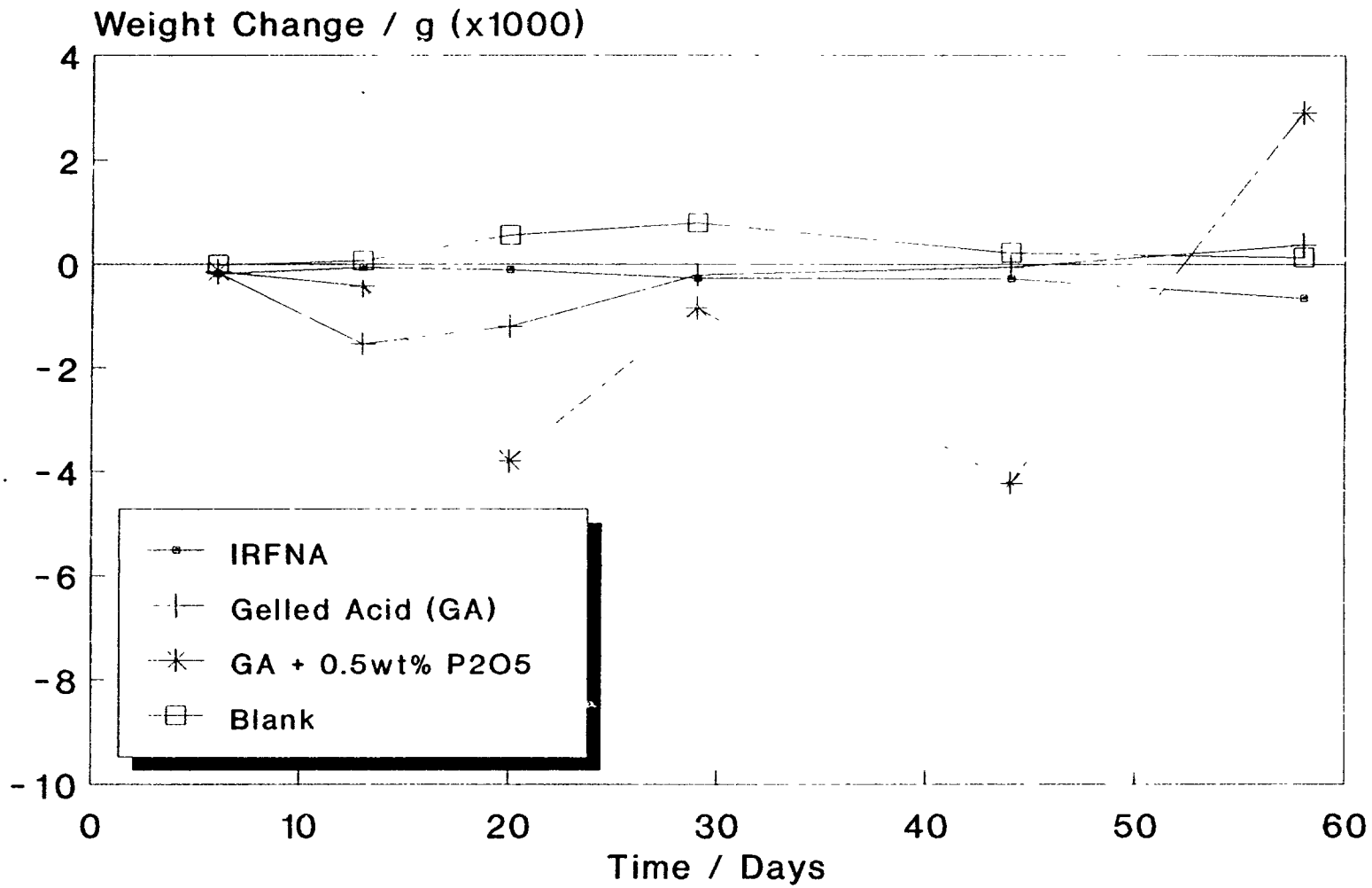

Figure 24 - Weight Change Study

Set B - ClF3 Pretreatment

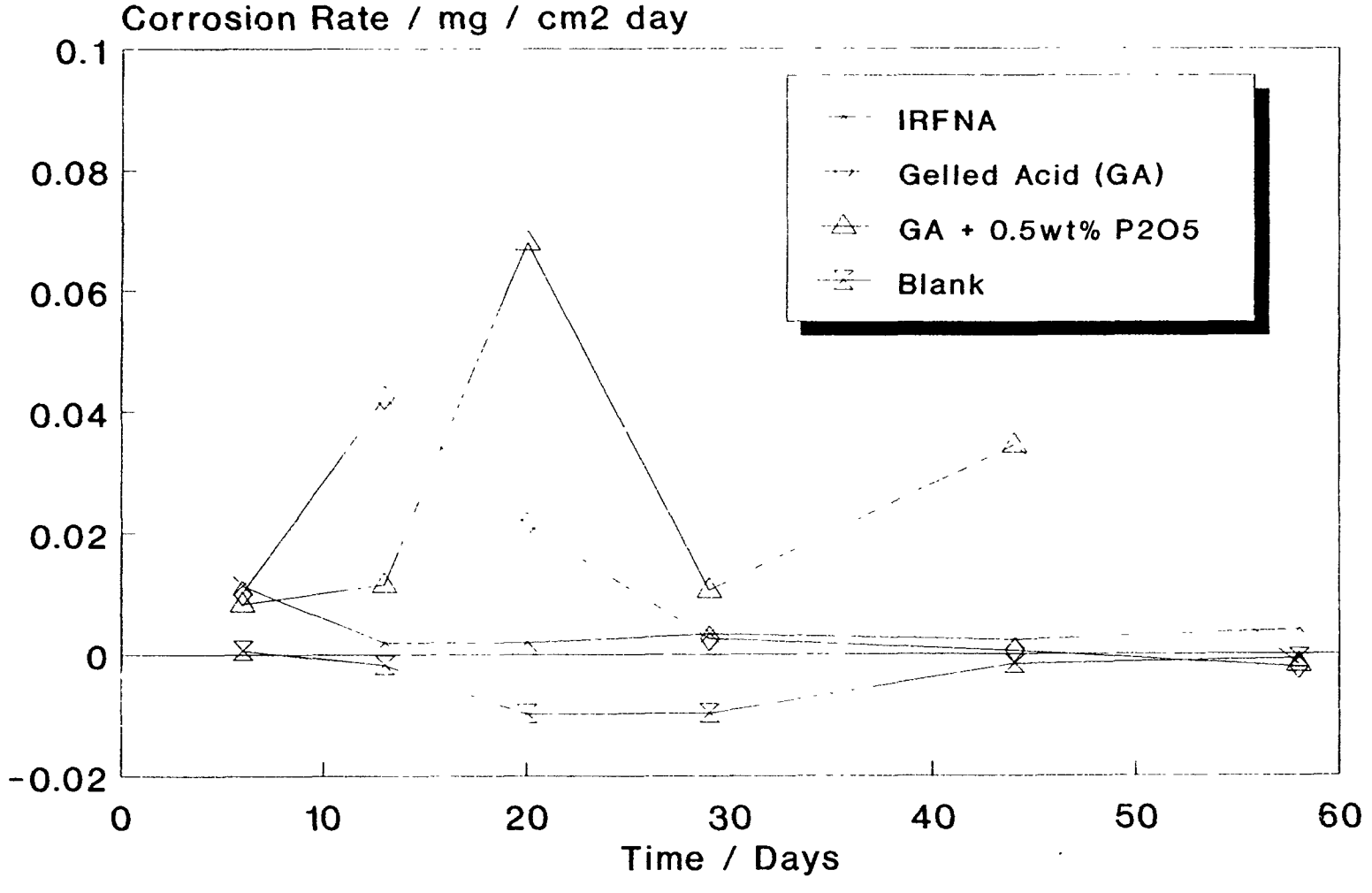

Figure 25 - Constant temperature (25C)

Ecorr and Rp vs Time
Cell GA3

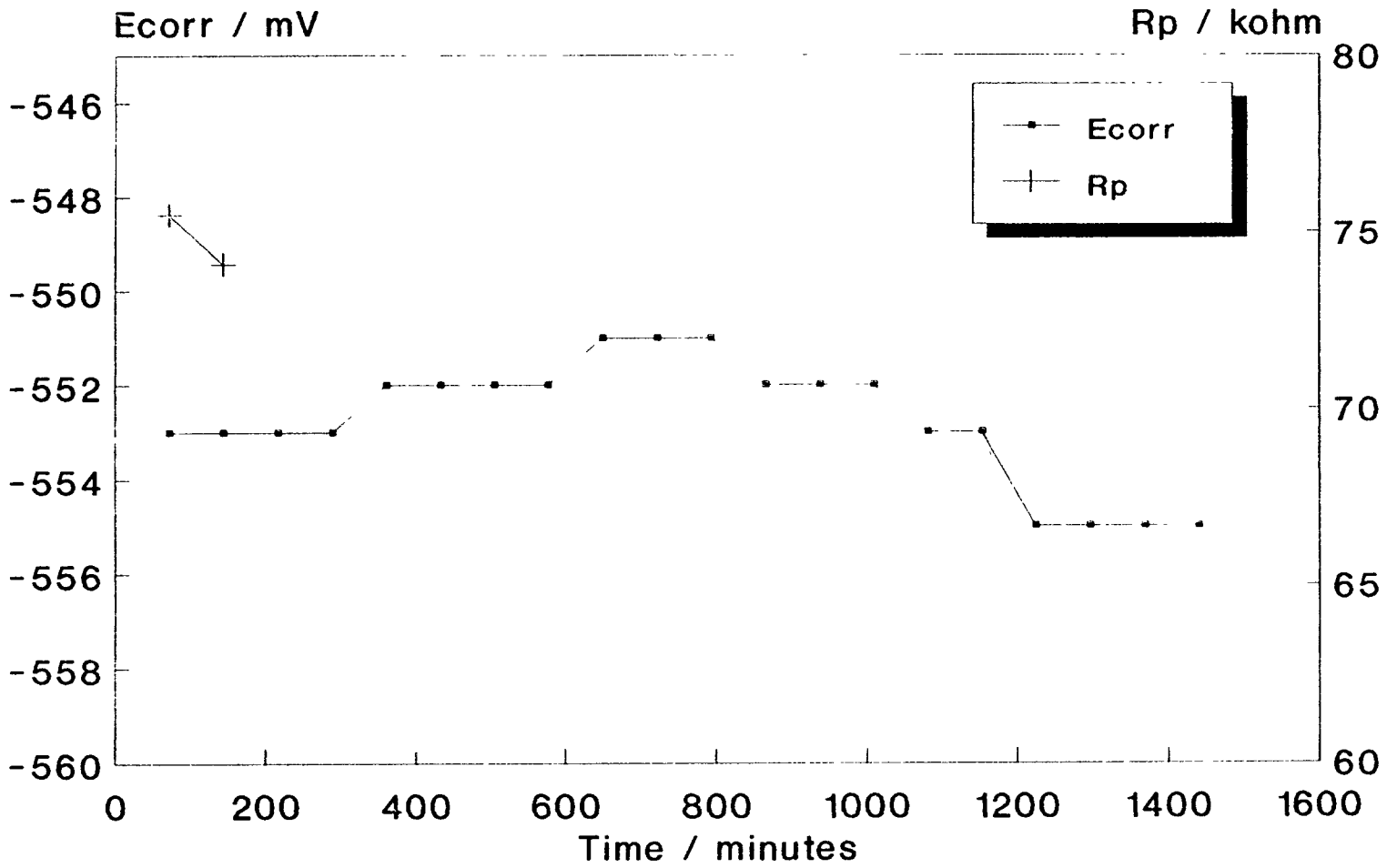

Figure 26 - Constant Temperature (25C)

Ecorr and Rp vs Time
Cell GA4

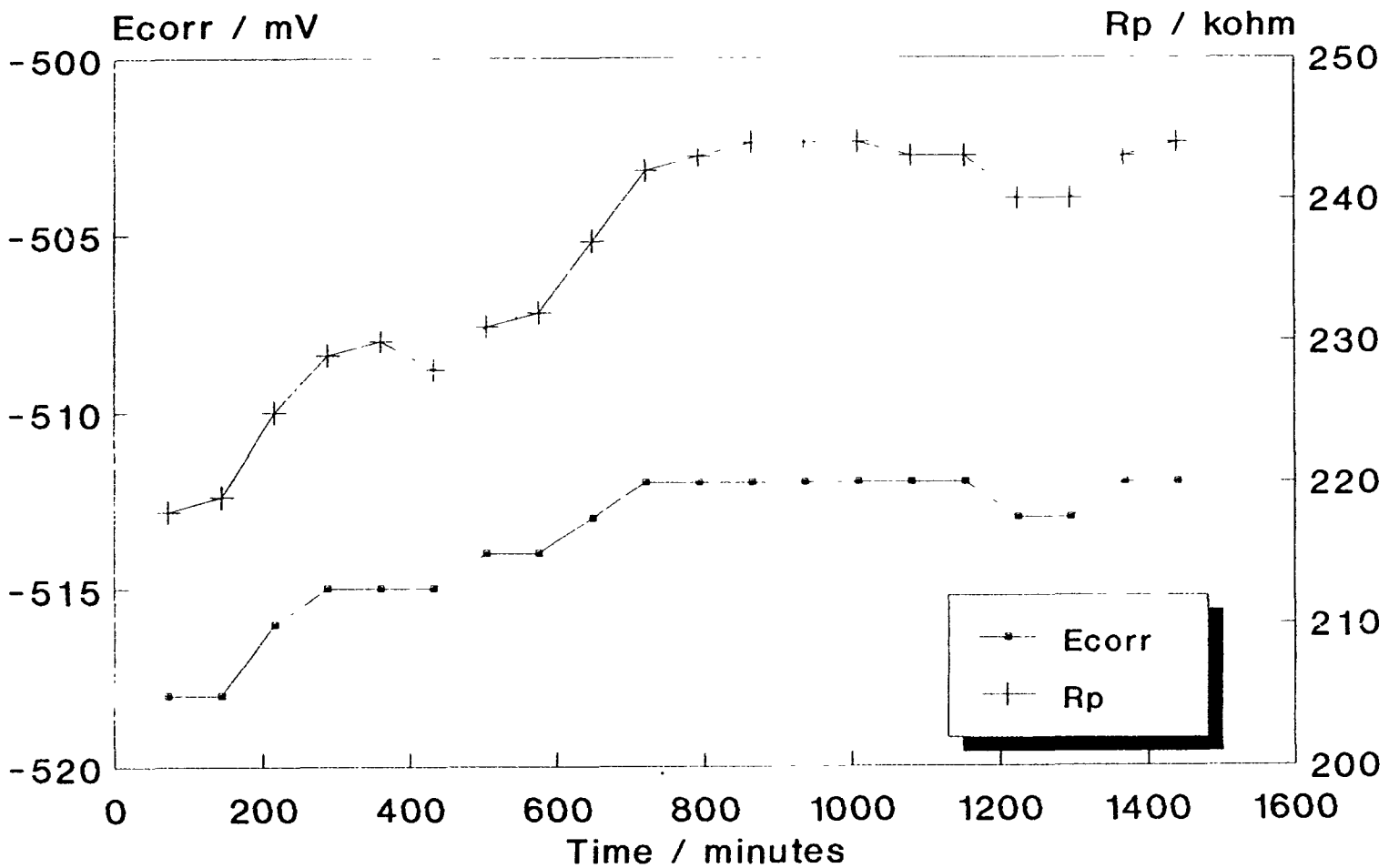

Figure 27 - Temperature cycle

From 5C to 45C

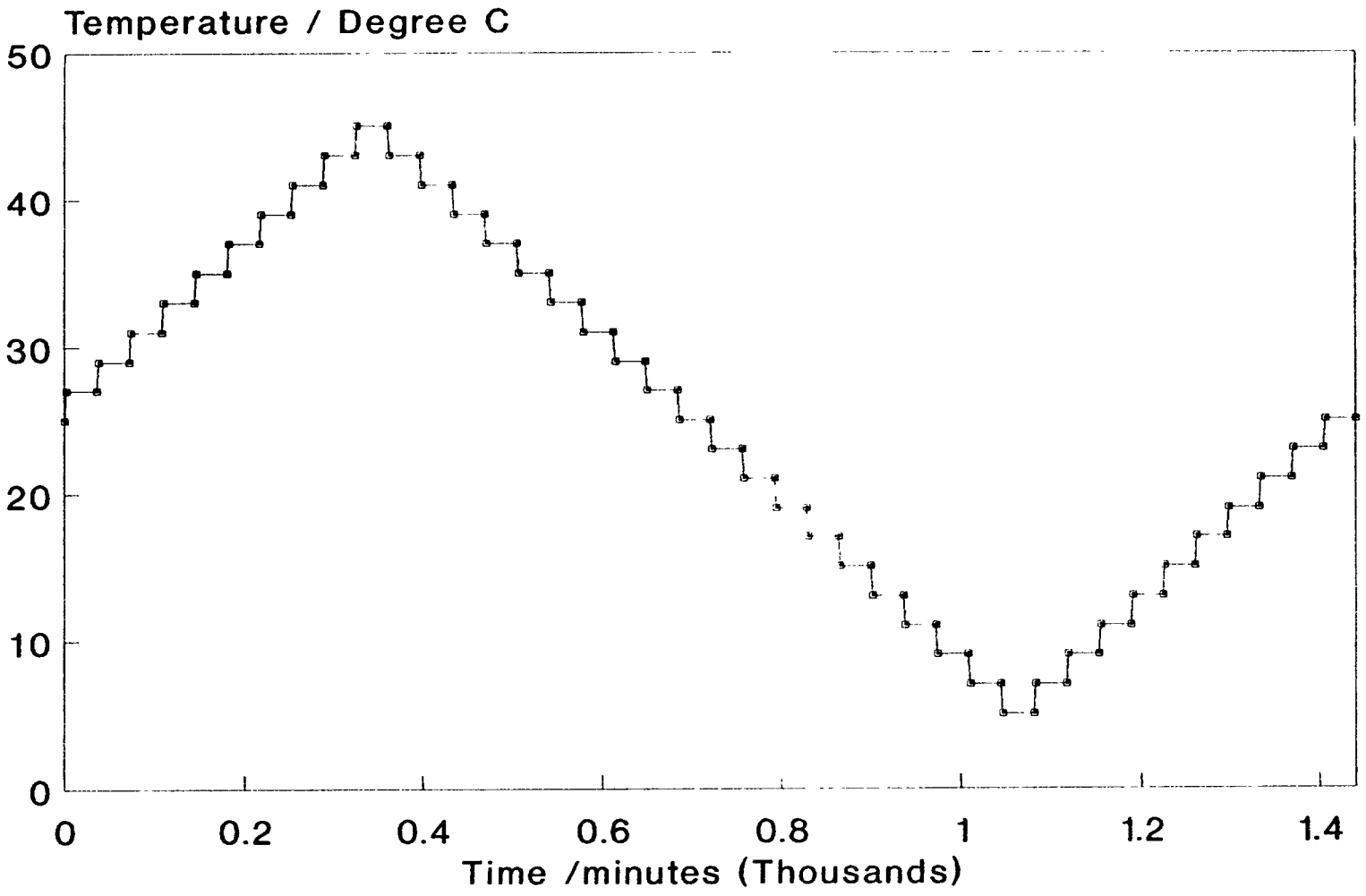

Figure 28 - Cell GA3

Ecorr and Rp vs Time

Temperature Cycle from 5C to 45C

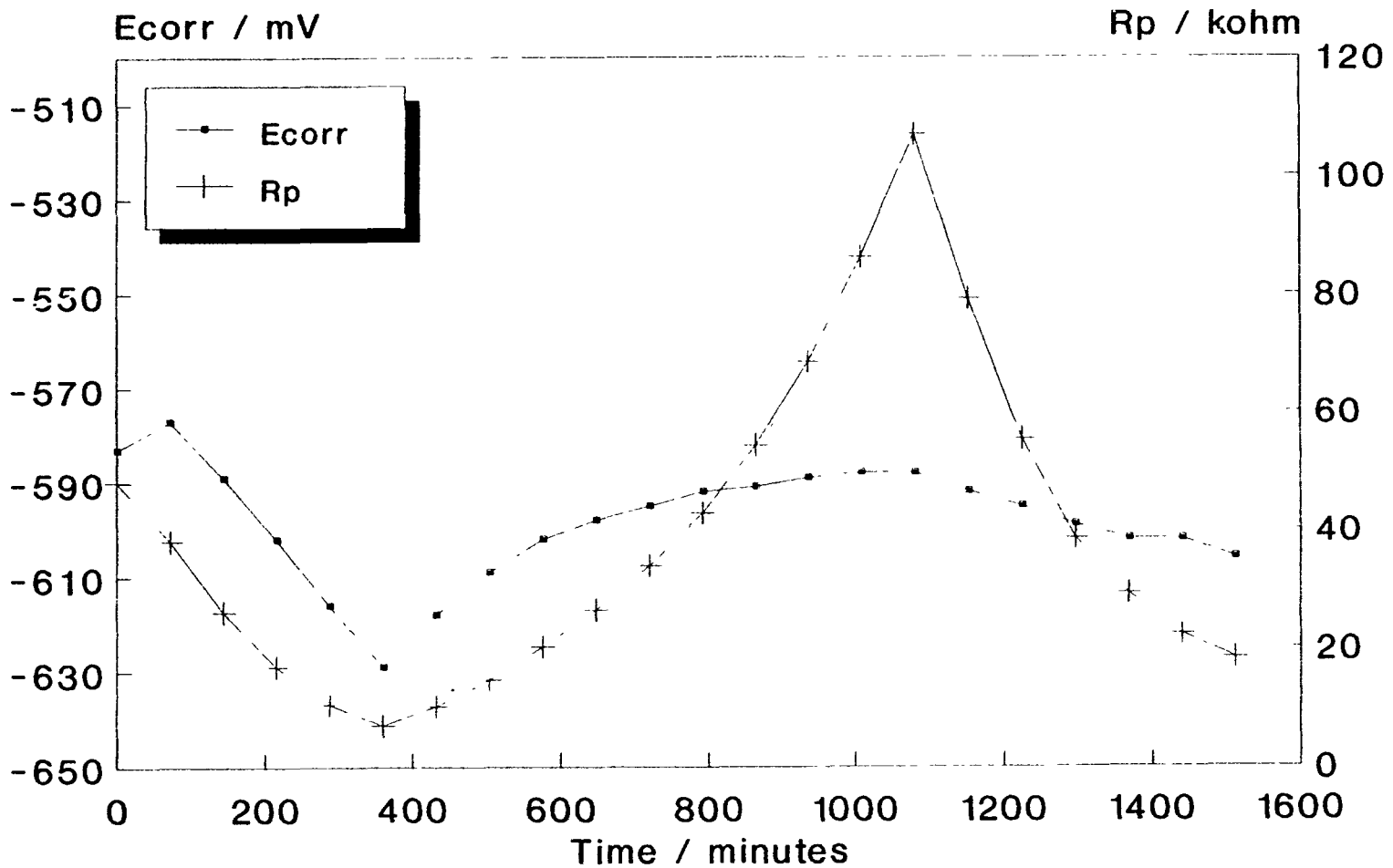

Figure 29 - Cell GA4

Ecorr and Rp vs Time

Temperature cycle from 5C to 45C

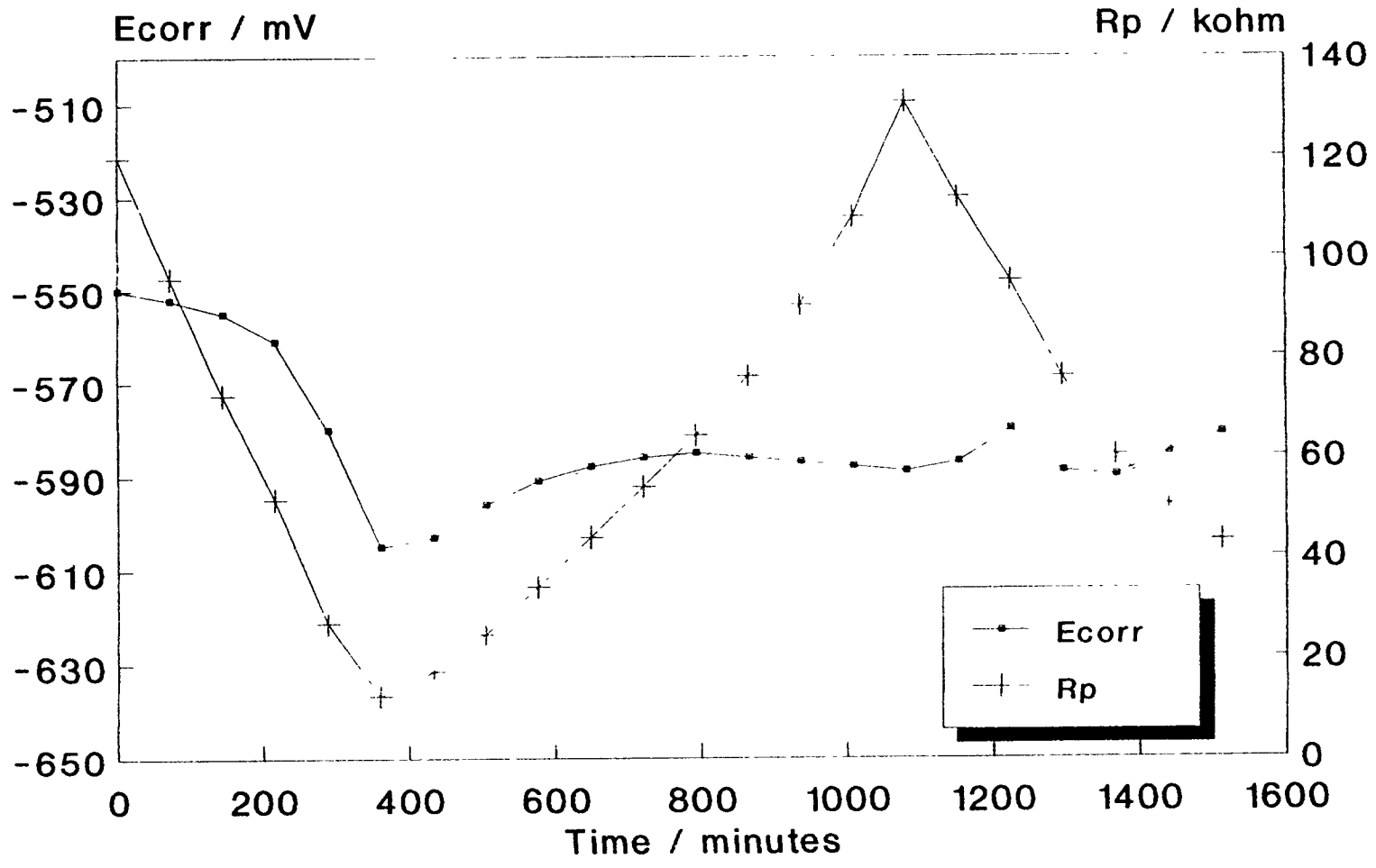

Figure 30 - Arrhenius Plot

Cells GA3 and GA4

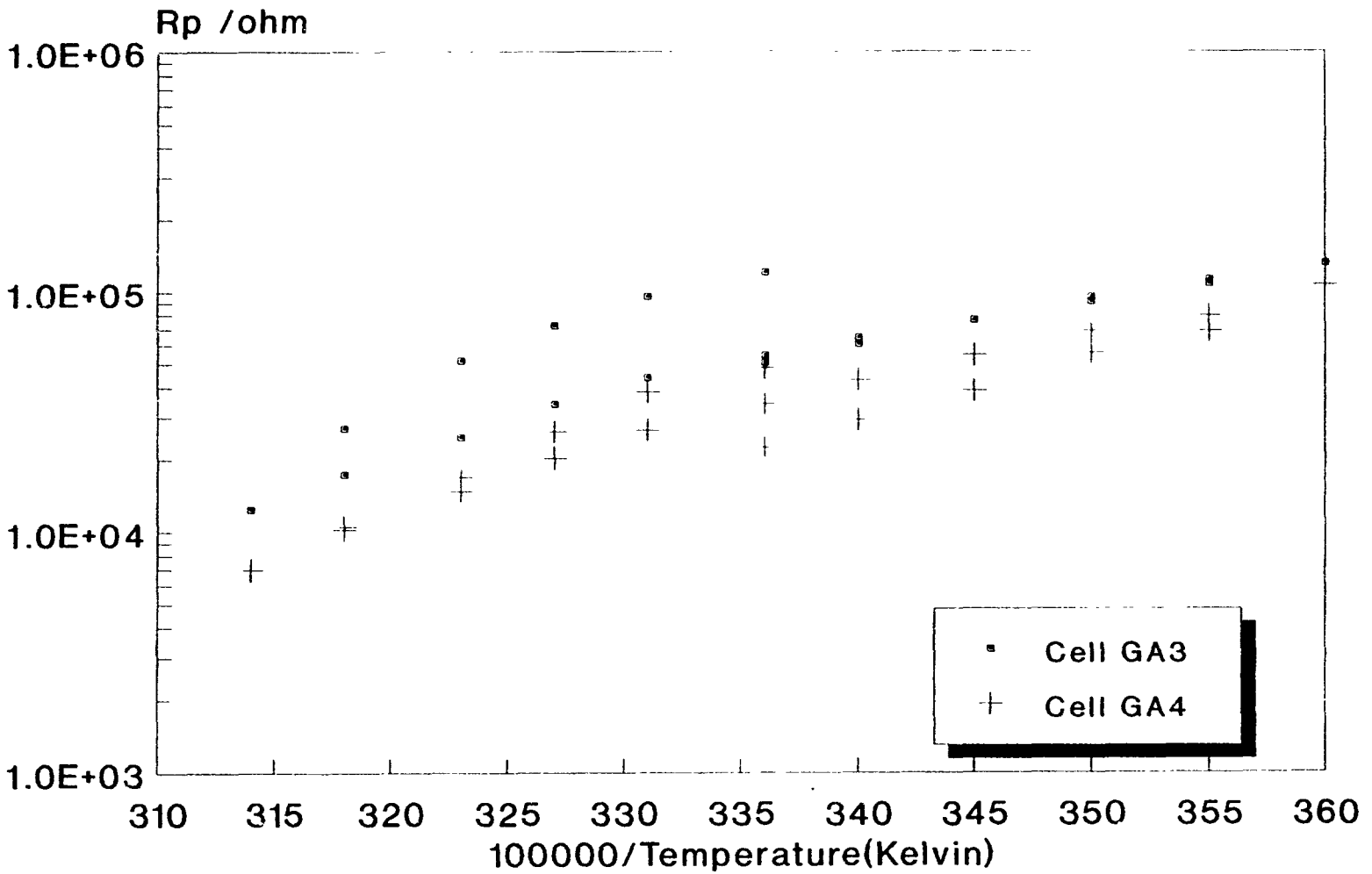

Figure 31 - Auger Depth Profile

2014Al GA + 0.5wt%P2O5
after 90 days immersion

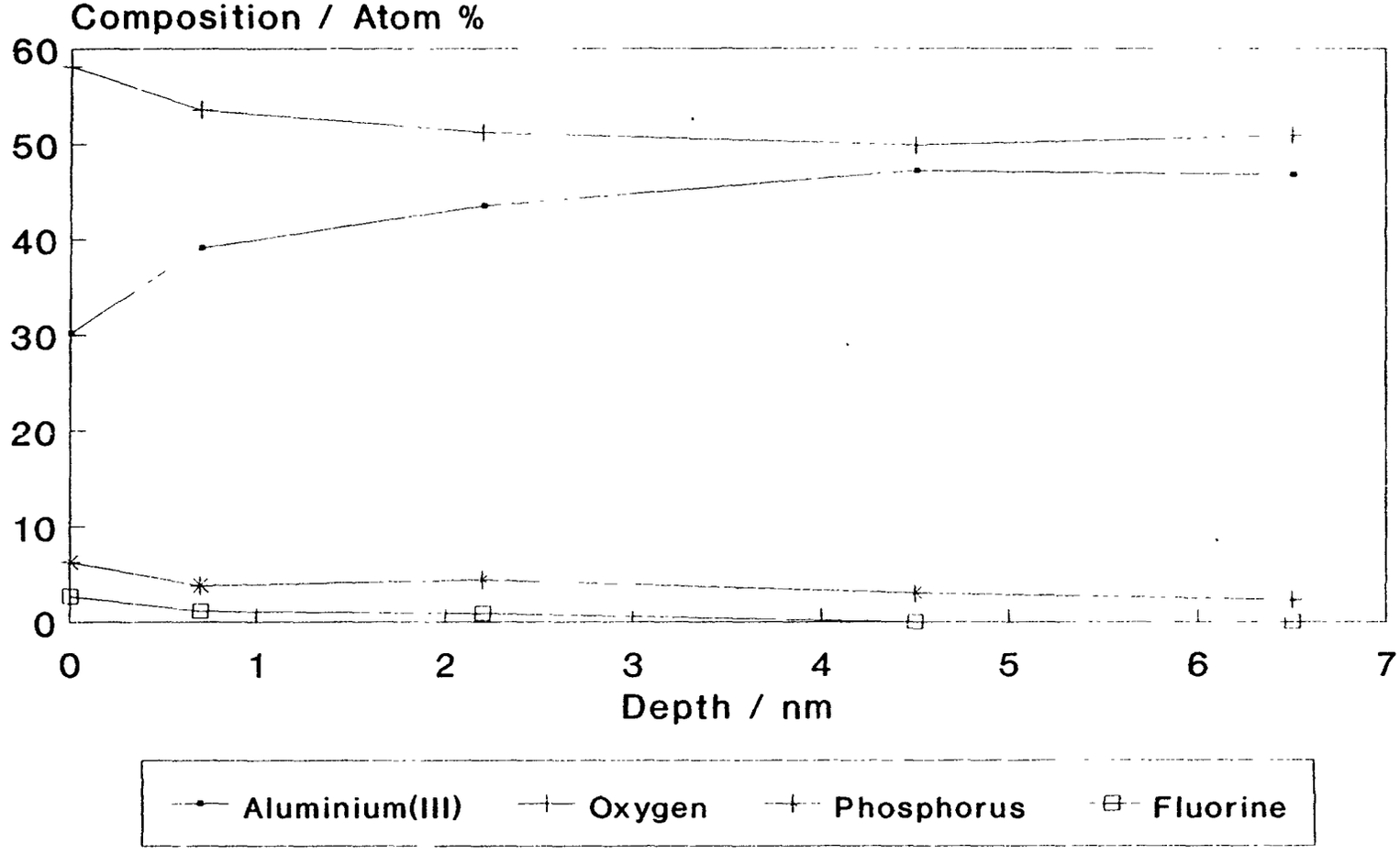

Figure 32 - Auger Depth Profile

2014Al (ClF3 Treated) GA+0.5wt%P2O5
after 90 days immersion

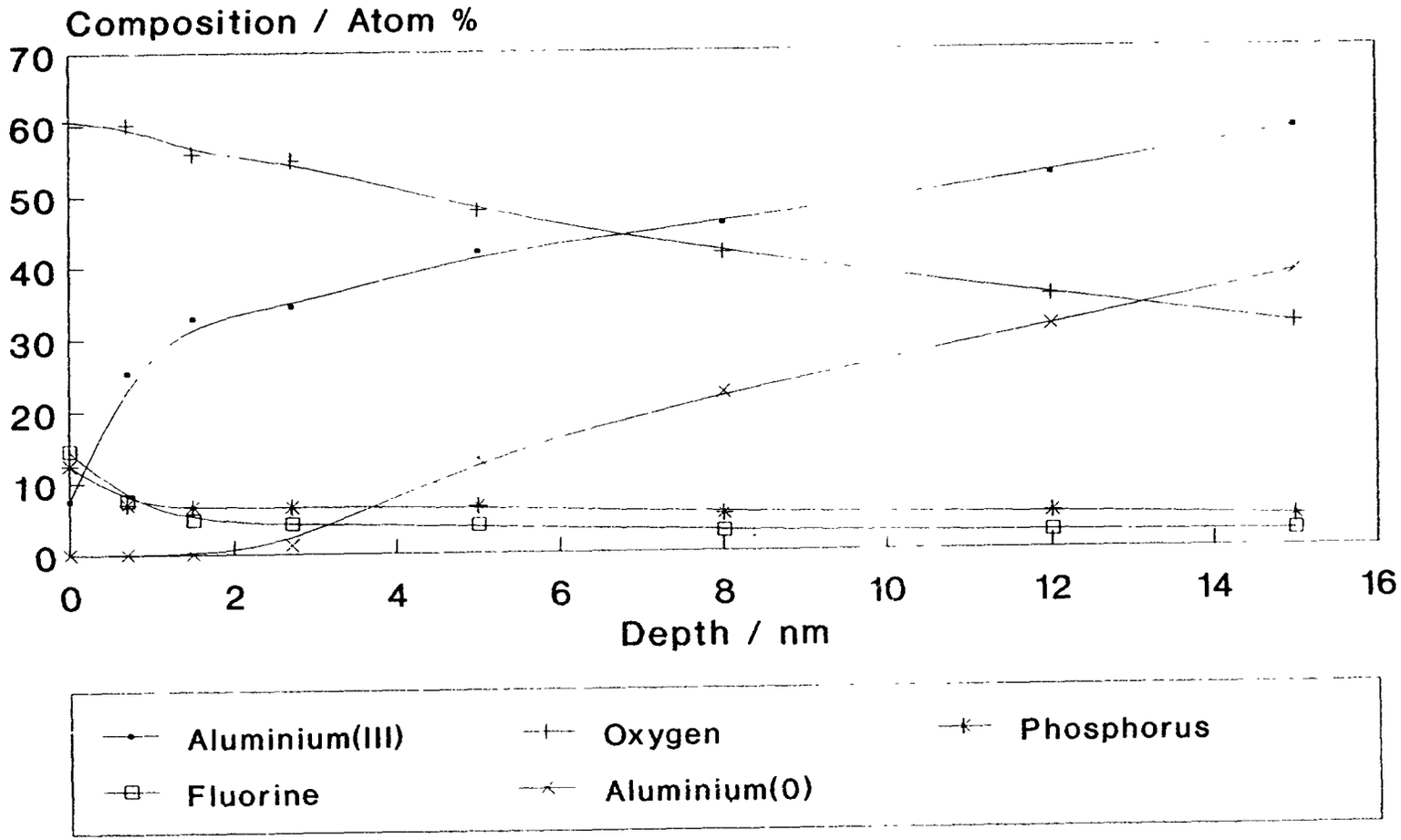

Table 1: Cell Details

Cell Code	Date Set up	Date Dismantled	Pretreatment	Acid Used	Charge of Acid/g
GA1	23/10/89	24/01/90	None	GA	16.54
GA2	23/10/89	06/11/89	None	GA	16.44
GA3	24/10/89		None	GA	16.64
GA4	24/10/89		None	GA	16.32
GA5	15/11/89	17/07/90	HF/F_2	GA	13.97
GA6	19/01/90	17/07/90	Electropolished and Anodised	GA	16.08
GA7	13/03/90		None	MGA-3	16.72
GA8	18/05/90		ClF_3	GA	16.44
GA9	18/05/90		ClF_3	GA	17.16
GA10	27/07/90		None	MIRFNA-3	14.39
GA11	27/07/90		None	MGA-3	17.51

GA = Gelled Acid (Gelled IRFNA)
MGA-3 = Modified Gelled Acid (containing 3wt% P_2O_5)
MIRFNA-3 = Modified IRFNA (containing 3wt% P_2O_5)

Table 2: XPS Data Obtained on Blank Sample of 2014 Aluminium

Table 2.1 - Surface composition

	Elemental Concentration / Atom %					
Etch time /minutes	C	O	Al	Si	F	Mg
0	23.6	37.9	23.6	11.7	2.0	1.3
1	18.0	36.0	31.6	10.1	1.1	1.3
4	6.8	41.6	37.3	10.0	0.8	0.8

Table 2.2 - Peak Binding Energies (Unetched surface)

Element	Peak	Binding Energy /eV
Al	2p	71.9 74.2
Si	2p	99.8
O	1s	531.8
F	1s	684.9

Table 3: XPS Data Obtained on a 2014 Aluminium Coupon Immersed In Gelled Acid at 25°C for 30 Days and Dried in a Stream of Dry Nitrogen

Table 3.1 - Surface Composition

	Elemental Concentration / Atom %					
Etch Time /minutes	C	O	Al	Si	F	N
0	27.0	42.0	9.7	7.5	4.5	7.6
1	19.1	41.0	17.9	13.5	6.2	2.4

Table 3.2 - Peak Binding Energies (Unetched surface)

Element	Peak	Binding Energy /eV
Al	2p	75.6
Si	2p	102.1
N	1s	407.7
O	1s	532.4
F	1s	687.6

Table 4: XPS Data Obtained on a 2014 Aluminium Coupon Immersed in Gelled Acid at 25°C for 30 Days and Water-Washed

Table 4.1 - Surface Composition

Etch Time /minutes	Elemental Concentration / Atom % C	O	Al	Si	F	N
0	25.2	46.2	13.5	6.2	4.5	4.5
1	9.9	46.1	24.9	12.8	5.2	0
4	10.6	42.8	27.9	14.1	3.0	0

Table 4.2 - Peak Binding Energies (Unetched surface)

Element	Peak	Binding Energy /eV
Al	2p	74.5
Si	2p	100.4
N	1s	407.1
O	1s	532.3
F	1s	685.4

Table 5: Weight Loss Experiments: Set A

(Comparing Gelled Acid with Gelled Acid Containing 3 wt% P_2O_5)

Number of Coupons	Type of Acid Used
8	Gelled Acid
8	Gelled Acid + 3wt% P_2O_5

The 2014 aluminium coupons used in set A were 2 x 1 x 0.2cm. The area of each coupon was 5.2cm^2. Temperature 25°C.

Table 6: Weight Loss Experiments: Set B

(Comparing Gelled Acid with Gelled Acid Containing 0.5 wt% P_2O_5)

Number of Coupons	Pretreatment	Type of Acid Used
8	None	Gelled Acid
8	None	Gelled Acid + 0.5 wt% P_2O_5
8	None	IRFNA
8	None	None
8	ClF_3	Gelled Acid
8	ClF_3	Gelled Acid + 0.5 wt% P_2O_5
8	ClF_3	IRFNA
8	ClF_3	None

The 2014 aluminium coupons used in set B were 1 x 1 x 0.2cm. The area of each coupon was 2.8cm^2. Temperature 25°C.

Table 7 : Arrhenius Parameters

Cell Code	Arrhenius Constant	Activation Energy /kJmol^{-1}	Correlation Coefficient
GA3	2.95×10^{3}	45.4	0.912
GA4	1.93×10^{1}	34.4	0.898

Table 8A

Estimated Polarisation Resistance (R_p) from Electrochemical Studies and Approximate Steady State Corrosion Rate (SSCR) from Weight Change Studies of 2014 Al Alloy in Various Corrosive Media after Specified Immersion Times.

Acid (Pre-treatment)	BW Cell	$R_p/k\Omega$+ 25d*	60d*	100d*	SSCR/mgcm^{-2}day^{-1}(60d*) Set A[a]	Set B[b]
GA	GA1	4.8	58.9	132.3(93d)	0.100	0.113(29d)
	GA3	4.4	18.5	113.6		
	GA4	24.4	214.8	324.3		
GA(ClF_3)	GA8	33.1	50.0(52d)	-	-	*ca.*0.000(58d)
	GA9	7.4	106.6(53d)	-		
GA(HF/F_2)	GA5	4.7	19.0	109.6	-	-
GA(E+A)	GA6	7.0	61.9	48.9	-	-
MGA-3	GA7	47.8	1000.0	9775.7	0.052	-
	GA11	46.6(23d)	-	-		
MIRFNA-3	GA10	6000.0(23d.)	-	-	-	-
IRFNA	-	-	-	-	-	0.001(59d)
IRFNA(ClF_3)	-	-	-	-	-	0.004(58d)
MGA-0.5	-	-	-	-	-	0.004(59d)
MGA-0.5(ClF_3)	-	-	-	-	-	*ca.*0.000(58d)

GA	Gelled Acid (Gelled IRFNA)
MGA-3	Modified Gelled Acid (containing 3wt.% P_2O_5)
MGA-0.5	" " " (" 0.5wt.% P_2O_5)
MIRFNA-3	Modified IRFNA (containing 3wt.% P_2O_5)
E+A	electropolishing and anodising pre-treatment
d	days
*	unless otherwise indicated
a	see Table 5 for details of experimental conditions
b	" " 6 " " " " "
+	to convert R_p (ohms) to the instantaneous corrosion rate of aluminium (mgcm^{-2}day^{-1}) at 298.15K(25C) use $\frac{205.2}{R_p}$

(see Appendix and also Table 8B).

Table 8B

Instantaneous Corrosion Rate (ICR) from Electrochemical Studies and Approximate Steady State Corrosion Rate (SSCR) from Weight Change Studies of 2014 Al Alloy in Various Corrosive Media after Specified Immersion Times.

Acid (Pre-treatment)	BW Cell	ICR/mgcm^{-2}day^{-1} 25d*	60d*	100d*	SSCR/mgcm^{-2}day^{-1} (60d*) Set A[a]	Set B[b]
GA	GA1	0.043	0.0035	0.0015 (93d)	0.100	0.113 (29d)
	GA3	0.0466	0.0111	0.0018		
	GA4	0.0084	0.0010	0.0006		
GA(ClF_3)	GA8	0.0062	0.0041 (52d)	-	-	*ca.* 0.000 (58d)
	GA9	0.0277	0.0019 (53d)	-		
GA(HF/F_2)	GA5	0.0437	0.0108	0.0019	-	-
GA(E+A)	GA6	0.0293	0.0033	0.0042	-	-
MGA-3	GA7	0.0043	0.0002	$\leq$ 0.0001	0.052	-
	GA11	0.0044 (23d)	-	-		
MIRFNA-3	GA10	$\leq$ 0.0001 (23d)	-	-	-	-
IRFNA	-	-	-	-	-	0.001 (59d)
IRFNA(ClF_3)	-	-	-	-	-	0.004 (58d)
MGA-0.5	-	-	-	-	-	0.004 (59d)
MGA-0.5(ClF_3)	-	-	-	-	-	*ca.* 0.000 (58d)

GA	Gelled Acid (Gelled IRFNA)
MGA-3	Modified Gelled Acid (containing 3wt.% P_2O_5)
MGA-0.5	" " " (" 0.5wt.% P_2O_5)
MIRFNA-3	Modified IRFNA (containing 3wt.% P_2O_5)
E+A	electropolishing and anodising pre-treatment
d	days
*	unless otherwise indicated
a	see Table 5 for details of experimental conditions
b	" " 6 " " " " "

Table 9

Optical Microscopy (200x) of 2014 Al Alloy Coupons

Corrosive Medium* (Metal Pre-treatment)	Immersion Time/ Days	Observation
GA	29	ic
GA(ClF_3)	58	uc
IRFNA	59	uc
IRFNA(ClF_3)	58	uc
MGA-0.5	59	ic + black film
MGA-0.5(ClF_3)	58	uc + black film

* see footnotes to Table 8A or 8B for abbreviations

ic non-uniform (e.g. intergranular) corrosion

uc uniform corrosion

Appendix

Calculation of the instantaneous corrosion rate of aluminium(ICR)/ $mgcm^{-2}day^{-1}$ from polarisation resistance(R_p)/Ω

Corrosion current density (i_{corr}) can be calculated from the Stern-Geary relationship

$$i_{corr} = I_{corr}/a$$

$$= b_a(-b_c)/[(b_a-b_c)2.303R_pa]$$

and using the theoretically calculated Tafel constants b_a and b_c such that

$$b_a = 2.303RT/[z_aF\beta] \text{ and } -b_c = 2.303RT/[z_cF(1-\beta)]$$

where $R = 8.31441JK^{-1}mol^{-1}$

$T = 298.15K$ (25°C)

$z_a = 3$ ($Al \rightarrow Al^{3+} + 3e^-$)

$z_c = 1$ ($NO_2^+ + e^- \rightarrow \frac{1}{2}N_2O_4$)

$F = 96484.6Cmol^{-1}$

$\beta = 0.5$ (the symmetry factor or transmission coefficient)

a = electrode area(m^2)

i_{corr} = corrosion current density (Am^{-2})

I_{corr} = corrosion current(A)

R_p = polarisation resistance (Ω)

the Stern-Geary equation becomes

$$i_{corr} = [0.0128/R_pa]Am^{-2}$$

$$= [B/R_pa]Am^{-2}$$

where $B = b_a(-b_c)/[(b_a-b_c)2.303]$

and 0.0128 is, therefore, the theoretical value of B at 25°C assuming $\beta = 0.5$.

It is useful to remember that when i_{corr} is in units of Am^{-2}, then

the value is approximately equal to the wastage rate (penetration) of the surface of the metal in mmyear^{-1}[5].

Alternatively, B can be determined using values of b_a and b_c obtained from Tafel polarisation measurements.

As pointed out earlier[8], results obtained at Nottingham for RFNA, IRFNA and WFNA appear to fit best when

$$B = 0.045 \quad (T = 25^{o}C)$$

To convert the corrosion current density, $i_{corr}(Am^{-2})$ = $B/R_p a$ to the instantaneous corrosion rate (ICR) of aluminium ($mgcm^{-2}day^{-1}$) for the working electrode ($a = 1.767 \times 10^{-4}m^2$) of the bottom working electrode (BWE) cells used in the electrochemical studies described in this Report, the detailed expression is

$$ICR/mgcm^{-2}day^{-1} = \frac{B \times 10^{-4} \times 60 \times 60 \times 24 \times 9 \times 10^{3}}{R_p \times 1.767 \times 10^{-4} \times 96484.6}$$

$$= \frac{4561.017B}{R_p}$$

which, when B = 0.045

$$= \frac{205.2}{R_p}$$

This conversion factor of 205.2 is therefore recommended for the R_p values of Table 8A (but see the cautionary note in Section 6.1 concerning the use of the ICR values in Table 8B).

Thus, considering the GA(ClF_3) system

for cell GA8

R_p(52 days) = 50000Ω (Table 8A)

and the ICR of aluminium

$$= \frac{205.2}{50000} = 0.0041 mgcm^{-2}day^{-1} \text{ (Table 8B)}$$

and for cell GA9

R_p(53 days) = 106600Ω (Table 8A)

and the ICR of aluminium

$$= \frac{205.2}{106600} = 0.0019 mgcm^{-2}day^{-1} \text{ (Table 8B)}$$

This is to be compared with the steady state corrosion rate (SSCR) of 2014Al alloy in the GA (ClF_3) system, determined by weight change after 58 days,

= *ca.*-0.000$mgcm^{-2}day^{-1}$ (Tables 8A and 8B).

References

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