AAEC/E270

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

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CORROSION OF ALUMINIUM IN PURE WATER AND DILUTE SOLUTIONS

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July 1973

ISBN 0 642 99585 0

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ABSTRACT

An investigation into the corrosion of aluminium in flowing near-neutral water at 50°C is reported. The corrosion rate passed through a minimum as the pH was changed from pH 5.0 to 8.0. The pH at the point of minimum corrosion was sensitive to atmosphere, being highest in oxygen-saturated water. The corrosion rate was reduced and spallation of the oxide film prevented by saturating the water with oxygen.

National Library of Australia card number and ISBN 0 642 99585 0

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ALUMINIUM; ALUMINIUM OXIDES; AQUEOUS SOLUTIONS; CHEMICAL REACTION KINETICS; CORROSION; DATA; ELECTRIC CONDUCTIVITY; EROSION; FILMS; HIFAR REACTOR; MEDIUM TEMPERATURE; OXIDATION; OXYGEN; PH VALUE; SILICON OXIDES; TABLES; WATER

CONTENTS

1. INTRODUCTION

The optimum operating conditions for minimum corrosion of the heavy water circuits of the HIFAR reactor have been a continuing source of debate since start-up in 1958. HIFAR is a DIDO class reactor with aluminium clad fuel elements immersed in heavy water contained in an aluminium tank. The circuit pipework and pumps, etc. are stainless steel.

The present operating conditions are based on the 15 years' operating experience with HIFAR and on the similar experience of overseas operators, particularly with the British reactors DIDO, PLUTO and DMTR, the Canadian experience with NRU and the French experience with EL2 and EL3.

The various operating philosophies and their associated problems were reviewed by Smith, Aitchison and Monohan (1969) and may be summarised as follows:

(a) Operation at high chemical purity

This system has been used on most of the reactors mentioned at various times in their operating life. The highest chemical purity in the heavy water circuits was obtained with the HIFAR reactor where a mixed bed ion-exchange unit was used continuously at a high flowrate (5 gal min^{-1}). The conductivity was maintained at a low value, $< 0.5\ \mu\text{S cm}^{-1}$ at 25°C and the pD averaged 6.5 [pD = pH x 1.07 based on Kw (H_2O)/Kw (D_2O) values of Cleaver (1968). The pH value is used throughout the remainder of this report and should be corrected for application to D_2O]. HIFAR was operated in this mode for the first 10 years of its life.

The advantages of this system are that:

(i) the chloride concentration which is a major cause of pitting in aluminium, is minimised,

(ii) the levels of impurities which cause radiolysis of the heavy water are minimised, and

(iii) the levels of soluble aluminium corrosion product are kept below the level at which precipitation of alumina takes place.

No other reactor working to this philosophy has achieved HIFAR's high state of purity in its heavy water circuits. This can be traced either to lower flowrates through the mixed bed ion-exchange units, or to intermittent use of the units. In some of the other reactors, difficulties were encountered with the precipitation of fine particle alumina from the heavy water circuit after very similar gestation periods (approximately 21 months of operation). The issue was confused by the differing power levels of each reactor resulting in different corrosion and aluminium release rates at the fuel element surfaces.

The precipitation was apparently due to the reactor being operated at a pH other than that for the minimum corrosion of aluminium (Smith et al. 1969; Hatcher and Rae 1961). This has been set in the pH range 5-6 by Pourbaix (1966), Hatcher and Rae (1961), Griess et al. (1961), Draley and Ruther (1956) and Troutner (1959), and leads to the alternative operating philosophy:

(b) Operation at a pH of 5.5 (pD 5.9)

This operation was achieved by injecting nitric acid into the circuit either directly or by injection of N_2 into the gas blanket. The conductivity usually rises to a maximum of 2.0 $\mu S\ cm^{-1}$ (Smith et al. 1969). The advantages and disadvantages are now reversed. In practice, formation of alumina precipitate is certainly suppressed but it becomes difficult to control the chloride concentration and radiolysis. However, alumina formation was experienced with DMTR while operating in this mode.

The evidence produced by reactor operating experience does not show the cause for precipitation of alumina. While the pH is certainly an important factor, there are other variables such as the power level, operation of the mixed bed ion-exchange unit, which includes choice of cation to anion resin ratio and the frequency of bed change, the degree of chemical control of the heavy water circuit and gas blanket, and any thermal cycling of the system.

Two water loops were built to study the corrosion of aluminium under various operating conditions relevant to the HIFAR reactor. This paper reports on the operation of these loops to date and describes the first experiments of an investigation of the effect of pH, conductivity and atmosphere. Future experiments will extend these conditions to include the presence of low concentrations of chloride ion.

2. EXPERIMENTAL

2.1 Apparatus

Two loops were constructed, a glass loop and a Vulcathene loop, allowing the effect of dissolved silica to be studied. The glass loop is illustrated in Figures 1 and 2. The apparatus, constructed from Quickfit industrial fittings, measured 7 ft high and 4 ft square, with a total capacity of 13 litres. Water was heated in the 5 litre flask and pumped to the base of the test section. The output from the top of the test section was returned to the flask. Flowrates could be controlled either by the choke valve on the pump outlet or by the bypass line. The heater was controlled by a Braun temperature controller positioned near the base of the test section. The loop temperature was measured at the top of the test section. Gas was bubbled into the top of the test section to saturate the water with the cover gas and the excess was vented in the heating flask. The conductivity was monitored with a Philips PW9515 conductivity cell connected to a Philips PW9501 conductivity meter. Vibration from the pump was damped by incorporating Teflon bellows in the output side of the pump.

The Vulcathene loop, also illustrated in Figures 1 and 2, was essentially the same design as the glass loop with the exception that stainless steel jacketed immersion heaters were used and different positions were chosen for the temperature controller, thermometer, conductivity cell and gas bubbler. The loop was constructed from 1 in. and 2 in. diameter Vulcathene piping and fittings. The individual pieces were welded together to form a small number of large units which could be bolted together with flange joints. The loop was of similar dimensions to the glass loop and had total capacity of 7 litres.

The flow through the glass loop with samples in the test section was determined by measuring the time taken to fill a 50 litre tank temporarily attached to the top return line. The maximum flow was 10 gal min^{-1} and the linear velocity through the test section was 80 ft min^{-1}. The Vulcathene loop test section had similar dimensions and was assumed to have the same flowrate. The calculated Reynolds number of 12,000 indicated that the flow in the test sections was turbulent. This flowrate was kept constant throughout the experiment.

2.2 Specimens and Methods

The specimens were ~ 10 cm by ~ 2 cm plates cut from 0.071 cm (0.028 inch) thick Australuco (Alcan) aluminium sheet (AA IS-H18) to BS 1470-SIB. A sample was submitted for spectrographic analysis with the following results:

Element	%	Element	%
Fe	0.42	Mg	< 0.1
Si	0.085	Ti	< 0.02
Cu	0.006	Zr	< 0.05
Mn	< 0.02	Cr	< 0.05
		Ni	< 0.05

0.5 cm diameter holes were drilled centrally in each specimen about 1 cm from each end. Each plate was die stamped with an identifying number. The surface was prepared as follows:

(i) buffed with Triple E polish;

(ii) degreased in boiling carbon tetrachloride vapour;

(iii) chemically polished for 90 seconds in a solution of 25 cm^3 concentrated sulphuric acid, 70 cm^3 of pure phosphoric acid and 5 cm^3 of nitric acid at 85°C. The specimen was washed in hot water, rinsed in ethanol and dried with hot air.

Once the surface was prepared the specimen was never touched by the hand. Each specimen was weighed to the nearest 0.0001 g and its area including the area of the edges was measured to 0.001 cm^2. It was then mounted on a Teflon holder illustrated in Figure 2. This holder was designed to keep the specimen rigid, stationary and parallel with the flow of water. The holder extended the complete length of the test section. The glass loop could accommodate 24 specimens while the Vulcathene loop held 16. Teflon was used because it was chemically inert and non-conducting. For the first run in the glass loop and all the runs in the Vulcathene loop, pairs of specimens were removed on a logarithmic time scale extending to 80 days. For all subsequent runs in the glass loop a set of four specimens was removed on the same time scale. The specimens were withdrawn from the top of the holder downwards. This insured that the remaining specimens continued to be immersed in the loop water so that thermal recycling and intermittent drying of the remaining specimens was avoided.

On removal, each set of specimens was rinsed in ethanol, allowed to dry in air and weighed. The weight change per unit area was calculated and the mean value for the set recorded. The weight of aluminium converted to oxide film was then determined by two independent methods.

2.2.1 The I_2/EtOH method - stripping and retention of the oxide film with an iodine ethanol solution

In this method the metal was dissolved and the oxide film retained. It was based on the method described by Bowen and Thiede (1957). Initially attempts were made to strip the surface film from the metal intact but were abandoned in favour of simple filtration of the broken film after dissolution of the under laying metal. 70 g of iodine was dissolved in 450 mℓ of ethanol contained in a 500 mℓ Quickfit flask. The flask was fitted with a 0-100°C thermometer and a double surface reflux condenser. A 500 mℓ bulb was placed between the reaction flask and condenser to control and retain any frothing. The reaction flask was surrounded by a removable heater. The surface film on the edge of one specimen from each group was abraded away to expose the raw metal and the specimen was dropped into the iodine-ethanol solution. After gently heating to reflux the heat source was removed and the reaction allowed to continue under its own reaction heat. When all the metal had dissolved the solution was filtered through a Whatman Number 42 filter paper and the oxide residues were washed onto the paper. The paper and residues were washed with ethanol until free of iodine. The paper was then charred in a platinum crucible before being ignited to constant weight at 1160°C. The final weight was recorded as weight of aluminium converted to oxide calculated according to the equation

$$A_a = \frac{0.5292Y}{T_f} \qquad \ldots(1)$$

The factor is the ratio of $2Al : Al_2O_3$.

2.2.2 The PO_4/CrO_4 method - dissolution of the oxide film, using a phosphoric-chromic solution

This method was the reverse of the $I_2/EtOH$ method. The oxide film was dissolved away using a solution recommended by Bowen and Thiede (1957) and the remaining metal weighed. One specimen of each group was immersed for 10 minutes in a boiling solution of 180 mℓ of water, 6 mℓ of phosphoric acid and 6 g of chromic oxide. The specimen was then washed with water, rinsed with acetone and allowed to dry. The treatment was repeated until constant weight was obtained. Normally only one repeat was necessary. Because a constant weight could be obtained it was considered that the solution specifically dissolved the oxide. Also no weight change could be detected when a freshly prepared specimen was treated.

The dissolved oxide was assumed to be a trihydrate, so the aluminium converted was calculated according to the equation

$$A_b = \frac{0.3458Z}{T_t} \qquad \ldots(2)$$

The factor is the ratio $2Al : Al_2O_3.3H_2O$.

2.2.3 Total aluminium lost

In addition to the aluminium converted to oxide some aluminium is lost to the loop water either by dissolution or erosion of the oxide film. Thus the total loss will be the weight difference between the initial weight of the specimen and the weight of the specimen after dissolving away the oxide film by the PO_4/CrO_4 method, given by equation

$$A_c = \frac{B-C}{T_t} \qquad \ldots(3)$$

2.2.4 Unaccounted aluminium

The aluminium lost either by dissolution or erosion of the oxide film was not determined experimentally and is, therefore, called the unaccounted aluminium. It will be the difference between the total aluminium lost and the value for aluminium converted to oxide by either the I_2/EtOH or PO_4/CrO_4 method.

$$A_d = A_c - A_a \text{ (or } A_b\text{)} \qquad \ldots(4)$$

3. RESULTS

To date 10 experiments have been run, each experiment taking approximately three months to complete. The experiments were designed to study the following effects:

- Low concentration of dissolved silica
- pH
- Cover gas
- Conductivity
- Erosion

At the beginning of each experiment the loop was filled with freshly prepared demineralised-distilled water having ion concentrations of < 0.2 mg ℓ^{-1} for aluminium and silica, < 0.005 for chloride, and a conductivity of < 1 µS cm^{-1} at 20°C. Unless otherwise stated all conductivity measurements quoted in this section were measured at loop temperature (50°C) and all pH measurements were made at 20°C.

3.1 The Glass Loop

Experiment G1 at pH ~ 6.5 - cover gas oxygen

This experiment was run using demineralised-distilled water with no additives. The initial pH was 6.46 which settled to 6.0 ± 0.15. The conductivity was not measured during this run . The final aluminium content of the water was 0.037 mg ℓ^{-1} and silica content 0.065 mg ℓ^{-1}. The mirror-bright specimens dulled and developed a brown interference film within two days of immersion. Subsequently a grey-white film developed on the surface; this film was chalky and could be rubbed off to leave a matt satin-white surface. The weight gains, oxide determinations, total aluminium losses and unaccounted aluminium are listed in Table 1.

Experiment G2 at pH ~ 6.5 - cover gas nitrogen

This experiment was identical to G1 except that the cover gas was changed to nitrogen. The initial pH of the water was 6.0; this settled down to pH 6.4 ± 0.2 with a conductivity of 2.0 ± 0.5 µS cm^{-1}. No final aluminium or silica concentration of the water was measured. Initially the specimen surfaces developed the same matt appearance as in experiment G1; however, towards the end of the run the last specimens brightened again. The results are listed in Table 2.

Experiment G3 at pH ~ 5.0 - cover gas oxygen

In this experiment the pH was controlled to 5.0 ± 0.1 by adding 0.1M nitric acid to the demineralised-distilled water. The conductivity remained steady at 6.5 ± 1.0 μS cm^{-1}. The final aluminium content of the water was less than 0.02 mg ℓ^{-1}, but the silica content was not measured. The specimen developed surface films similar to those in the previous experiments. The results are listed in Table 3.

Experiment G4 at pH ~ 5.0 - cover gas nitrogen

In this experiment the pH was controlled to 5.0 ± 0.1 by adding 0.1M nitric acid to the demineralised-distilled water. The conductivity was initially 4.0 μS cm^{-1} but quickly rose to 16.0 ± 2.0 μS cm^{-1}. The final aluminium content of the water was < 0.02 mg ℓ^{-1} and the silica content 0.118 mg ℓ^{-1}. The initially bright specimens quickly developed the matt satin-white finish observed in previous runs. Towards the end of the experiment the remaining specimens developed brighter patches on their surface. The results are listed in Table 4.

Experiment G5 at pH ~ 5.0 - cover gas nitrogen and conductivity controlled to ~ 5.0 μS cm^{-1}

In this experiment the conductivity was controlled by occasionally replacing some of the loop water. Demineralised-distilled water was used with small additions of 0.1M nitric acid to maintain the pH to 5.0 ± 0.3. The initial conductivity was 3.0 μS cm^{-1}. It was allowed to rise to 6.0 μS cm^{-1}; then some water was replaced until the conductivity had dropped to approximately 4.0 μS cm^{-1}. The aluminium content of the water did not exceed 0.02 mg ℓ^{-1} throughout the experiment. The silica content was not measured. Surface films developed in a similar pattern to the previous experiments. The results are listed in Table 5.

Erosion experiment G6 at neutral pH - cover gas nitrogen

In some of the runs, the final specimens spalled. It was suggested that this was due to the position of the specimens in the rig. To check this, a full set of specimens was placed in the glass loop and the loop was run for 84 days with demineralised-distilled water. No samples were removed for the period of the experiment. The conductivity was initially 0.55 μS cm^{-1} and slowly rose to 1.05 μS cm^{-1}, during the run. The pH remained steady at

6.5 ± 0.2. The aluminium and silica content of the water was not measured. The results, listed in Table 6, show that corrosion of the specimens is independent of their position in the rig.

3.2 The Vulcathene Loop

Experiment V1 at pH ~ 6.5 - cover gas oxygen

This experiment was made under conditions identical to those in experiment G1 to study the effect of silica in circuit. The experiment was run using demineralised-distilled water with no additives. The initial pH was 6.1 and settled to 6.3 ± 0.2 with a conductivity of 3.0 ± 1.0 $\mu S\ cm^{-1}$. The final aluminium content was not measured. The specimens initially developed a light brown film similar to those of experiment G1. Two days later the brown film disappeared leaving the specimen bright again. The specimens then developed a matt satin-white finish sometimes having darker patches and spots on the surface with flow lines around the support pegs. The results are listed in Table 7.

Experiment V2 at pH ~ 8.0 - cover gas oxygen

In this experiment the pH was controlled to 8.0 ± 0.5 by adding sodium hydroxide to the demineralised-distilled water. Initially the conductivity was 5.5 $\mu S\ cm^{-1}$ after the sodium hydroxide addition but rose gradually over the period of 84 days to 40.0 $\mu S\ cm^{-1}$. The final aluminium content was 0.097 mg ℓ^{-1}. The samples developed a light brown film after 3 days. This film quickly thickened and became matt white in colour. After 60 days bright spots appeared on the remaining specimens. The results are listed in Table 8.

Run V3 at pH ~ 8.0 - cover gas nitrogen

This experiment was identical to run V2 but with the cover gas changed to nitrogen. The conductivity was initially 10.0 $\mu S\ cm^{-1}$ after the sodium hydroxide addition but gradually rose to 16.0 $\mu S\ cm^{-1}$. The final aluminium content was 0.197 mg ℓ^{-1}.

The samples developed a light brown interference film within two days. This later developed into a matt satin-white film which darkened towards the end of the experiment. The last samples had a few bright spots on their surfaces. The results are listed in Table 9.

Run V4 at pH ~ 8.0 - cover gas nitrogen and the conductivity controlled to ~ 5.0 $\mu S\ cm^{-1}$

In this experiment the conductivity was controlled by occasionally replacing some of the loop water as in experiment G5. Demineralised-distilled water was used with small additions of 0.1M sodium hydroxide to maintain the pH at 8.0 ± 0.2 to 0.5. The initial conductivity with sodium hydroxide addition was 4.6 $\mu S\ cm^{-1}$. The conductivity rose slowly to 6.0 $\mu S\ cm^{-1}$ and was controlled between 4.0 - 6.0 $\mu S\ cm^{-1}$ by replenishment with fresh water. The aluminium concentration fluctuated between 0.90 and 0.10 mg ℓ^{-1} during the first 30 days. Subsequently, with the progressive replacement of the water, the aluminium content dropped to below 0.02 mg ℓ^{-1}. The specimens developed surface films similar to those of the previous experiments. The results are listed in Table 10.

The results for the above experiments are plotted on Figures 4 to 8 to illustrate the various effects of silica content, pH, cover gas and conductivity control.

4. DISCUSSION

4.1 Effect of Silica

When the loops were being built it was suggested that silica leached from the glass could affect the corrosion rates. Accordingly, one loop was built of glass and the other of Vulcathene and an identical experiment was run in each loop using demineralised-distilled water with oxygen as the cover gas and no pH or conductivity control. (See experiments G1 and V1; Section 3). The results are illustrated by Figure 3 (a) to (d). The initial and final silica content of the water in the glass loop was <0.02 and 0.065 mg ℓ^{-1} respectively, indicating a slight leaching. However, the graphs show no significant difference between the two experiments in terms of weight gain, aluminium converted to oxide, or total aluminium lost; the unaccounted aluminium was too low for a worthwhile comparison to be made. It may be concluded that at these low concentrations dissolved silica has no affect on the corrosion rate. To be an effective inhibitor the silicate concentration is usually 1000 mg ℓ^{-1} (Wilson 1971). In view of these results it was no longer considered necessary to continue with identical experiments in each loop. Subsequently the glass loop was used for the more acidic experiments (~ pH 5.0) and the Vulcathene loop for the more alkaline experiments (pH 8.0).

4.2 The Oxide Film

The remarkable stability of aluminium in view of its chemical reactivity is attributed to its protective surface film of aluminium oxide. The growth and destruction of this film is the controlling feature of aluminium corrosion. In this work the overall growth of the film has been studied by two independent methods. The results reported are shown as weight of aluminium converted to oxide in Figures 3(b), 4(b), 5(b) and 7(b). The two methods are in reasonable agreement although in practically all cases the iodine-ethanol value was slightly larger than the chromate-phosphate value. This may have been due to a consistent experimental error in one of the methods or to an incorrect assumption over the stoichiometry of the hydrated film.

In the iodine-ethanol method the oxide film was detached from the metal by dissolving away the supporting aluminium. The possible errors in the method are as follows:

(a) Slight solubility of the oxide film in the iodine-ethanol solution either as a simple or a complexed species. Neither reaction is thought to occur to a significant extent.

(b) Precipitation of the product aluminium iodide from solution. This was avoided by using an excess of ethanol.

(c) Hydrolysis of the product aluminium iodide to an insoluble oxide/hydroxide. This was avoided by using dry ethanol. However the error was checked by adding 10 volume per cent water to a filtrate, allowing to stand overnight and refiltering the solution. The residue found was only slightly greater than the quoted ash content of the filter paper, so the error was considered negligible.

(d) Incomplete ignition of the aluminium oxide to Al_2O_3. This error was minimised by repeating the ignition to constant weight.

This method does not have to make any assumptions about the stoichiometry of the hydrated oxide film. Assuming that the above errors are negligible, the simple proportionation gives the actual weight of aluminium converted to oxide.

In the chromate-phosphate method the oxide film was dissolved away leaving behind the clean metal. The possible errors in this method are:

(a) The formation of a significant chromate-phosphate film.

(b) Some of the metal is stripped off by the solution.

(c) Not all the oxide film is stripped off.

(d) The film is not exactly $Al_2O_3.3H_2O$.

Errors (a) and (b) are considered to be insignificant since no weight changes could be detected with a freshly prepared specimen. Error (c) will be present, although it is below the limit of detection. Altenpohl (1962), using a slightly weaker stripping solution of 20 g of chromic oxide and 35 cm^3 of 85% phosphoric acid made up to 1 litre with distilled water, reported that successive layers of oxide film could be stripped off leaving a final insoluble layer of amorphous oxide. This final barrier film is usually about 10 to 20 Å thick and is always present in an oxygen atmosphere or aqueous environment. It will have been retained in the I_2/EtOH method but stripped off in the PO_4/CrO_4 method. However, because it is so thin its weight would be insignificant. The most likely error is the incorrect stoichiometry of the film. If there were x moles of water in the film then Equation (2) would become

$$A_{b,t} = \left\{\frac{53.94}{101.94 + x18.02}\right\} \frac{Z}{T_t} \qquad \ldots(5)$$

where $A_{b,t}$ is the true value of A_b. In the iodine-ethanol method the ignited oxide film is weighed directly and can be assumed to give the true value for aluminium converted to oxide, thus

$$A_a = A_{b,t} \qquad \ldots(6)$$

and we may then use the values of A_a and A_b to solve for x since

$$A_b - A_a = \frac{Z}{T_t}\left\{\frac{53.94}{156.00} - \frac{53.94}{101.94 + x18.02}\right\} \qquad \ldots(7)$$

Therefore

$$x = 8.657\,\frac{A_b}{A_a} - 5.657 \qquad \ldots(8)$$

Values for x have been listed in the tables of results. There is a general pattern independent of pH, cover gas and conductivity control. For the nine experiments the mean initial value is 2. This rises over a period of 20 days to 3 before slowly falling back towards 2.

The stoichiometry of the oxide film also can be calculated from the weight gain measurements. The weight gain will be due to the addition of oxygen and water to the sample in forming the oxide film minus the dissolved aluminium, assuming this is the unaccounted aluminium. Thus for the iodine-ethanol results

$$D = A_a\,\frac{[O_3 + yH_2O]}{2[Al]} - (A_c - A_a) \qquad \ldots(9)$$

Solving for y and substituting the molecular weights

$$y = \frac{1}{18.02}\left\{\left(\frac{(D + A_c - A_a)\ 53.96}{A_a}\right) - 48.0\right\} \qquad \ldots(10)$$

Values for y using the iodine-ethanol results have been listed in the tables of results. A difficulty arises when using the chromate-phosphate results due to the incorrect stoichiometry used in calculating A_b originally. The true value of aluminium converted to oxide by the chromate-phosphate method is

$$A_{b,t} = A_b \cdot \left[\frac{Al_2O_3\ .\ 3H_2O}{Al_2O_3\ .\ zH_2O}\right] \qquad \ldots(11)$$

If Equation (11) is substituted into Equation (9) we obtain after suitable rearrangement

$$D = A_b\left(\frac{156.0}{101.96 + z18.02}\right)\left(1 + \frac{(48.0 + z18.02)}{53.96}\right) - A_c \qquad \ldots(12)$$

Solving for z

$$z = \frac{294.82\ A_b - 101.94\ A_c - 101.94\ D}{18.02\ D + 18.02\ A_c - 52.10\ A_b} \qquad \ldots(13)$$

On substituting values for weight gain, A_b and A_c, unrealistic negative values for z were obtained. This was due to the nature of Equation (12). Both the numerator and denominator are the result of subtraction of two numbers larger than z, so that the value of z lies within the errors of the values for the weight gain, A_b and A_c. Consequently, values for z obtained by the chromate-phosphate method have not been listed.

The values for y were slightly higher than x and followed the same variation. Assuming the weight of the barrier oxide layer is negligible and that there are no significant errors in determining A_a then these calculations show that the hydrated oxide film contains a non-stoichiometric amount of water. Draley, Mori and Loess (1963) reached a similar conclusion using a slightly different technique. They determined the total aluminium lost using an eddy current gauge and the amount of aluminium in solution by chemical analysis. This was equated with the weight gain of the sample. The stoichiometric ratio obtained by them showed a slightly different variation with time. It was initially 3.0 and then decreased to 2.7. This may have been due to the higher operating temperature of 70°C and almost stagnant conditions.

This non-stoichiometric amount of water would account for the slight difference between the two methods for determining the amount of aluminium converted to oxide.

4.3 Effect of pH and Cover Gas

The weight gain, aluminium converted to oxide, total aluminium lost and unaccounted aluminium have been plotted in Figure 4(a) to (d) for the results at pH 5.0, 6.0 and 8.0 under an oxygen atmosphere. Similarly the results using nitrogen as the cover gas are plotted in Figure 5(a) to (d). The overall effect of pH and cover gas is more clearly illustrated by Figure 6(a) to (d) where the interpolated values at 40 days have been plotted as a function of pH. These figures show that the formation and dissolution of the oxide film is dependent on the pH and the cover gas. At pH 5.0 the total aluminium lost is independent of the cover gas and is completely accounted for by formation of the oxide film; there is no detectable solution of the film. As the pH is increased the film under a nitrogen atmosphere thickens and begins to dissolve until at pH 8.0 a quarter of the total aluminium lost is due to solution of the oxide. As the pH is increased from pH 5.0 under an oxygen atmosphere, the formation of oxide film is reduced to a minimum value at pH 6.0 before it increases again. At pH 8.0 almost half of the total aluminium lost is due to solution of the oxide. It is likely that the formation and dissolution of the oxide film under a nitrogen atmosphere also passes through a minimum value at about pH 5.0. Thus the overall effect of pH is for the growth of oxide to be reduced from a high level in acidic solutions to a minimum value around pH 5.0 to 7.0, before increasing again in alkaline solutions. This observation is in accordance with those of Draley and Ruther (1956) and Troutner (1957, 1959), who found that a point of minimum corrosion rate or oxide formation at pH 6.0 - 6.5 in air-saturated water for temperatures below 100°C. The pH at which this minimum occurred is dependent upon the cover gas. In an oxygen-depleted environment it moves to a more acidic pH. This dependence on atmosphere has not been previously noted and the explanation is not clear. Draley et al. (1959, 1963, 1967) claim to have observed that oxygen diminishes the local pH increase observed at the specimen during the initial stages of corrosion. Such an effect, if present, would tend to move the observed minimum to a higher pH in an oxygenated atmosphere and is a possible factor during the earlier stages of corrosion.

The mechanism for dissolution of the oxide will differ either side of the minimum. In acid solutions the oxide will dissolve to form aluminic ions:

$$Al_2O_3 + 6H^+ = 2Al^{3+} + 3H_2O \qquad ...(13)$$

The Al^{3+} ion will probably hydrolyse to a number of complexes of the general formula

$$[Al_g(OH)^{p+}_{3g-p}]$$

(Dezelic, Belinski and Wolf 1971). In alkaline solutions the oxide will dissolve to form the aluminate ion:

$$Al_2O_3 + H_2O = 2Al_2O^- + 2H^+ \qquad ...(14)$$

The degree of solution will depend on the equilibrium constants of Equations (13) and (14).

The 'unaccounted aluminium' is an indication of the amount of dissolved oxide. However, the value will also include all oxide lost by spallation and remaining in the apparatus as particulate matter, the errors arising from incorrect stoichiometry in the calculations and any experimental errors, so the unaccounted aluminium will give only a qualitative picture of the situation. Figures 4(d) and 5(d) show that, irrespective of the cover gas, the amount of unaccounted (dissolved) aluminium below pH 7.0 is very small but as the solution becomes more alkaline the dissolution rate increases. Thus aluminium is more soluble in slightly alkaline solutions than slightly acid solutions.

The results show that the rate of formation of oxide is dependent on pH since the variation of aluminium converted to oxide with pH is greater than the variation of unaccounted aluminium with pH (see Figure 6(b) and (d)). However, the kinetics for the formation of the oxide cannot be deduced from these experiments. Only the overall reaction rate can be determined. This is obtained from the graphs for total aluminium lost, Figures 4(c) and 5(c) which show that the overall reaction rate proceeds in a logarithmic stepwise manner, the size and breadth of the step depending on the environmental conditions. This stepwise reaction rate is similar to that reported by Draley (1959) for 2SS aluminium in water at 70°C, although he found a much shorter initial step. Using X-ray diffraction techniques he was able to identify a thin, protective film produced during the initiation period as boehmite (nominally AlOOH) while bayerite was formed as a heavy, porous non-protective layer after longer exposures (Draley et al. 1959; 1963). This was in agreement with Hart (1957) who showed that the oxide film produced when pure aluminium was immersed in water below 60°C had a layered structure, being amorphous at the metal-oxide interface, followed by a boehmite layer and finally a bayerite layer at the oxide water interface. Such a structure would account for the fractional stoichiometry of the film. Since the factor x was close to 3 for most of the films we may conclude that the bulk of the corrosion product was bayerite. From a limited number of samples up to 1000 days, Draley (1963) concluded that the stepwise kinetics would continue indefinitely.

The overall effect of changing the cover gas from oxygen to nitrogen is that the rate of formation of oxide film will be increased and the minimum in the rate of formation will be shifted from pH 6.0 to pH 5.0. Also under a nitrogen atmosphere the oxide film would spall after 60-80 days. This effect was independent of pH and occurred in both loops. The erosion experiment G6 showed that the effect did not depend on the position of the specimen in the loop. The oxygen run at pH 8.0 also spalled at 70 days but this was the only example for the oxygen series. Examination of the calculated stoichiometry of the films showed no significant variation between the two cover gases. Hence, the cover gas has no effect on the degree of hydration of the oxide. Spallation is associated with dissolved oxygen concentration in the water since the effect can be prevented by running the loops under oxygen-saturated conditions. A possible explanation is that spallation occurs only above a certain minimum film thickness which, over the timescale of these experiments, is reached in nitrogen but not oxygen. Successive spallations under an inert atmosphere may be a contributory cause of the turbidity found in various reactors. It could be occurring in the HIFAR reactor but remains undetected due to the efficient 'clean-up' of the moderator heavy water. This spallation effect is being further investigated.

4.4 Effect of Conductivity

One of the earliest indicators of corrosion of the heavy water circuits is a rise in the conductivity. In part this will be due to the accumulation of corrosive impurities such as chloride, but also it will be due to an increasing concentration of dissolved aluminium. In the first experiment the conductivity and concentration of aluminium would increase as the run progressed. It would be expected, if dissolution is the rate controlling step, that according to the law of mass action the presence of aluminium ions in the loop water would lower the corrosion rate.

Such a dependence has been noted by Dillon (1959), Dickinson (1965), Wilkins, Dalton and Wanklyn (1961) and Draley and Ruther (1967) at temperatures between 150°C and 300°C and at lower temperatures by Hatcher and Rae (1961) and Troutner (1957; 1959). However, Draley and Mori (1967) reached a different conclusion when they reported that no dependence existed between corrosion rate at 70°C and corrosion product concentration. In fact, earlier work (Draley et al. 1963) showed that the corrosion rate at 70°C was increased when the number of specimens was increased or the flowrate was decreased. To study this effect two pairs of experiments were run at different pHs in which the conductivity of one experiment was uncontrolled, while in the other it was controlled by replenishment of the loop water. The two pairs were:

Experiment	Conductivity	pH	Gas
G4	Uncontrolled and rose to 16.0 μs cm^{-1}.	5.0 ± 0.1	N_2
G5	Controlled to 3.0-6.0 μs cm^{-1}.	5.0 ± 0.3	N_2
V3	Uncontrolled and rose to 16.0 μs cm^{-1}.	8.0 ± 0.2-0.5	N_2
V4	Controlled to 3.0-6.0 μs cm^{-1}.	8.0 ± 0.2-0.5	N_2

The results may be compared in Figure 7(a)-(d). At pH 5.0 there was very good agreement within the pair of experiments for weight gain, aluminium converted to oxide, total aluminium lost and unaccounted aluminium. Also, both experiments showed identical spallation effects. At pH 8.0 the total aluminium lost was independent of the conductivity but there was more unaccounted (dissolved) aluminium and a smaller weight gain when the conductivity was controlled by replacement of the loop water. This would indicate that, at pH 8.0 and for the concentration range under study (maximum 0.9 Al mg ℓ^{-1}), the aluminium concentration did not affect the rate of oxide growth and hence the corrosion rate, but would affect the rate of oxide dissolution; presumably, the lower the aluminium concentration the higher the dissolution rate of the outer porous bayerite layer. The expected change in the weight of oxide film did not occur however, and further measurements will be required before any definite conclusion can be reached.

At pH 5.0 any changes of this kind, if present, are small and within the experimental error of the measurements. This lack of sensitivity to conductivity changes for pH levels within the minimum corrosion range is to be expected from the observations of Draley and Ruther (1956) who found that corrosion rate was not sensitive to flowrate within this range.

5. SUMMARY

The results of preliminary studies on the corrosion of aluminium in high purity flowing water at 50°C have been presented. The overall weight gains, aluminium converted to oxide, total aluminium lost and the unaccounted (dissolved or spalled?) aluminium were reported. The amount of aluminium converted into oxide was determined by two independent methods. There was a consistent small difference between the results; this was attributed to the oxide film being a non-stoichiometric hydrated oxide. Trace silica (less than 0.065 mg ℓ^{-1}) had no effect on the corrosion rate. The dissolution rate of the aluminium was very low, below pH 7.0,but increased markedly at pH 8.0. Results indicated that dissolved aluminium would suppress the solution rate of the oxide film at pH 8.0 without influencing the corrosion rate. No effect could be discerned at pH 5.0. The corrosion rate passed through a minimum as the pH was changed from pH 5.0 to pH 8.0. The position of the minimum was determined by the oxygen concentration being pH 6.0 at oxygen saturation and pH 5.0 or less with oxygen depletion through nitrogen saturation. Oxygen saturation reduced the rate of build-up of oxide film and prevented spallation of the oxide film within the 100 days' duration of the experiment. The significance of these results to the corrosion and operation of the HIFAR reactor will be discussed in a later report.

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7. LIST OF SYMBOLS

Symbol	Definition	Identifying Equation
A_a	Weight of aluminium converted to oxide determined by iodine-ethanol method, g cm^{-2}.	1
A_b	Weight of aluminium converted to oxide determined by phosphate-chromate method and applying Equation (2), g cm^{-2}.	2
$A_{b,t}$	True weight of aluminium converted to oxide, g cm^{-2}.	6

Symbol	Definition	Identifying Equation
A_c	Total aluminium lost determined by phosphate-chromate method, g cm^{-2}.	3
A_d	Unaccounted aluminium.	4
B	Weight of specimen before immersion, g.	3
C	Weight of specimen after immersion, g.	3
D	Weight gain of specimen, g.	9
T_f	Surface area of the specimen minus the area of the abraided edges, cm^2.	1
T_t	Total surface area of the edges, cm^2.	2
x	Water stoichiometry in oxide film.	5
Y	Weight of ignited residues in the iodine-ethanol method, corrected for ash content of filter paper.	1
y	Stoichiometry of water.	9
Z	Weight loss in phosphate-chromate method, g.	2
z	Stoichiometry of water.	11
[ ]	Molecular weight of species inside brackets.	

TABLE 1 - EXPERIMENT G1

Time in Days	Weight Gain	Aluminium Converted to Oxide		Total Aluminium Lost	Unaccounted Aluminium		x	y
		I_2/EtOH Method	PO_4/CrO_4 Method		From I_2/EtOH Method	From PO_4/CrO_4 Method		
2	15.9	9.3	9.3	11.0	1.7	1.7	3.0	3.0
6	17.4	11.0	10.3	12.3	1.3	2.0	2.5	2.4
12	18.7	8.4	11.1	12.8	4.4	1.8	5.7	5.6
22	21.2	18.7	10.7	13.5	-ve	2.7	-ve	3.2
47	19.2	10.9	12.0	13.8	3.0	1.9	3.9	3.4
81	18.9	11.0	11.0	13.6	2.6	2.6	3.0	3.2

<u>Conditions:</u> Temperature 50°C
Demineralised-distilled water
pH uncontrolled, mean value 6.0 ± 0.15
Cover gas - oxygen
Conductivity not measured
Chloride - nominally $\leq$ 0.005 mg ℓ^{-1}
All values are in g cm^{-2} x 10^5

TABLE 2 - EXPERIMENT G2

Time in Days	Weight Gain	Aluminium Converted to Oxide		Total Aluminium Lost	Unaccounted Aluminium		x	y
		I_2/EtOH Method	PO_4/CrO_4 Method		From I_2/EtOH Method	From PO_4/CrO_4 Method		
1.3	16.2 ± 0.16	14.4	9.3	10.7	-ve	1.4	-ve	0.7
4	33.5 ± 0.25	20.7	18.3	19.7	-ve	1.4	2.0	2.2
11	66.9 ± 2.6	30.1	33.7	34.6	4.4	0.8	4.0	4.4
21	76.9 ± 4.0	43.6	38.5	39.3	-ve	0.8	2.0	2.6
46	73.0 ± 6.2	42.4	43.0	42.9	0.5	-ve	3.1	2.5
82	51.2 ±13.9	38.4	31.2	37.9	-ve	6.6	1.4	1.3

Conditions:

Temperature $50^{\circ}C$
Demineralised-distilled water
pH uncontrolled, mean value 6.4 ± 0.2
Cover gas - nitrogen
Conductivity - uncontrolled, mean value 2.0 ± 0.5 $\mu S\ cm^{-1}$
Chloride - nominally ≤ 0.005 mg ℓ^{-1}
All values are in g $cm^{-2} \times 10^5$

TABLE 3 - EXPERIMENT G3

Time in Days	Weight Gain	Aluminium Converted to Oxide		Total Aluminium Lost	Unaccounted Aluminium		x	y
		I_2/EtOH Method	PO_4/CrO_4 Method		From I_2/EtOH Method	From PO_4/CrO_4 Method		
2	47.4 ± 0.13	25.1	25.0	24.6	-ve	-ve	3.0	2.9
6	55.1 ± 0.41	29.5	29.0	28.1	-ve	-ve	2.8	2.8
14	56.5 ± 0.34	31.0	29.3	28.9	-ve	-ve	2.5	2.6
23	55.9 ± 0.24	31.9	29.7	29.9	-ve	+0.2	2.4	3.0
47	57.0 ± 0.62	32.4	29.7	29.8	-ve	+0.1	2.3	2.4
79	56.4 ± 1.3	30.9	30.6	30.5	-ve	-ve	2.9	2.7

<u>Conditions:</u> Temperature $50^{\circ}C$
Demineralised-distilled water (with nitric acid additions)
pH controlled to 5.0 ± 0.2 pH
Cover gas - oxygen
Conductivity - uncontrolled, 6.5 ± 1.0 $\mu S\ cm^{-1}$
Chloride - nominally < 0.005 mg ℓ^{-1}
All values are in g $cm^{-2} \times 10^5$

TABLE 4 - EXPERIMENT G4

Time in Days	Weight Gain	Aluminium Converted to Oxide		Total Aluminium Lost	Unaccounted Aluminium		x	y
		I_2/EtOH Method	PO_4/CrO_4 Method		From I_2/EtOH Method	From PO_4/CrO_4 Method		
2	32.4 ± 2.0	17.9	16.2	16.6	-ve	0.4	2.2	2.8
6	50.9 ± 0.52	20.9	26.5	26.2	-ve	-ve	2.0	1.9
14	49.8 ± 1.6	26.9	26.8	26.7	-ve	-ve	2.9	2.9
23	51.0 ± 1.1	30.9	27.6	27.8	-ve	0.2	2.1	2.3
45	50.7 ± 3.0	30.8	28.4	28.4	-ve	0.1	2.3	2.3
80	40.5 ± 5.1	28.2	22.1	24.1	-ve	2.0	1.1	1.6

Conditions: Temperature $50^{\circ}C$
Demineralised-distilled water (with nitric acid additions)
pH controlled to 5.0 ± 0.1
Cover gas - nitrogen
Conductivity - uncontrolled, mean value 16.0 ± 2.0 $\mu S\ cm^{-1}$
Chloride - nominally < 0.005 $mg\ \ell^{-1}$
All values are in $g\ cm^{-2} \times 10^5$

TABLE 5 - EXPERIMENT G5

Time in Days	Weight Gain	Aluminium Converted to Oxide		Total Aluminium Lost	Unaccounted Aluminium		x	y
		I_2/EtOH Method	PO_4/CrO_4 Method		From I_2/EtOH Method	From PO_4/CrO_4 Method		
1.3	26.6 ± 0.34	17.1	14.3	14.9	-ve	0.6	1.6	2.0
4	45.8 ± 0.18	27.6	24.4	24.5	-ve	1.6	2.0	2.3
10	48.3 ± 0.50	32.0	25.3	25.5	-ve	0.2	1.2	1.8
22	49.0 ± 0.53	30.5	25.7	26.3	-ve	0.5	1.7	2.1
45	50.5 ± 1.3	32.2	27.4	28.0	-ve	0.6	1.7	2.1
80	43.8 ± 2.4	29.3	24.3	25.6	-ve	1.3	1.5	1.8

Conditions:
Temperature 50^0C
Demineralised-distilled water (with nitric acid additions)
pH controlled to 5.0 ± 0.3
Cover gas - nitrogen
Conductivity - controlled to 3.0 - 6.0 $\mu S\ cm^{-1}$
Chloride - nominally ≤ 0.005 mg ℓ^{-1}
All values are in $g\ cm^{-2} \times 10^5$

TABLE 6 - EXPERIMENT G6

Top of Loop

Position	Weight Gain
1	76.4
2	77.0
3	76.6
4	77.5
5	76.2
6	75.6
7	76.2
8	76.2
9	77.7
10	77.3
11	76.6
12	77.6
13	76.5
14	76.2
15	76.8
16	77.4
17	77.3
18	78.0
19	76.1
20	77.3
21	76.9
22	75.8
23	75.7
24	75.8

Bottom of Loop

Conditions:
Temperature 50°C
Demineralised-distilled water with no additions
pH uncontrolled, 6.5 ± 0.2
Cover gas - nitrogen
Conductivity - uncontrolled initially 0.55 μS cm^{-1}
and rose to 1.05 μS cm^{-1}
All values are in g $cm^{-2} \times 10^5$

TABLE 7 - EXPERIMENT V1

Time in Days	Weight Gain	Aluminium Converted to Oxide		Total Aluminium Lost	Unaccounted Aluminium		x	y
		I_2/EtOH Method	PO_4/CrO_4 Method		From I_2/EtOH Method	From PO_4/CrO_4 Method		
2	7.8	7.9	4.9	6.8	-ve	1.9	-ve	0.3
5	19.4	13.4	11.5	13.7	0.3	2.2	1.8	1.7
12	18.1	15.4	11.4	14.7	-ve	3.3	0.8	0.9
22	21.0	12.5	12.6	15.2	2.8	2.7	3.1	3.0
34	20.2	16.0	12.1	15.0	-ve	3.0	0.9	1.1
47	19.9	17.1	12.6	16.3	-ve	3.7	0.8	0.8
83	18.5	15.0	12.8	18.4	3.4	5.6	1.7	1.7

Conditions:

Temperature $50^{\circ}C$
Demineralised-distilled water
pH uncontrolled, mean value 6.3 ± 0.2
Cover gas - oxygen
Conductivity - uncontrolled, mean value 3.0 ± 1.0 $\mu S\ cm^{-1}$
Chloride - nominally ≤ 0.005 mg ℓ^{-1}
All values are in g $cm^{-2} \times 10^{5}$

TABLE 8 - EXPERIMENT V2

Time in Days	Weight Gain	Aluminium Converted to Oxide		Total Aluminium Lost	Unaccounted Aluminium		x	y
		I_2/EtOH Method	PO_4/CrO_4 Method		From I_2/EtOH Method	From PO_4/CrO_4 Method		
0.96	23.9	19.1	17.1	14.1	5.0	7.0	2.1	1.9
3.7	30.8	22.9	21.1	31.9	9.0	10.9	2.3	2.5
6.0	31.0	23.0	22.8	34.8	11.8	12.0	2.9	2.9
11	31.2	23.8	24.5	37.9	14.1	13.4	3.3	3.0
20	32.7	26.6	25.6	40.6	13.8	14.9	2.7	2.5
40	32.9	26.9	26.7	42.0	15.1	15.4	2.9	2.7
62	13.7	24.0	23.1	55.7	31.7	32.6	2.7	3.0
84	38.1	32.5	31.3	49.2	16.8	17.9	2.7	2.4

Conditions: Temperature 50°C
Demineralised-distilled water (with sodium hydroxide additions)
pH controlled, mean value 8.0 ± 0.5
Cover gas - oxygen
Conductivity slowly rose from 5.5 to 40.0 $\mu S\ cm^{-1}$
Chloride - nominally $<$ 0.005 $mg\ \ell^{-1}$
All values are in $g\ cm^{-2} \times 10^5$

TABLE 9 - EXPERIMENT V3

Time in Days	Weight Gain	Aluminium Converted to Oxide		Total Aluminium Lost	Unaccounted Aluminium		x	y
		I_2/EtOH Method	PO_4/CrO_4 Method		From I_2/EtOH Method	From PO_4/CrO_4 Method		
2	13.2	13.8	11.4	19.4	5.7	8.1	1.5	1.4
6	41.3	29.4	27.4	41.1	11.7	13.6	2.4	2.7
14	82.6	53.7	48.7	63.8	10.2	15.2	2.2	2.5
23	88.6	58.1	56.4	69.9	11.8	13.5	2.7	2.5
36	88.5	60.2	56.9	75.9	15.6	18.9	2.5	2.5
44	90.1	59.3	57.9	76.3	16.9	18.4	2.8	2.7
62	87.1	61.8	59.8	89.2	27.4	29.4	2.7	2.9
79	33.8	59.4	57.6	137.7	78.3	80.3	2.7	3.0

Conditions: Temperature $50^{\circ}C$
Demineralised-distilled water (with sodium hydroxide additions)
pH controlled, mean value 8.0 ± 0.2 - 0.5
Cover gas - nitrogen
Conductivity - uncontrolled, mean value 16.0 ± 2.0 $\mu S\ cm^{-1}$
Chloride - nominally ≤ 0.005 mg ℓ^{-1}
All values are in g $cm^{-2} \times 10^5$

TABLE 10 - EXPERIMENT V4

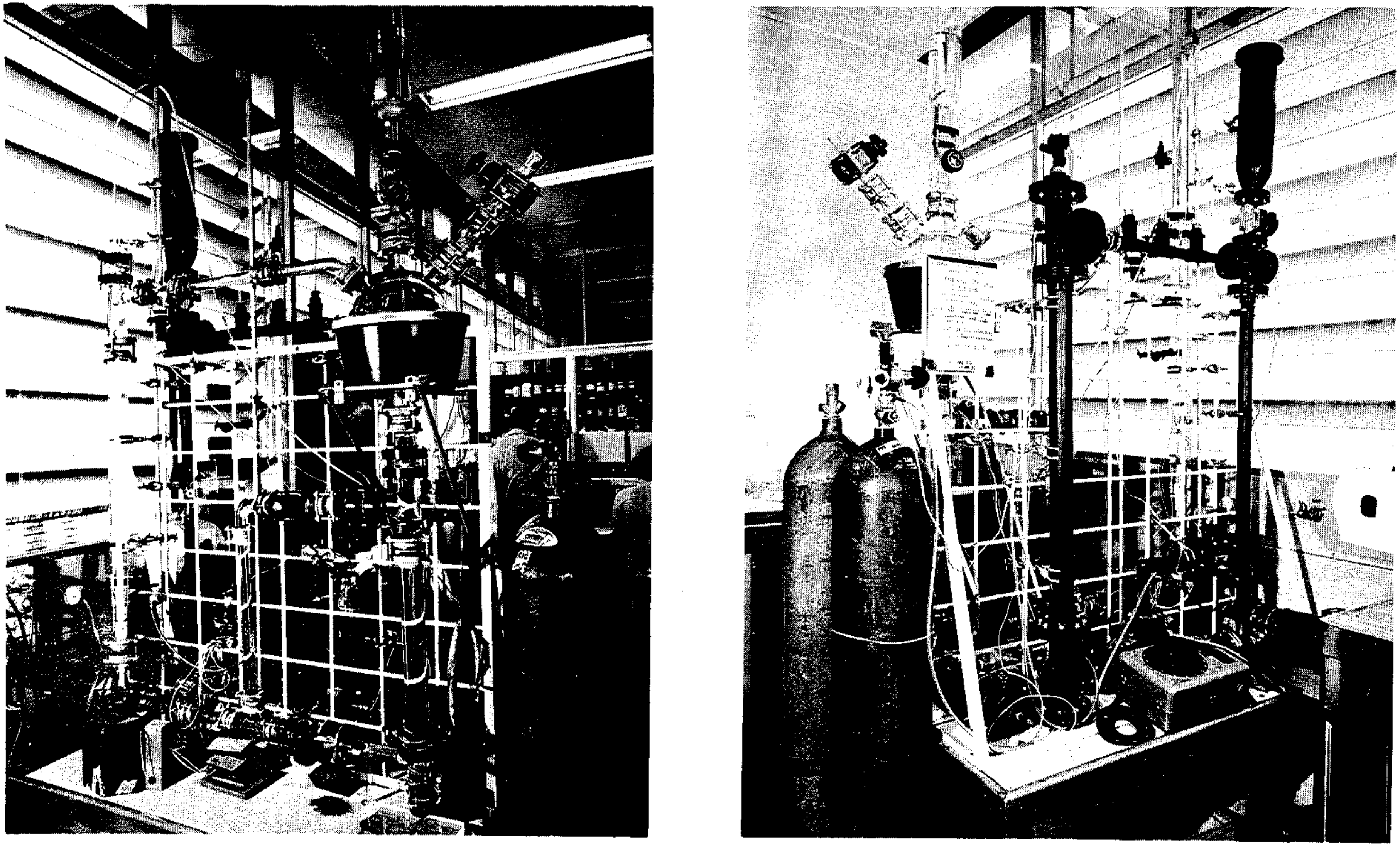
Time in Days	Weight Gain	Aluminium Converted to Oxide		Total Aluminium Lost	Unaccounted Aluminium		x	y
		I_2/EtOH Method	PO_4/CrO_4 Method		From I^2/EtOH Method	From PO_4/CrO_4 Method		
2	18.1	16.5	13.3	24.1	7.6	10.8	1.3	2.0
6	51.0	34.3	36.5	47.1	12.8	10.6	3.6	2.9
10	62.9	44.3	43.2	62.0	17.6	18.8	2.8	2.8
20	70.7	50.3	48.2	69.5	19.3	21.4	2.6	2.7
35	71.6	54.0	54.3	78.2	24.2	24.0	3.0	2.6
50	66.1	56.1	52.8	93.4	37.3	40.6	2.5	2.8
64	26.1	58.8	52.1	109.6	50.7	57.5	2.0	1.2
80	78.8	65.6	62.7	96.0	30.4	33.3	2.6	2.3

Conditions: Temperature 50°C
Demineralised-distilled water (with sodium hydroxide additions)
pH controlled to 8.0 + 0.2 - 0.5
Cover gas - nitrogen
Conductivity - controlled 4.0 - 6.0 $\mu S\ cm^{-1}$
Chloride - nominally < 0.005 mg ℓ^{-1}
All values are in g $cm^{-2} \times 10^5$

NOTE

Figures 3 to 7 inclusive are divided into four sections:

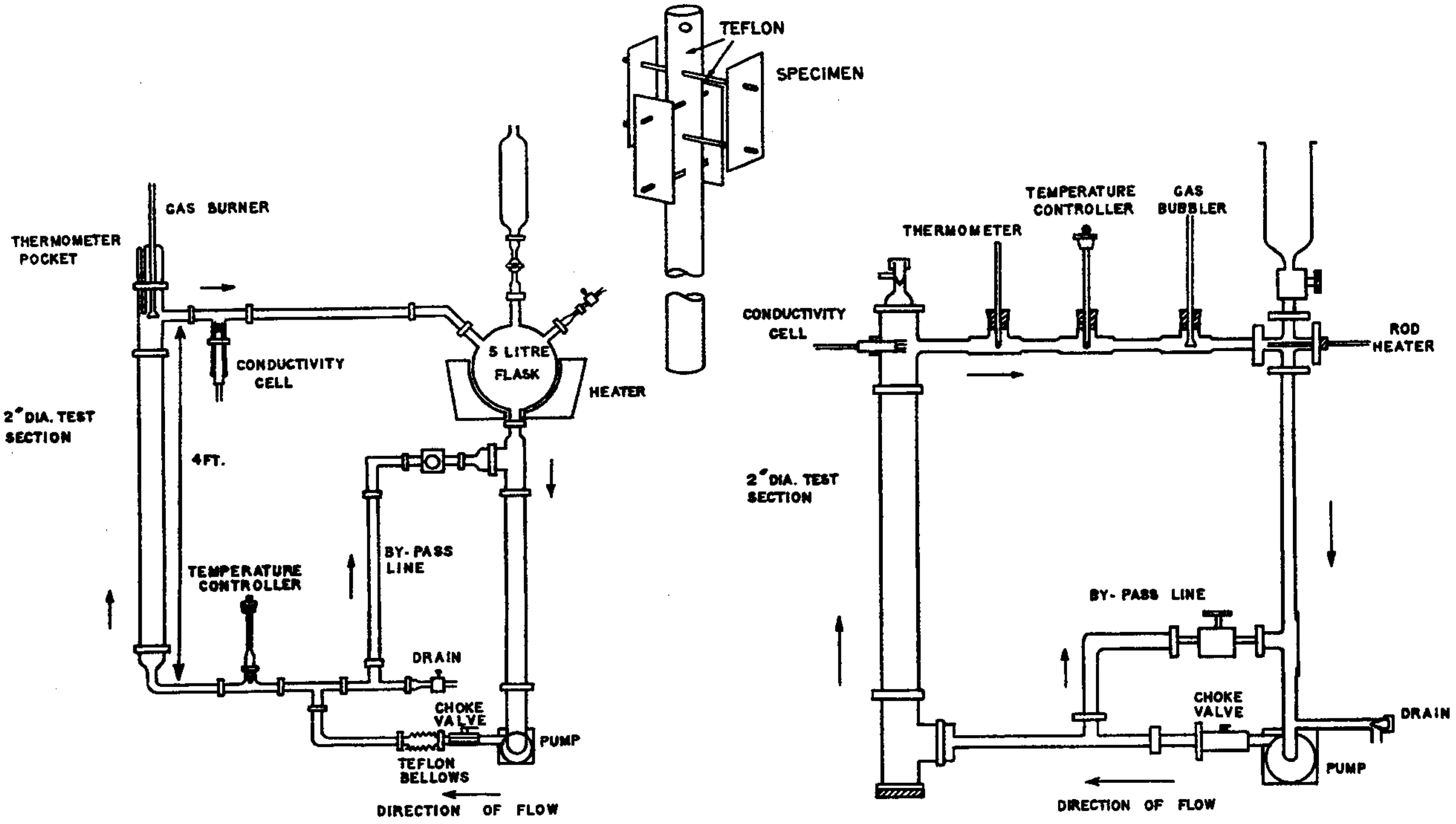
- *(a) The effect on total weight gained*
- *(b) The effect on aluminium converted to oxide*
- *(c) The effect on total aluminium lost*
- *(d) The effect on unaccounted aluminium*



(a) The Glass Loop

(b) The Vulcathene Loop

FIGURE 1. THE TWO EXPERIMENTAL LOOPS *in situ*



(a) THE GLASS LOOP

(b) THE VULCATHENE LOOP

FIGURE 2. SCHEMATIC DIAGRAMS OF THE TWO EXPERIMENTAL LOOPS

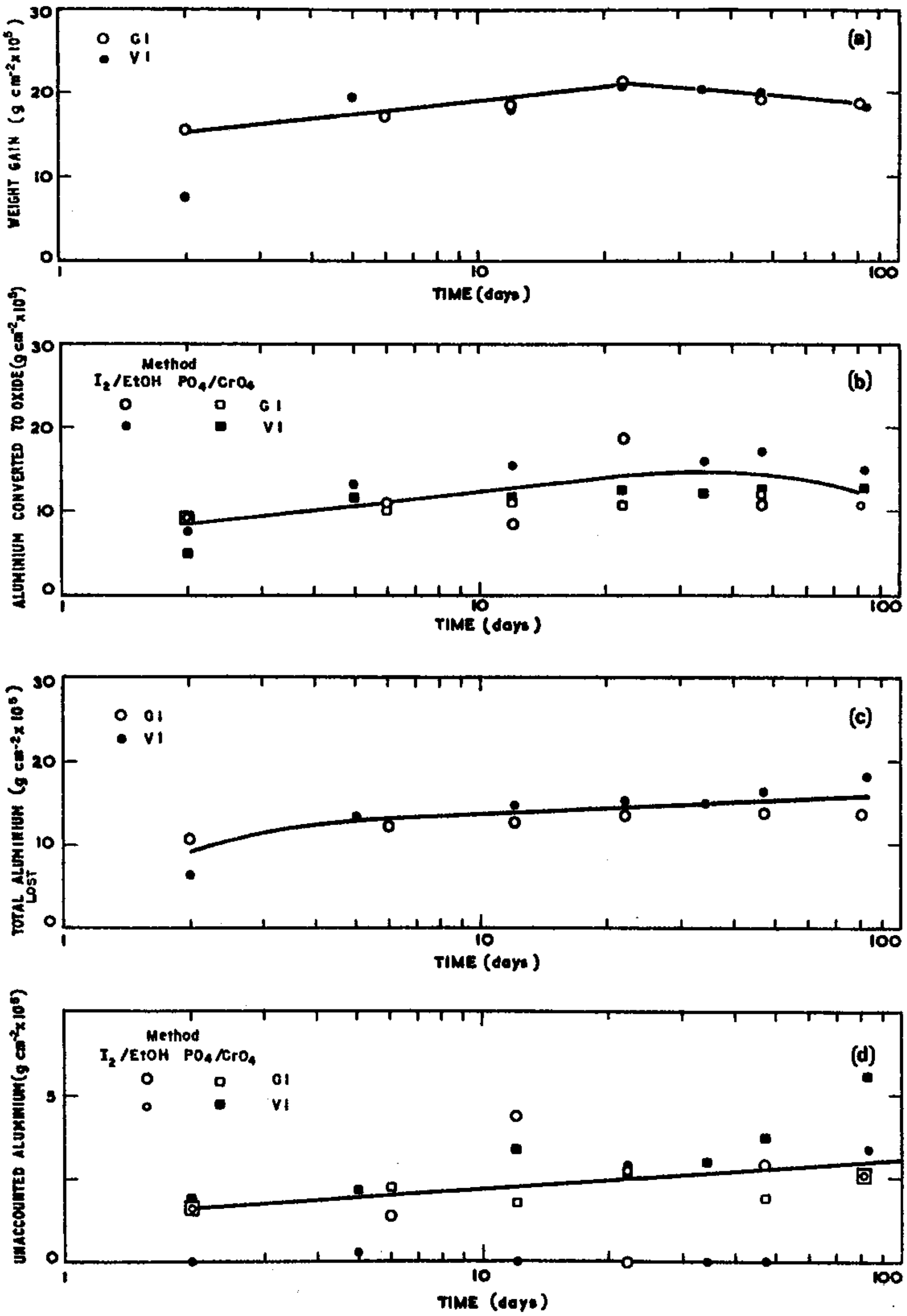


FIGURE 3. COMPARISON BETWEEN GLASS AND VULCATHENE LOOPS, EFFECTS OF SILICA

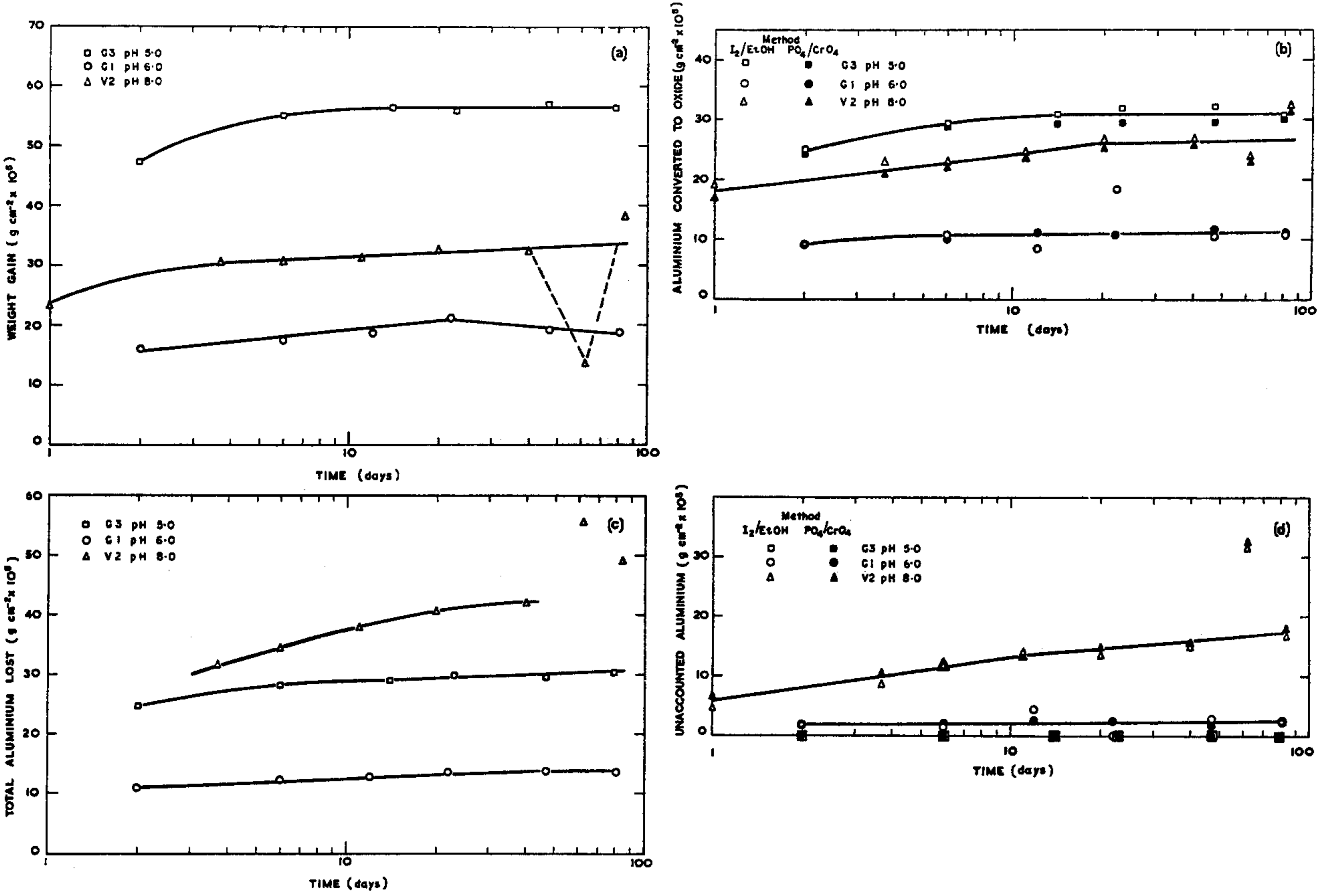


FIGURE 4. THE EFFECT OF pH IN AN OXYGEN ATMOSPHERE

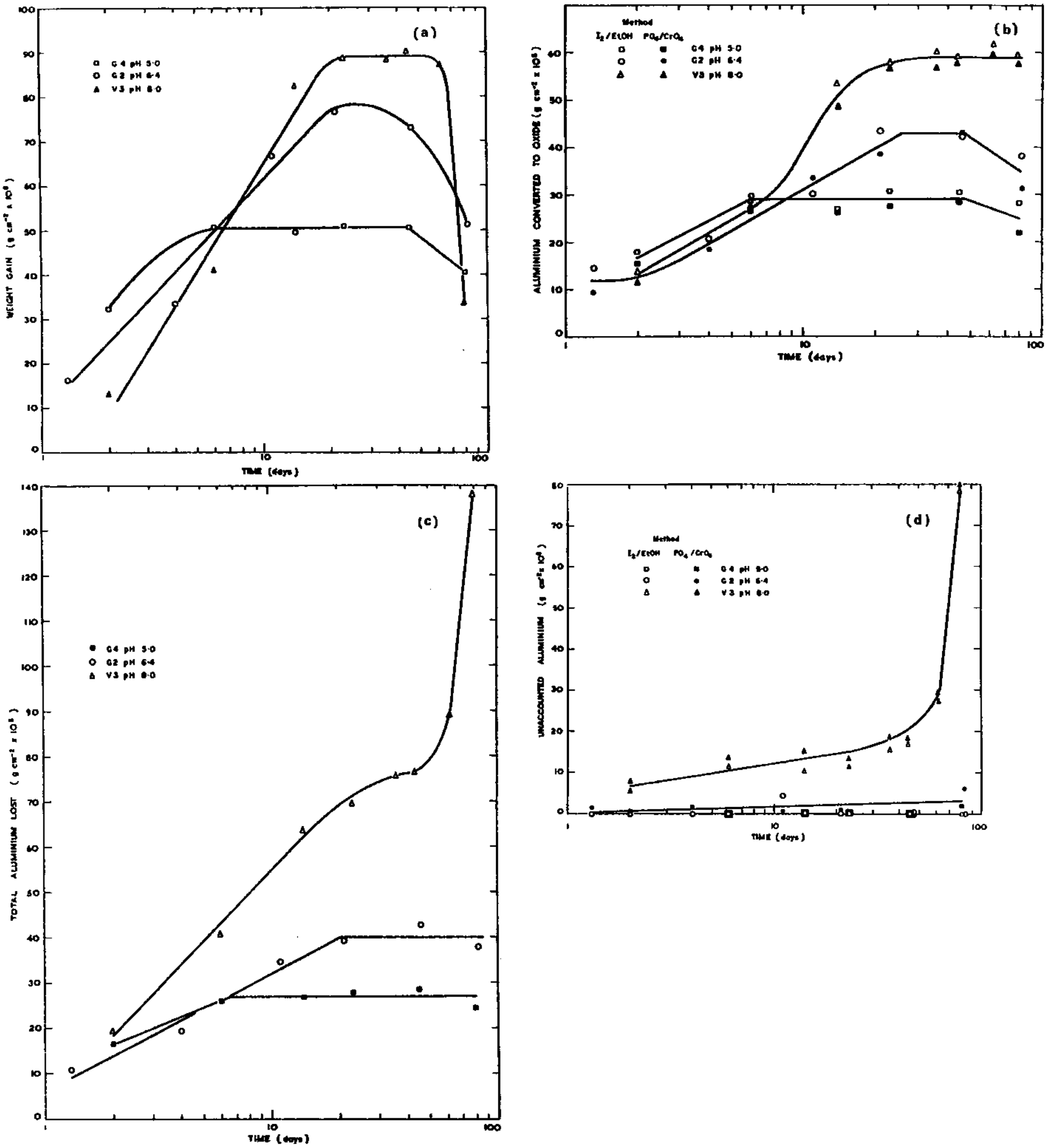


FIGURE 5. THE EFFECT OF pH IN A NITROGEN ATMOSPHERE

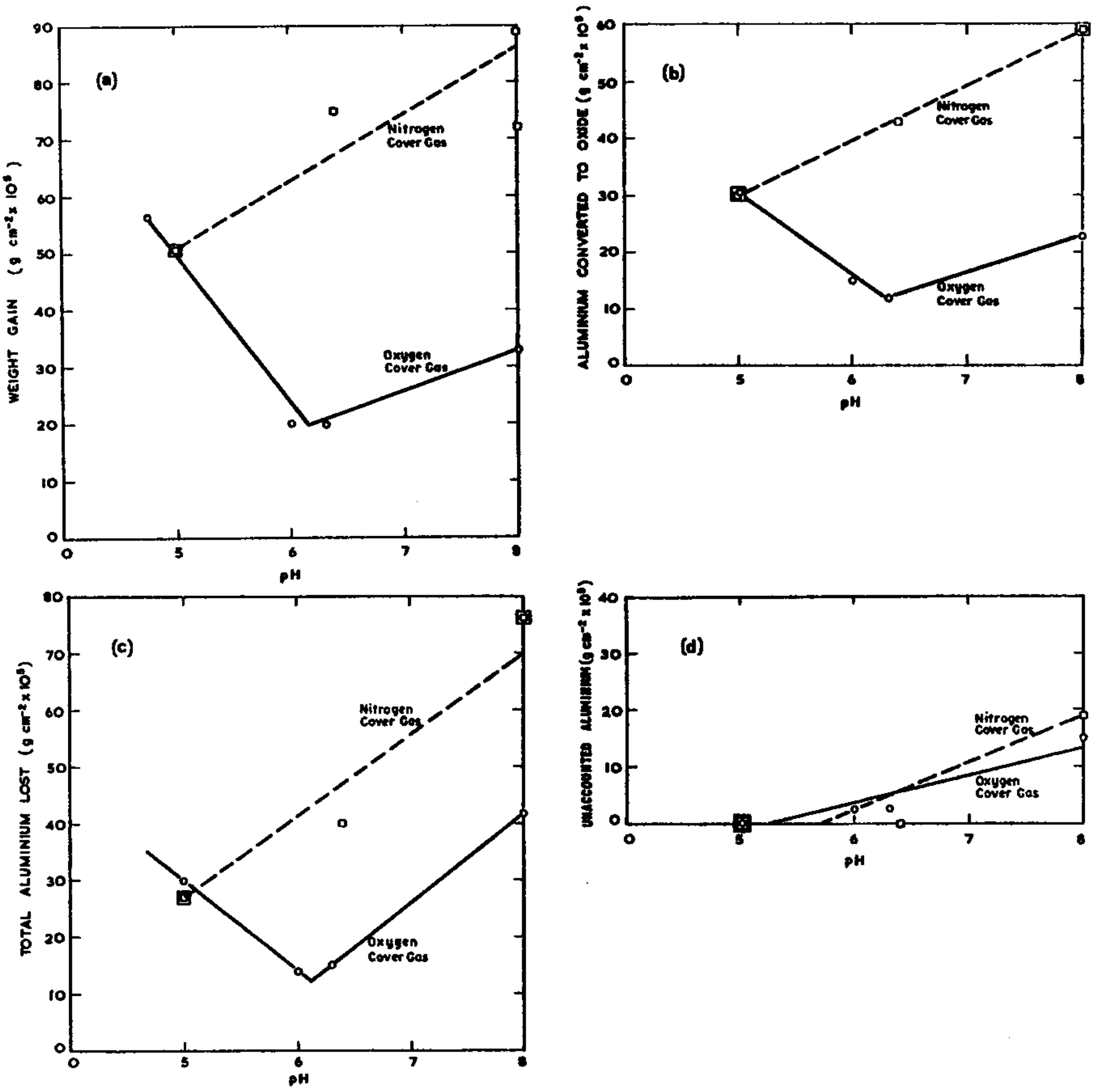


FIGURE 6. THE EFFECT OF pH

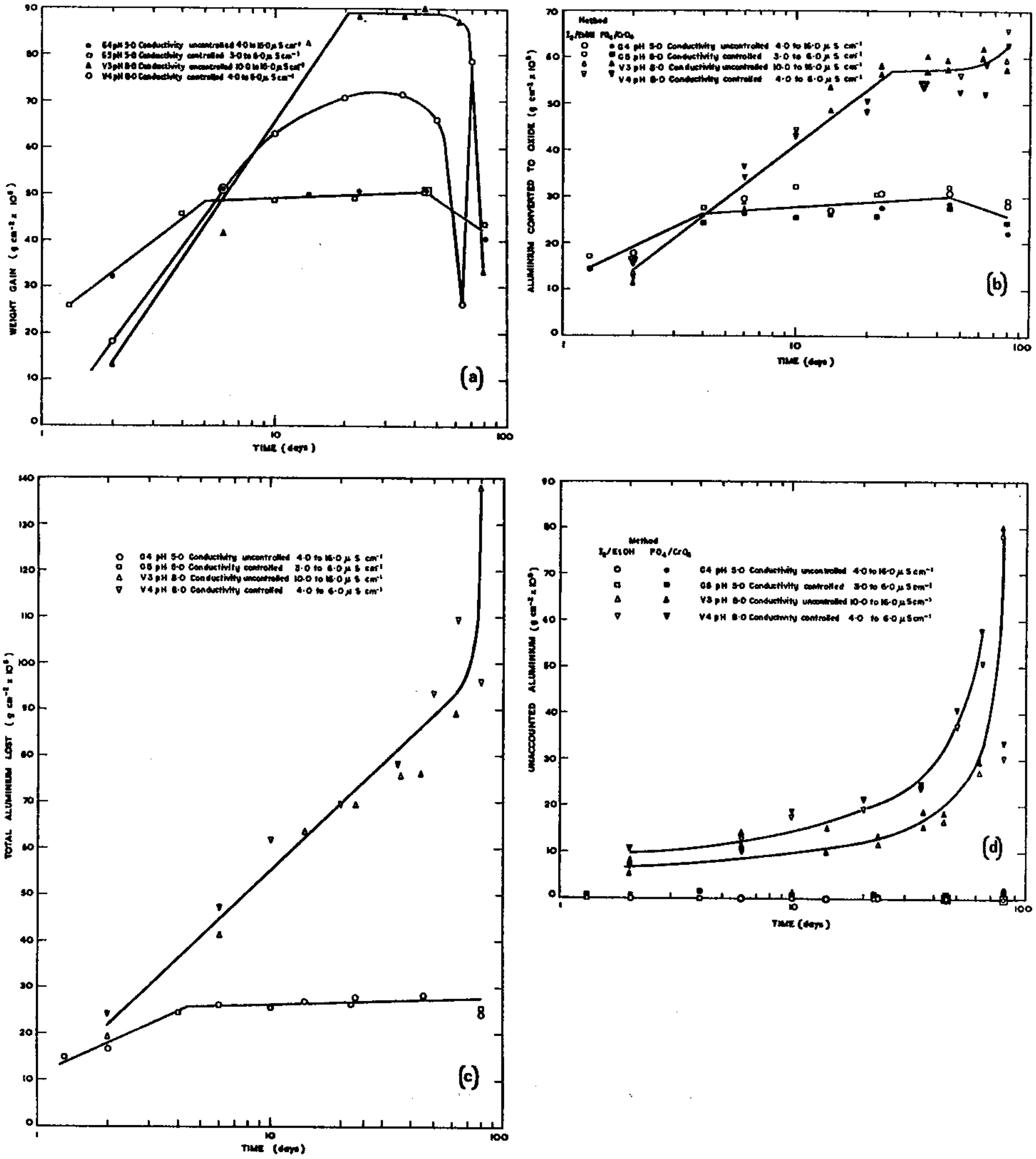


FIGURE 7. THE EFFECT OF CONTROLLING THE CONDUCTIVITY WITH NITROGEN AS COVER GAS