

The Anodic Dissolution of Uranium with
Particular Reference to the Design of
Critically Safe Equipment

by

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Abstract.

Anodic dissolution of uranium metal was effected in tubular dissolvers whose dimensions fell within the limits of criticality safety ($\frac{3}{4}$ in. and $1\frac{1}{2}$ in. I.D.). A randomly stacked bed of cylindrical uranium metal pellets was contained inside a vessel made up of two sections of tantalum tube forming the electrodes, separated by a length of plastic insulating material. The dissolver was operated **vertically with** current entering and leaving through the metal sections and flowing via the uranium bed. A circulating electrolyte, usually 3N nitric acid, carried away the heat of reaction.

The arrangement used resulted in a number of cells being set up in series by the pellets forming the bed, largely within the insulating section of the dissolver. Current efficiencies of approximately 20 equivalents of hexavalent uranium dissolved per faraday were thus achieved at voltage gradients of up to 8V/cm. and current densities of up to 7 amp/cm². Under the best conditions, uranium dissolved at a rate of $\frac{1}{2}$ kg U/hr.

Experiments using a simplified model of the dissolver were carried out to study multi-cell formation within the dissolver bed. It was found that current utilisation in a multi-cell system depended on the ease with which the current could bypass the pellets interposed between the electrodes and thus increased with the number of interposed pellets. Experiments with a single uranium cell and nitric

acid electrolyte showed that uranium passed into solution as a hexavalent metal.

Various sizes of packing and dissolver tube diameter were used to test two available correlations for pressure drop estimation in packed beds where the particle diameter is large compared with the tube diameter. A relationship developed by Max Leva was considered to be the most suitable in scale-up calculations.

Based on experiments using the tubular dissolver, the design of a suitable plant-size unit is proposed. Such a unit of critically safe dimensions ($2\frac{1}{2}$ in. I.D.) and capable of operating under remote control would process 8.2 tonne of uranium per year at a voltage gradient of 8V/cm. and a current density of 1.25 amp/cm^2 .

Contents.Page Nos.

Abstract.	2.
Acknowledgements.	6.
Chapter 1. Introduction.	7.
Chapter 2. Historical Review of Work.	12.
Chapter 3. Selection of the Anodic Dissolution Process.	38.
Chapter 4. Preliminary Work.	44.
Chapter 5. Anodic Dissolution of Uranium in a Stainless Steel Dissolver.	63.
Chapter 6. Anodic Dissolution of Uranium in a Tantalum Dissolver.	121.
Chapter 7. Model Experiment.	153.
Chapter 8. Discussion and Conclusions.	199.

(Contents - contd.).

	<u>Page Nos.</u>
Chapter 9. Design Suggestions for Plant-Size Dissolver.	276.
Appendix A. Electrode Potential Measurements.	288.
Appendix B. Pressure Drop Test Data and Calculations.	293.
Appendix C. Analytical Methods.	305.
Appendix D. Determination of the Valency of Uranium.	308.
Appendix E. Gas Evolution during Electrolysis.	313.
Appendix F. Measurements of Resistance.	320.
References.	326.

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Chapter 1.

Introduction.

Introduction.

The speedy and efficient head-end processing of spent reactor fuel elements forms an important cost-reducing factor in fuel reprocessing. The comparative ease with which nitric acid dissolves the majority of fuel elements and claddings, as well as the efficiency with which both uranium and plutonium can be solvent extracted from nitrate-rich solutions, have both been important reasons why most presently operating head-end processing systems are based on nitric acid dissolution.

Uranium, uranium-aluminium alloys, and claddings such as Magnox or aluminium react readily with nitric acid without the formation of any appreciable amounts of sludge or precipitate. The dissolution of this type of fuel element has been studied extensively in the laboratory and practised widely on a plant-scale. The results of these studies and experience have formed the subject of a complete symposium ⁽¹⁾ and parameters involved in the dissolution of uranium in nitric acid on a laboratory and semi-plant scale have been reported even earlier by Tonkin⁽²⁾.

The effect on uranium dissolution of such factors as the temperature and concentration of nitric acid and the concentration of NO_2 in solution, have been studied recently, on a more fundamental basis, by Salzman⁽³⁾ who also found that irradiated samples of uranium tended to dissolve faster than unirradiated ones.

The emergence of newer, advanced reactor systems operating at high temperatures and pressures and often to high burn-up, necessitated the introduction of more resistant cladding materials, e.g. stainless steel or zirconium. The high chemical inertness of these metals and alloys which remain either unaffected or are attacked only very slowly by nitric acid, has led to the investigation of new head-end processing techniques using more corrosive media, e.g. aqua regia (in the case of stainless steel) and hydrofluoric acid in the dissolution of zirconium and Zircaloy. Details of these processes have been given by Blanco⁽⁴⁾ and Culler⁽⁵⁾.

The ultimate goal of most research work in this field, however, has been the successful development of a universal dissolution process, capable of dealing with as many of the existing and proposed fuel elements and claddings as possible, and preferably using nitric acid as solvent. The solutions resulting from such a process could then be treated conveniently in existing solvent extraction systems. The need for building new dissolution plant equipment from highly corrosion resistant materials, e.g. titanium, would also be obviated, with consequent saving in capital expenditure.

Anodic dissolution of both the cladding and fuel core itself has shown much promise as a practical head-end processing step of almost universal application. Reasonable rates of attack, proportional to the current flowing, are encountered even in fairly dilute (3N) acid.

Nitric acid can conveniently be used as the electrolyte in the dissolution of a wide variety of metals and alloys, but other electrolytes e.g. HCl-methanol have also been employed where special conditions exist, e.g. in the electrolytic dissolution of zirconium and Zircalloy-clad UO_2 fuel elements⁽⁶⁾⁽⁷⁾.

Two major problems, however, have hindered the development of a successful electrolytic dissolution process. These are:

(1) the provision and continuous maintenance of efficient contact between the fuel elements and the metal forming the anodic connection, and

(2) the prevention of excessive sludge formation. A bad contact leads to undesirable side effects of overheating and arcing, whilst high uranium losses have been associated with sludge formed during electrolytic dissolution.

The application of highly enriched fuels both in thermal and fast reactor systems has introduced the criticality problem into the head-end processing of nuclear fuel elements. It has therefore been the object of this research to develop a practical electrolytic dissolver of critically safe dimensions capable of operating under plant conditions.

Criticality control may be achieved by limiting quantities of fissile material in any section of the plant (administrative control), by geometric control or even by addition of materials of large cross-section (nuclear poisons) to process solutions. The latter method has not been applied on an industrial scale. Administrative control has

been used on all presently operating large-scale plant but this method requires an exceptionally large team of plant operators and analysts and even then the danger of human error is not eliminated completely. The ideal plant is that designed for geometry control, i.e. every section of the plant is designed strictly on the basis of "eversafe" dimensions. Specifications for the sizes of spheres, cylinders or slabs may be made such that under no circumstances can the vessel become critically unsafe. ⁽⁸⁾ These parameters impose, however, severe restrictions on the size of the vessel which can be used e.g. the critically safe diameter of a water reflected, infinitely long cylinder of uranium-235 metal is 2.5 inches.

Whilst "eversafe" mixer-settlers, pulsed columns, evaporators and storage vessels have been described and some are in use, ⁽⁹⁾⁽¹⁰⁾ considerable difficulty has been met in the design of a satisfactory dissolver. This is due to the problem of achieving sufficiently high dissolution rates in a small unit which can be operated continuously and yet is so simple and reliable in construction as to be suitable for remote control operation.

Such a dissolver has been developed and operated successfully for the dissolution of natural uranium metal pellets in 3N nitric acid as electrolyte.

Chapter 2.

Historical Review of Work.

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Historical Review of Work.

- 2.1. Introduction.
 - 2.2. Anodic Dissolution - Early Investigations.
 - 2.3. Anodic Fuel Element Dissolution.
 - 2.3.1. Research and Development carried out at the Idaho Chemical Processing Plant of Phillips Petroleum Company.
 - 2.3.2. Research and Development carried at the Savannah River Laboratory of E.I. du Pont de Nemours & Co.
 - 2.3.3. Research and Development carried out on the Anodic Dissolution of Zirconium and its Alloys.
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2.1. Introduction.

American workers have been responsible for nearly all the papers and reports published on the subject of electrolytic dissolution of nuclear fuel elements in general and uranium in particular. Research and development work carried out in this field under the auspices of the United States Atomic Energy Commission (U.S.A.E.C.) has been concentrated in two main groups : The Idaho Chemical Processing Plant of the Phillips Petroleum Company and The Savannah River Laboratory of E.I. du Pont de Nemours & Co.

Much of this literature has been published since the work reported here commenced and is surveyed below (Section 2.3.). Results of investigations reported at the time work on this project was started are first reviewed.

2.2. Anodic Dissolution - Early Investigations.

Sborgi⁽¹¹⁾ was one of the earlier workers to study the anodic behaviour of uranium. He carried out experiments to determine the electrochemical equivalent of uranium. Using rather impure uranium samples, he found that in the majority of electrolytes under investigation, uranium behaved electrochemically as a quadrivalent metal, but dissolved to give the hexavalent ion in some experiments involving oxidising media (e.g. $\frac{N}{10}$ H_2SO_4 , $\frac{N}{10}$ Na_2SO_4 , $\frac{N}{10}$ KNO_3 , acetates). The potential-time behaviour of uranium in $\frac{N}{10}$ H_2SO_4 , $\frac{N}{10}$ HCl and $\frac{N}{10}$ HNO_3 was also studied by Sborgi, who concluded that uranium was not a metal which could be anodically passive.

McLaren and co-workers⁽¹²⁾ were one of the first teams to carry out a systematic laboratory study of the possibilities of electrolytic dissolution of uranium as a head-end process for dissolving fuel elements. They investigated a wide variety of acids, bases and salts. Using a nickel cathode, and a nickel or platinum anode basket, they found that saturated tartaric acid, sodium bicarbonate and 1.5 N nitric acid solutions were the most satisfactory electrolytes from the stand-point of concentration of uranium achieved, rates of corrosion and condition of electrodes. Under bench-scale conditions uranium in electrolyte concentrations of up to 80 gU/l were achieved at current efficiencies of 75-120%. Relatively low ($\approx 0.1 \text{ amp/cm}^2$) current densities were reached and direct current was found to have better dissolution properties than alternating current. Hydrogen peroxide was recommended as a complexing agent to increase the solubility of uranium in basic electrolytes.

Beederman⁽¹³⁾ investigated the suitability of several metals for providing electrical contact with the bulk of the uranium which was to be dissolved anodically in 3M H_2SO_4 . He found that zirconium was the most suitable metal for an anode basket operating with 3M H_2SO_4 and at 35°C.

The disintegration of zirconium metal in 3M HCl was investigated by Blanco and co-workers⁽¹⁴⁾ at current densities of up to 0.27 amp/cm^2 . Zirconium dissolution efficiencies of up to 0.95 g Zr. dissolved/amp were obtained. Using a.c., zirconium metal and

Zircaloy-2 were found to disintegrate readily in 15 M HNO_3 , but poor uranium recoveries ($< 80\%$) were obtained when U-Zr fuel element sections were attacked anodically. Stainless steel dissolved in 10 M HNO_3 using d.c. and current efficiencies of 76.5-78.0% were obtained at temperatures between 50 and 90°C.; the dissolution rate being proportional to current density. Off-gas evolution was less with 5 M than with 10 M HNO_3 and in most cases hydrogen formed only a small fraction of the gases evolved.

Anodic dissolution of stainless steel in 3 M HCl was also reported by Blanco⁽⁴⁾. Current efficiencies from 83-97% at 2.5-3.0 volts were quoted and, by 1957, electrolytic dissolution was becoming recognised as a possible universal head-end process for future nuclear fuels.

Further studies on the electrolytic dissolution of Zircaloy-2 in 3 M HCl, carried out by Culler and Blanco⁽⁵⁾, showed that between 2-25% of the zirconium did not dissolve completely but remained dispersed as a metallic sol. This was considered an undesirable phenomenon as any uranium retained in such sludge would be lost. Both stainless steel and uranium dissolved readily, however, when made anodic in an electrolytic cell using 3 M nitric acid as the electrolyte.

Larsen and co-workers⁽¹⁵⁾ investigated the electrolytic dissolution of stainless steel and Zirconium-clad UO_2 fuel elements. The following points were listed as being essential requirements for a successful dissolution process:

- (a) complete dissolution of all U in a recoverable form,
- (b) continuous operation,
- (c) remote control capability,
- (d) preferably universal application,
- (e) preferably nitrate solution medium.

3 N HNO_3 was found to be the best overall electrolyte for stainless steel dissolution as it gave the highest dissolution rate at a given current density, and at temperatures higher than 60°C . was extremely efficient in dissolving UO_2 . Nitric acid (3N) proved also to be a successful electrolyte in the dissolution of 10% Nb-90% U alloy. 3 N HCl was chosen for the dissolution of zirconium, however, as it gave less sludge in the product as compared with HNO_3 . Small quantities of HF added to the HCl electrolyte decreased the amount of sludge formed even further. It was suggested that an upper limit of 1 M be placed on the metal ion concentration in the electrolyte, to prevent overheating due to a rise in resistance of the solution. Larsen, however, reported a rather low power consumption efficiency which was presumed to be due to the platinum anode charge holder, and consequent oxygen evolution. Titanium and tantalum are mentioned as suitable anodic materials for a basket-type dissolver, a form of apparatus which was rejected because it was suitable for batch-type operation only. Typical hydrogen concentration in the off-gas was 4.24 mole %.

Uranium was recovered from unirradiated fuel element scrap by Jasny and co-workers⁽¹⁶⁾ who used rectangular and cylindrical stainless steel vessels acting as cathodes to dissolve strips of uranium-stainless steel alloy clamped inside by means of stainless steel clamps which also served to carry the anodic current : 4 M HNO_3 at 80-90°C. was used as electrolyte and a total current of 1200 amps at 5-6V was passed through an array of 10 dissolver units. This corresponded to a current density of 0.2 amp/cm² giving a throughput of 2 kg of alloy/hr. and a dissolution rate of 0.25 g/amph.

Preliminary experiments to investigate the anodic dissolution of stainless-steel and stainless steel- UO_2 cermets have been carried out by Martin and Waterman⁽¹⁷⁾, under a wide variety of conditions with respect to electrolyte (nitric acid) concentration and current density, using both a.c. and d.c. It was found that current efficiency with a.c. was only 54-63% compared with 100% for d.c., current densities being equal. Dissolution potentials for the stainless steel anode - platinum cathode system were observed in 1-7 M nitric acid. Complete dissolution of the immersed sections of both the stainless steel and cermet (18% UO_2) samples was obtained, external clamps being used in all experiments to supply the anodic current. The specific conductivity of ferric nitrate - nitric acid solutions containing up to 8 equivalents of cations/l was measured. An average specific conductivity value of 0.4 mho was deduced from these experiments. No detailed suggestions were made concerning the design of a

possible electrolytic dissolver. It was recommended, however, that a stainless steel dissolver vessel be completely insulated from both electrodes as stainless steel was found to corrode cathodically, thus making it inadvisable for the vessel itself to be used as the cathode.

Hartland ⁽¹⁸⁾ suggested the use of a tubular basket-type dissolver for the continuous anodic dissolution of uranium under critically safe conditions. The dissolver consisted of a tubular stainless steel anode joined on to a perforated p.t.f.e. basket, surrounded by a stainless steel tubular cathode. The basket was to be filled with uranium pieces extending into the anode tube and thus maintaining electrical contact. A "sacrificial" mild steel liner was included in the design to protect the anode portions from corrosion. Nitric acid was pumped through the dissolver to serve both as coolant and electrolyte. Assuming a current density of 50 amps/cm^2 , and a voltage drop of 50V, a 4 inch diameter dissolver would take approximately 4000 amps and dissolve 150 kgU/day at a cost of £275/tonne, (assuming 2d/kWh for d.c. power). The figures calculated were based on experiments showing uranium to be hexavalent, i.e. 40g uranium dissolving per Faraday.

The experiments with the basket dissolver suggested the possibility of a more simple system, in which a bed of randomly stacked uranium pellets would extend vertically from a tube forming the anode to a tube forming the cathode. The two stainless steel tubular

electrodes would be separated by a length of non-conducting tube e.g. p.t.f.e., thus forcing the current to flow partly through the electrolyte and partly through the uranium bed. By a suitable choice of conditions, it was considered possible to obtain within the uranium bed a system whereby a series of electrolytic cells would be set up with each of the pellets composing the uranium bed acting both as an anode and a cathode to the pellet next to it. On the basis of the same current density and voltage values as quoted above for the basket-type dissolver, and assuming a 5 inch diameter dissolver, tentative calculations indicated that such a system would have a throughput of 2800 kg U/day at an approximate cost of £55/tonne. A current of 6300 amps would be passing through the dissolver at this rate.

A summary of the results reviewed in this section is given in Table 2.1.

2.3. Anodic Fuel Element Dissolution.

More recent American work on the electrolytic dissolution of nuclear fuel elements has been concerned mainly, at Idaho, with the more fundamental and theoretical problems involved⁽¹⁹⁻³⁰⁾ (Section 2.3.1.), whilst at Savannah River the work has been concentrated mainly on the practical aspects and possibilities of operating semi-works and plant-scale dissolvers⁽³¹⁻⁴²⁾ (Section 2.3.2). A review of work dealing with the anodic dissolution of zirconium and Zircaloy-2 is given in Section 2.3.3.

Table 2.1.

ANODIC DISSOLUTIONComparison of Results obtained by Early Workers on Electrolytic
Dissolution Systems.

Material Dissolved	Metal forming anode contact material.	Electrolyte used or recommended.	Current Density, (anode) amps/cm ² .	Overall current amp.	Overall voltage V.	Dissolution Rate. mg/cm ² .min.	Current Utilis-ation. g/amp-hr	Current Effi-ciency. %	Ref.
Uranium Metal	Ni or Pt basket.	satd. NaHCO ₃ " tartaric acid. 1.5N HNO ₃ .	0.12	0.4-2.0	12-15	0.46-0.57 ^(a)	-	74-124	(12)
Uranium Metal.	Zr or Pt basket.	3M H ₂ SO ₄	-	<90	-	-	-	-	(13)
Zirconium Metal.	-	3N HCl	0.017-0.27	-	-	-	0.88-1.53	-	(14)
Stainless Steel.	-	10N HNO ₃	-	-	-	-	-	76.5-78.0	
Stainless Steel.	Pt basket	3N HNO ₃	-	30A	5.8-13	~2.0	0.8	-	(15)
10% Nb-90% U Alloy.		3N HNO ₃	-	-	-	-	-	-	
Zirconium Metal.		3N HCl	-	-	-	-	1.0	-	
U-SS Alloy	SS Clamps	4N HNO ₃	0.2	1200	5-6	5.6 ^(a)	0.25	-	(16)
UO ₂ -SS Cermet.	SS Clamps	1-12 N HNO ₃	0.2-1.5	-	-	-	-	18-100	(17)
Uranium Metal.	S.S. Tube	0.01-16 N HNO ₃	0.01-70.0	0.2-280	0.2-65	0.2-1500	-	>50	(18)

Note: (a) Figures calculated from values quoted in reference.

2.3.1. Idaho Investigations

2.3.1.(a) Electrochemical Aspects of Electrolytic Dissolution.

Both qualitative and quantitative studies of the electrochemical behaviour of iron and stainless steel (Type 304) in nitric were carried out and the results reported in a number of Idaho Chemical Processing Plant Quarterly Progress Reports⁽¹⁹⁾⁽²⁰⁾⁽²¹⁾. A summary of these findings has appeared in a report by Slansky and co-workers⁽²²⁾. Polarisation relationships both for metal oxidation and nitric acid reduction as well as the behaviour of cell voltage as a function of current density (including an analysis of the overvoltage component) were investigated. A difference in the limiting current density of stainless steel in the transpassive region was revealed at concentrations less than 6 N HNO_3 ⁽²³⁾.

A temperature range of 60-70°C. was recommended⁽²⁴⁾⁽²⁵⁾ for the efficient anodic dissolution of stainless steel. Under these conditions minimum interference from such phenomena as secondary passivation, limiting current and gas evolution was observed over a suitably wide range of solution compositions and at current densities up to 2 amp/cm².

Investigations of the potential-current density behaviour of pure chromium⁽²⁶⁾ and Nichrome⁽²⁷⁾ in various concentrations of nitric acid - nitrate solutions showed marked similarity between the two metals. In both cases an absence of secondary passivation and a tendency towards concentration polarisation at higher current densities were observed.

2.3.1.(b) Electrode Materials.

A perforated cylindrical anode basket, made of a metal exhibiting the electrolytic valve effect (Section 6.1.) was considered as the best means of making and maintaining anodic contact with fuel pieces during dissolution ⁽¹⁹⁾⁽²²⁾. Metals which have this property of valve action (e.g. niobium or tantalum) allow current to flow through metal-to-metal contact, an oxide film formed under anodic conditions in nitric acid preventing any flow of anodic current directly to the electrolyte. As the efficiency of dissolution thus depends on the efficiency of the anode-fuel contact mechanism, both the ⁽²²⁾⁽²⁸⁾ potential-thickness of oxide film and pressure-resistance of contact ⁽¹⁹⁾⁽²²⁾ relationships between niobium and fuel pieces were studied. Results obtained did not show any clear correlation between the variables considered, but a general trend was observed which indicated that the contact and resistance varied inversely with the pressure and the thickness of the oxide film formed increased with the voltage supplied.

Corrosion tests carried out on stainless steel (Carpenter - 20) showed ⁽¹⁹⁾⁽²¹⁾⁽²²⁾ that it could be used as short-lived material of construction for the cathode provided certain conditions of current density and solution composition were adhered to ($< 0.5 \text{ amp/cm}^2$, $\text{NO}_3^- > 4.5\text{M}$, $\text{H}^+ > 0.5\text{M}$). Niobium appeared

acceptable as material of construction for longer-lived cathodes⁽²²⁾.

Its suitability was further proved when extensive tests⁽²³⁾ showed little hydrogen embrittlement on a niobium cathode.

2.3.1.(c) Dissolver Characteristics.

Bench experiments were carried out to establish flowsheet conditions for the anodic dissolution of stainless steel-clad -UO_2 fuel elements, as well as various samples of stainless steel⁽¹⁹⁾⁽²⁰⁾⁽²¹⁾⁽²²⁾⁽²⁸⁾. To ensure equilibrium conditions, steady state concentrations of the various salts were maintained in the electrolyte at an acid concentration of $3.0 \pm 0.27 \text{ N HNO}_3$. Anode dissolution efficiencies greater than 96% (based on Cr^{vi}) were achieved at current densities of $0.5\text{-}1.5 \text{ amp/cm}^2$. It was found that $1.17 - 1.45$ moles of nitric acid were consumed per equivalent of metal dissolved (based on Cr^{iii} , the ion species ultimately present in solution), including acid consumed on uranium oxidation. Experiments indicated that chemical dissolution of UO_2 occurred readily in electrolyte solutions at temperatures above 50°C , thus providing a convenient means for the integral processing of stainless steel-clad fuels.

Anode sludge formed $1 - 7\%$ of total anode weight loss, but further tests indicated that lower temperatures (40°C vs 90°C) resulted in less sludge formation. High current density-high acidity and low current density-low acidity also favoured low sludge deposition. It was suggested⁽²²⁾ that loss of uranium to sludge would be reduced and an increase in the uranium

processing capacity for a given solvent extraction system would result if the stainless steel cladding was first dissolved anodically and the UO_2 core then processed chemically in a separate batch dissolver. A flow diagram of a proposed electrolytic dissolution pilot plant, based on results obtained in the bench scale experiments, was given⁽²⁸⁾.

Based on a dissolver model made up of a cylindrical valve metal anode basket and surrounded by a cylindrical cathode, the heat output which accompanies electrolytic dissolution of stainless steel in nitric acid, was evaluated^{(22) (28)}. Heat generated from three different sources was considered, viz. heat due to the enthalpy change (ΔH), ohmic heat (I^2R) and electrical polarisation energy at the electrodes ($V_p I$ where V_p = polarisation voltage).

Experiments were carried out⁽²¹⁾ with various anode basket hole arrangements in order to determine the influence of such arrangements and the anode-cathode separation distance on the ohmic heat evolved during electrolytic dissolution.

Conductive rubber sheeting has been used instead of a niobium dissolver basket in an effort to establish the effect of electrode and cell geometry on the current paths within a dissolver⁽²³⁾. Current paths were plotted by deduction from lines of equal potential joining cathode and anode. It was

found that although current was fairly evenly distributed on the cathode surface, the greatest current concentration on the anode occurred along the portions nearest the cathode. Stray current paths in an electrolyte were also studied using conductive rubber sheeting⁽²⁶⁾, in an attempt to forestall possible corrosive situations in electrolytic process equipment. Various cell configurations were investigated and experimental evidence showed that little electrolytic corrosion of metal pipes connected to the dissolver would occur provided the pipes were sufficiently insulated from the dissolver vessel.

2.3.1.(d) Corrosion and Irradiation Resistance of Materials.

Investigations into the corrosion resistance of materials likely to be used in the construction of electrolytic dissolution plant were carried out. Corrosion tests on stainless steel (Type 304L) in electrolytic dissolver product solutions showed⁽¹⁹⁾⁽²²⁾ that its use would be limited to the construction of cooled raffinate storage tanks. Titanium, however, proved to have excellent corrosion resistance⁽²³⁾⁽²⁶⁾, even in boiling raffinate solutions. A number of plastic materials were also tested for stability in boiling electrolytic dissolver solutions⁽²⁶⁾. Only fluorocarbon, polyethylene and p.v.c. plastics proved sufficiently resistant, however. Corrosion tests on specimens of various metals suspended near the electrodes

of an operating bench-scale electrolytic dissolver showed⁽²⁴⁾⁽²⁶⁾ that only titanium and niobium were sufficiently resistant to both electrolytic and chemical corrosion.

Plastics which were shown earlier to be resistant to chemical attack in electrolytic dissolver solutions⁽²⁶⁾, were irradiated in the dissolver product medium at levels up to 10^9 R⁽²⁴⁾. Only a polyethylene - type plastic proved sufficiently stable under these conditions to warrant further consideration as a possible insulating and supporting material in dissolver construction. Further chemical and irradiation tests on other non-conducting materials showed that samples of a glass fabric - silicone resin, a fluorocarbon (Kynar) and alumina were also sufficiently resistant⁽²⁹⁾.

2.3.1.(e) Series Dissolver.

In an attempt to overcome the major disadvantages of the electrolytic dissolution of nuclear fuels in an inert anode basket, (e.g. loss of contact between fuel and basket, the need for low potential - high current power supply) the concept of a series electrolytic dissolver was evolved⁽²⁴⁾⁽²⁹⁾⁽³⁰⁾. Bomar⁽³⁰⁾ has described laboratory experiments involving the use of glass dissolvers either U-shaped or straight tubular. Fuel pieces (stainless steel, aluminium or zirconium) were placed in the dissolver through which the electrolyte solution was circulated. Current passed through the whole system by means of electrodes inserted at each end of the dissolver, not necessarily in contact with the fuel pieces inside the vessel. It was found that a series of electrolytic cells were thus formed within the dissolver, each fuel piece in turn acting both as an anode and a cathode. Both a.c. and d.c. were tested but it was found that the dissolution rate with a.c. was only about 40% of that obtained with d.c. Current utilisation factors of up to 10.7 were obtained when using d.c. for the dissolution of stainless steel in 8 M HNO_3 . The current utilisation factor was defined as

$$\text{Current Utilisation Factor} = \frac{(\text{Grams of metal dissolved})}{(\text{Electrochemical Equiv.})(\text{Faradays of Metal.})}$$

A maximum dissolution rate of $2.5 \text{ mg/cm}^2 \text{ min.}$ was obtained for stainless steel in 8 M HNO_3 at 2.5-3.1 amp and 105-130V.

A simplified mathematical approach to the series dissolver has been attempted⁽²⁹⁾. An equation was derived relating percentage current utilisation per piece (U), solution resistance (R_s) and polarisation resistance (R_p) as follows :

$$\frac{100}{U} = 1 + \frac{R_p}{R_s} \quad \dots (2.1)$$

Based on equation 2.1. a correlation of the results was established which showed that the current utilisation, U , decreased with decreasing current and piece length. This decrease in current utilisation was attributed to an increase in polarisation resistance and a relative decrease in solution path resistance, respectively.

2.3.2. Savannah River Investigations.

Work at the Savannah River Laboratory has been directed at the practical problems associated with the operation of an electrolytic dissolver which would be compatible with existing aqueous-solvent reprocessing plants constructed in stainless steel.

2.3.2.(a) Bench-Scale Investigations.

Simple experiments using a single stainless steel rod as the anode showed ⁽³¹⁾⁽³²⁾ that stainless steel dissolution rates were directly proportional to the current within a wide range of temperature, electrolyte concentration and current density conditions. Current efficiencies obtained were higher with d.c. than with a.c. and samples of off-gas were found to consist mainly of nitric oxide, with no hydrogen being detected.

Electrolytic dissolution experiments with stainless steel-clad UO_2 cermet and graphite - uranium fuel in 10 M HNO_3 showed⁽³³⁾⁽³⁴⁾ that a small amount (0.4%) of uranium was entrained in the sludge resulting from the dissolution of the cermet. This amount could be reduced by about 50% after leaching of the sludge with boiling 10 M HNO_3 . Less than 0.01% of uranium was lost, after leaching, in the sludge resulting from the anodic dissolution of stainless steel-clad UO_2 fuel elements in 10 M HNO_3 ⁽³⁴⁾. No complications were observed when irradiated stainless steel-clad UO_2 rods were dissolved electrolytically in 7 M HNO_3 ⁽³⁵⁾.

Anodic dissolution of aluminium was achieved⁽³⁵⁾, using both a.c. and d.c., under a wide range of current densities (0.03-1.0 amp/cm²), solution temperatures (25-108°C.) and electrolyte concentrations (0-1 M Al, 1.5 - 6.0 M HNO_3). Dissolution rates of 0.37 g/amp were obtained for both types of current.

Efficient dissolution of both stainless steel and stainless steel-clad UO_2 in 4 M HNO_3 was obtained using a tantalum basket as the anode holder⁽³⁶⁾. Loss of electrical contact between the stainless steel and tantalum was, however, the main disadvantage of such a system. Pressure was applied to the charge in the basket to help maintain electrical contact, whilst arcing was prevented to a large extent by the insertion of an aluminium liner above the level of the solution.

Investigations were carried out to observe fuel element - anode basket contact behaviour and to determine the best operating conditions which are necessary to achieve a high throughput without damaging the basket⁽³⁷⁾. It was found that no current flowed across points of contact between stainless steel and niobium immersed in nitric acid until the potential reached a value of about 0.30V. Once this potential has been achieved and the oxide film broken, the voltage could be reduced without loss of contact. Current was found to be directly proportional to the contact force when a constant potential of 0.30V was applied across the contact points.

2.3.2.(b) Semiworks and Prototype Scale Basket Dissolvers.

Extended electrolytic dissolution runs in a semiworks-size plant, using a niobium basket, were reported⁽³³⁾⁽³⁸⁾. Successful dissolution of stainless steel-clad UO_2 fuel elements was achieved in 10 M HNO_3 at 95°C. Stainless steel charges of up to 7 kg. were dissolved electrolytically in 7 M HNO_3 at 70°C. Currents up to 400 amp and a cathode-anode potential difference of 16V were used. Current efficiencies of 80-90% were obtained and an intermittent mechanical vibratory device was used to maintain efficient contact between the fuel pieces and the anode basket.

Based on laboratory and semiworks experience a plant prototype electrolytic dissolver was designed⁽³³⁾⁽³⁹⁾. This consisted of a rectangular niobium anode basket, surrounded by a rectangular niobium cathode and contained in a stainless steel tank. A maximum

power supply of 5000 amp d.c. (or 1900 amp a.c.) at a potential of 20V. was envisaged. At maximum power input, a dissolution rate of 7 lb. of stainless steel per hour was anticipated. The prototype dissolver was successfully tested using charges of aluminium and stainless steel rods⁽³⁵⁾. Electrolytes used were 8 M and 4.5 M HNO_3 respectively. Severe arcing occurred, however, during the dissolution of the stainless steel charge resulting ultimately in failure of the bottom of the anode basket. Contact between the fuel rods and the anode basket was maintained by means of periodic vibrations from an automatic hammer and, in order to minimise the arcing, arrangements were made to shut off the current whenever the hammer was used. Despite attempts to overcome arcing in the anode basket, it was found that the only practical way of avoiding damage due to local overheating was by imposing an upper limit of 15V. on the potential applied to the dissolver⁽³⁷⁾. A current of about 2000 amp appeared to be the limit under these conditions, thus cutting down the projected output of the prototype dissolver.

Further charges of stainless steel could be dissolved, however, at an average current of 3000 amp and 15V. (maximum)⁽⁴⁰⁾. Electrolyte used was 4.5 M HNO_3 at $85 \pm 5^\circ\text{C}$. From these figures it was deduced that a full scale electrolytic dissolver could process more than 1 ton of uranium per day, assuming an uranium to cladding ratio of 3:1.

2.3.2.(c) Liquid Contact Dissolvers.

In order to obviate the problems associated with the maintenance of efficient metal-to-metal contact, the use of a "liquid contact" dissolver was suggested⁽³⁷⁾. Based on the experiments with the series electrolytic dissolver reported by Bomar⁽³⁰⁾, such a dissolver would operate by conducting current to the charge through the electrolyte rather than by direct metal-to-metal contact. Anodic dissolution would then occur on the side of the charge facing the cathode, provided the geometrical arrangement of the charge with respect to the electrodes was such that the current flowed preferentially through the charge rather than through the electrolyte.

The S.R.L. basket dissolver⁽³³⁾⁽³⁹⁾ was modified⁽⁴¹⁾ so that it could be operated as a liquid contact dissolver. Tests showed that arcing was eliminated and a current density of 3-3.5 amp/cm² of anode surface would be maintained thus doubling the throughput of a given size dissolver as compared with the metal-to-metal contact method. A platinum anode of 0.7 ft.² area was used in the successful dissolution of various stainless steel fuel assemblies in 5.5 M HNO₃, a voltage of 15-20V. being necessary to conduct the desired amount of current (3-3.5 amp/cm²).

Various types of "insulating" fuel baskets were proposed for use with the liquid contact dissolver⁽⁴²⁾. These were intended to contain the fuel element charge and to prevent it from coming

in contact with the electrodes. Successful electrolytic dissolution of aluminium was achieved in the liquid contact dissolver but electrolytic disintegration of Th-0.5% U alloy proved less promising⁽⁴²⁾. Despite leaching with 6 M nitric acid, an overwhelming proportion of the uranium (70.5%) remained in the thorium oxide sludge.

2.3.3. Zirconium and its Alloys.

A considerable amount of research has been carried out on the anodic dissolution of zirconium and its alloys, a method which could be an attractive head-end processing step, obviating the need for corrosive solutions containing HF, necessary in purely chemical processing. It has been found that the electrolytic reaction of zirconium and zirconium alloys in nitric acid and nitrate solutions is one of "disintegration" rather than dissolution as about 70% of the zirconium flakes off the anode in the form of an insoluble ZrO_2 sludge. No sludge, however, is produced when zirconium is dissolved anodically in HCl - methanol electrolyte.

2.3.3.(a) Bench-Scale Experiments.

Clark and Petersen⁽⁴³⁾ investigated the possibilities of electrolytic disintegration in situ of Zircaloy-2 screens from a reactor vessel. Zircaloy-2 was found to dissolve best at 60°C. in 8 M HNO_3 . Similar results were obtained from investigations carried out by workers at Idaho⁽²³⁾⁽²⁶⁾⁽⁴⁴⁾ who also showed that 6-28% of uranium was lost in the sludge when Zircaloy-2 clad UO_2 fuel elements

were disintegrated electrolytically in nitric acid at various temperatures and acid concentrations⁽⁴⁴⁾.

Successful electrolytic dissolution of both Zircaloy-2 clad UO_2 and zirconium clad U-Mo alloys in 10 M nitric acid was achieved, however, by S.R.L. workers⁽³⁴⁾⁽⁴⁵⁾. Only a small fraction of the uranium remained in the zirconium sludge after leaching with 10 M HNO_3 . Results similar to those obtained by Clark and Petersen⁽⁴³⁾ were observed in the case of zirconium and Zircaloy-2 dissolution⁽⁴⁵⁾⁽³⁸⁾⁽⁴⁶⁾, but attempts to reduce the amount of uranium lost to the sludge (10-50%) from the electrolytic disintegration of Zr-low U (5-15%) alloys proved largely unsuccessful⁽⁴⁶⁾⁽³⁸⁾⁽³³⁾⁽³⁴⁾⁽³⁹⁾⁽⁴⁷⁾. Variations in the electric power supply (half-rectified a.c. and interrupted d.c.), chemical composition and temperature of the electrolyte had little effect on the uranium loss.

Current utilisation during anodic dissolution of Zircaloy-2 was found to remain constant at 1.0 ± 0.1 g/amph throughout a wide range of nitric acid concentrations (1-10 M)⁽⁴⁰⁾.

Although Zircaloy-2 was found to disintegrate anodically in the series electrolytic dissolver⁽³⁰⁾, equilibrium conditions could not be established as no provision for sludge removal from the dissolver was made and the run had to be stopped.

Early work on the anodic dissolution of zirconium in aqueous HCl solutions indicated⁽⁵⁾ that up to 25% of the zirconium removed

from the anode remained in the electrolyte in the form of a finely divided sludge of alpha-zirconium. To obviate this sludge formation, anhydrous HCl mixtures, notably HCl-methanol, were tried⁽⁴⁸⁾ (19)(28). Based on these experiments, an equation which correlates the current density on a zirconium anode in HCl-methanol solutions with the overvoltage, temperature and HCl concentration was developed⁽²⁹⁾. Preliminary results indicated also that stainless steel, iron, nickel and chromium dissolved anodically in HCl-methanol solutions, while aluminium and uranium dissolved chemically. No sludge formation was observed in the case of any of the above metals.

Studies of current density-potential relationships for zirconium in HCl-methanol solutions revealed the existence of two distinct, anodic overvoltage dependent reactions⁽⁴⁹⁾. At low overvoltage values (0-0.4V.) anodic dissolution was accompanied by the separation of a certain amount of finely divided sludge of alpha-zirconium and the rate of attack was independent of HCl concentration. As the anodic overvoltage rose (> 0.5) a region of electropolishing was reached with complete dissolution off the anode and current density largely independent of the applied potential.

2.3.3.(b) Semiworks and Prototype Dissolvers.

Zircaloy-2 clad UO_2 fuel elements were dissolved electrolytically in 10 M HNO_3 using the basket-type semiworks dissolver⁽³⁴⁾. An average alternating current of 65 amp at a constant potential of about 19V. was applied. Little loss of uranium to the sludge was observed.

Electrolytic dissolution of a charge of Zircaloy plates was tried in 4.5 M HNO_3 at 90°C . using the prototype electrolytic basket dissolver⁽⁴⁰⁾. Poor contact between the Zircaloy and the niobium basket, due to excessive zirconium oxide resistance, limited the current flow to 1100-1200 amp d.c. at 15V. A dissolution rate of 2.5 lb. Zr/hr. was obtained, an anode striker being used on a 1 minute cycle to improve contact.

When Zircaloy-clad UO_2 fuel assemblies were dissolved in 8 M HNO_3 in the prototype liquid contact dissolver⁽⁴²⁾, it was found that the current utilisation figure was only 35-40% of the value obtained when the metal-to-metal contact method was used. This effect was attributed to the fact that the current bypassed the charge through the electrolyte, due to the high resistance of the oxide film formed on the surface of the Zircaloy.

Chapter 3.

Selection of the Anodic Dissolution
Process.

Chapter 3.

Selection of the Anodic Dissolution Process

- 3.1. Introduction.
- 3.2. Choice of Dissolver Vessel.
- 3.3. Choice of Electrolyte.
- 3.4. Conclusions.

3.1. Introduction.

Severe limitations on the design of the proposed electrolytic dissolver for the head-end treatment of irradiated, highly enriched fuel elements were imposed both by criticality considerations (Section 1) and by the need for remote control operation. The former governed the size of the dissolver which had to conform to critically-safe dimensions, whilst the latter precluded the use of complicated equipment and fuel treatment methods, as safe, maintenance-free operation would be required from any apparatus situated in a radioactive plant cell.

The desirable characteristics of any dissolution system (e.g. universal application, satisfactorily high processing rates and compatibility of resulting product solutions with existing liquid-liquid extraction processes and equipment) were outlined previously (Section 1). Continuous dissolution was preferred both to give a uniform product composition and to provide a convenient means of cooling the dissolver charge by way of the continuously circulating electrolyte.

3.2. Choice of Dissolver Vessel.

3.2.1. Vessel Shape.

Based on known dimensions for critically safe geometries, two possible configurations of dissolver vessel were considered originally, viz. a cylinder and a slab. Maximum dimensions quoted in literature⁽⁸⁾ for the two shapes, based on U^{235} metal as the fissile material, are given below:

safe, infinitely long cylinder - 2.5 in. dia.

(water reflected)

safe, infinitely long and broad slab - 0.6 in. slab depth
(water reflected).

It must be noted that the figures quoted above refer to safe and not critical dimensions, i.e. a factor of about 2 has been applied in arriving at safe dimensions. If Pu^{239} were to be considered as the fissible material to be processed, the dimensions quoted above would have to be reduced further by a factor of 2-3.

Figures given above show that the size of a safe slab imposes very severe restrictions on the shape and dimensions of the fuel fragments which can be processed. In addition, a slab possesses inherent structural disadvantages (e.g. presence of corners) which will increase the complications of manufacture and maintenance and decrease the margin of safety. A cylindrical shape was therefore chosen as being preferable both from the point of view of the current investigation and future plant-size development.

The suggestion that an annular pipe dissolver be used was put forward during the course of the work described here. The characteristics of such a vessel are discussed in a subsequent chapter (Chapter 9).

3.2.2. Anode Connection.

In a continuously operating electrolytic dissolver, simple but adequate provision for the conveyance of the electric current to and from the dissolver charge had to be provided. Factors such as a bed composed of a large number of individual fuel pieces and the need for corrosion protection of the electrical contacts precluded the supply of

current by the simple expedient of a direct connection between the fuel element and the current source as used by other workers in previous laboratory experiments ⁽¹⁶⁾ ⁽¹⁷⁾.

The use of an anode basket ⁽¹²⁾ ⁽¹³⁾ holding the fuel fragments and surrounded by a cylindrical cathode forming the outside wall of the dissolver vessel was also considered. Such an arrangement, however, would reduce the volume ⁱⁿ ~~to~~ which the fuel could be ^{placed} ~~charged~~ even further as clearance between the cathode walls and the anode basket had to be provided to prevent short-circuiting. In addition the basket had to be made of a material which itself exhibited negligible anodic corrosion, (e.g. Pt or Ta). These metals introduced complications e.g. evolution of oxygen in the case of certain electrolytes (HNO_3) from the platinum and poor contact characteristics when a tantalum basket was used. ⁽¹⁵⁾. In general, too, a basket-type dissolver was considered as being more suitable for a batch process ⁽¹⁵⁾ rather than a continuous one.

The idea of a mercury pool anode was rejected on grounds of the high reactivity of mercury with electrolyte solutions.

The simplest solution to the problem seemed to be based on a suggestion by Hartland ⁽¹⁸⁾ who proposed a tubular dissolver vessel in which the two stainless steel parts forming the electrodes were aligned along the same vertical axis and separated by a length of electrically inert material (e.g. p.t.f.e.). Heat generated at contact points was removed by continuously circulating electrolyte and current was conveyed directly from the walls of the vessel to the charge. The possibility that

a number of electrolytic cells might be set up within such a system (Section 2.2), thus increasing the current efficiency, added to the attraction of the proposal and it was therefore decided to investigate further the practical implications of this particular means of conveying current to the dissolver charge.

3.3. Choice of Electrolyte.

In order to obtain dissolver product solutions compatible with existing uranium solvent extraction processes, aqueous electrolytes only were considered. Based on reported evidence ⁽¹²⁾, two of these, viz. saturated sodium bicarbonate solution and nitric acid were chosen as being the most suitable both from the point of view of uranium dissolution and minimum sludge formation.

3.4. Conclusions.

From considerations outlined above, a tubular electrolytic dissolver vessel, in which current from the anodic to the cathodic section flowed through a bed of uranium pellets, was chosen as the system to be investigated. An aqueous electrolyte, preferably nitric acid solution, was to be used as the dissolving medium.

CHAPTER 4

Preliminary Work.

Chapter 4.Preliminary Work.

- 4.1. Potential - Time Behaviour of Uranium in Nitric Acid.
 - 4.1.1. Introduction.
 - 4.1.2. Experimental Procedure.
 - 4.1.3. Results and Observations.
 - 4.1.4. Discussion and Conclusions.
 - 4.2. Measurement of Pressure Drop.
 - 4.2.1. Introduction.
 - 4.2.2. Experimental Procedure.
 - 4.2.3. Results and Calculations.
 - 4.2.4. Discussion and Conclusions.
-

4.1.1. Introduction.

A number of experiments were carried out to observe quantitatively the behaviour of uranium electrode in nitric acid. Potential-time curves were plotted to investigate the behaviour at different concentrations of nitric acid.

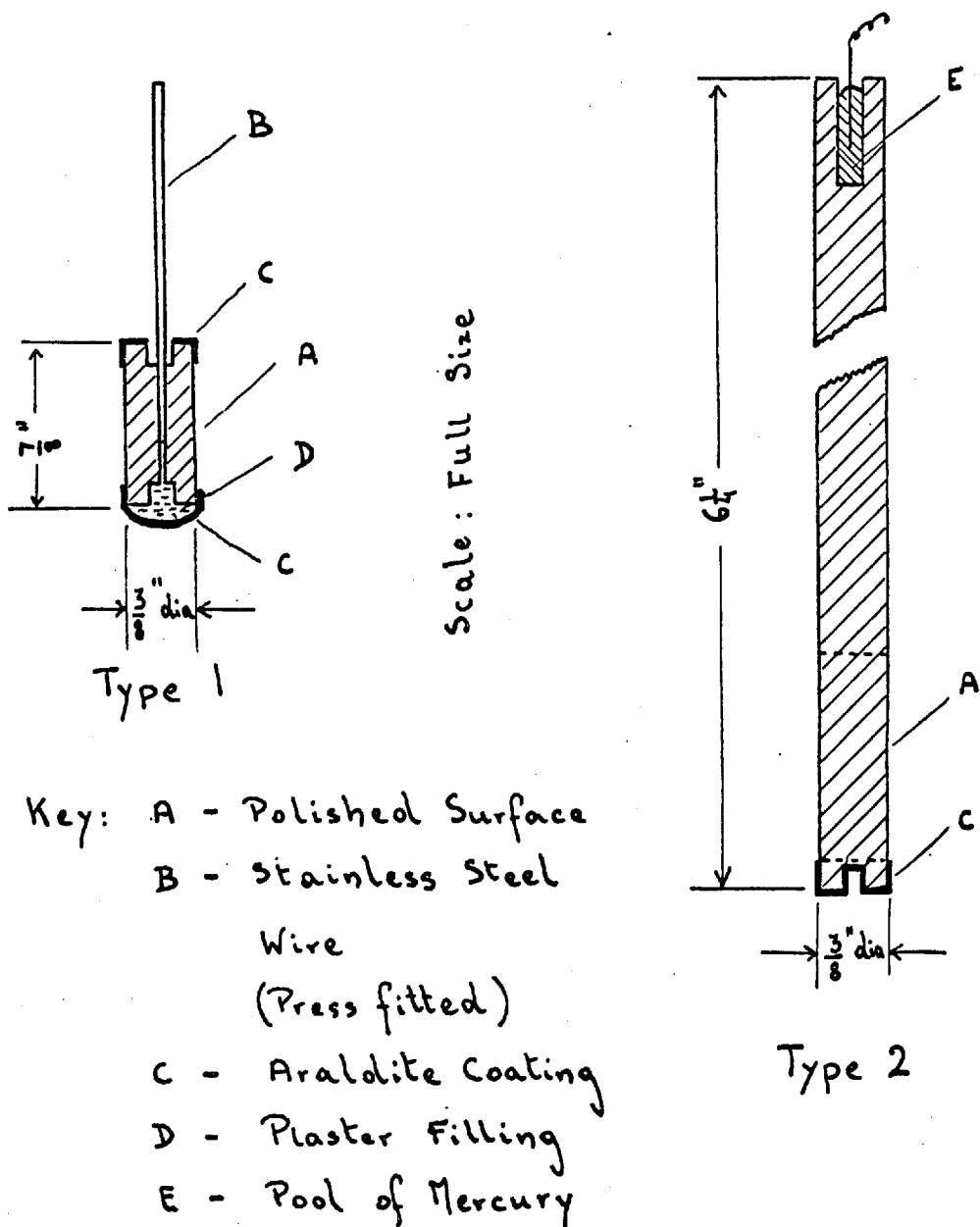
4.1.2. Experimental Procedure.

The test circuit was the standard potentiometric bridge circuit used in electrode potential measurements; the main components being a Pye Model "S" potentiometer, a Pye Taut Suspension Pointer Galvanometer and a Weston standard cell for calibration. A normal calomel electrode, prepared as recommended by Findlay⁽⁵⁰⁾, formed the reference electrode, its potential being taken as + 0.281V at 25°C.⁽⁵¹⁾

Three concentrations of nitric acid were used as the test electrolyte, viz. 3N, 6N and 9N, and a saturated potassium nitrate salt bridge provided the electrical link between the reference electrode and the test electrode. The electrolyte was not stirred and was contained in a vessel open to the atmosphere.

A number of uranium pieces were selected from a batch of uranium metal specimens provided by A.E.R.E., Harwell. Two of these were chosen as being more easily adaptable to form the uranium electrode used in the experiments (Fig. 4.1). The uranium electrodes were first cleaned by dipping in 6N nitric acid and were then polished anodically before the start of each experiment using a method described by Stebbens⁽⁵²⁾. An 18-8, 16 s.w.g. stainless steel wire formed the cathode.

Fig. 4.1. Two Types of Uranium Rod adapted for Use as Electrodes in the Study of Potential-Time Behaviour of Uranium in Nitric Acid.



A copper-saturated copper sulphate electrode was chosen as reference. It was considered to be both simple from the point of view of use and construction and accurate enough for the purposes of the experiment. The copper foil dipping in the saturated copper sulphate solution was prepared as described by Findlay⁽⁵³⁾, and the value of the potential of this electrode system was taken as 0.318V at 25°C.⁽⁵⁴⁾

4.1.3. Results and Observations.

Results of potential-time measurements for the uranium electrode are given in Tables A1, A2 and A3 (See Appendix A) and are plotted in Figs.4.2 and 4.3. Results of circuit test readings using the Cu-CuSO₄ electrode are given in Table A.4 (Appendix A). It was noted that the high concentrations of nitric acid (6N and 9N) very rapidly attacked the electropolished surface of the uranium electrode causing severe pitting if the reaction was allowed to proceed for too long. Hence, experiments were limited to about 10 minutes each in order to protect the electrode from undue corrosion. This effect was less marked in the case of 3N nitric acid.

4.1.4. Discussion and Conclusions.

The electrolytes chosen were 3N, 6N and 9N nitric acids. These were considered to be most likely used in an industrial-scale dissolver. Values of electrode potential of uranium obtained appear to be (Figs.4.2 and 4.3) + 0.06V, + 0.35V and + 0.40V (vs NCE) in 3N, 6N and 9N acid respectively. Whilst no direct comparison can be made between these

Fig. 4.2. Potential - Time Behaviour of a Uranium Electrode
in 3N Nitric Acid.

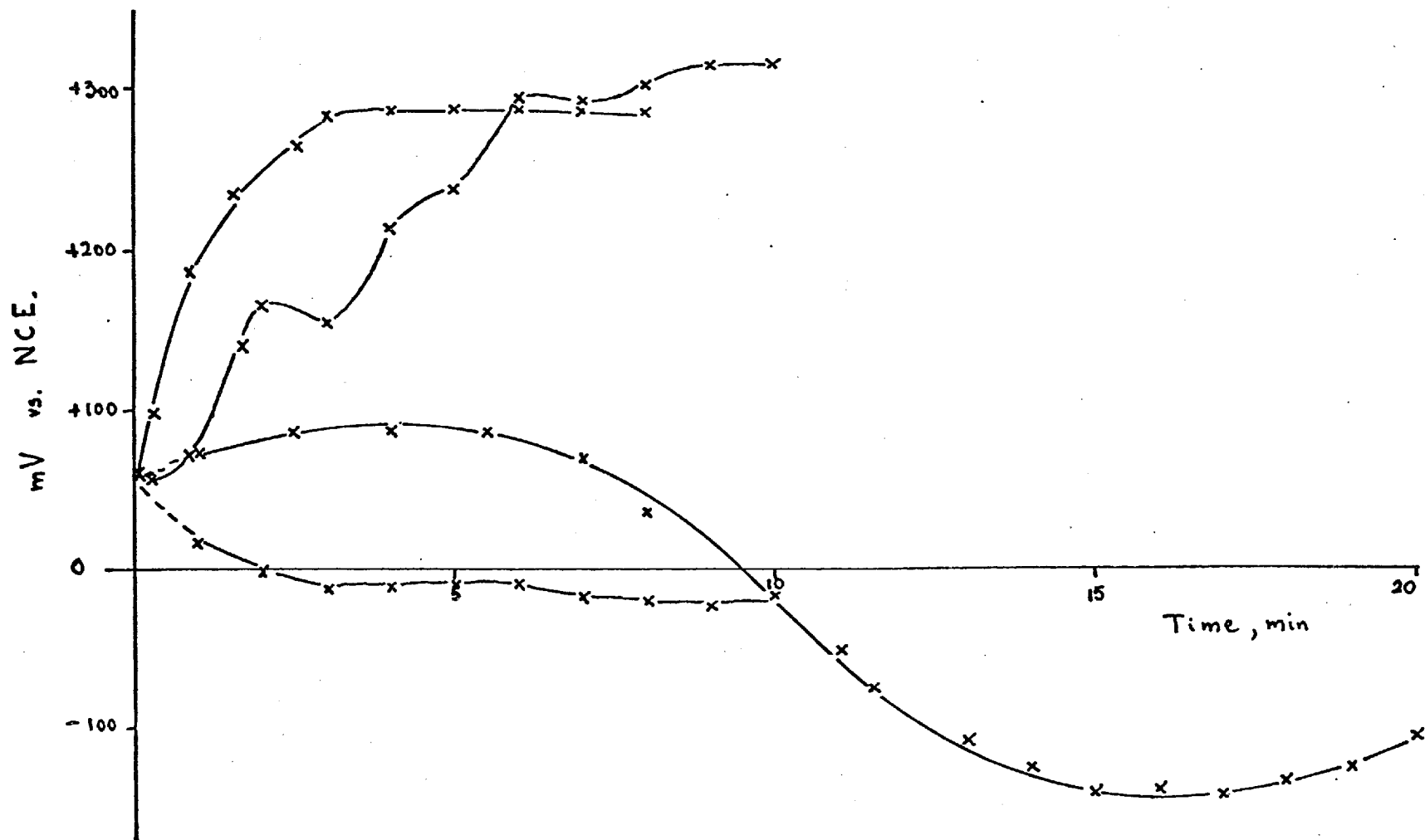
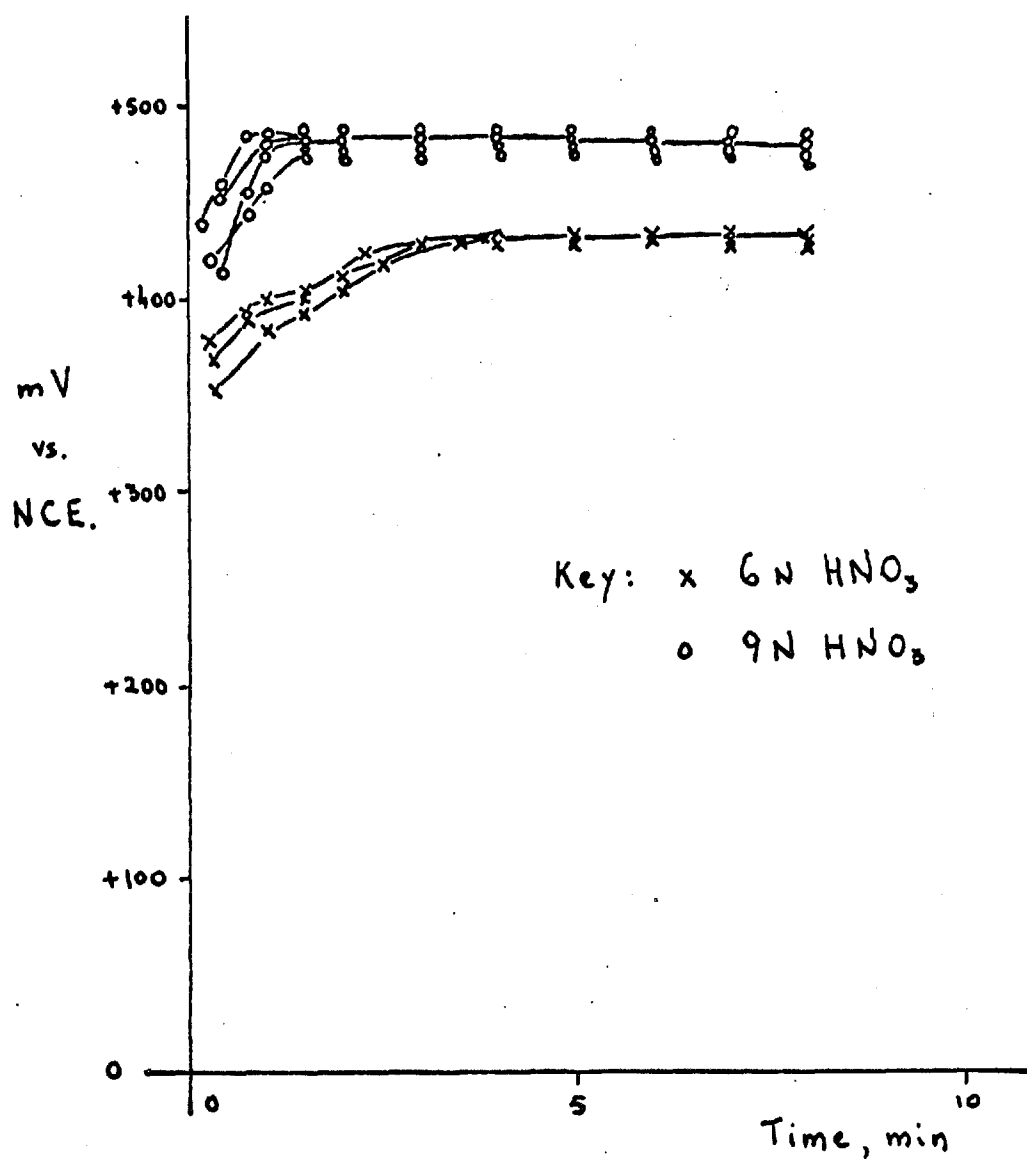


Fig. 4.3. Potential-Time Behaviour of a Uranium Electrode in 6N and 9N Nitric Acid.



values and those obtained by other workers studying the behaviour of uranium in other oxidising media, the figures noted above fall within the range observed generally under oxidising conditions^{(52) (55)}.

A comparison of the graphs in Figs.4.2. and 4.3. shows also that the reaction equilibrium was achieved much more rapidly in the case of the more concentrated acids. The more noble values of electrode potential under these conditions may be attributed partly to the greater oxidising power of concentrated nitric acid tending to passivate the surface of the uranium. The rapid rise in concentration of uranyl ions, due to the higher dissolution rate of uranium in 6N and 9N acid, would also contribute towards an increase in potential, according to the equation

$$E_u = E_u^0 + \frac{RT}{nF} \ln a_u^{6+}$$

where E = e.m.f. of the uranium electrode

E_u^0 = standard electrode potential

R = gas constant

T = temperature, °K.

F = faraday.

n = valency change.

a_u^{6+} = activity of the uranyl ion in solution.

It would thus appear that a rise in acid concentration, whilst beneficial on purely chemical considerations, might lead to a more stable electrolytic condition needing a higher over-voltage than would be the case with 3N nitric acid.

4.2. Measurement of Pressure Drop.

Nomenclature.

A	-	surface area of particle, ft^2 .
D_P	-	diameter of particle, ft.
D_T	-	diameter of tube, ft.
e	-	overall bed voidage fraction, dimensionless.
G	-	mass rate of flow, lb/hr.ft^2 .
g_c	-	gravitational constant, ft/hr^2 .
ΔH_B	-	pressure drop in packed tube, ft.
ΔH_T	-	pressure drop in empty tube, ft.
L	-	bed height, ft.
Δp	-	pressure drop in packed tube, lb/ft^2 .
V	-	volume of particle, ft^3 .
λ	-	particle shape factor, dimensionless.
ϕ_s	-	particle shape factor, dimensionless = $\frac{1}{\lambda}$
μ	-	fluid viscosity, lb/hr.ft .
ρ_F	-	fluid density, lb/ft^3 .

4.2.1. Introduction.

In order to provide a useful correlation between fluid flow and pressure drop in the dissolver system under study, a series of controlled experiments was carried out using various sizes of packing and dissolver diameters. Most of the proved relationships which were available⁽⁵⁶⁾ referred to fluid flow across packed beds where the $\frac{D_T}{D_P}$ ratio is large and a correlation based on a modified Reynolds number could, in general, be used. It was considered necessary, therefore, to test some of the correlations available in the literature⁽⁵⁷⁾ ⁽⁵⁸⁾ for packed beds of small $\frac{D_T}{D_P}$ ratios as obtained in the present work.

The use of such expressions would then be advantageous in scale-up calculations when pressure drops in plant size dissolvers would have to be determined.

The correlation developed by Chennakesavan and Laddha⁽⁵⁷⁾ was considered particularly useful as the range of $\frac{D_T}{D_P}$ ratios which they investigated, viz. 2 to 12, corresponded very closely with that which was most likely to occur in the dissolver. This range was assumed for the dissolver on the basis that the diameter of a full-scale, critically safe tubular dissolver would not be more than 2.5-5 inches⁽⁸⁾, packed with $\frac{3}{8}$ - $\frac{1}{2}$ inch diameter uranium pellets. The correlation is given by the following equation:

$$\frac{\Delta H_B^4}{\phi H_T} = 24.8 \left[\left(\frac{D_T}{D_P} \right) (1.5) (1-e) \lambda + 1 \right] - 22.3 \quad \dots (4.10)$$

where, for all particles, the Leva shape factor⁽⁵⁹⁾ λ , is taken as

$$\lambda = \frac{0.205A}{V \frac{2}{3}} \quad \dots (4.11)$$

A more general relationship, developed by Leva⁽⁵⁸⁾ was also tested. Under most turbulent-flow conditions, and for smooth-surfaced particles, this relationship is given as

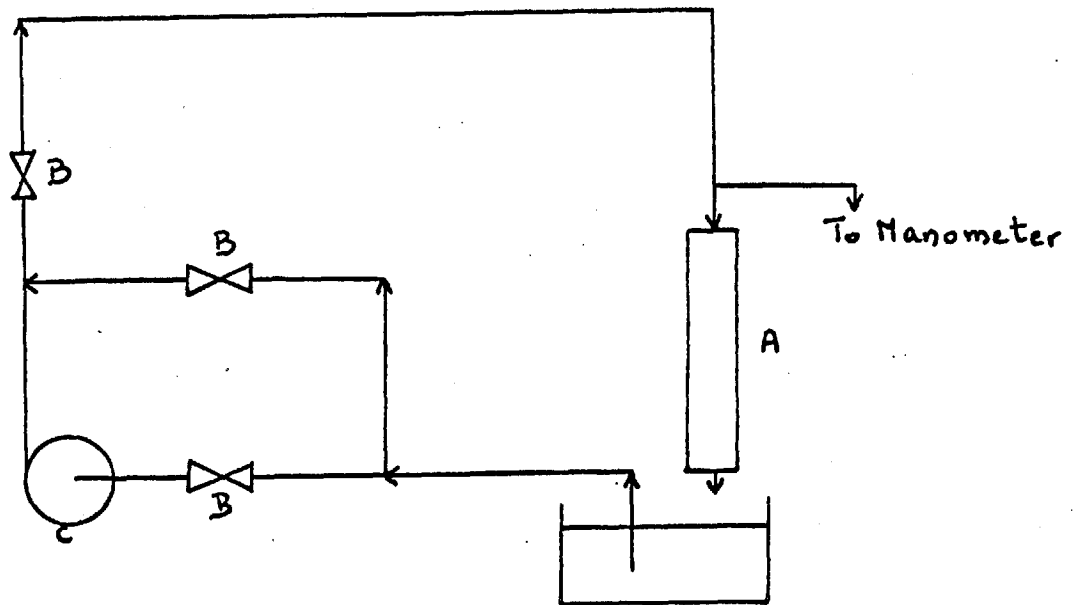
$$\frac{\Delta p}{L} = \frac{3.50G^{1.9} \mu^{0.1} (1-e)^{1.1}}{D_P^{1.1} \phi_s^{1.1} \rho_F g_c e^5} \quad \dots (4.12)$$

As will be seen from results quoted later (Sec.4.2.3.), both Eqn.4.10. and Eqn.4.12 can be used to estimate pressure drop values which obtain in the system under investigation.

4.2.2. Experimental Procedure.

Three different sizes of packing were used in the experiments viz. 5-7 mm. diameter glass beads, $\frac{3}{8}$ inch diameter and $\frac{1}{2}$ inch diameter ^{or} porcelain spheres. The ~~p~~^{or} porcelain spheres were a type normally used in industrial applications and were obtained from Hydronyl Ltd. Two tube sizes, viz. $\frac{3}{4}$ inch and $1\frac{1}{2}$ inch internal diameter were tested using 12 in. long, 18-8 stainless steel tubes. Only the two smaller sizes of packing were used with the $\frac{3}{4}$ in. I.D. tube. In all cases, bed lengths of 3 and 6 in. were investigated, the packed bed being supported on a plug of stainless steel mesh. The whole packed bed assembly was incorporated into the dissolver flow circuit (Fig.4.4.) as used in some of the earlier dissolution runs, with water as the testing fluid. Pressure drop across the bed was measured by means of a mercury manometer and liquid flow rates were obtained from measurements of time taken for a unit volume to flow through the bed.

Fig. 4.4. Pressure Drop Tests
Flow Diagram



Not to Scale

- A : Packed Bed Assembly
- B : 15 mm I.D. Glass Stop-Cocks
- C : No 12 Stuart - Turner Pump.

4.2.3. Results and Calculations.

Full results obtained are given in Appendix B (Tables B.1 and B.2) and plotted in Figs. 4.5. and 4.6. The correlations (Eqns. 4.10 and 4.12) were tested by substituting in them the appropriate values of flow rate, tube and particle diameter, voidage fraction etc. The figures for pressure drop thus obtained were then compared with those observed experimentally. A comparison of these values, expressed in cm. mercury/foot length of bed, is given in Table 4.1.

In order to reduce any influence of end-effects on the observed pressure drop values, the experimentally observed figures as quoted in Table 4.1. are based on the difference in pressure drop observed for a 6 inch bed and a 3 inch bed.

Thus

$$\Delta^{obs}/_{foot} = 4 (\Delta^{obs}/_{6 \text{ inches}} - \Delta^{obs}/_{3 \text{ inches}})$$

Values of voidage fraction, e , used in the calculations involving Eqns. 4.10 and 4.12 are those given by Leva⁽⁶⁰⁾ and are quoted in Table 4.2. As only beds composed of spherical particles were tested, the value of the particle shape factor (λ or ϕ_s) was taken as unity. Specimen calculations of pressure drop values using Eqns. 4.10. and 4.12. are included in Appendix B.

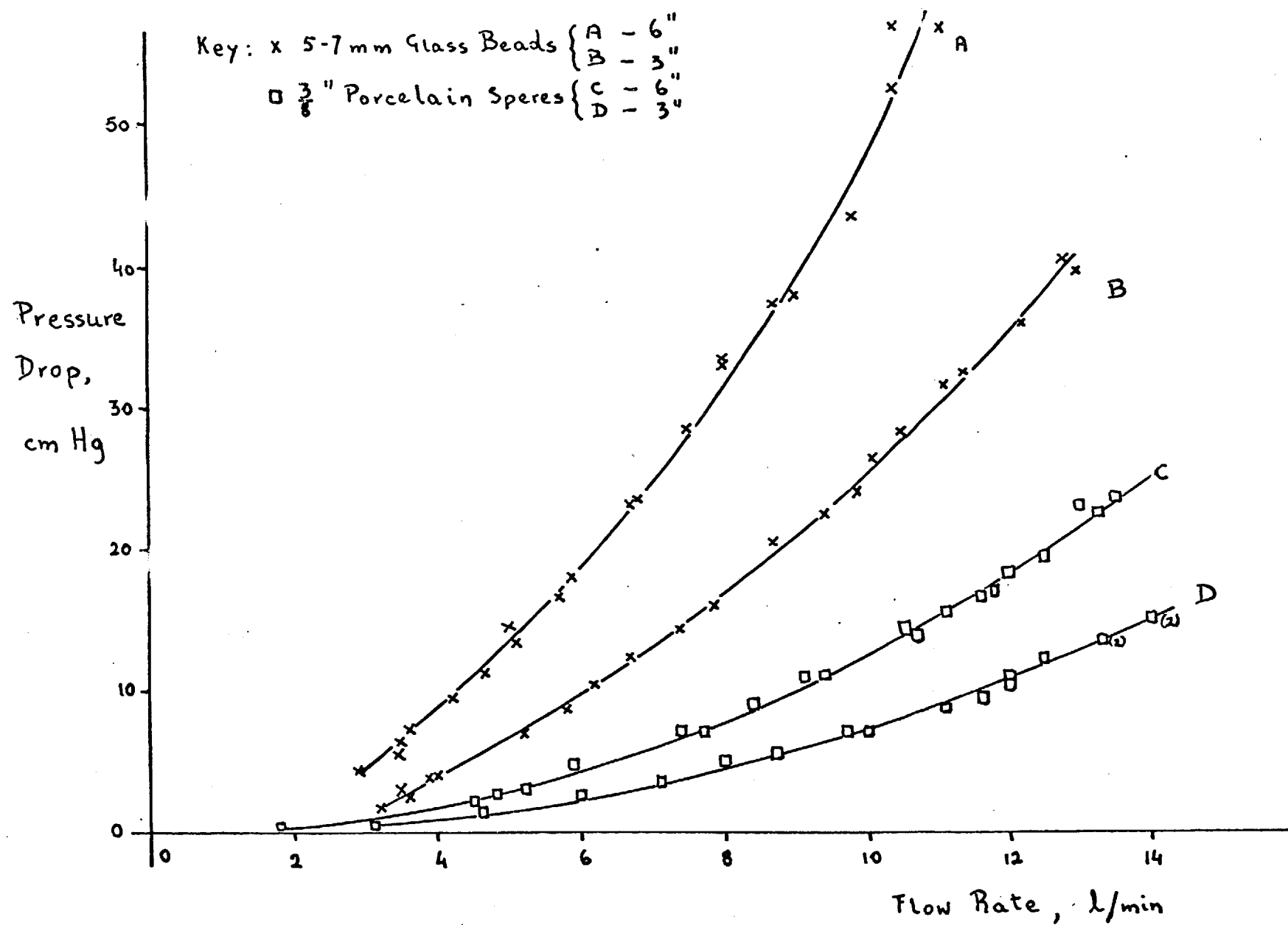
Fig. 4.5. Pressure Drop TestsPressure Drop vs. Flow Rate - $\frac{3}{4}$ in I.D. Tube

Fig. 4.6. Pressure Drop Tests

Pressure Drop vs. Flow Rate - $1\frac{1}{2}$ in I.D. Tube

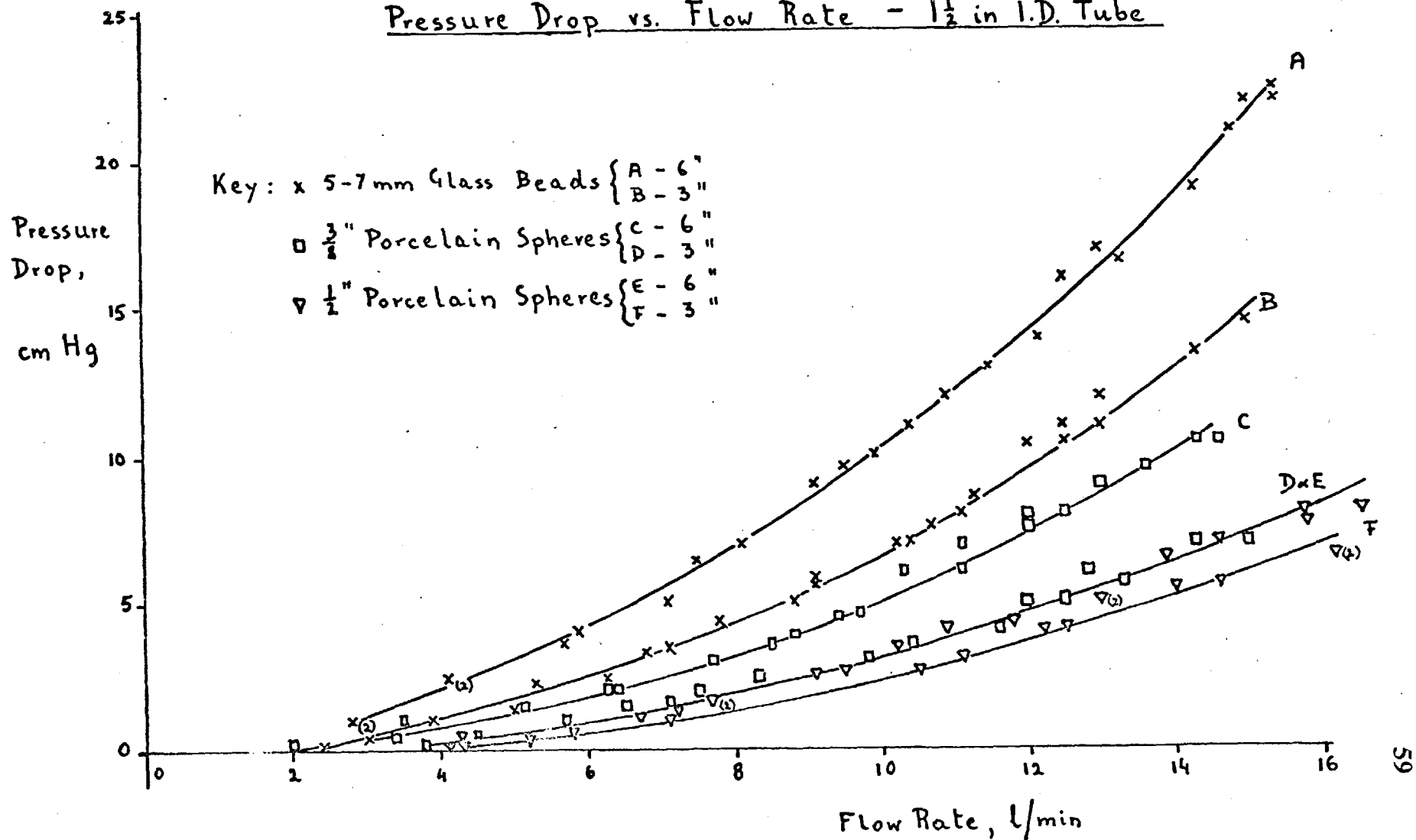


Table 4.1.

60.

A Comparison of Δp Values obtained experimentally and those calculated using the Leva (58)
and Chennakesavan and Laddha (57) Equations.

Flow Rate, l/min.

Notes:

Δp_1 : Pressure
Drop Values
from Eqn.
4.12.

Δp_2 : Pressure
Drop Values
from Eqn.
4.10.

Δp_3 : Observed
Drop Values.
Pressure
Drop Values
in cm.
mercury.

Tube Diameter. D_T	Particle Diameter D_p	6			8			10			12			14		
		Δp_1	Δp_2	Δp_3	Δp_1	Δp_2	Δp_3	Δp_1	Δp_2	Δp_3	Δp_1	Δp_2	Δp_3	Δp_1	Δp_2	Δp_3
$\frac{3}{4}$ inch	5-7 mm. glass beads.	33.8	32.0	35.6	59.6	53.8	56.8	91.6	111	90.0						
	$\frac{3}{8}$ inch porcelain spheres.	12.1	10.7	8.4	20.9	18.1	13.6	32.1	26.0	22.0	45.3	35.6	30.0			
	5-7 mm. glass beads.	5.1	6.0	6.4	8.8	9.6	10.4	13.5	14.3	14.8	19.0	19.3	18.8	25.4	25.4	23.2
	$\frac{3}{8}$ inch porcelain spheres.	2.1	2.4	2.8	3.6	3.8	5.0	5.6	5.7	8.0	7.9	7.7	10.4	10.6	10.1	14.0
	$\frac{1}{2}$ inch porcelain spheres.	1.1	1.2	1.0	2.0	2.0	2.0	3.0	2.9	2.8	4.3	4.0	4.4	5.7	5.3	5.2

Table 4.2.

Values of e , based on a graph by M. Leva (60).

Tube Diameter, D_T	Particle Diameter, D_P	$\frac{D_P}{D_T}$	e
$\frac{3}{4}$ inch	5-7 mm. glass beads.	0.33	0.47
	$\frac{3}{8}$ inch porcelain spheres.	0.50	0.54
$1\frac{1}{2}$ inch	5-7 mm. glass beads.	0.16	0.39
	$\frac{3}{8}$ inch porcelain spheres.	0.25	0.435
	$\frac{1}{2}$ inch porcelain spheres.	0.33	0.47

Note: 6 mm. was taken as the average diameter size of the glass beads.

4.2.4. Discussion and Conclusions.

A comparison of the figures listed in Table 4.1. shows a satisfactory degree of agreement between the calculated and observed values of pressure drop, bearing in mind the experimental errors involved. Most of the results fall within the limits of accuracy claimed by the respective authors⁽⁵⁷⁾⁽⁵⁸⁾. Figures obtained from the work of Chennakesavan and Laddha⁽⁵⁷⁾ show perhaps a slightly better correlation with the observed values than those based on the more general equation developed by Leva⁽⁵⁸⁾. In the latter case, the only significant lack of correlation occurs when $\frac{D_P}{D_T} = 0.5$. Under these circumstances, as

randomness of packing cannot really be achieved, correct estimation of the voidage fraction is difficult.

Equation 4.12 shows that under high voidage conditions, the value of pressure drop depends greatly on the voidage **f**raction estimate, a small variation in voidage resulting in a relatively large change of Δp . Such extreme conditions, however, are unlikely to occur in a full-scale dissolver, and Eqn.4.12 can be assumed to apply under most plant conditions likely to be encountered.

Either of the equations tested here can thus be used satisfactorily to obtain an estimate of the pressure drop resulting from a given length of bed in a dissolver, provided the flow-rate, tube diameter and average particle diameter are known.

Chapter 5

Anodic Dissolution of Uranium in a
Stainless Steel Dissolver.

Anodic Dissolution of Uranium in a
Stainless Steel Dissolver.

5.1. Introduction

5.2. Sodium Bicarbonate Electrolyte.

5.2.1. Experimental Procedure.

5.2.2. Results and Discussion.

5.3. Nitric Acid Electrolyte - Preliminary Circuit.

5.3.1. Experimental Procedure.

5.3.2. Results and Discussion.

5.4. Nitric Acid Electrolyte - Pilot Plant Circuit.

5.4.1. Experimental Procedure.

5.4.2. Results and Discussion.

5.5. Conclusions.

Chapter 5.

5.1. Introduction.

Experiments carried out with the stainless steel dissolver represent progressive stages of development of the dissolver circuit, starting with a simple assembly consisting only of a pump, reservoir and dissolver (Section 5.2.1), and leading up to the construction of the pilot plant (Section 5.4.1.) used subsequently throughout the course of this work.

The use of stainless steel as material of construction for the dissolver vessel had to be abandoned, however, due to excessive anodic corrosion of the stainless steel tube forming part of the dissolver.

Saturated sodium bicarbonate solution, which was reported to be one of the few alternative electrolytes, suitable for the anodic dissolution of uranium metal⁽¹²⁾, was used in the first set of experiments. (Section 5.2.). The ease and safety of handling a relatively weak alkaline solution also influenced its choice in preference to nitric acid under such conditions that splashing and spillage was likely to occur.

Nitric acid of various concentrations was used, however, in all further experiments carried out in safer, more closely controlled dissolver circuits.

5.2. Sodium Bicarbonate (Saturated Solution) Electrolyte.

In order to form some idea of the flow behaviour and the current and voltage characteristics of the dissolver system under

investigation, a number of runs were carried out using the simplest possible flow circuit assembly with a saturated sodium bicarbonate solution as electrolyte.

5.2.1. Experimental Procedure.

5.2.1.(a) Dissolver Vessel.

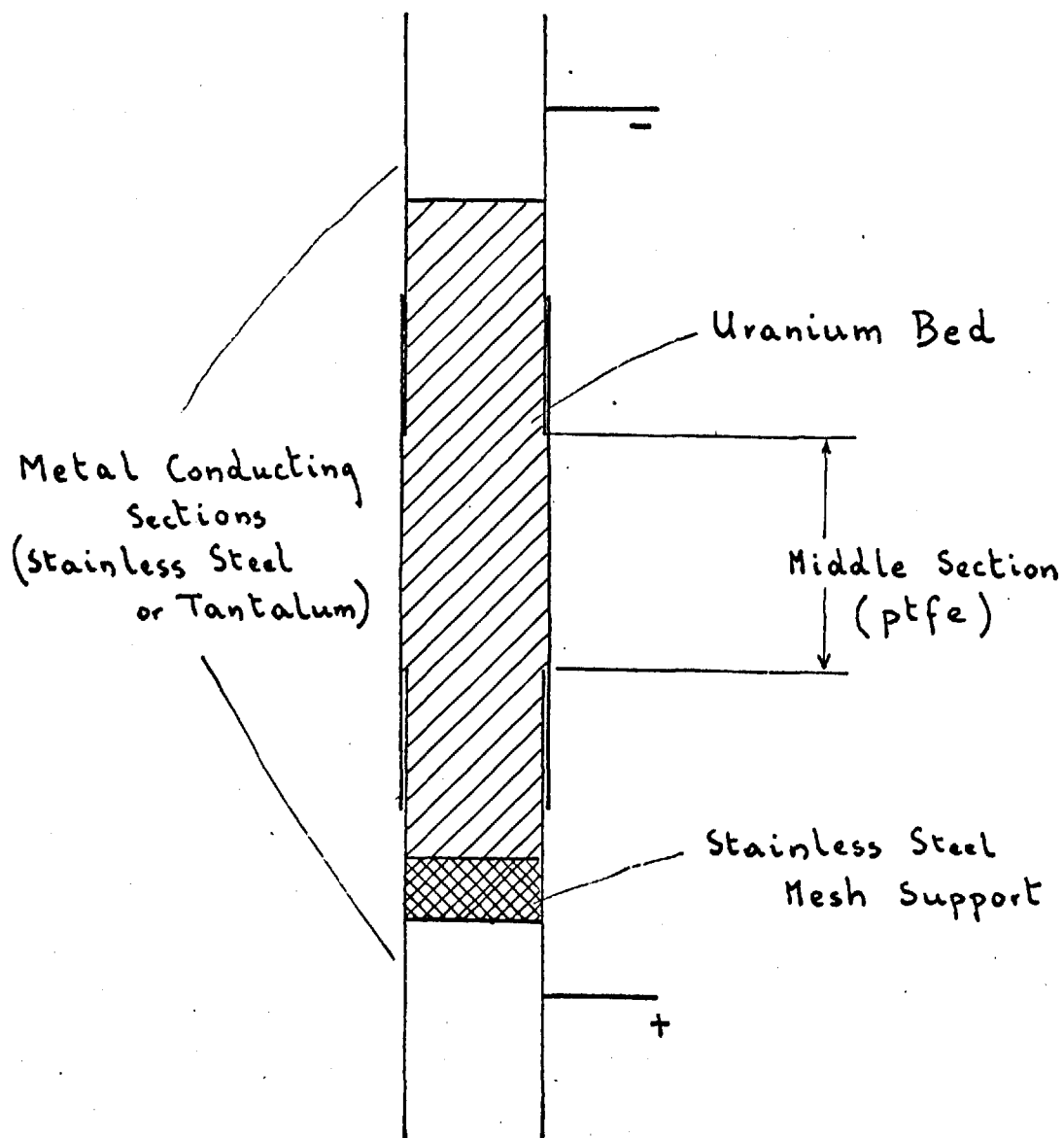
The dissolver vessel was made up of two sections of 18-8 stainless steel tube, $\frac{3}{4}$ in. i.d., $\frac{7}{8}$ in. o.d., each of the sections being 6 in. long. These metal sections, which conveyed the current to and from the dissolver, were joined by a length of p.t.f.e. tube, $\frac{7}{8}$ in. i.d. and 9 in. long. Varying degrees of separation between the two metal sections could thus be achieved, whilst at the same time sufficient overlap was ensured to provide a leakproof press-fit joint between the metal and the plastic. In order to provide an additional safeguard against leakage and to prevent the metal tubes from slipping under the weight of the uranium bed contained within the dissolver, "Jubilee" clips were attached round both ends of the p.t.f.e. tube. The bed of uranium pellets was supported on a stainless steel mesh plug which was inserted into the lower of the two stainless steel sections, the dissolver being operated vertically. A diagram of the dissolver vessel is given in Fig. 5.1.

5.2.1.(b) Uranium Bed.

With a separation distance of between 3-4 inches between the metal sections, a bed was made up consisting of 23 - $\frac{3}{8}$ in. diameter,

Fig. 5.1. Anodic Dissolution of Uranium

Diagram of Dissolver



Not to Scale

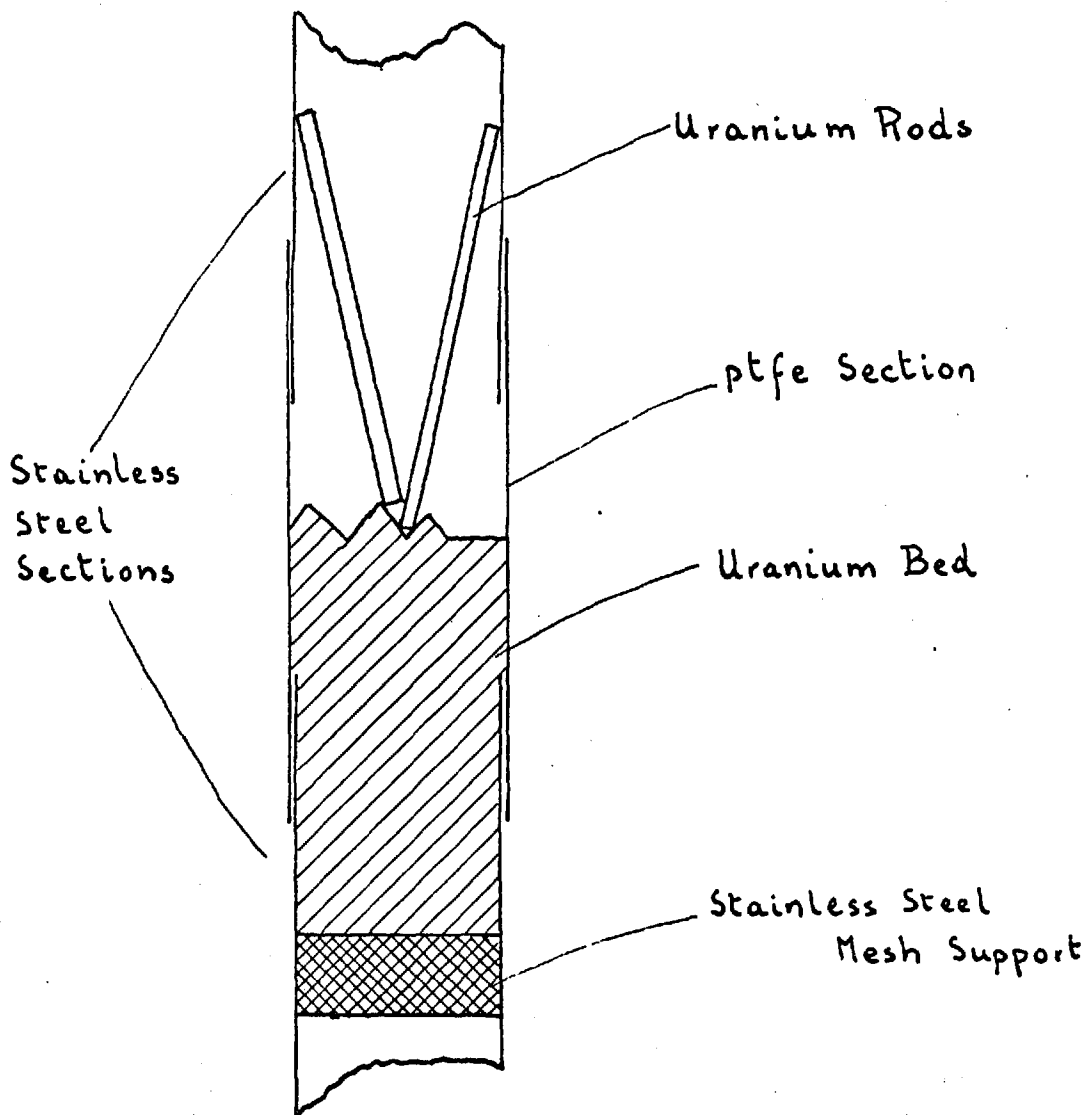
$\frac{7}{16}$ in. long cylindrical uranium pellets. It was found, however, that the bed did not reach the upper stainless steel section, thus failing to maintain proper electrical contact. Three 6 in. long $\frac{3}{8}$ in. diameter, uranium rods were therefore inserted inside the dissolver in the case of the first three runs (BC 1-3) to ensure adequate contact between the bed and the stainless steel tube. (Fig. 5.2.). In subsequent runs (BC 4-10), the distance separating the two stainless steel sections was decreased to 1 inch, thus enabling the bed, now made up of 18 $\frac{3}{8}$ in. x $\frac{7}{16}$ in. pellets, to touch both sections without the aid of the uranium rods. The majority of runs (BC 1 & 2, and BC 6-10) were carried out with the lower section of the dissolver forming the positive terminal, the polarities of the stainless steel sections being reversed for the remainder of the runs in the series (BC 3-5).

5.2.1.(c) Flow Circuit.

A saturated solution of sodium bicarbonate, made up with distilled water, was used as the electrolyte. It was circulated continuously through the dissolver by means of a No.12 Stuart centrifugal pump, fitted with a stainless steel impeller and impeller casing. The dissolver vessel was completely open to the atmosphere, thus limiting the flow of electrolyte through it to about 4-5 l/min. The pump output was controlled by means of a glass stop-cock attached to the inlet side. A diagram of the flow circuit is given in Fig.5.3.

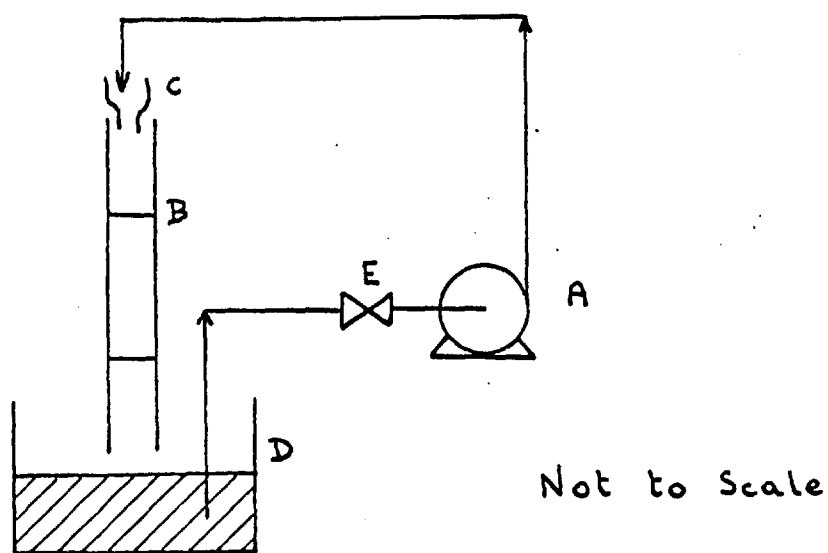
The source of D.C. power used for the anodic dissolution was a Heyberd battery charger with a maximum output of 3A at 12 V. A "blank"

Fig. 5.2. Anodic Dissolution of Uranium
Detail of Uranium Bed in
Dissolver (Runs BC 1-3)



Not to Scale

Fig. 5.3. Anodic Dissolution of Uranium
Flow Diagram - Sodium Bicarbonate
Electrolyte



A : No 12 Stuart-Turner Pump

B : Dissolver Vessel

C : Glass Funnel

D : Glass Tank

E : Glass Stop-Cock

run (BC 8), i.e. a run during which no current or voltage was applied, was also carried out. The temperature of the electrolyte remained within the range 19-35°C. throughout the series of runs.

5.2.1.(d). Method of Analysis.

Samples of electrolyte were taken after each run and analysed from uranium using the thiocyanate method described by Currah and Beamish⁽⁶¹⁾. The determination is based on the estimation of the colour produced by the uranyl-thiocyanate complex. The optical density of the coloured complex was measured on a Unicam SP.500 spectrophotometer at a wavelength of 335 m μ . Details of the analytical procedure are given in Appendix C, Section C.1.

5.2.2. Results and Discussion.

Results for uranium dissolution quoted in table 5.1. are based on the analysed content of uranium of the samples of electrolyte taken and the total volume of electrolyte which varied between 3.6-6.0 l. Allowance has been made for the volume of solution withdrawn during sampling.

Values of current density have been expressed in terms of amperes per square centimetre of cross-sectional area of the dissolver tube ($\frac{3}{4}$ in. i.d.), whilst dissolution rate figures have been calculated on the basis of the superficial area of the uranium pellets contained within that volume of the dissolver which separated the two metal sections, i.e. the p.t.f.e. section. This part of the dissolver will be referred to from now on as the "middle section". It was found when the uranium bed from the dissolver was examined after runs BC1-3,

Table 5.1. Anodic Dissolution of Uranium in a Saturated Solution of Bicarbonate as Electrolyte.

72.

Expt. No.	Duration mins.	Volts	Voltage Gradient volts/cm.	Amps	Current Density, amps/cm ² (cross-section)	Fara-days F	Wt. of Uranium Dissolved g.	Equivalents U ^{VI}	Equivalents $\frac{U^{VI}}{F}$	Conc. of uranium in elec. g/l.	Dissol. Rate ⁽¹⁾ , mg/min. cm. ²	Length of middle section. cm.
BC 1	120	15.0	2.0	0.4	0.14	0.030	4.25	0.107	3.5	1.06	0.53	7.5
2	90	15.0	2.0	0.4	0.14	0.022	4.25	0.107	4.7	2.24	0.73	
3	90	15.0	2.0	0.4	0.14	0.022	3.2	0.081	3.7	3.29	0.55	
4	150	12.0	4.8	1.0	0.36	0.093	7.5	0.189	2.0	3.20	2.7	
5	240	13.0	5.2	0.5	0.18	0.075	10.1	0.254	3.4	5.45	2.3	2.5
6	120	8.5	3.4	0.4	0.14	0.030	0.9	0.023	0.8	5.03	0.41	
7	120	9.0	3.6	0.2	0.07	0.015	0.6	0.015	1.0	5.70	0.27	
8	120	-	-	-	-	-	0.1	-	-	5.93	0.04	
9	120	12.6	5.0	0.6	0.21	0.045	3.8	0.096	2.1	6.92	1.71	
10	120	12.5	5.0	0.6	0.21	0.045	2.6	0.065	1.4	8.10	1.17	

Notes: (1) Estimated superficial area of pellets in middle section, taken as 4.7 cm²/pellet.

that 14 of the 23 pellets were dissolved to a slightly greater extent than the remaining nine. It was thus assumed that those 14 pellets were contained within the middle section.

$$\begin{aligned}\text{Surface area of 14, } \frac{3}{8} \text{ in. dia.} \times \frac{7}{16} \text{ in. long, pellets} \\ &= 0.737 \text{ in}^2 \times 14 \\ &= 66.5 \text{ cm}^2\end{aligned}$$

$$\begin{aligned}\text{Volume of 14 pellets} \\ &= 11.1 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\therefore \text{Volume occupied by 14 pellets within dissolver tube, assuming} \\ \text{55\% voidage}^{(60)} \\ &= 24.6 \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\therefore \text{Length equivalent to this volume within a } \frac{3}{4} \text{ in. i.d.} \\ \text{dissolver vessel} \\ &= 8.85 \text{ cm.} \\ &\text{or approx. } 3\frac{1}{2} \text{ inches.}\end{aligned}$$

In the case of runs BC4-10, when the length of the middle section was 2.5 cm., the number of pellets contained within that section would be

$$\begin{aligned}\frac{2.5}{8.85} \times 14 &= 4 \text{ pellets approx.} \\ \therefore \text{Surface area} &= 19 \text{ cm}^2\end{aligned}$$

The surface area of the three rods inserted into the dissolver in Runs BC 1-3 (Section 5.2.1.(b)), was disregarded from the point of view of dissolution rate calculations as it was considered that these served purely ^{as} ~~as~~ conductors between the uranium bed and the metal section.

Values for total current flowing through the dissolver are given in Table 5.1. It has been assumed that this is equal to the current flowing through the uranium bed, disregarding any fraction which may

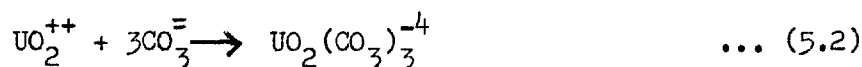
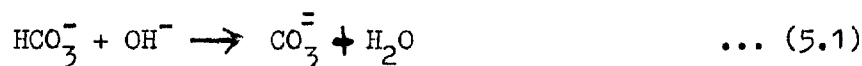
pass directly through the electrolyte from one stainless steel section to the other. This assumption is valid as only a negligible (<0.2 amp) current flowed through the dissolver in the case of Runs BC 1-3, before the uranium rods were inserted.

Frequent tapping of the dissolver was necessary to maintain a flow of current which tended to drop off to zero if no attempt was made to improve contact within the bed.

In order to be able to compare the voltages applied across uranium beds of different lengths, the concept of "Voltage Gradient" was introduced, where Voltage Gradient (volts/cm.)

$$= \frac{\text{Total Volts applied}}{\text{Length middle section (cm.)}}.$$

Although figures obtained in these runs indicated that the dissolution proceeded satisfactorily in terms of current efficiency, the resistance (overall) of the system remained excessively high with consequently low current densities and dissolution rates. In the presence of excess bicarbonate, uranium forms a soluble sodium uranyl carbonate complex^{(62) (63)}:-



The high resistance of the uranium bed could, however, be attributed to the formation of a basic hydrated oxide film on the anodic surfaces of the uranium. The formation of such a film in saturated sodium bicarbonate solution was observed by McLaren⁽¹²⁾.

It was thus decided to carry out a few preliminary runs using nitric acid electrolyte in order to compare its efficiency and speed of dissolution.

5.3. 6N Nitric Acid Electrolyte - Preliminary Experiments.

In order to test the behaviour of nitric acid as an electrolyte in anodic dissolution of uranium, a more sophisticated flow circuit was constructed. A limited number of runs were carried out which showed that, although the current efficiency level remained of the same order as that achieved with sodium bicarbonate electrolyte, the dissolution rate increased appreciably.

5.3.1. Experimental Procedure.

5.3.1.(a) Dissolver Vessel and Circuit.

Both the dissolver vessel and the bed of uranium used in these experiments were the same as described previously (Section 5.2.1.). The middle section of the dissolver was 2.5 cm. (1 in.) long and the uranium bed consisted of the same 18, $\frac{3}{8}$ in. x $\frac{7}{16}$ in. uranium pellets as used in the sodium bicarbonate dissolution runs. Prior to being incorporated in the new circuit, however, the uranium bed was washed with distilled water. The lower section of the dissolver formed the positive terminal.

The dissolver was connected to a flow circuit constructed from $\frac{5}{8}$ in. i.d. P.V.C. tubing with $\frac{5}{8}$ in. i.d. glass stop-cocks providing the means of flow control. A by-pass loop was included on the pump to facilitate the control of flow rate. A diagram of the circuit,

which was the same as that used for the flow rate - pressure drop experiments, (Section 4.2) was given previously (Fig.4.4). A manometer was, however, not included in the flow circuit. Flow of the electrolyte was maintained at the rate of 4.5 l/min. throughout the experiments and the temperature range was 22-49°C., no external cooling being provided. The strength of the nitric acid electrolyte, nominally 6N, ranged from 6-7 N and its volume from 3.65-4.00 l. The source of d.c. power was again a battery charger with a nominal output of 3A at 12V. No tapping of the dissolver was needed to maintain the current at a satisfactory level.

5.3.1.(b) Analytical Methods.

In order to obviate the interference of iron or any other metal present in the nitric acid electrolyte, the samples obtained from the dissolution runs were analysed using the tetrapropylammonium uranyl trinitrate complex method developed by Maeck et al⁽⁶⁴⁾. This is an extraction method specific for uranium and consequently does not suffer from the limitations imposed on the concentrations of interfering cations as in the case of the thiocyanate method⁽⁶¹⁾. Strong absorption by the uranyl complex in hexone was found at the stated wavelength of 452 m μ . Details of Maeck's method are given in Appendix C, Section C.2.

Acidities of the electrolyte in the presence of uranium were determined by pH titration with standard alkali after first complexing the uranium in situ with potassium oxalate solution. Details of the method are given in Appendix C, (Section C.3).

5.3.2. Results and Discussion.

The choice of the normality of the electrolyte was dictated by its electrical resistance which is at its lowest when the nitric acid concentration is approximately 3-6N⁽⁶⁵⁾. The higher concentration was chosen, however, as previous electrode potential measurements (Section 4.1.) showed that electrochemical equilibrium was likely to be achieved quicker in 6N rather than 3N nitric acid. As before, the current density was expressed in terms of the cross-sectional area of the dissolver and the dissolution rate in terms of the superficial area of the pellets contained in the middle section.

Results of the experiments are given in Table 5.2, Runs NA 1-5. Both current density and dissolution rate were far higher, at a given voltage gradient, than in the case of sodium bicarbonate electrolyte. It was thus considered that nitric acid had definite advantages as an electrolyte for the anodic dissolution of uranium and in all subsequent experiments nitric acid only was used.

Two columns of figures are given in Table 5.2. whenever values involving the measurement of current are quoted. These columns, headed "Total" and "Net" refer respectively to (1) current values as measured during the course of an experiment and (2) values of current flowing through the uranium bed, allowing for maximum current to flow directly through the electrolyte from one stainless steel terminal of the dissolver vessel to the other. The figures for the current flowing through the electrolyte are based on experimental evidence reported

Table 5.2. Anodic Dissolution of Uranium in Nitric Acid Electrolyte -

78.

Stainless Steel Dissolver Vessel.

Expt. No.	Duration mins.	V.	Voltage Gradient, volts/cm.	Amperes.		Current Density, amps/cm. ² , cross-section.		Fara-days		Weight of U. dissolved. g.	Equiv. U ⁶⁺	Equivalents U ⁶⁺ F	
				Total	Net.	Total	Net.	Total	Net.			Total	Net.
NA1	60	4.8	1.9	2.20	1.68	0.79	0.60	0.08	0.06	5.0	0.13	1.6	2.0
2	60	7.6	3.0	3.80	2.46	1.36	0.88	0.14	0.09	11.8	0.30	2.1	3.3
3	120	7.4	3.0	4.20	2.86	1.51	1.03	0.32	0.21	29.5	0.74	2.3	3.5
4	120	9.2	3.7	3.10	1.38	1.12	0.50	0.23	0.10	37.2	0.94	4.1	9.4
5	120	10.1	4.0	2.00	1.02	0.72	0.37	0.15	0.08	16.3	0.41	2.8	5.1
ED1	35	20.0	4.0	5.00	2.70	1.80	0.97	0.11	0.06	33.6	0.84	7.6	14.0
2	35	20.0	4.0	6.00	3.70	2.16	1.33	0.13	0.08	19.3	0.48	3.7	6.0
3	65	25.0	5.0	9.00	6.06	3.24	2.18	0.36	0.25	62.1	1.55	4.3	6.2
4	33	25.0	5.0	7.50	4.54	2.70	1.63	0.15	0.09	25.7	0.64	4.3	7.1
EDA1	33	25.0	5.0	1.75	1.19	0.63	0.43	0.04	0.02	13.3	0.33	8.3	16.5
2	30	25.0	5.0	2.00	1.44	0.72	0.52	0.04	0.03	14.9	0.37	9.3	12.3
3	45	25.0	5.0	2.00	1.44	0.72	0.52	0.06	0.04	19.5	0.49	8.2	12.3
EDB1	30	25.0	5.0	4.00	2.65	1.44	0.95	0.07	0.05	26.8	0.67	9.7	13.4
2	30	25.0	5.0	4.0	2.65	1.44	0.95	0.07	0.05	19.0	0.48	6.9	9.6
3	20	25.0	5.0	4.0	2.65	1.44	0.95	0.05	0.03	18.0	0.45	9.0	15.0
4	30	-	-	-	-	-	-	-	-	4.0	0.10	-	-
EDC1	20	25.0	5.0	8.50	5.80	3.07	2.08	0.11	0.07	21.5	0.54	4.9	7.7

Table 5.2. - continued.

Expt. No.	Duration mins.	V.	Volt- age Grad- ient.	Amperes.		Current Density amps/cm ² cross- section.		Faradays		Wt. of U dis- solved. g.	Equiv. U ⁶⁺	Equivalents U ⁶⁺ F	
			volts/ cm.									Total	Net.
EDL3C													
1	30	25.0	5.0	7.50	4.80	2.70	1.72	0.14	0.09	21.5	0.54	3.9	6.0
2	40	25.0	5.0	6.00	3.30	2.16	1.18	0.15	0.08	38.0	0.95	6.3	11.9
3	30	25.0	5.0	4.00	1.30	1.44	0.47	0.07	0.02	21.0	0.52	7.4	(26.0)
4	40	25.0	5.0	4.00	1.30	1.44	0.47	0.10	0.03	20.0	0.50	5.0	16.7
5	40	-	-	-	-	-	-	-	-	3.6	0.09	-	-
EDCEB													
1	60	25.0	2.5	2.90	1.55	1.04	0.56	0.11	0.06	34.0	0.88	8.0	14.7
2	40	25.0	2.5	3.00	1.65	1.08	0.59	0.08	0.04	16.0	0.40	5.0	10.0
3	30	25.0	2.5	3.00	1.65	1.08	0.59	0.06	0.03	30.0	0.76	12.7	(25.4)
4	30	25.0	2.5	3.00	1.65	1.08	0.59	0.06	0.03	34.0	0.88	14.7	(29.4)
5	20	-	-	-	-	-	-	-	-	4.0	0.10	-	-
7	30	20.0	2.0	1.57	0.52	0.57	0.19	0.03	0.01	4.0	0.10	3.3	10.0
8	30	20.0	2.0	1.89	0.84	0.68	0.30	0.04	0.02	8.5	0.21	5.3	10.5
9	30	20.0	2.0	1.98	0.93	0.71	0.33	0.04	0.02	10.5	0.26	6.5	13.0
10	30	15.0	1.5	1.40	0.63	0.51	0.23	0.03	0.01	4.0	0.10	3.3	10.0
11	30	15.0	1.5	1.30	0.53	0.47	0.19	0.02	0.01	2.5	0.06(3)	2.6	6.3
								(4)					
12	30	10.0	1.0	0.73	0.28	0.26	0.10	0.01	0.005	1.9	0.05	3.4	9.6
								(4)					
13	30	10.0	1.0	0.63	0.18	0.23	0.06	0.01	0.003	3.1	0.08	6.5	(26.0)
								(2)					

Table 5.2.-contd.

Expt. No.	Duration. mins.	V.	Volt- age Grad- ient.	Amperes.		Current Density amps/cm ² cross- section.		Faradays		Wt.of U dis- solved.	Equiv. U ⁶⁺	Equivalents U ⁶⁺ F	
			volts/ cm.	Total	Net.	Total	Net.	Total	Net.	g.		Total	Net.
EDCSB													
1	30	15.0	6.0	12.9	9.8	4.65	3.53	0.24	0.18	28.1	0.71	3.0	3.9
2	30	15.0	6.0	8.0	4.9	2.87	1.76	0.15	0.09	18.2	0.46	3.1	5.1
3	30	15.0	6.0	7.3	4.2	2.63	1.51	0.14	0.08	24.8	0.63	4.5	7.9
4	30	20.0	8.0	10.5	6.3	3.78	2.27	0.20	0.12	27.3	0.69	3.5	5.8
5	30	20.0	8.0	9.3	5.05	3.33	1.82	0.17	0.09	27.3	0.69	4.1	7.7
6	30	25.0	10.0	10.0	4.6	3.60	1.66	0.19	0.09	50.6	1.28	6.7	14.2
8	30	10.0	4.0	4.0	2.2	1.44	0.79	0.08	0.04	18.1	0.46	6.1	11.5
9	30	10.0	4.0	3.5	1.7	1.26	0.61	0.07	0.03	10.0	0.25	3.9	8.3
10	30	10.0	4.0	3.2	1.4	1.15	0.51	0.06	0.03	12.8	0.32	5.3	10.7
11	30	25.0	10.0	16.3	10.9	5.85	3.93	0.30	0.20	61.7	1.56	5.2	8.8
12	30	25.0	10.0	12.0	6.6	4.33	2.38	0.22	0.12	51.2	1.29	5.9	10.7
13	30	25.0	10.0	9.3	3.9	3.35	1.40	0.17	0.07	36.0	0.91	5.4	13.0

Table 5.2 - contd.

Expt. No.	Concentration U in electrolyte, g/l.	Dissol. Rate ⁽¹⁾ mg/min.cm. ²	Length of middle section. cm.	Normality (nominal) of acid.
NA1	1.25	4.51	2.5 cm.	6-7
2	4.20	10.6		
3	12.00	13.3		
4	22.25	16.8		
5	27.25	7.2		
ED1	4.35	8.01	5.0 cm.	6.0
2	6.18	4.60		
3	11.95	7.97		
4	14.50	6.49		
EDA1	2.70	3.36		0.4
2	4.15	4.14		
3	6.10	3.62		
EDB1	8.35	7.45		1.0
2	10.25	5.28		
3	12.06	7.50		
4	12.50	0.56 ⁽²⁾		
EDC1	13.40	8.96		2.5-3.0
EDLBC1	13.40	5.98		
2	16.86	7.92		
3	19.16	5.83		
4	21.06	4.17		
5	21.66	0.25 ⁽²⁾		

) Different size of
) pellets.
) Early dissolver
) system.

(1) Estimated superficial area of pellets in middle section.

(2) " " " " " in total length of bed.

Table 5.2 - contd.

82.

Expt. No.	Concentration U in electrolyte, g/l.	Dissol. Rate ⁽¹⁾ mg/min.cm. ²	Length of middle section. cm.	Normality (nominal) of acid.
EDCEB				
1	24.80	2.36	10 cm.	3.0
2	26.50	1.67		
3	29.50	4.17		
4	33.00	4.72		
5	17.10	0.44 ⁽²⁾		
7	17.60	0.54		
8	18.50	1.18		
9	19.64	1.46		
10	20.10	0.54		
11	20.44	0.35		
12	20.70	0.26		
13	21.10	0.43		
EDCSB				
1	23.8	15.6	2.5 cm.	3.0
2	25.8	10.1		
3	28.5	13.8		
4	31.5	15.2		
5	34.5	15.2		
6	40.0	28.1		
8	44.3	10.0		
9	45.5	5.6		
10	47.0	7.1		
11	53.5	34.2		
12	59.0	28.5		
13	63.0	20.0		

(1) Estimated superficial area of pellets in middle section.

(2) " " " " " in total length of bed.

later (Section 5.4) which gives the resistance of the electrolyte & Appendix F flowing across a non-conducting bed. The values of "Net" current quoted can thus be taken as representing the minimum amount of current which would pass through the uranium bed and take part in the dissolution reaction. The true value of current passing through the bed, however, lies somewhere between the two extremes. This assumption is illustrated clearly by the results obtained in Run NA.4 where the current efficiency value (Equivalents of uranium dissolved per Faraday) based on the "net" current figure is far higher than that theoretically possible. As there are only 4 pellets in the middle section of the dissolver (Section 5.2.2.) the maximum number of cells which can conceivably be formed is 5, whilst a figure of 9.4 is calculated on the basis of "net" current.

5.3.2.(a) Uranium and Nitric Acid Balance.

(1) Weight of Uranium dissolved = 99.5 g.

(by analysis, see Table 5.2).

(2) Weight of uranium dissolved = 97.5 g.

(by direct weighing of bed before
and after Runs 1-5).

The dissolution efficiency in the case of runs NA 1-5 was 4.0 g.U/amp compared with 3.7 gU/amp obtained for the sodium bicarbonate dissolution runs.

The values for the nitric acid balance are given in Table 5.3. below.

Table 5.3. Acidity ConsumptionRuns NA 1 - NA 5.

Run No.	Normality of Electrolyte	Volume of electrolyte l.	Wt. of HNO_3 in electrolyte. g.	Difference in HNO_3 content. g.
NA 0	6.85	4.00	1726	-
NA 5	6.19	3.65	1423	303

Note: Sample NA 0 represents the conditions of the fresh electrolyte as added to the dissolver at the start of the experiments.

Now we have acid lost by leaking and removal by sampling = 350 ml.

At a mean normality of 6.5N, this represents $6.5 \times 0.35 \times 63$

$$= 144 \text{ g } \text{HNO}_3$$

∴ Net nitric acid consumed

$$= 303 - 144$$

$$= 159 \text{ g.}$$

$$= 2.5 \text{ moles.}$$

Also uranium dissolved

$$= 97.5 \text{ g.}$$

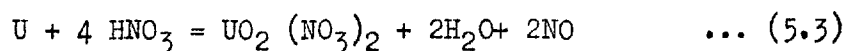
$$= 0.41 \text{ moles}$$

∴ Acid consumption

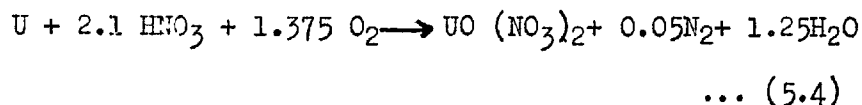
$$= \frac{2.5}{0.41}$$

$$= 6 \text{ moles } \text{HNO}_3 / \text{mole uranium diss.}$$

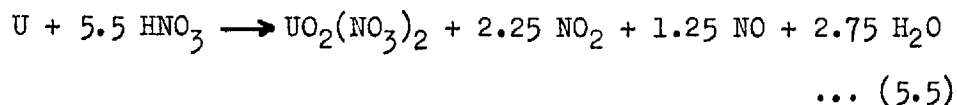
The principal equation for the chemical dissolution of uranium in nitric acid of concentrations less than 8N is given by ^{(2) (66)}



When the off-gases from the chemical dissolution of uranium are allowed to react with oxygen, virtually fumeless dissolution is achieved according to the equation⁽⁶⁷⁾:



Under these conditions, closely stoichiometric consumption of nitric acid results, compared with the 4 moles HNO_3 /mole of uranium as represented by equation 5.3. The figure of 6 moles nitric acid consumed per mole of uranium can be compared with 5.5 moles obtained in actual chemical dissolution practice⁽⁶⁸⁾ as is shown by the reaction



when no attempt at scrubbing or efficient removal of nitrogen oxides is made.

It must thus be assumed that a certain amount of acid from the dissolver circuit was lost due to the inability of the relatively small volume of electrolyte to reabsorb the oxides of nitrogen formed by the chemical and electrolytic decomposition of nitric acid.

5.3.2.(b). Anodic Corrosion of the Stainless Steel Dissolver.

Two observations were made when the dissolver assembly was examined after the completion of Run NA 5 : (1) the level of the uranium bed dropped so low in the dissolver due to dissolution, that direct contact between the uranium and the upper (cathodic) section

of the dissolver was lost and (2) closer examination of the dissolver vessel revealed considerable corrosion of the lower (anodic) stainless steel section.

The loss of direct contact between the stainless steel section and the uranium bed led to a change in resistance of the system with consequent drop in current density and dissolution rate as can be seen from Table 5.2. It also contributed to the anodic corrosion of the stainless steel section by forcing more current to flow directly from one stainless steel section to the other.

The weight of the stainless steel lost was estimated from the length of the tube as follows:

Assume length of tube dissolved = 1 in.

. . . Volume of ring 1 in. long, $\frac{3}{4}$ in. i.d., $\frac{7}{8}$ in. o.d.

$$= 0.16 \text{ in}^3$$

$$= 2.61 \text{ cm}^3$$

Assuming density of stainless steel = 7.8 g/cm^3

We have, weight of stainless steel
dissolved = 20.2 g.

= 20 g, say.

As 24.4 amph were consumed during the series of Runs NA 1-5, this gives a dissolution rate of 23.3 g/Faraday which leads to a current efficiency greater than 100% if one assumes 19.1 g of stainless steel to dissolve per Faraday⁽³²⁾. One can thus assume that a stainless

steel cell was operating continuously throughout the whole series of Runs NA 1-5. It was observed also that the anodic corrosion of the dissolver tube did not take place along its whole length, but only from the part nearest to the cathodic section of the dissolver.

5.4. Nitric Acid Electrolyte-Pilot Plant Dissolver Circuit.

A new, permanent pilot plant flow circuit incorporating the dissolver assembly was constructed in order to carry out a more extensive study of the anodic dissolution of uranium in nitric acid electrolyte. The main variables investigated were: (1) nitric acid concentration and (2) voltage gradient applied across the middle section of the dissolver. A new 6 in. section of stainless steel tube to serve as the positive terminal was substituted for the corroded one in the dissolver assembly. The end of this tube which was nearest the cathodic part of the dissolver was painted with acid-proof paint and coated with a number of layers of "Araldite" in an attempt to stop, or at least reduce the rate of anodic corrosion.

5.4.1. Experimental procedure.

5.4.1.(a) Dissolver Vessel and Uranium Bed.

The dissolver was again made up from $\frac{3}{4}$ in i.d. stainless steel tube (Section 5.2.1.) but a new anodic section was inserted (Section 5.4.). Due to continuing corrosion, however, this too had to be replaced, in runs EDCSB 7-13, by another (unpainted) section of stainless steel tube. The lower metal part of the

dissolver vessel formed the positive terminal of the system throughout the series of runs reported in this section.

The uranium bed was made up of $\frac{1}{8}$ in. diameter x $\frac{5}{16}$ in long pellets. This size was chosen in preference to the $\frac{3}{8}$ in diameter pellets used previously, as the smaller size gave a more realistic diameter of tube to diameter of particle ratio, resulting in a voidage factor for the bed of approximately 0.4. Such a bed would represent more closely the conditions obtaining in a plant scale dissolver. The overall initial length (i.e. length within the middle section and length within stainless steel sections) of the uranium bed in the dissolver varied largely with the length of the middle section, which ranged from 2.5-10.0 cm. thus resulting in a corresponding variation in voltage gradient. In the majority of the experiments the length of bed contained in the lower, positive section of the dissolver ranged from 4-5 cm. Four different initial lengths of bed were used:

(1) 15 cm (6 in) in the case of Runs EDI-EDCI (experiments carried out consecutively) and Runs EDCSB 8-13;

(2) 20 cm. (8 in.) in Runs EDLBC 1-5 in which the length of uranium bed within both the positive and negative stainless steel sections was increased to 7.5 cm. (3 in.) in each section;

(3) 22.5 cm. (9 in.) in Runs EDCEB 1-13;

(4) 10 cm. (4 in.) in Runs EDCSB 1-6.

In each case the initial length was measured before the start of a series of runs. As dissolution of the uranium proceeded the length of the bed would thus fall during consecutive experiments

until such time as fresh pellets were added to the bed to make up a convenient length for the next set of runs.

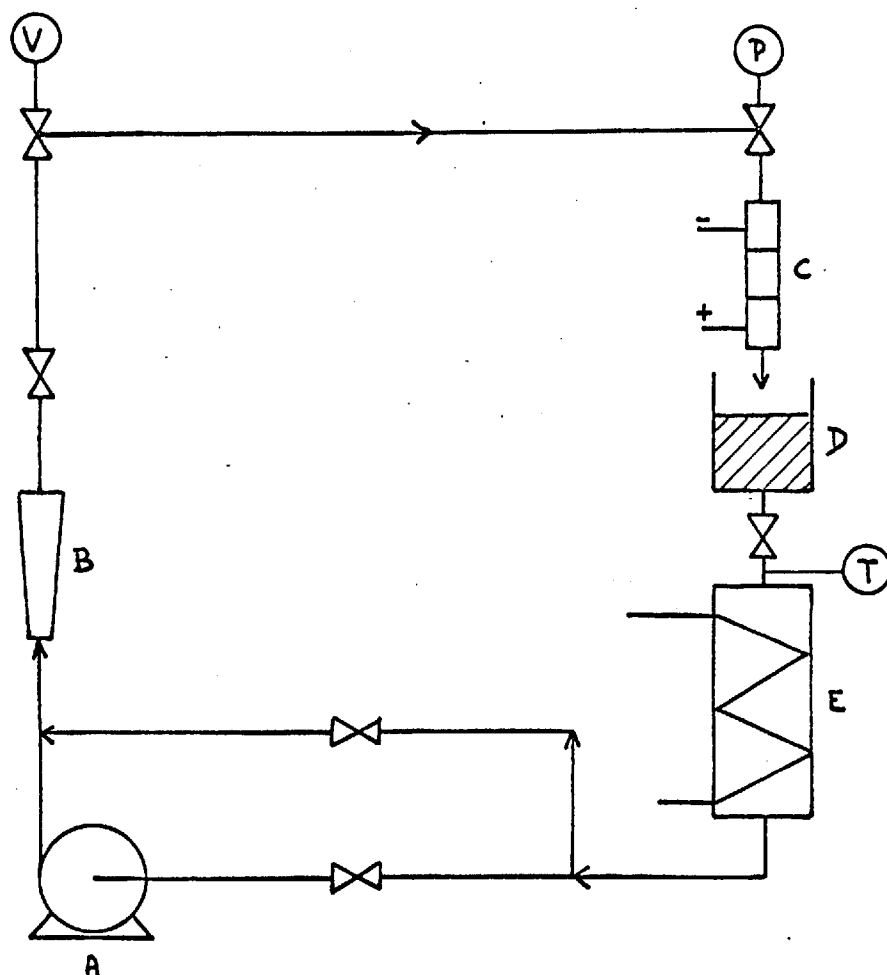
5.4.1.(b). Flow Circuit.

Four strengths of nitric acid were tested (0.4, 1.0, 3.0 and 6.0N, nominal concentrations), the total volume of the circulating electrolyte ranging from 9.66 - 11.0 l. Careful estimate was made of the volume lost by leakage and sampling during each run, the total volume being kept approximately constant by periodic additions of fresh nitric acid electrolyte. In order to achieve thorough mixing, fresh electrolyte was recirculated for 10-15 minutes prior to the start of a series of runs. Electrolyte solutions were made up from nitric acid already containing a certain concentration of uranyl nitrate. Final concentrations of uranium in solution ranged from 2.70 - 63.0 g uranium/l.

The flow circuit was constructed of 1 in. i.d. Q.V.F. glass pipework, the dissolver being connected to it by means of a flanged joint. A diagram of the dissolver circuit is given in Fig.5.4. An all-glass Q.V.F. cooler with a total cooling area of 28 ft.² was included in the circuit, whilst pressure drop developed across the dissolver bed was measured on a 0-60 p.s.i.g. pressure gauge fitted with a stainless steel diaphragm. The same pump was used as in previous dissolver circuits (Section 5.2.1.(c)), the rate of flow being measured by means of a No.18 Metric Rotameter. D.C. power was

Fig. 5.4. Anodic Dissolution of Uranium

Flow Diagram - Nitric Acid Electrolyte



Not to Scale

A: Pump

B: Flowmeter

C: Dissolver Assembly

D: Overflow Vessel

E: Cooler

(P): Pressure Gauge

(T): Temperature Pocket

(V): Vent

supplied from a 25V. 50A rectifier. "Blank" runs, using 1N and 3N nitric acid, were carried out to determine the fraction of uranium dissolved by chemical means alone.

5.4.1.(c). Electrical Resistance Determinations.

The resistance of a dry uranium bed was determined by applying a fixed voltage and measuring the current flowing. These measurements were repeated on a "wet" uranium bed. Electrolyte (3N nitric acid, containing 17-17.5 gU/l) was allowed to circulate over a bed of uranium contained in the dissolver (length of middle section = 10 cm.). The flow of electrolyte was then stopped and current values at a given voltage measured at fixed time intervals after the flow had ceased.

The resistance of the electrolyte (0.4, 1.0 and 3.0N nitric acid containing 2.2, 5.4 and 13.4 gU/l respectively) was estimated by substituting the uranium bed in a dissolver (length of middle section = 5 cm.) with an equivalent length bed composed of 5 - 7 mm. dia. glass beads and then measuring the current passing at a given voltage whilst the electrolyte was being circulated.

5.4.1.(d). Analytical Methods.

Samples taken at the end of each run were analysed for uranium content and acidity using methods outlined previously (Section 5.3.1.(b)).

5.4.2. Results and Discussion.

Both "total" and "net" current values are given in Table 5.2. which lists results of all the runs carried out using the stainless steel dissolver. "Net" current figures appear only for comparison, however, and have not been used in the plotting of the curves which characterise the behaviour of the dissolver. The current-voltage relationship of the system is shown in Fig.5.5. for voltage gradient values ranging from 1.0-10.0 volts/cm. Figures obtained previously with 6N nitric acid electrolyte (Runs NA 1-5, Section 5.3) are also plotted, with the exception of the figure obtained for Run NA 5 where an abnormal increase in resistance and consequently low current density were caused by loss of contact between the uranium bed and the metal section of the dissolver (Section 5.3.2.(b)). Current density - voltage gradient results for electrolytic dissolution using sodium bicarbonate electrolyte (Section 5.2) are also included in Fig.5.5. Similarly, corresponding values both for dissolution in sodium bicarbonate and Runs NA 1-5 are shown in Fig.5.6. in which the relationship between current density and dissolution rate is plotted. As before, the dissolution rate values are based on the superficial area of pellets contained within the middle section when dissolution under electrolysis is considered. In the case of the "blank" runs, however, (Runs EDB 4, EDLBC 5 and EDCBB 5, Table 5.2.) the dissolution figures are based on the estimated superficial area of all the pellets composing the bed.

Whilst dissolution under electrolytic conditions

Voltage Gradient vs. Current Density

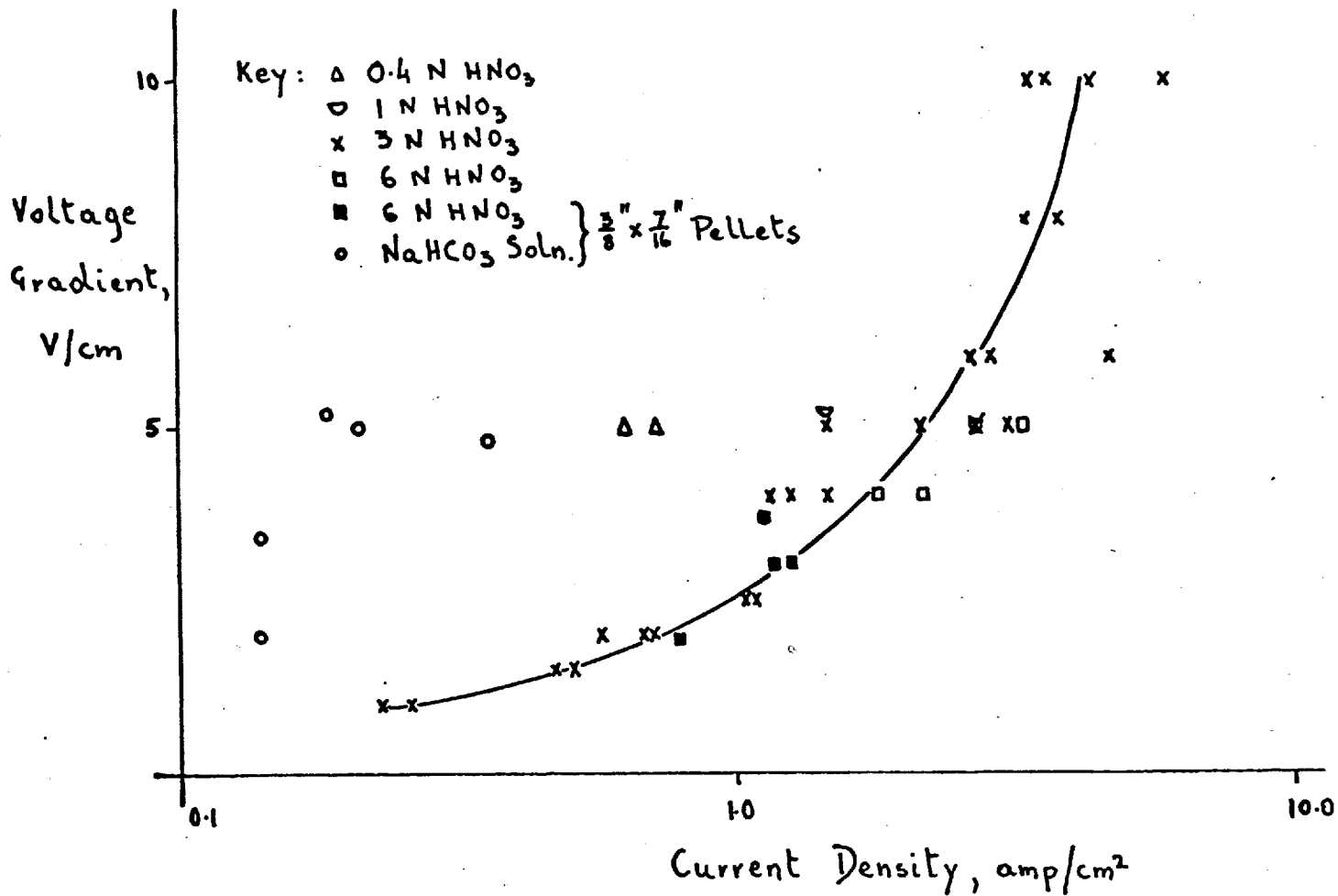
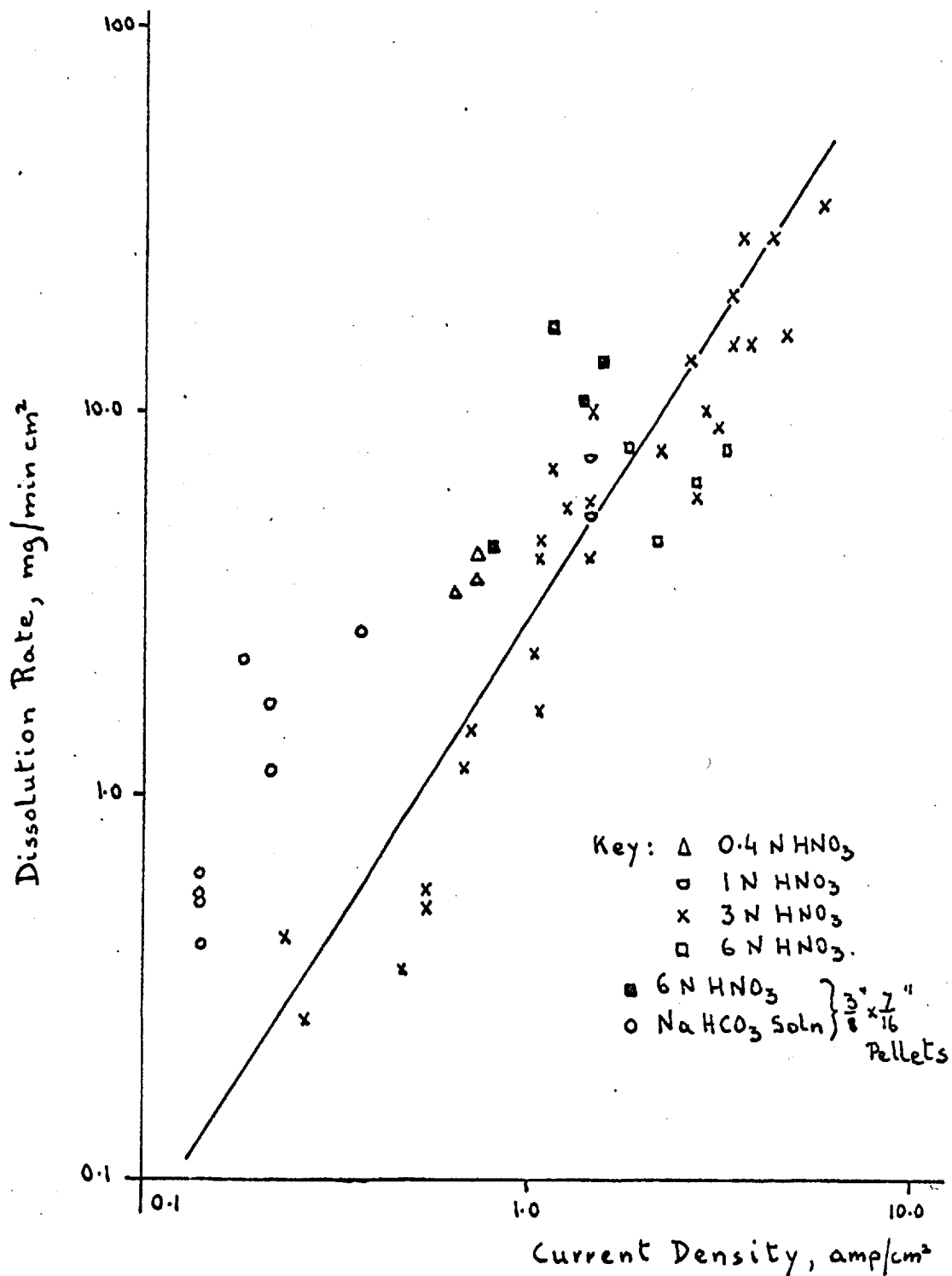


Fig. 5.6. Anodic Dissolution of Uranium
Stainless Steel Dissolver
Dissolution Rate vs. Current Density



occurred mainly in the middle section thus providing a basis for dissolution rate calculations in the former case, there were no reasons to suppose that, in the latter, chemical dissolution alone would not take place uniformly along the whole length of the bed. This difference in the basis for calculation was ignored in the case of run BC 8 (Section 5.2.2.) as the amount of uranium dissolved in sodium bicarbonate due to chemical attack alone was insignificantly small.

The dissolver was tapped frequently, particularly at lower voltage gradients and nitric acid concentrations, in order to promote higher current flow and consequently higher dissolution rates. Although an increase of up to 25% in the current values was normally achieved when the dissolver was tapped, this effect was not consistent and at times tapping did not give any marked rise in current flow. In the majority of cases tapping was done by means of a plastic or wooden rod with which the dissolver was struck periodically. The frequency of striking depended on the behaviour of the current but on the average occurred at intervals of about five minutes. In an attempt to improve the reproducibility of the tapping action, an electric fire alarm mechanism was installed (Runs EDCEB 3-13) in such a way that the hammer which normally struck a gong, struck the dissolver vessel instead when the circuit was closed. It was found, however, that the vibrations produced by the hammer did not lead to any increase in current flow and in fact, if continued for too long (periods longer than 5 minutes) were observed to result in a decrease of current.

The use of the hammer mechanism was therefore discontinued after Run EDCEB 13.

At high voltage gradients, when the length of the middle section of the dissolver was reduced to 2.5 cm. (Runs EDCSB 1-13), spontaneous arcing between uranium pellets in the middle section was observed. As tapping of the dissolver tended to result in arcing, the frequency of tapping was reduced significantly during this set of runs (average interval 10 minutes). The arcing within the bed caused violent current fluctuations, which made the estimation of average current values from ammeter readings alone very doubtful. Time-current curves were therefore plotted and figures for average current obtained by integration of the area under the curve. Although they helped to raise the amount of current passing through the dissolver, both tapping and arcing were to some extent responsible for the scatter of the results obtained, as can be seen from Figs. 5.5. and 5.6.

As expected from conductivity values given in the literature⁽⁶⁵⁾ for pure nitric acid solutions, the uranium bed - electrolyte system shows lower resistance when 6N nitric acid ^{is} ~~is~~ used as the electrolyte if compared with 3N, 1N or 0.4N nitric acid solutions. This point is illustrated in Fig. 5.7, where current densities at a given nitric acid concentration for the uranium bed - electrolyte system, are compared with current densities which would be obtained were pure nitric acid alone responsible for the flow of current through the

Fig. 5.7. Anodic Dissolution of Uranium

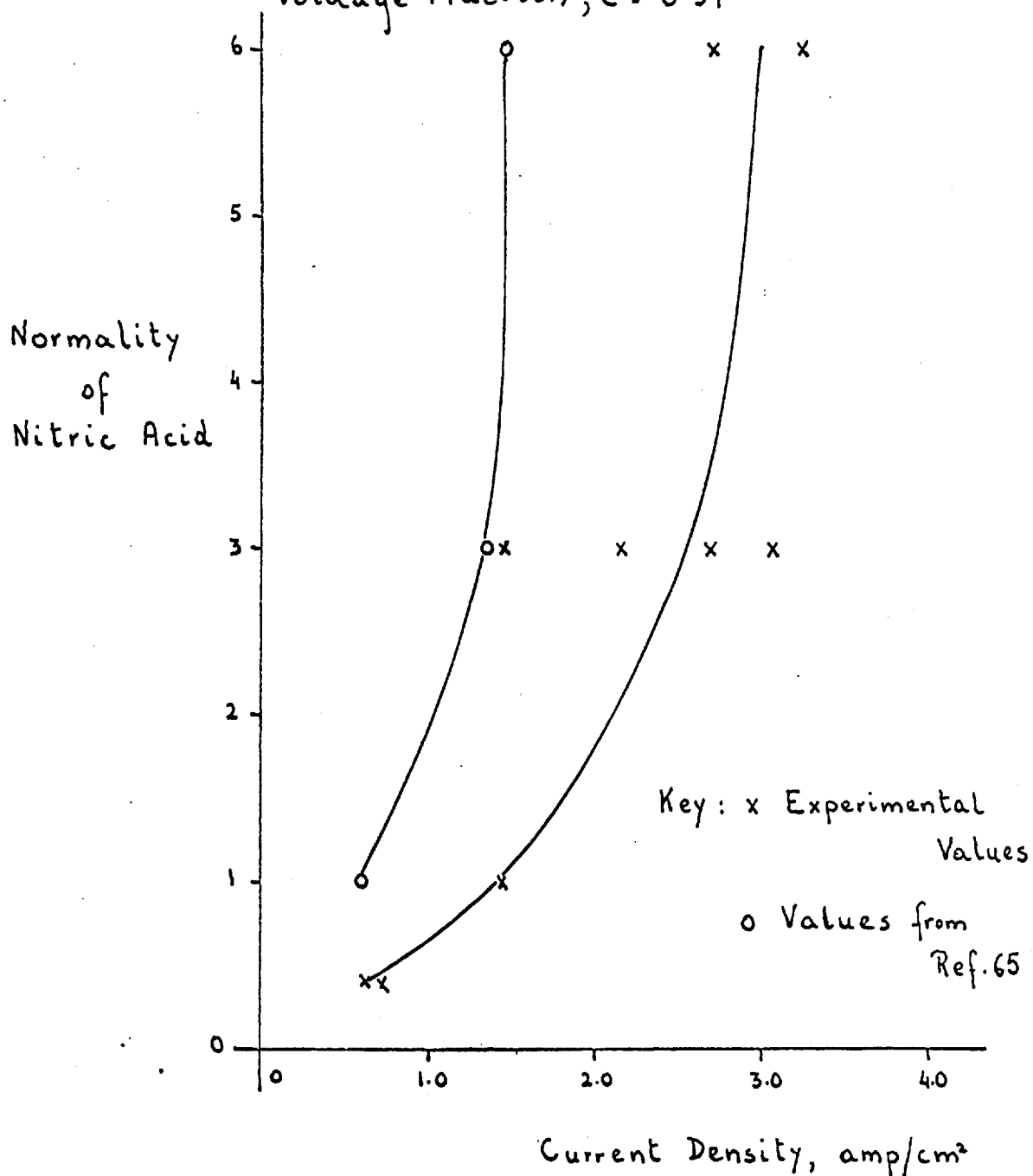
Stainless Steel Dissolver

Normality of Nitric Acid vs. Current Density.

Voltage Gradient - 5 V/cm

Length of Middle Section - 5 cm

Voidage Fraction, $\epsilon = 0.39$



dissolver under the same conditions of potential difference and voidage. It can be seen, however, that the conductivity does not change greatly if the concentration of nitric acid is 3N or higher and as 3N nitric acid is safer and more convenient to handle than 6N, the former was chosen as the standard nitric acid concentration in the electrolyte for all subsequent experiments. An added factor in favour of 3N nitric acid is its low chemical reactivity with uranium at room temperature, the rate of dissolution with 6N nitric acid under the same conditions having been reported as being 10 times greater⁽³⁾. Less error was thus likely to be caused by the assumption that electrolytic action alone was responsible for the dissolution of a given weight of uranium. At a constant current density and same length of middle section, no significant difference in dissolution rate was found, however, between 3N and 6N nitric acid although Larsen et al⁽¹⁵⁾ reported a higher dissolution rate when 3N nitric acid was used in the anodic dissolution of stainless steel.

All electrolytic dissolution runs were carried out with a certain amount of uranyl nitrate present in the electrolyte from the start. This would tend to minimise the effect of too rapid a change in the concentration of uranium on the dissolution rate, an effect which could occur had the uranium concentration been allowed to build up from zero. The presence of a certain amount of uranium in the electrolyte throughout the duration of a run also gave conditions closer to those to be expected in plant operation.

The concentration of uranium in solution was allowed to build up gradually during the course of the experiments, reaching a maximum of 63.0 g U/l (Run EDCSB 13).

Pressures throughout the series of experiments recorded in this chapter ranged from 4.0 p.s.i.g. (Run EDCSB 6) for a flow rate of 9.0 l/min across a bed 2.5-4.0 cm. long, composed largely of small particles of uranium remaining from the partial dissolution of the original pellets, to 7.7 p.s.i.g. (Run EDLBC 1) at 6.0 l/min across a 20 cm. long bed of largely unattacked pellets. More generally, a pressure drop of about 11-14 p.s.i.g. across a foot length of bed of original, unattacked pellets, was observed for a flow rate of 3.4 ft/sec. (6.2 l/min).

Flow rates ranged from 4.1 (Run EDCEB 1) to 9.2 l/min (Run EDCSB 5) but both pressure and flow rate varied little during the course of an experiment, the main factor influencing both parameters being the height of the uranium bed in the dissolver. A self-imposed limit of about 10 p.s.i.g. was chosen for the maximum pressure allowed across the dissolver bed. This limit was dictated by the use of taps incorporated in the flow circuit. These had a maximum working pressure of 20 p.s.i.g. (as quoted by the makers) but in practice it was found that they tended to leak at pressures in excess of about 10 p.s.i.g.

The extremes of the temperature range recorded throughout the course of the experiments were 18-37°C. but the range during the

major portion of any particular run did not exceed 10°C as it was found that the temperature of the electrolyte rose very rapidly initially - about 3°C in five minutes at the start of a run - and then increased only slowly as thermal equilibrium in the system was established. In the majority of experiments temperature was allowed to rise unchecked i.e. no water flowed through the cooler, as the heat output from the dissolver was not sufficiently high to warrant the use of the heat exchanger. Thus initial temperatures of the electrolyte ranged mainly from $21\text{--}25^{\circ}\text{C}$ rising to $25\text{--}30^{\circ}\text{C}$ at the end of a run. Where cooling was used, ^{the} temperature dropped close to ambient (less than 5°C difference) within 1-2 minutes from the time the water was switched on.

It was considered that the variation in chemical dissolution rate within the range of temperatures observed was too small compared with the overall dissolution rate to have a significant bearing on the dissolution figures obtained.

An example of a full data and results table showing in detail the manner in which the figures quoted in Table 5.2. were obtained is given in Table 5.4. For the sake of simplicity, however, total current values only are shown, the calculations in the case of net current figures being identical, involving simply a change in numbers and not in procedure.

5.4.2.(a) Uranium Mass Balance.

A comparison of mass balance of uranium figures as obtained by direct weighing and by analysis of the uranium content of the electrolyte is given in Table 5.5.

Table 5.4. Anodic Dissolution of Uranium in Nitric Acid Electrolyte
Stainless Steel Dissolver Vessel.

101.

Detailed Calculations Sheet - Runs EDCSB 1-13.

Run EDCSB No.	Duration of Run, min.	A (total)	V	Voltage Gradient, volts/cm.	Current Density, amp/cm ²	Volume of Electro- lyte, ℓ	Optical ⁽¹⁾ Density	Conc. U mg/ml. (ali- quot).	Conc. U g/ℓ (sample).
0				-	-	9.68	0.067	2.08	20.8
1	30	12.9	15	6.0	4.65	9.64	0.077	2.38	23.8
2	"	8.0	15	6.0	2.87	9.60	0.083	2.58	25.8
3	"	7.3	15	6.0	2.63	9.56	0.092	2.85	28.5
4	"	10.5	20	8.0	3.78	9.52	0.102	3.15	31.5
5	"	9.3	20	8.0	3.33	9.48	0.112	3.45	34.5
6	"	10.0	25	10.0	3.60	9.44	0.130	4.00	40.0
7		-	-	-	-	9.90	0.137	4.23	42.3
8	"	4.0	10	4.0	1.44	9.85	0.143	4.43	44.3
9	"	3.5	10	4.0	1.26	9.82	0.147	4.55	45.5
10	"	3.2	10	4.0	1.15	9.78	0.152	4.70	47.0
11	"	16.3	25	10.0	5.85	9.74	0.173	5.35	53.5
12	"	12.0	25	10.0	4.33	9.70	0.191	5.90	59.0
13	"	9.3	25	10.0	3.35	9.66	0.204	6.30	63.0

Note: (1) Optical density of aliquot solution as analysed.

Table 5.4. - continued.

Run EDCSB No.	Dilution of Sample.	Total Weight U in Soln.	Difference g.	Equiv. U v1	F	$\frac{Eq}{F}$	Dissol. Rate mg/min.cm. ²
0	1:9	201.4		-	-	-	-
1	"	229.5	28.1	0.71	0.24	3.0	15.6
2	"	247.7	18.2	0.46	0.15	3.1	10.1
3	"	272.5	24.8	0.63	0.14	4.5	13.8
4	"	299.8	27.3	0.69	0.20	3.5	15.2
5	"	327.1	27.3	0.69	0.17	4.1	15.2
6	"	377.7	50.6	1.28	0.19	6.7	28.1
7	"	418.7		-	-	-	-
8	"	436.8	18.1	0.46	0.075	6.1	10.0
9	"	446.8	10.0	0.25	0.065	3.9	5.6
10	"	459.6	12.8	0.32	0.060	5.3	7.1
11	"	521.3	61.7	1.56	0.30	5.2	34.2
12	"	572.5	51.2	1.29	0.22	5.9	28.5
13	"	608.5	36.0	0.91	0.17	5.4	20.0

Table 5.5. Stainless Steel DissolverMass Balance of Uranium.

Run Nos.	Weight of U Dissolved g		Difference as % of (a).
	(a)	(b)	
ED1-4	170.0	155.0 ^(c)	-8.8
EDA1-EDC1	133.0	137.0	+3.0
EDCLE1-5	114.0	104.0	-8.8
EDCEB1-13	143.0	152.5	+6.6
EDCSB1-6	177.0	176.3	-0.4
EDCSB8-13	179.0	189.0	+5.6

Notes: (a) Weight determined by weighing U bed before and after a set of runs.

(b) Weight determined by analysis.

(c) Includes 14.3 g U dissolved in preliminary, non-electrolytic Run EDQ, not given in Table 5.2.

The discrepancy between the two sets of figures given in Table 5.5. is largely due to inaccuracies in the assessment of leakage losses from the dissolver circuit which in turn made the estimation of the volume of electrolyte difficult.

Values of overall uranium dissolution efficiency, expressed in terms of grams uranium dissolved per ampere-hour of electricity passed

through the bed, are given below:

Runs	Efficiency
ED1-4	8.0
EDAl-EDCl	10.5
EDLBGl-5	8.1
EDCEBl-13	11.8
EDCSBl-6	6.1
EDCSB8-13	8.4

These figures are based on weights of uranium dissolved as determined by analysis and total values of current. In a system where only one cell would operate, with uranium going into solution at the anode, 1.48 g U/amph would dissolve at 100% cell efficiency, assuming uranium to go into solution in the hexavalent state.

5.4.2.(b). Consumption of Nitric Acid.

The figures for moles of nitric acid consumed per mole of uranium dissolved in the various sets of runs are given in Table 5.6. These were calculated on the basis of the drop in acidity of the electrolyte, corrected for the amount of nitric acid lost from the bulk of the solution by leaking and sampling, as described earlier (Section 5.3.2.(a)). Again, weights of uranium dissolved as determined by analysis were used in the calculations but, as the volume of the electrolyte could not be assessed very accurately, the results given in

Table 5.6. are of a rather qualitative nature

Table 5.6. Consumption of Nitric Acid in the
Electrolytic Dissolution of Uranium.

Run Nos.	Nominal Acidity of Electrolyte, as HNO_3 .	Moles of Nitric Acid consumed.	Moles of Uranium dissolved.	Moles HNO_3
				Mole U
ED 1-4	6.0	2.49	0.65	3.8
EDA 1-3	0.4	0.51	0.20	2.5
EDB 1-4	1.0	0.51	0.28	1.8
EDC 1	3.0	0.38	0.09	4.2
EDLBC 1-5	3.0	1.22	0.44	2.8
EDCEB 1-5	3.0	0.52	0.49	1.1
EDCEB 7-13	3.0	0.19	0.14	1.4
EDCSB 1-6	3.0	1.62	0.74	2.2
EDCSE 8-13	3.0	1.84	0.80	2.3

and merely indicate the order of nitric acid consumption. By comparison, however, with the figure of 6 moles nitric acid consumed per mole of uranium, obtained in preliminary runs (Section 5.3.2.(a)), results in Table 5.6. indicate that the greater volume of electrolyte had a beneficial effect on the absorption of nitrogen oxides liberated in the reaction, bringing the nitric acid consumption nearer the stoichiometric value of 2 moles nitric acid per mole uranium. No satisfactory reason could be found for the extremely low values of consumption found in the case of runs EDCB.

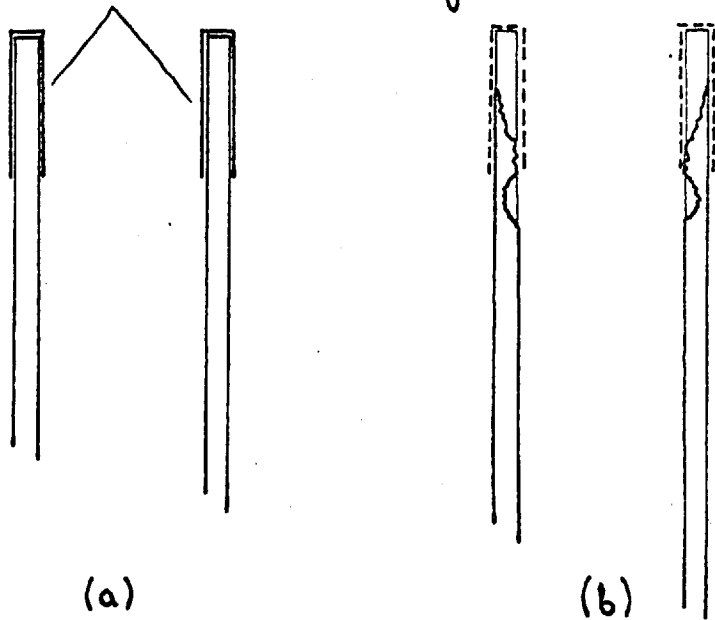
5.4.2.(c). Corrosion of the Dissolver Vessel.

Despite attempts made to protect the end of the positive section of the dissolver from anodic attack (Section 5.4.), it was found that corrosion of the stainless steel tube continued and after about 85 amph the section had to be replaced. Because the end of the tube was protected, however, corrosion started immediately past the Araldite layer, undermining it and eventually leading to its complete disintegration. An approximate cross-section (longitudinal) of the tube as it appeared after about 43 amph of use is shown in Fig.5.8. The experiment with the Araldite coating was not repeated when the new section was inserted in Run EDCSB 7. A table giving the corrosion rate of the stainless steel tube is given (Table 5.7). It must be noted, however, that no weight loss throughout the whole series of runs was observed from the stainless steel gauze supporting the uranium bed which was

Fig. 5.8. Stainless Steel Dissolver

Corrosion of Positive Section

Araldite and paint coating



(a) Appearance before start of runs

(b) Appearance after 43 amph

inserted in the positive section of the dissolver. This confirmed the earlier observation (Section 5.3.2.(b)), illustrated subsequently in Fig.5.8, that corrosion of the stainless steel tube took place preferentially from the part nearest the negative (cathodic) section of the dissolver vessel. Quantitative tests on the negative section of the dissolver were not carried out as no comparable corrosion was observed.

Table 5.7. Stainless Steel Dissolver Vessel - Corrosion Rate of Positive Section.

Run Nos.	Weight of s.s. dissolved, g.	amph	g s.s./amph
ED1-EDLBC 5	21.0	42.94	0.5
EDCEB1-13	4.9	12.65	0.4
EDCSB1-6	14.3	28.98	0.5

5.4.2.(c). Evaluation of the Surface Area of Pellets contained within a Unit Length of the Dissolver Bed.

The dissolution rate figures appearing in Table 5.2 were, as before, calculated on the basis of surface area of the pellets contained within the middle section of the dissolver. For this purpose an estimate of the average value of surface area of pellets contained in a unit length of dissolver bed was made. The estimate is based on a weight-surface area relationship as represented by a sample of 10

unattached uranium pellets, chosen at random. The method of calculation is shown below whilst full results are given in Table 5.8.

Average dimensions of pellet - 7.14 x 3.0 mm.

(based on measurement of 10 pellets)

$$\begin{aligned} \therefore \text{Surface area} &= \pi (7.14 \times 3 + 4.5) \text{ mm}^2 \\ &= 82 \text{ mm}^2 \\ &= 0.82 \text{ cm}^2 \end{aligned}$$

$$\therefore \text{Surface area of 10 pellets} = 8.2 \text{ cm}^2$$

$$\text{Also weight of 10 pellets} = 10.83 \text{ g.}$$

Now, in the case of ~~Runs~~ ED1-4, where the total length of bed was originally 6 in. (15.0 cm.) and weighed 470 g, we have,

$$\text{number of 10 pellet units} = \frac{470}{10.83}$$

$$= 43.4$$

$$\therefore \text{Equivalent surface area} = 356 \text{ cm}^2$$

$$\begin{aligned} \text{i.e. Surface area per inch length of bed} &= \frac{356}{6} \text{ cm}^2 \\ &= 59.3 \text{ cm}^2 \end{aligned}$$

Similarly, results calculated for other lengths and weights of bed are given in Table 5.8.

Table 5.8. Evaluation of Surface Area of Pellets in Unit Length
of Dissolver Vessel, $\frac{3}{4}$ in. i.d.

Run Nos.	Weight of bed, g.	No. of units of 10 pellets.	Surface area (total) of bed, cm^2 .	Length of bed in.	Surface Area per inch, $\text{cm}^2/\text{in.}$
EDA-EDC	490	45.2	371	6	61.8
EDLBC	573	52.9	433	8	54.2
EDCEB	729	67.2	551	9	61.2
EDCSB1-6	305	28.2	231	4	57.7
EDCSB7-13	408	37.7	309	$5\frac{1}{2}$ -6	53.8
(a) EDCTNB	618	56.8	465	8	58.2
(a) EDSTN	772	71.3	585	10	58.5
1-21					

Note: (a) Figures refer to Runs carried out later, using a tantalum dissolver vessel.

Based on figures given in Table 5.8 a value of $60 \text{ cm}^2/\text{in.}$ or $24 \text{ cm}^2/\text{cm.}$ length of bed was chosen to represent the surface area of pellets per unit length of bed in a dissolver vessel, $\frac{3}{4}$ in. i.d. As mentioned, the figures calculated in Table 5.8 are based on the dimensions of unattacked pellets and thus the value of surface area chosen is representative of conditions which obtain only at the start of a series of runs. Examination of the uranium bed after electrolysis

revealed, however, that no increase in the surface roughness of the pellets had occurred. No change in surface area due to a change in surface roughness was thus likely to result. As pellets dissolved and became smaller, their numbers per unit volume of bed would increase, thus maintaining the surface area at a relatively constant value. The value chosen was considered therefore a fair approximation of the surface area of pellets contained at any one time within the dissolver bed.

5.4.2.(e) Sludge Formation.

It was noticed during the course of the dissolution runs that small amounts of sludge were deposited throughout the system. About 2 g. of flocculent, grey-black sludge resulted from the dissolution of 914 g uranium and 52 g stainless steel, (from the corrosion of the stainless steel dissolver), assuming that 0.5 g s.s./amp dissolved in runs EDCSB 7-13 where no direct check on the corrosion of the stainless steel tube was made. The sludge was filtered off from the solution, dried and ashed, the ash forming 66% by weight of the dry solid. The ashed residue was analysed spectrographically (at A.E.R.E., Harwell) and results of the analysis are given in Table 5.9(A). Table 5.9(B) gives the composition of the stainless steel forming the tube and used in the construction of the dissolver.

Comparison of the analysis figures shows that at least part of the sludge originated from the dissolution of the stainless steel components of the dissolver vessel. American workers⁽²⁰⁾ investigating

sludge formation resulting from the anodic dissolution of Type 304 stainless steel in nitric acid found that at 40°C . and current densities of 0.4 and 1.2 amp/cm², 0.2-2.6 g of sludge were deposited for every 100 g of stainless steel which dissolved. Nominal composition figures of Type 304 stainless steel are given in Table 5.10.

Table 5.9. Stainless Steel Dissolver

Analyses of Sludge and Stainless Steel Tube.

(A) Sludge Analysis⁽¹⁾

Element	%	Element	%	Element	%
Fe	7	Al.	3	Ca.	0.06
Cr	3	Mg.	1	B	0.02
Ni	1.5	Mo.	0.3	Sn.	0.02
Si	20	Ti.	0.2	Co.	0.03
C	15.8	Mn.	0.2	Cd.	0.01
O	4	W.	0.15	Cu.	0.06
		Ba.	0.06		

(B) Composition of Stainless Steel Tubes
used as Conducting Sections in
Dissolver Vessel⁽²⁾.

	Cr.	Ni.	C.	Mn.	Ti.	Nb.	Co.
Element % by weight.	19.1	8.1	0.22	0.35	0.75	0.05	0.02

Notes: (1) Figures given in weight % of original (dried) material

(2) Stainless Steels of the type analysed contain an average of 0.6% Si^(69,70).

Table 5.10. Nominal Composition of Type 304
Stainless Steel ⁽⁷¹⁾.

Element % (wt.).						
C	Cr.	Ni.	Mn.	P	S	Si.
0.08	18-20	8-12	2.0	0.045	0.030	1.0

Based on the similarity in contents of the main elements in Type 304 and the steel used in the construction of the dissolver, the assumption can be made that not more than half (or about 1 g) of the sludge found in the dissolver circuit came originally from the stainless steel tubes making up the dissolver vessel. The rest (about 1 g) of the sludge was thus contributed by the uranium. Unfortunately no analysis figures could be obtained for the batch of uranium which on dissolution contributed to the sludge for which analysis figures are given in Table 5.9(A). Chemical and spectrographic analyses, however, of a typical batch of natural uranium used in subsequent dissolution runs are given in Table 5.11. The absence of uranium in the sludge confirms the findings of Hartland⁽¹⁸⁾ and, together with a comparison of the respective compositions of sludge and uranium, suggests strongly that formation of sludge from the electrolytic dissolution of uranium is caused mainly by the presence of metal impurities.

5.4.2.(f) Valency of Uranium during Anodic Dissolution.

The electrochemical equivalent of uranium and consequently the values of current efficiency quoted in Table 5.2. are based on uranium being hexavalent. Although uranium in nitrate solutions is always

Table 5.11. Anodic Dissolution of UraniumAnalysis of a Typical Batch ofNatural Uranium⁽⁷²⁾.

(A). Chemical Analysis.

Element, p.p.m.				
C	Si	Al	N	Fe
300	15	95	15	65

(B). Spectrographic Analysis.

Element	ppm.	Element	ppm.
Fe	60	Va	)
Ni	50	Mo	)
Mn	10	Co	10
Cr	8	Pb	)
As	)	Ge	)
Bi	)	Tl	)
In	)	Gd	)
Cu	)	Cd	)
B	)	Be	)
Mg	)		

observed as the uranyl ion (UO_2^{++})⁽⁷³⁾, it is conceivable that a lower valency ion is initially formed but becomes oxidised immediately on leaving the anode.

In order to establish the valency of uranium during electrolytic dissolution in nitric acid and thus provide a firm basis for the current efficiency figures, experiments using a single cell with uranium as the anode were carried out. Details of the apparatus used and the results obtained are given in Appendix D. Good agreement was shown between the weights of uranium dissolved as obtained by direct weighing of the anode and by analysis of the uranium content of the electrolyte. An electrochemical equivalent of uranium of about 40g and a valency of 6 were observed. Values of current density on the anode ranged from 0.15 to 1.04 amp/cm².

5.4.2.(g). Gas Evolution during Electrolysis.

A limited number of experiments was carried out in order to obtain some estimate of the amount of gaseous products evolved during electrolytic dissolution. Details of the apparatus used and the results obtained are given in Appendix E. Both stainless steel and uranium cathodes were used in combination with a uranium anode and 3N nitric acid as electrolyte. Current densities ranged from 0.2-0.3 amp/cm² on the anode and 0.25-0.3 amp/cm² and 0.7-0.9 amp/cm² on the uranium and stainless steel cathodes respectively.

It was found that almost all ($\leq 99\%$) the gas evolution occurred at the cathode. On the basis of the few experiments carried out, no significant difference in volumes of gas evolved per mole of uranium dissolved was observed. A figure of 18-24 l gas (at 20-25°C.) per mole uranium dissolved was obtained, corresponding to 110-150 ml/amp when expressed in terms of current consumption. This gas evolution rate may be compared with a figure of 47.6 l gas (at 30°C) per mole uranium dissolved quoted by Gresky⁽⁶⁶⁾ for the chemical dissolution of uranium slugs in 55% nitric acid.

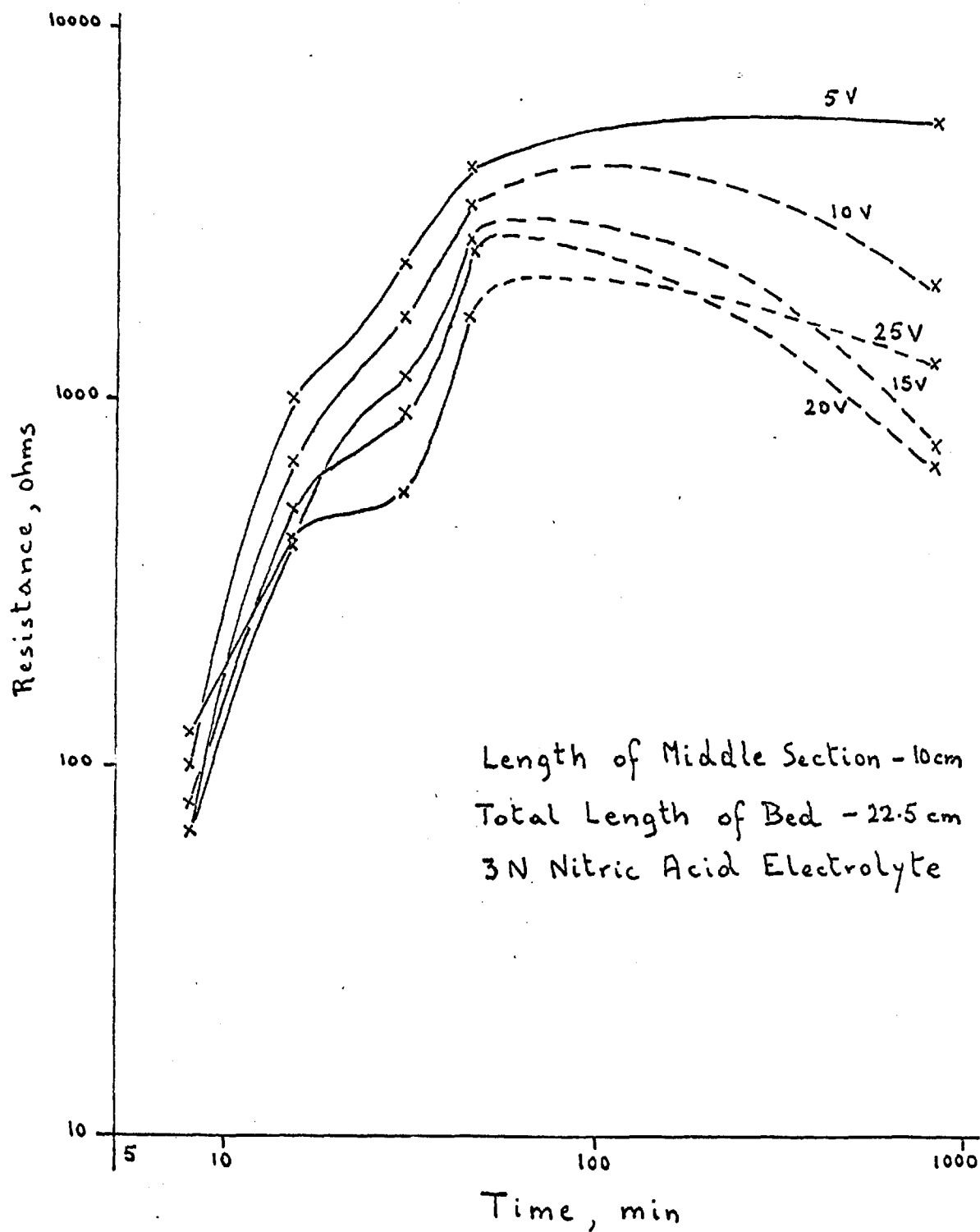
Qualitative observations of the behaviour of the cathodic gases evolved tended to indicate that nitrogen oxides formed the major portion of the mixture with perhaps a greater fraction of NO present in the off-gas when a uranium cathode (as compared with a stainless steel cathode) was used.

Hydrogen content of the gas mixture was determined in the case of two of the runs when a stainless steel cathode was used. Figures obtained showed that 1-2% H₂ was present in the off-gas. This result compares with the findings of other workers^{(15) (22)} who observed the presence of hydrogen in the gases evolved from a stainless steel cathode at current densities of the same order of magnitude as used in the experiments described above. The absence of hydrogen in the off-gas produced at low cathodic current densities (0.0003-0.03 amp/cm²) was noted by Henry⁽³²⁾, however, during experiments involving the anodic dissolution of stainless steel in 2-10N nitric acid.

5.4.2.(h). Measurements of Resistance (Uranium bed and electrolyte).

Results of measurements involving both beds composed of dry uranium pellets and pellets moistened with electrolyte are given in Appendix F, Tables F.1 and F.2. Very high resistance values, ranging from 10-300 Ω per cm. length of bed in the middle section depending on conditions, were obtained in the case of a uranium bed composed of dry pellets. As expected, an increase in the length of bed contained within the conducting stainless steel sections, decreased the resistance, as more contact points between the uranium and the stainless steel were provided. An increase in overall bed length, leading to an increased overall bed weight, would also result in decreased resistance owing to an increase of pressure on individual uranium-to-uranium contact points within the dissolver bed. The resistance of such a system, however, was still very large and indicated that no appreciable amount of current was likely to flow through a bed of uranium pellets in the absence of a suitable electrolyte.

This effect was clearly illustrated by results quoted in Table F.2, which gives the increase in resistance of a uranium bed with time after drainage of the circulating electrolyte. A graphical presentation of these results is given in Fig.5.9. The very high values of resistance observed after overnight drainage are possibly due both to oxide film formation on the surface of the uranium pellets and the formation of a layer of $\text{UO}_2(\text{NO}_3)_2$ crystals resulting

Fig. 5.9. Stainless Steel DissolverUranium Bed Resistance vs. Time (after draining)

from the evaporation of a film of electrolyte.

Resistance measurements of the electrolyte (Table F.3) showed that the observed values were approximately double those quoted in literature for an equivalent strength of nitric acid. Thus, we have, assuming a voidage factor = 0.47 for the case of a bed composed of 5-7 mm. dia. glass spheres within a $\frac{3}{4}$ in. dia. tube, (Section 4.2.2.)

$$\text{Resistance of electrolyte (3N)} = \frac{10 \times 2.78 \times 0.47}{5}$$

$$= 2.61 \text{ ohms/cm.cube}$$

$$\text{Resistance of 3N Nitric Acid} = 1.45 \text{ ohms/cm.cube}^{(65)}$$

assuming an observed resistance of 10 ohms and 5 cm. long middle section. Similarly, in the case of 1N nitric acid electrolyte, we have,

$$\text{Resistance (observed)} = 5.22 \text{ ohms/cm.cube}$$

$$\text{Resistance of 1N nitric acid} = 3.2 \text{ ohms/cm.cube}$$

Higher figures than the theoretical would be expected as the observed values were affected by the polarisation resistance on the stainless steel electrodes. Small variations in pressure and flow rate did not appear to have any effect on the observed resistance values.

5.4.2.(i) Use of A.C.

No experiments using a.c. were carried out. This decision was influenced largely by results of other workers⁽¹²⁾⁽¹⁷⁾⁽³²⁾ who found that current efficiencies using a.c. were only about 60% of the value obtained with d.c. under the same conditions.

When during Run ED1, however, the power supply was switched over momentarily to a.c., it was noticed that both current and voltage were lower than with d.c. at the same Variac setting. During a number of subsequent runs, the power supply was switched over to a.c. for a few seconds at a time in an attempt to boost the level of the current when the system was switched back to d.c. No improvement, however, was noticed during any of the runs.

5.5. Conclusions.

Although successful electrolytic dissolution of uranium was accomplished and, using a bed of uranium pellets, current efficiencies many times greater than 100% were achieved in the majority of runs, the following points became obvious during the course of the experiments:

- (1) excessive corrosion of the anodic section of the stainless steel dissolver showed that a more corrosion resistant metal was needed;
- (2) in order to achieve better reproducibility of the results, further dissolution runs needed to be conducted under more stable equilibrium conditions. This meant minimum use of tapping, resulting in a possible drop of current efficiency.
- (3) the need for the installation of a d.c. amperehour meter or some other current-time integrating instrument became apparent as violent current fluctuations during the course of a run (even without tapping) made an accurate estimation of the current consumed impossible.

Chapter 6.

Anodic Dissolution of Uranium in a
Tantalum Dissolver.

Chapter 6Anodic Dissolution of Uranium in a Tantalum Dissolver.

- 6.1. Introduction.
 - 6.2. $\frac{3}{4}$ in. I.D. Dissolver Vessel.
 - 6.2.1. Experimental Procedure.
 - 6.2.2. Results and Discussion.
 - 6.3. $1\frac{1}{2}$ in. I.D. Dissolver Vessel.
 - 6.3.1. Experimental Procedure.
 - 6.3.2. Results and Discussion.
 - 6.4. Conclusions.
-

6.1. Introduction.

Severe corrosion encountered on the anodic section of the dissolver vessel when stainless steel was used as material of construction (Sections 5.3.2. and 5.4.2.) led to the consideration of other metals which could be used to maintain electrical contact with the fuel charge in the dissolver, without themselves suffering from electrolytic corrosion. Several workers⁽¹⁹⁾⁽³⁶⁾⁽⁴⁶⁾ have shown that both tantalum and niobium could be used successfully as materials of construction for a basket which contained the fuel charge being dissolved anodically in an electrolytic cell. These metals were chosen because they both belong to a group of metals (other typical members Hf, Zr, W) which exhibit the so-called "electrolytic valve" effect. Anodic polarization of metals in this group results in the formation of a high-resistance oxide film which prevents the occurrence of any other electrode process. In the case of tantalum, an electrolytically inert oxide coating is formed in almost any aqueous electrolyte with the exception of hydrofluoric acid solutions⁽⁷⁴⁾. An overvoltage value of about 180V. was noted for tantalum (40V. for niobium) in 70% nitric acid at a constant current density of 1 mA/cm^2 at 25°C.⁽⁷⁵⁾ Thus, when a length of tantalum tubing is made the anodic section of a dissolver vessel, no current will flow from it

directly to the nitric acid electrolyte and the tube itself, therefore, will not dissolve provided the applied voltage does not exceed the overvoltage. The electrical circuit can be completed, however, by direct contact between the fuel charge and the tantalum anode either by conduction through the oxide film or direct metal-to-metal contact through local penetration of the film.⁽²⁸⁾

The use of a noble metal e.g. platinum as a means of making anodic contact with the uranium charge in the dissolver was also considered. Oxygen evolution, however, occurs at a platinum anode in nitric acid solutions⁽⁷⁶⁾. This was regarded as undesirable in view of the presence of small amounts of hydrogen found in the dissolver off-gas (Section 5.4.2.) and the consequent formation of possibly explosive hydrogen-oxygen mixtures. In addition, oxygen evolution represents a competing side reaction on the anode which will tend to lower the current efficiency of the dissolution process. It has been found⁽¹⁹⁾, however, that provided the noble metal anode was sufficiently covered by the fuel charge in contact with it, oxygen evolution was reduced and the dissolution proceeded satisfactorily. It was considered unlikely, however, that such conditions could be ensured constantly in an operating dissolver and tantalum was chosen therefore as material of construction of the dissolver vessel.

In order to improve the reproducibility of the experimental values observed, tapping of the dissolver vessel was avoided and current values were based on readings using a d.c. ampere hour meter.

Dissolution runs were carried out using both different sizes of uranium pellets for the dissolver charge and different diameters of the dissolver vessel.

6.2. 3/4 in I.D. Dissolver Vessel.

6.2.1. Experimental Procedure.

Both the construction of the dissolver vessel and the flow circuit were the same as described previously (Chapter 5, Figs. 5.1 and 5.4). The anodic and cathodic stainless steel sections of the dissolver, however, were replaced by 6 in. lengths of tantalum tube, 3/4 in. i.d. and 7/8 in. o.d. With the exception of 3 runs during which the polarities of the tantalum sections were reversed, the lower section formed the positive terminal, a stainless steel mesh plug inserted in it acting as support for the uranium bed. Electrolyte used throughout the course of the runs was 3N HNO_3 , containing 0.55 - 85g U/l, its volume ranging from 8.8 - 15.4 l. Acidity level was maintained and some control on the uranium concentration exercised by periodical withdrawals of portions of the electrolyte which were then replaced with fresh 3N HNO_3 .

6.2.1.(a) Uranium Bed.

The majority of runs were carried out on beds composed of the same size of uranium pellets as used previously (Section 5.4.1.) (Size 2) viz. $1/8$ in. dia. x $5/16$ in. long. Three different lengths of middle section, 2.5, 5.0 and 10.0 cm., were investigated, the overall initial lengths of the uranium charge in the dissolver ranging from 20-29 cm. Details of dimensions and compositions of the dissolver charges are given in Table 6.1.

Table 6.1. $3/4$ in. dia. Tantalum Dissolver.

Dimensions and Composition of Uranium Charges

Run Nos.	Overall length of bed, cm.	Length of bed in anode section, cm.	Length of middle section, cm.	Pellet Size No.
EDCTNB 1-5	20	7.5	5	2
EDSTN 1-21	25	10	5	
EDSTN 22-42	23	10	2.5	
EDNT 1-3	20	5	5	
4-6	21	5	5	
7-9	23	5	5	
10-12	21	5	5	
13-15	25	5	10	
16-18	29	5	10	
19-21	28	5	10	
EDNTE 1-3	24	7.5	5	1
4-6	24	7.5	5	2
7-9	25	7.5	5	
10-12	26	7.5	5	
13-15	26	7.5	5	
16-18	26	7.5	5	2

Values of voltage gradient varied between 1-12 V/cm. in the case of the 5 cm. length of middle section, the two other lengths having been

tested within a narrower range. The behaviour of the bed when composed of two other sizes of pellets was also examined. Both smaller, size 1, ($\frac{1}{16}$ in. dia. x $\frac{1}{8}$ in. long) and larger, size 3, ($\frac{1}{4}$ in. dia. x $\frac{3}{8}$ in. long) pellets were dissolved in beds with a 5 cm. length of middle section at voltage gradients ranging from 7.8 to 13.6 V/cm. for the smaller and 5.0 - 8.6 V/cm. for the larger size.

6.2.1.(b) Electrical Circuit.

D.C. supply obtainable from the 0-48A, 0-25V rectifier unit (Section 5.4.1.), limited the voltage gradient to 10 V/cm. even when a length of middle section of only 2.5 cm. was used. A mains 30A, 220V. d.c. supply was used therefore to obtain higher voltage gradients and current densities, especially when testing 5.0 cm. and 10.0 cm. lengths of middle section. The flow of current to the dissolver was controlled by means of a system of resistances included in series in the circuit. With the exception of the first five runs, all values of current obtained were calculated from readings observed on an ampere-hour meter, calibrated by the London Electricity Board and capable of being read to ± 0.001 ampere-hour. An ammeter was also included in the circuit, however, to keep a visual check on the behaviour of the current.

6.2.1.(c) Electrical Resistance of Bed.

The resistance of a bed of uranium composed of size 2 pellets, through which water of known conductivity was flowing, was determined.

The overall length of bed was 25 cm. with 10 cm. each contained in the anodic and cathodic sections of the dissolver, the middle section being 5 cm. long. Both a.c. and d.c. current-voltage readings were obtained at various values of water conductivity.

6.2.1.(d) Analytical Procedure.

Concentrations of uranium in the electrolyte were determined before and after each run using the method of analysis described previously (Section 5.3.1.).

6.2.2. Results and Discussion.

Runs carried out on 2.5 and 5.0 cm. lengths of middle section (up to a voltage gradient of 5V/cm. only in the case of the 5 cm. middle section) are reported in Table 6.2. (Runs EDSTN 1-42). Although the results as given in Table 6.2. appear in order of their voltage gradients, the order in which the runs were carried out originally was random in an attempt to minimise any effects of a progressive voltage increase on the current-voltage behaviour of the bed. Voltage gradient, current density and dissolution rate values are based on parameters defined previously (Section 5.2.2.).

The dissolver vessel was tapped during runs EDCTNB 1-5 but was not tapped during Runs EDSTN 1-42.

Blank runs (EDSTN 21 and 42) were carried out to measure the extent of chemical dissolution. As before (Section 5.4.2.) dissolution rates quoted for the blank runs in Table 6.2. are based on the estimated surface area of all the pellets composing the bed.

Table 6.2. Anodic Dissolution of Uranium in Nitric Acid $\frac{3}{4}$ in. dia. Tantalum Dissolver.

129.

2.5 and 5.0 cm. Lengths of Middle Section.

Expt.No.	Duration, mins.	amph.	Faradays	amp.	V	Voltage Gradient, Volts/cm.	Current Density, amp./cm ²	Weight of U dissolved, g.	Equiv. U ⁶⁺	Equiv.U ⁶⁺ F	Conc.U in elec- trolyte, g/l.	Dissol. Rate, mg/min.cm. ²
EDCTNB 1	20		0.12	9.5	25.0	5.0	3.4	34.0	0.86	7.2	65.3	14.2
2	30		0.07	3.9	25.0	5.0	1.4	34.8	0.88	12.6	69.2	9.7
3	30		0.11	5.9	25.0	5.0	2.1	38.2	0.96	8.7	73.5	10.6
4	30		0.09	4.7	25.0	5.0	1.7	38.0	0.96	10.7	77.8	10.6
5	30		0.11	6.0	25.0	5.0	2.2	30.8	0.78	7.1	81.5	8.6
EDSTN 1	30	1.346	0.050	2.7	25.0	5.0	0.97	9.0	0.23	4.6	2.40	2.50
2	30	1.672	0.062	3.3	25.0	5.0	1.19	12.7	0.32	5.2	6.00	3.54
3	30	1.798	0.065	3.6	25.0	5.0	1.29	16.2	0.41	6.3	9.55	4.50
4	30	2.140	0.080	4.3	25.0	5.0	1.55	16.9	0.43	5.4	11.75	4.69
5	30	0.910	0.034	1.8	20.0	4.0	0.63	5.43	0.14	4.1	1.45	1.52
6	30	1.032	0.039	2.1	20.0	4.0	0.76	8.33	0.21	5.4	3.95	2.31
7	30	1.136	0.042	2.3	20.0	4.0	0.83	8.86	0.22	5.2	7.35	2.46
8	30	0.945	0.035	1.9	20.0	4.0	0.69	6.20	0.16	4.6	13.18	1.72
9	30	0.511	0.019	1.0	15.0	3.0	0.36	2.73	0.069	3.6	2.70	0.76
10	30	0.637	0.024	1.3	15.0	3.0	0.47	4.66	0.12	5.0	4.60	1.30
11	30	0.524	0.020	1.1	15.0	3.0	0.40	1.85	0.047	2.4	6.35	0.51
12	30	0.483	0.018	1.0	15.0	3.0	0.36	2.60	0.066	3.7	12.10	0.72
13	40	0.570	0.021	0.85	10.0	2.0	0.31	3.15	0.079	3.8	0.88	0.66
14	30	0.298	0.011	0.60	10.0	2.0	0.22	0.86	0.022	2.0	6.12	0.24
15	30	0.271	0.010	0.54	10.0	2.0	0.19	0.81	0.020	2.0	9.68	0.23
16	30	0.383	0.014	0.77	10.0	2.0	0.28	2.00	0.050	3.6	12.38	0.56
17	60	0.267	0.010	0.27	5.0	1.0	0.10	3.01	0.076	(7.6)	3.05	0.42
18	45	0.192	0.007	0.26	5.0	1.0	0.09	1.06	0.027	3.9	4.08	0.20
19	45	0.241	0.009	0.32	5.0	1.0	0.12	3.06	0.077	(8.6)	7.72	0.57
20	45	0.210	0.008	0.28	5.0	1.0	0.10	0.59	0.015	1.9	9.81	0.11
21	40	-	-	-	-	-	-	5.34	0.13	-	0.55	0.20

Table 6.2. - contd.

130.

Expt. No.	Duration, mins.	amph.	Faradays	amp.	V	Voltage Gradient, Volts/cm.	Current Density, amp/cm ²	Weight of U dissolved, g.	Equiv. U ⁶⁺	Equiv. U ⁶⁺ F	Conc. U in electrolyte, g/l.	Dissol. Rate, mg/min.cm ²
EDSTN 22	20 ^{1/2}	5.621	0.21	16.5	25.0	10.0	5.95	54.5	1.37	6.5	17.3	44.3
23	20	5.458	0.20	16.4	25.0	10.0	5.90	47.9	1.21	6.1	25.7	39.9
24	20	4.473	0.17	13.4	25.0	10.0	4.83	46.3	1.17	6.9	33.4	38.7
25	20	3.079	0.12	9.2	25.0	10.0	3.32	26.4	0.67	5.6	36.3	22.0
26	30	0.970	0.036	1.94	20.0	8.0	0.70	4.1	0.10	2.8	18.1	2.28
27	30	1.401	0.052	2.80	20.0	8.0	1.01	11.8	0.30	5.8	26.5	6.57
28	30	1.351	0.050	2.70	20.0	8.0	0.97	4.2	0.11	2.2	28.3	2.34
29	32	1.949	0.073	3.66	20.0	8.0	1.32	8.0	0.20	2.7	38.26	4.17
30	30	0.558	0.021	1.12	15.0	6.0	0.40	2.1	0.053	2.5	18.40	1.17
31	30	0.853	0.032	1.70	15.0	6.0	0.61	7.6	0.19	5.9	19.96	4.22
32	30	0.495	0.017	1.00	15.0	6.0	0.36	3.5	0.088	5.2	27.0	1.95
33	30	0.673	0.025	1.35	15.0	6.0	0.49	5.4	0.14	5.6	37.0	3.00
34	30	0.665	0.024	1.33	12.5	5.0	0.48	5.8	0.15	6.3	11.7	3.20
35	30	0.530	0.020	1.06	12.5	5.0	0.38	2.4	0.061	3.1	19.1	1.34
36	30	0.372	0.014	0.74	12.5	5.0	0.27	1.2	0.030	2.1	27.2	0.67
37	30	0.381	0.014	0.76	12.5	5.0	0.27	4.7	0.12	8.6	39.4	2.61
38	30	0.385	0.014	0.77	10.0	4.0	0.28	3.0	0.076	5.4	17.6	1.67
39	30	0.434	0.016	0.87	10.0	4.0	0.31	3.0	0.076	4.7	18.8	1.67
40	30	0.355	0.013	0.71	10.0	4.0	0.26	1.7	0.043	3.3	27.2	0.95
41	30	0.281	0.010	0.56	10.0	4.0	0.20	3.0	0.076	7.6	38.8	1.67
42	30	-	-	-	-	-	-	0.7	0.018	-	27.4	0.04

Notes: (1) Length of Middle Section Runs 1-20 = 5 cm. Runs EDCTNB 1-5 = 5 cm.
Runs 22-42 = 2.5 cm.

(2) Normality of electrolyte = 3N as HNO₃.

The high weight of uranium dissolved in Run EDSTN 21 was attributed to the dissolution of uranium oxide film present on the surface of fresh, unattacked uranium pellets, Run EDSTN 21 having been carried out first, before any of the other electrolytic dissolution runs in the series.

Higher voltage gradients (≈ 5 V/cm) were obtained on uranium beds with a 5 cm. length of middle section using the 30A-220V d.c. mains power supply. Results recorded in these experiments are given in Table 6.3. (Runs EDNT 1-12). In the case of Runs EDNT 10-12, the polarities of the tantalum tubes conveying current to the uranium charge were reversed, i.e. the upper (previously cathodic) section became the anode and the lower the cathode. A slight improvement in the current density values obtained at a given voltage gradient was noticed. This was to be expected as a thinner layer of oxide, offering lower electrical resistance, would be present on the normally cathodic tantalum section compared with the layer of oxide on the usually anodic lower section. With the new source of d.c. power it was possible to obtain sufficiently high voltage gradients for uranium beds of 10 cm. lengths of middle section to be tested (Table 6.3., Runs EDNT 13 -21).

All the runs reported in Tables 6.2. and 6.3. were carried out on uranium beds composed of Size 2 pellets and current density - voltage gradient relationships obtained with each of the three lengths of middle section investigated are given in Fig.6.1.

Table 6.3. Anodic Dissolution of Uranium in Nitric Acid.

132.

 $\frac{3}{4}$ in. dia. Tantalum Dissolver.

5.0 and 10.0 cm. Lengths of Middle Section (Higher Voltage Gradients).

Expt. No.	Duration mins.	amph.	Fara- days.	amp	V	Voltage Gradient Volts/cm.	Current Density amp/cm ²	Weight U dissolved g.	Equiv. U ⁶⁺	Equiv. U ⁶⁺ F	Conc. U in elec- trolyte g/l	Dissol. Rate mg/min. cm. ²
EDNT 1	30	4.721	0.176	9.44	35.0	7.0	3.40	59.4	1.50	8.53	35.35	16.5
2	19 $\frac{1}{2}$	3.082	0.115	9.49	35.0	7.0	3.41	24.9	0.63	5.48	37.10	10.7
3	33	5.333	0.199	9.69	35.0	7.0	3.48	66.0	1.66	8.34	43.25	16.7
4	25	7.037	0.262	16.9	47.5	9.5	6.08	95.2	2.40	9.17	48.15	31.7
5	30	8.453	0.316	16.9	50.0	10.0	6.08	114.5	2.88	9.12	55.90	31.8
6	31	8.636	0.322	16.7	50.0	10.0	6.02	142.0	3.58	11.1	66.65	31.8
7	21	8.141	0.304	23.3	52.5	10.5	8.38	136.6	3.45	11.3	42.10	54.2
8	21	7.741	0.289	22.1	57.5	11.5	7.95	117.9	2.97	10.6	50.35	46.8
9	18 $\frac{1}{2}$	6.375	0.238	20.7	60.0	12.0	7.45	84.7	2.14	9.00	56.35	38.2
10	30	4.897	0.183	9.79	30.0	6.0	3.52	65.0	1.64	8.96	30.75	18.1
11	33	5.258	0.196	9.56	32.5	6.5	3.44	81.6	2.06	10.5	37.85	20.6
12	34	5.515	0.206	9.74	30.0	6.0	3.50	81.2	2.05	9.95	43.85	19.9

Table 6.3. - contd.

133.

Expt. No.	Duration mins.	amph.	Fara-days.	amp	V	Voltage Gradient Volts/cm.	Current Density, amp/cm ²	Weight U dissolved g.	Equiv. U ⁶⁺	$\frac{\text{Equiv. U}^{6+}}{F}$	Conc. U in electrolyte g/l	Dissol. Rate mg/min.cm. ²
EDNT 13	26	3.731	0.139	8.61	50.0	5.0	3.10	70.3	1.77	12.7	25.65	11.3
14	35	5.231	0.195	8.97	50.0	5.0	3.22	105.6	2.66	13.6	32.75	12.6
15	26	3.879	0.145	8.95	50.0	5.0	3.22	73.0	1.84	12.7	38.15	12.7
16	29	7.246	0.270	15.0	65.0	6.5	5.40	220.1	5.55	20.6	52.15	31.6
17	26	6.483	0.242	14.9	68.0	6.8	5.36	181.0	4.56	18.9	64.50	29.0
18	24	5.582	0.208	14.0	75.0	7.5	5.03	146.0	3.68	17.7	74.85	25.4
19	20	6.636	0.248	19.9	75.0	7.5	7.17	207.3	5.22	21.0	58.50	43.2
20	20	6.550	0.244	19.7	78.0	7.8	7.09	221.8	5.58	22.7	73.95	46.8
21	21	5.324	0.199	15.2	115.0	11.5	5.47	140.0	3.53	17.7	85.05	27.8

Notes: (1) Length of Middle Section Runs 1-12 = 5 cm.
Runs 13-21 = 10 cm.

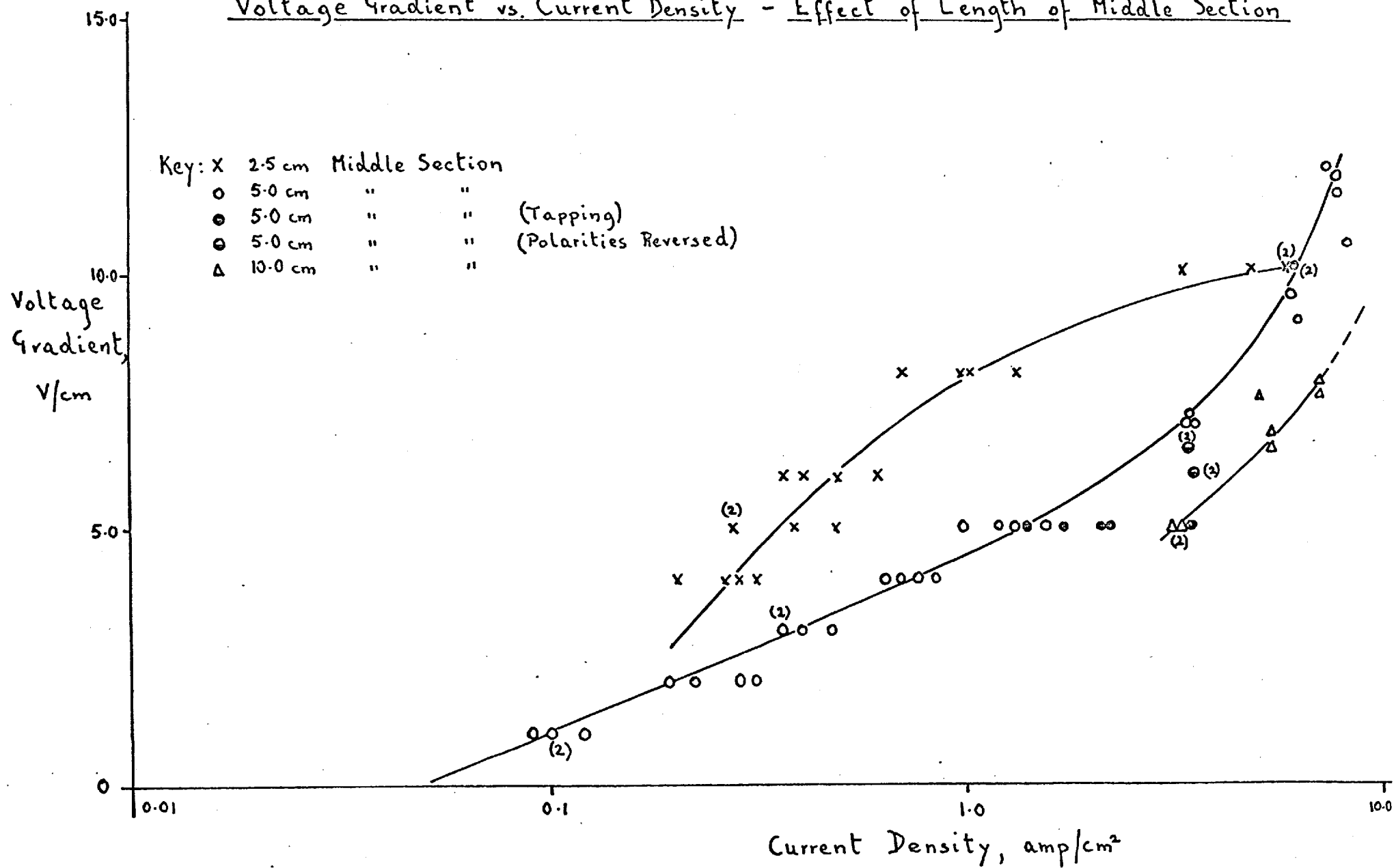
(2) Normality of electrolyte 3N as HNO₃.

(3) Polarity of electrodes reversed in Runs 10, 11, 12.

Fig. 6.1. Anodic Dissolution of Uranium in Nitric Acid

Tantalum Dissolver ($\frac{3}{4}$ in dia.)

Voltage Gradient vs. Current Density - Effect of Length of Middle Section



Results obtained when Size 1 and Size 3 pellets were used to make up a dissolver charge are given in Table 6.4. (Runs EDNTE 1-6 and 10-15 respectively). The effect of a change in pellet size on the current-voltage characteristic of a uranium bed, keeping the length of middle section constant (5 cm.), is illustrated (Fig.6.2). Runs EDNTE 7-9 shown in Table 6.4. were carried out with Size 2 pellets as a check on the similarity of experimental conditions as compared with those obtaining in previous electrolytic dissolution experiments. Higher average temperatures of electrolyte were used during Runs EDNTE 16-18 (Table 6.4).

The variation of dissolution rate with current density at constant pellet size and various lengths of middle section is shown in Fig.6.3. The influence of pellet size on the current density - dissolution rate relationship is illustrated in Fig.6.4. It must be noted that current values quoted in Tables 6.2., 6.3. and 6.4. refer to the total current flowing through the system as no current was assumed to flow directly from the anodic tantalum section to the electrolyte.

Flow rates and pressure drops recorded during the course of the runs ranged from 2.3-3.8 l/min. at 9.5-11.0 p.s.i.g., 2.6-7.3 l/min. at 3.0-10.0 p.s.i.g. and 6.7-8.1 l/min. at 3.5-4.0 p.s.i.g. in the case of uranium beds made up of Size 1, Size 2 and Size 3 pellets respectively.

Table 6.4. Anodic Dissolution of Uranium in Nitric Acid

136.

 $\frac{3}{4}$ in. dia. Tantalum Dissolver.

Run No.	Duration of Run, min.	amph.	F	amp (calc.)	V (aver- age)	Voltage Gradient, Volts/cm.	Current Density, amp/cm ²	Weight of U dis- solved, g	Equiv. U ^{vi}	Equiv. U ^{vi} F	Conc. U in elec- trolyte, g/l	Dissol. Rate, mg/min.cm. ²
EDNTE 1	36	5.766	0.215	9.63	39	7.8	3.46	50.0	1.26	5.86	8.72	5.2
2	34	5.302	0.198	9.37	40	8.0	3.37	70.3	1.77	8.94	13.49	7.7
3	25	6.820	0.254	16.35	55	11.0	5.88	93.4	2.36	9.30	20.00	14.0
4	26	7.103	0.265	16.40	55	11.0	5.90	117.8	2.97	11.20	28.65	17.0
5	23	7.791	0.291	20.35	65	13.0	7.31	105.2	2.66	9.15	36.00	17.1
6	19	6.599	0.246	20.85	68	13.6	7.50	143.2	3.62	14.73	46.00	28.2
7	29	4.780	0.178	9.89	35	7.0	3.56	51.5	1.30	7.31	49.75	14.8
8	24	6.933	0.258	17.30	45	9.0	6.23	63.2	1.59	6.16	54.35	22.0
9	19	6.908	0.258	21.80	58	11.8	7.85	54.8	1.38	5.35	58.35	24.1

Notes: (1) Runs EDNTE 1-6 : No.1 Size Pellets.

(2) Runs EDNTE 7-9 : No.2 Size Pellets (Control Runs).

Table 6.4. - contd.

137.

Run No.	Duration of Run, min.	amph.	F	amp (calc.)	V (average)	Voltage Gradient, Volts/cm.	Current Density, amp/cm ²	Weight of U dissolved, g.	Equiv. U ^{vi}	Equiv. U ^{vi} / F	Conc. U in electrolyte, g/l	Dissol. Rate, mg/min.cm ²
EDNTE 10	35	5.946	0.222	10.20	25	5.0	3.67	51.7	1.30	5.86	31.35	27.1
11	34	5.674	0.212	10.00	28	5.6	3.60	30.9	0.78	3.68	33.50	16.7
12	23	6.717	0.251	17.50	40	8.0	6.30	52.6	1.33	5.30	37.10	42.0
13	26	8.098	0.302	18.70	33	6.6	6.73	67.6	1.70	5.63	41.25	47.7
14	23	8.673	0.324	22.60	43	8.6	8.15	69.1	1.74	5.37	46.00	55.2
15	27	10.518	0.393	23.40	43	8.6	8.42	99.3	2.50	6.36	52.85	67.5
16	32	5.952	0.222	11.20	35	7.0	4.03	70.4	1.77	7.98	28.10	18.3
17	27	10.266	0.383	22.80	50	10.0	8.20	92.8	2.34	6.12	34.50	28.7
18	26	7.641	0.285	17.60	43	8.6	6.35	77.5	1.95	6.85	39.90	24.8

Notes - contd. :

(3) Runs EDNTE 16-18 : No.2 Size Pellets (Temp. of Electrolyte 32-50°C.).

(4) Runs EDNTE 10-15 : No.3 Size Pellets.

(5) Length of middle section = 5 cm. Electrolyte 3N HNO₃ in all runs.

Fig. 6.2. Anodic Dissolution of Uranium in Nitric Acid

Tantalum Dissolver ($\frac{3}{4}$ in dia.)

Voltage Gradient vs. Current Density - Effect of Pellet Size

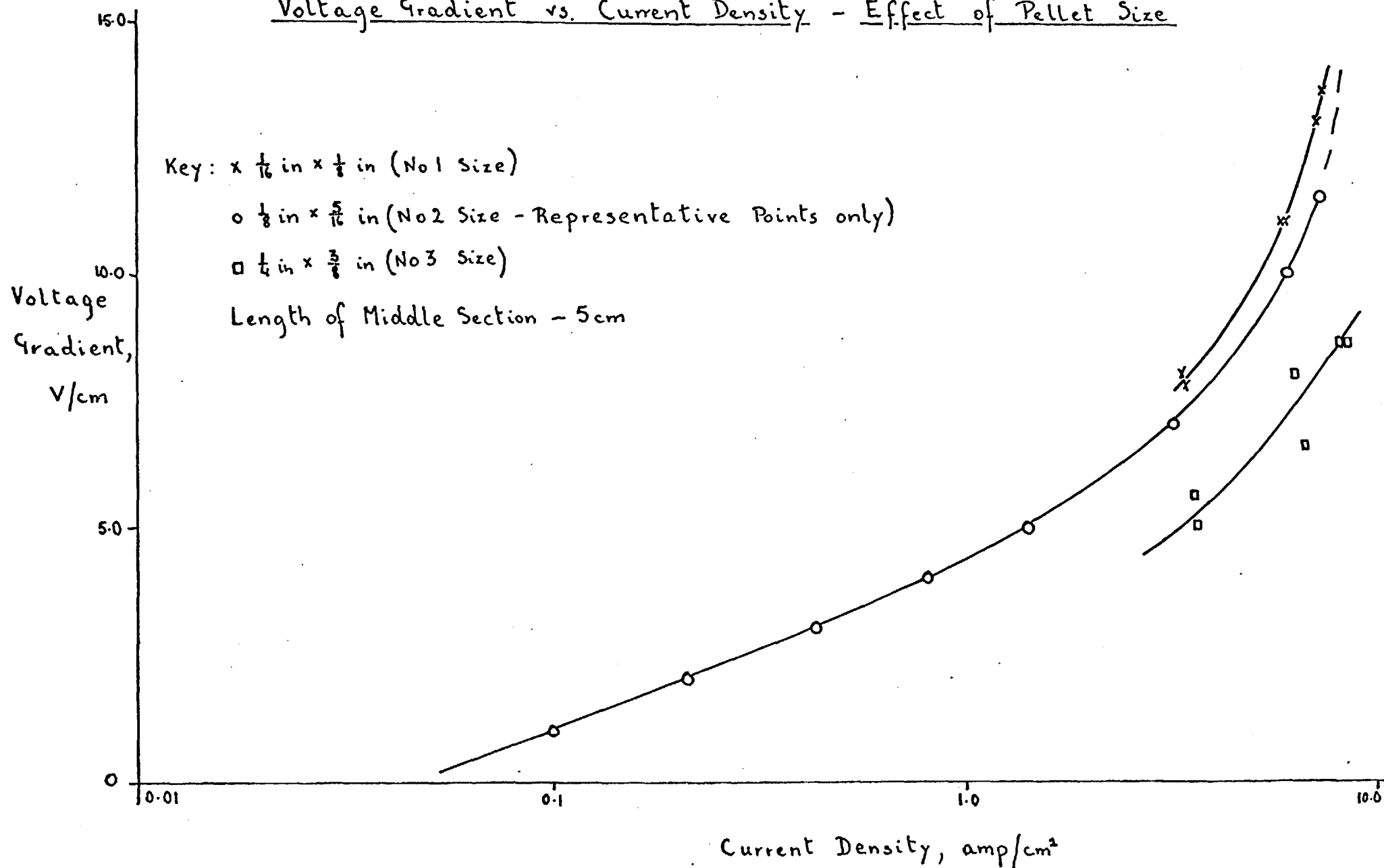


Fig. 6.3. Anodic Dissolution of Uranium in Nitric Acid

Tantalum Dissolver ($\frac{3}{4}$ in dia.)

Dissolution Rate vs. Current Density
(Effect of Length of Middle Section)

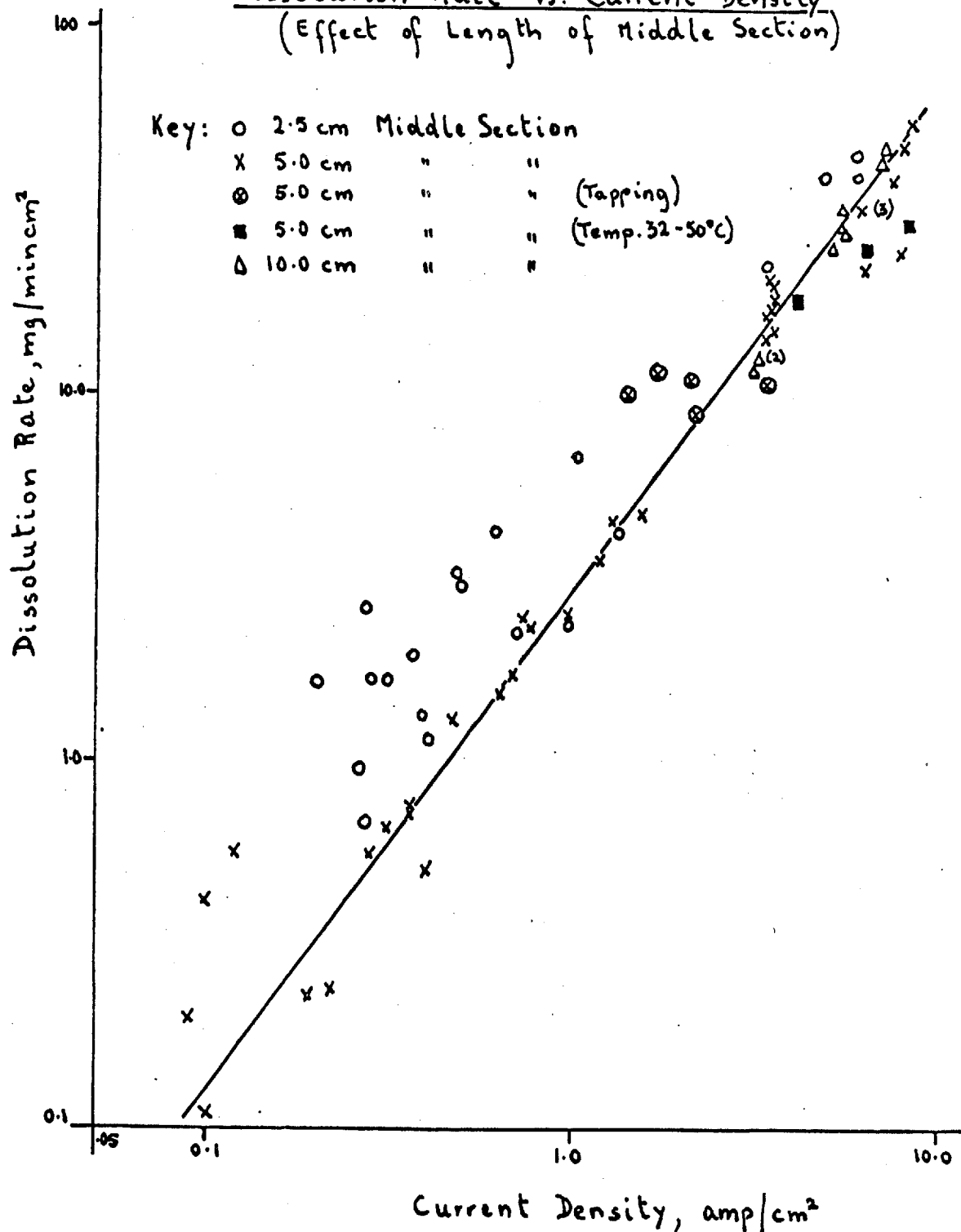
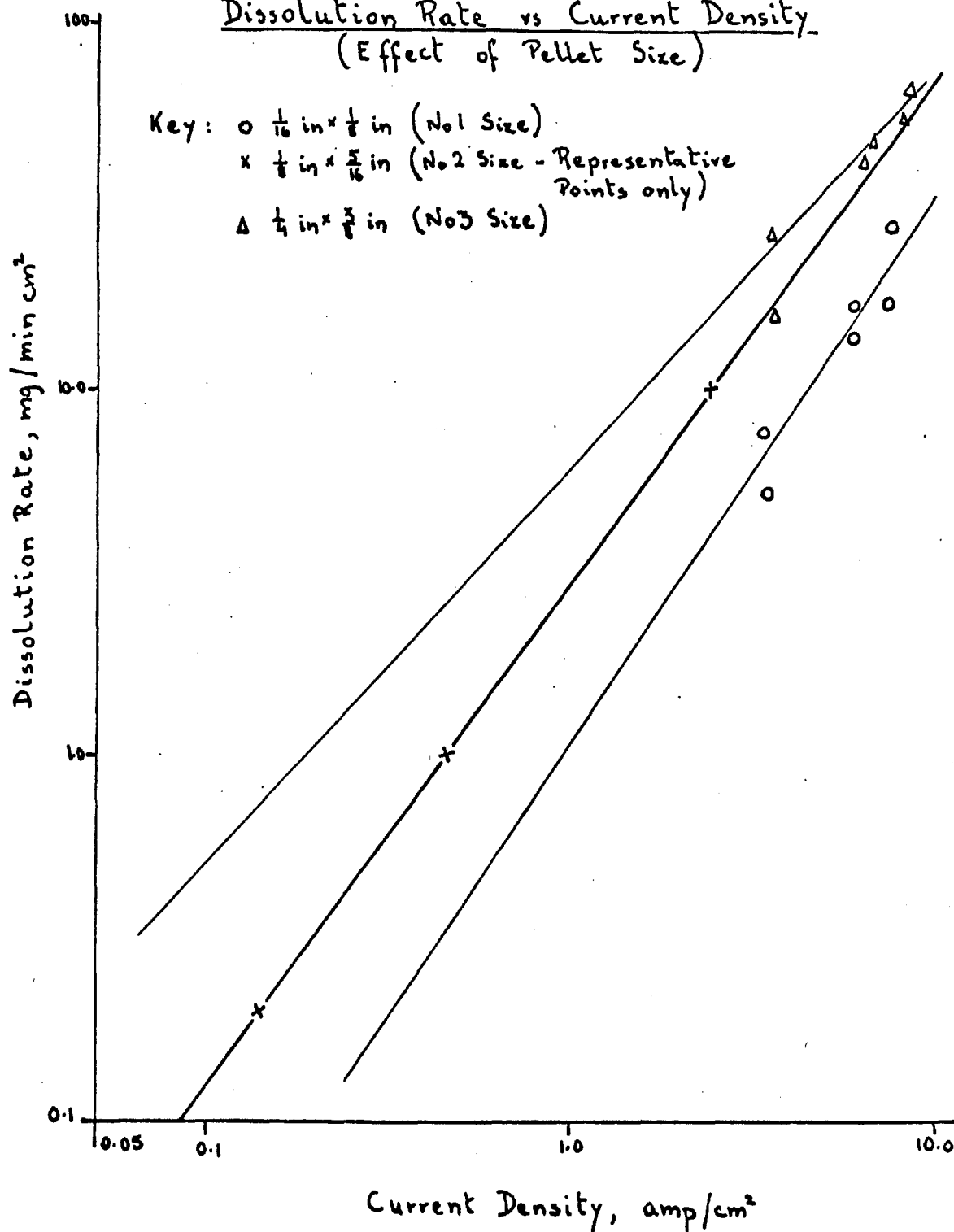


Fig. 6.4. Anodic Dissolution of Uranium in Nitric Acid

Tantalum Dissolver ($\frac{3}{4}$ in dia.)

Dissolution Rate vs Current Density
(Effect of Pellet Size)



Except in the case of Runs EDNTE 16-18 (Table 6.4.) when the electrolyte was heated and its temperature maintained in the range 32-50°C., temperatures during the course of the majority of experiments were held within 20-35°C. Temperature was allowed to rise unchecked, however, during Runs EDNT 8, 17 and 20 (Table 6.3.) when temperatures up to 55°C. were observed towards the end of a run. Evolution of brown NO₂ fumes was noticed in each case as the temperature of the electrolyte rose above 35-40°C.

6.2.2.(a) Mass Balance of Uranium.

As before, (Section 5.4.2.) weights of uranium dissolved as obtained by direct weighing and by analysis, are compared. Results obtained are shown in Table 6.5. No reasonable explanation could be found for the rather large discrepancy observed between the two figures in the case of Runs EDSTN 22-42. Based on observation of the uranium bed level at the end of these runs, it would appear, however, that the figure obtained by direct weighing is more correct. Displacement from the normal curve of dissolution rate values obtained in Runs EDSTN 22-42 (Fig.6.3.) tends to support this observation.

6.2.2.(b) Corrosion of Tantalum Anode.

The anodic section of the dissolver vessel was re-weighed after the first five runs (EDCTNB 1-5) when 13.4 amph had passed through the dissolver. A weight loss of 0.08 g tantalum was observed.

Table 6.5. $\frac{3}{4}$ in. dia. Tantalum Dissolver.Mass Balance of Uranium.

Run Nos.	(a) g	(b) g	Difference % ± on (a).
EDCTNB 1-5	173	176	+ 1.6
EDSTN 1-21	116	115	- 0.9
EDSTN 22-42	193	247	+28.0
EDNT 1-3	127	150	+18.1 ⁽¹⁾
4-6	350	352	+ 0.6
7-9	324	339	+ 4.6
10-12	202	228	+12.9 ⁽¹⁾
13-15	-	249	- (2)
16-18	532	547	+ 2.8
19-21	558	569	+ 2.0
EDNTE 1-3	230	214	- 7.0
4-6	360	366	+ 1.7
7-9	177	170	- 4.1
10-12	131	135	+ 3.1 ⁽¹⁾
13-15	228	236	+ 5.3 ⁽¹⁾
16-18	241	241	0.0

Notes: (a) Figures obtained by direct weighing.

(b) " " " analysis.

(1) Uranium bed removed for examination prior to weighing.

(2) Uranium bed removed for examination - not weighed.

This loss was attributed largely to tantalum removed from the rough edges of the tube remaining round the circumference where the tube was sawn. No weight loss was found after a further 44.4 amph. This observation confirms the findings of other workers⁽³⁶⁾ who detected no loss in weight of a tantalum anode basket even after several hundred ampere-hours of charge. Examination of the anodic section of the dissolver revealed signs² of pitting, however, presumably where arcing had occurred between the tantalum and the uranium bed. The stainless steel mesh support for the uranium bed was frequently found corroded after a series of runs and had to be replaced.

6.2.2.(c) Arcing within Dissolver Bed.

Spontaneous arcing within the dissolver bed was found to occur at voltage gradients above 5V/cm., and more frequently at values greater than 7V/cm. This behaviour seemed independent of whether tapping was used or not (no tapping at all Runs EDSTN; limited tapping, at most once or twice during a run, in Runs EDNT and EDNTE) - often tapping did not result in arcing. Greater tendency towards arcing was observed with the smaller sizes of pellets and during some runs using Size 1 arcing was almost continuous for periods up to 1 minute. Proportionately more arcing took place nearer the anodic rather than the cathodic section of the dissolver.

6.2.2. (d) Evaluation of Surface Area of Pellets.

The surface area of Size 1 and Size 3 pellets was estimated in a manner analogous to that described previously for the case of Size 2 pellets (Section 5.4.2.). A value of $54 \text{ cm}^2/\text{cm}$ length of bed was obtained, for Size 1, and $11 \text{ cm}^2/\text{cm}$ for Size 3 pellets.

6.2.2.(e). Measurements of Uranium Bed Resistance.

Resistances of a bed of uranium composed of Size 2 pellets, with water circulating through the dissolver, were measured at successive time intervals. By measuring the conductance of the circulating water, the overall resistance of the bed (i.e. uranium + water) could be used to give resistance values of the uranium bed alone. Results and details of calculations are given in Appendix F (Table F.4.). Based on figures obtained with a.c. the resistance of the uranium bed alone rose from an estimated value of about 60 ohms/cm. to a calculated value of about 140 ohms/cm. length of middle section. (Time interval between Expts. 1-3 and Expts. 4-7 : 3 weeks). The rise in resistance was attributed to a gradual build-up of oxide on the surface of the uranium pellets which was unattacked in the non-corrosive, aqueous medium. A similar rise in resistance was observed with d.c. but the actual value of resistance was 4-5 times higher as compared with a.c., due to polarisation effects.

6.3. 1 $\frac{1}{2}$ in. I.D. Dissolver Vessel.

Experiments using a wider dissolver vessel were carried out in order to gain a further insight into the behaviour of the electrolytic dissolution system and thus also provide a better basis for any future scale-up development of the dissolver vessel. All parameters with the exception of the diameter were kept within limits investigated on the $\frac{3}{4}$ in. I.D. vessel to allow for a greater degree of certainty in the comparison between the behaviour patterns of the two dissolver units.

6.3.1. Experimental Procedure.

The 1 $\frac{1}{2}$ in I.D. dissolver vessel was made up of two 6 in. lengths of tantalum tube, separated by a p.t.f.e. section as shown previously (Fig.5.1.). As before, the lower tantalum section served as the anode, a stainless steel mesh plug serving as a support for the uranium bed. The charge consisted of Size 2 pellets and one length of middle section only was investigated (9.5 cm.). Initial overall bed lengths ranged from 23-26 cm. with 5-6 cm. within the anodic section. Voltage gradient values between 0.5-7.5 V/cm. were applied across the middle section, both the 48A-25V rectifier unit and the d.c. mains supply (Section 6.2.1.) having been used as sources of power. Current values were obtained from integrated time-current figures recorded on the d.c. ampere-hour meter (Section 6.2.1.).

The dissolver vessel was incorporated in the flow circuit described earlier (Section 5.4.1., Fig.5.4.). Uranium concentrations in the 3N HNO₃ electrolyte ranged from 10.5 - 67.0 gU/l. Uranium content of samples taken before and after each run was determined according to the method described earlier (Section 5.3.1.).

6.3.2. Results and Discussion.

Results of all runs carried out on the 1½ in. dia. dissolver are given in Table 6.6. The current density-voltage gradient relationship is plotted in Fig.6.5, the rise of dissolution rate with increase in current density being illustrated in Fig.6.6. A blank run (Run EDWT 16) was carried out and the dissolution rate value given for it was again based on the surface area of all pellets within the dissolver (Section 6.2.2.). Based on surface area estimates for Size 2 pellets calculated previously (Section 5.4.2.), the total surface area of pellets within the middle section of the 1½ in. dia. dissolver amounts to about 910 cm². A value of 900 cm² was, however, taken for the purposes of calculations quoted in Table 6.6.

Temperatures were allowed to rise unchecked during Runs EDWT 23, 24, 26 and 28 and reached 42-48°C. at the end of a run, when evolution of NO₂ gas was noticed. A temperature of 20-35°C. was maintained during the majority of the remaining runs. Electrolyte flow rates of 7.5-10.0 l/min. were observed at pressures ranging from 1.5-3.5 p.s.i.g.

Table 6.6. Anodic Dissolution of Uranium in Nitric Acid.

147.

1 1/2 in dia. Tantalum Dissolver.

Expt.No.	Duration, mins.	amph.	F (Fara- days).	amp	V	Voltage Gradient Volts/cm.	Current Density, amp/cm ²	Weight U dis- solved, g.	Equiv.U ⁶⁺	Equiv.U ⁶⁺ F	Conc.U in elec- trolyte g/l	Dissol. Rate mg/cm ² .min.
EDNT 1	17	0.180	0.007	0.64	5.0	0.53	0.06	3.6	0.09	12.9	10.45	0.24
2	35	0.380	0.014	0.65	5.0	0.53	0.06	4.8	0.12	8.58	10.85	0.15
3	60	0.595	0.022	0.60	5.0	0.53	0.05	3.8	0.10	4.55	11.30	0.07
4	31	1.070	0.040	2.07	10.0	1.05	0.18	6.2	0.16	4.00	11.77	0.22
5	31	1.276	0.048	2.47	10.0	1.05	0.22	6.0	0.15	3.13	12.23	0.22
6	30	1.089	0.041	2.18	10.0	1.05	0.19	6.4	0.16	3.90	12.72	0.24
7	23	1.155	0.043	3.01	15.0	1.58	0.26	2.7	0.07	1.63	12.96	0.13
8	36	1.664	0.062	2.78	15.0	1.58	0.24	8.2	0.21	3.39	13.58	0.25
9	33	1.519	0.056	2.76	15.0	1.58	0.24	6.9	0.17	3.04	14.14	0.23
10	31	1.873	0.070	3.63	20.0	2.10	0.32	9.1	0.23	3.29	14.84	0.33
11	35	2.111	0.079	3.62	20.0	2.10	0.32	15.8	0.40	5.06	16.02	0.50
12	31	1.938	0.072	3.75	20.0	2.10	0.33	13.4	0.34	4.72	17.04	0.48
13	31	2.873	0.107	5.56	25.0	2.63	0.49	21.6	0.54	5.05	18.66	0.76
14	32	2.759	0.103	5.17	25.0	2.63	0.45	23.1	0.58	5.63	20.40	0.80
15	32	2.857	0.107	5.35	25.0	2.63	0.47	22.4	0.57	5.33	22.10	0.78
16	61	-	-	-	-	-	-	5.0	0.13	-	22.54	0.04

Table 6.6. - contd.

148.

Expt.No.	Dura- tion, mins.	amph.	F (Fara- days).	amp	V	Voltage Gradient Volts/cm.	Current Density, amp/cm ²	Weight U dis- solved, g.	Equiv.U ⁶⁺	Equiv.U ⁶⁺ F	Conc.U in elec- trolyte g/l	Dissol. Rate mg/cm ² .min.
EDWT 17	31	5.071	0.189	9.81	40.0	4.20	0.86	58.6	1.48	7.84	29.85	2.10
18	32	5.028	0.188	9.43	40.0	4.20	0.83	62.4	1.57	8.35	35.35	2.17
19	32	5.053	0.189	9.49	40.0	4.20	0.83	76.0	1.92	10.2	41.10	2.64
20	25 ¹ / ₄	5.045	0.188	12.0	47.5	5.00	1.05	64.3	1.64	8.73	25.25	2.83
21	30	5.995	0.224	12.0	47.5	5.00	1.05	86.3	2.17	9.69	31.35	3.20
22	28	5.561	0.208	11.9	47.5	5.00	1.05	88.4	2.23	10.7	37.70	3.51
23	30	7.228	0.270	14.5	49.0	5.15	1.27	128.5	3.24	12.0	29.25	4.77
24	30	7.003	0.261	14.0	53.0	5.70	1.23	116.0	2.92	11.2	38.25	4.30
25	26	5.959	0.222	13.8	55.0	5.80	1.21	98.3	2.48	11.2	45.40	4.21
26	19	5.022	0.187	15.9	60.0	6.30	1.39	103.7	2.61	13.9	30.50	6.07
27	34	9.111	0.340	16.1	58.0	6.10	1.41	139.1	3.51	10.3	41.35	4.55
28	31	8.151	0.304	15.8	60.0	6.30	1.38	147.6	3.72	12.2	53.25	5.29
29	30	11.125	0.420	22.3	65.0	6.80	1.95	254.7	6.42	15.3	42.25	9.08
30	30	10.836	0.405	21.7	68.0	7.14	1.90	210.4	5.31	13.1	57.15	7.80
31	16	5.426	0.202	20.4	73.0	7.67	1.79	129.3	3.26	16.1	67.00	8.96

Notes: Length of middle section : 9.5 cm.

Normality of electrolyte : 3N as HNO₃.

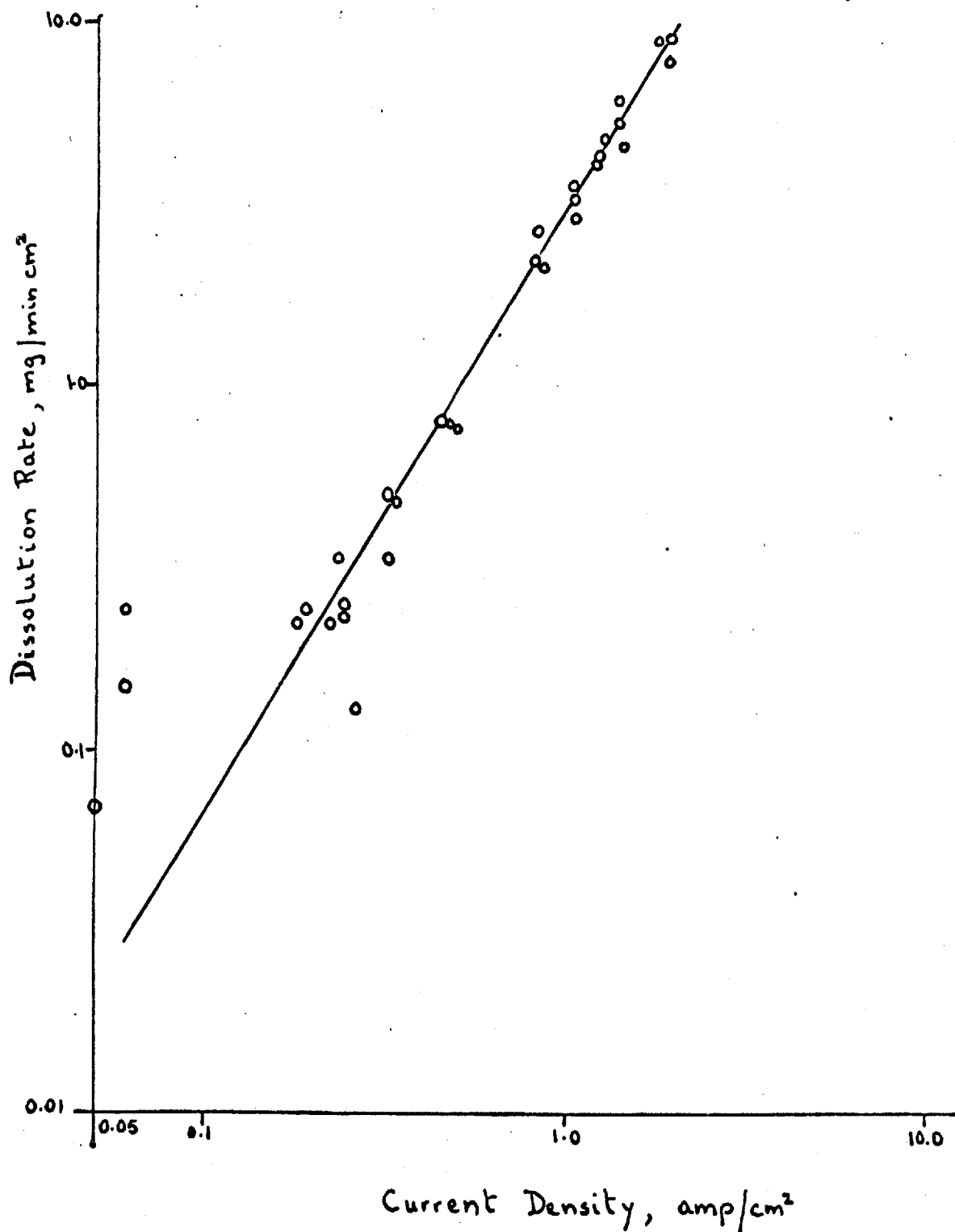
Key: $\times 1\frac{1}{2}$ " Dissolver
 $\Delta \frac{3}{4}$ " Dissolver (10 cm Middle Section)



Fig. 6.6. Anodic Dissolution of Uranium in Nitric Acid

Tantalum Dissolver (1½ in. dia.)

Dissolution Rate vs. Current Density



6.3.2.(a) Mass Balance of Uranium.

Weights of uranium dissolved during the course of the runs, as obtained by direct weighing and by analysis, are given in Table 6.7.

Table 6.7. 1 $\frac{1}{2}$ in. dia. Tantalum Dissolver.

Mass Balance of Uranium.

Run Nos.	(a) g	(b) g	Difference % ± on (a).
EDWT 1-22	676	645	-4.6
23-28	751	733	-2.4
29-31	591	594	+0.6

Notes: (a) Figures obtained by direct weighing.
(b) " " " analysis.

6.3.2.(b) Appearance of Anode.

Apart from a few pitting marks, observed also in the case of $\frac{3}{4}$ in. dia. dissolver (Section 6.2.2.), no corrosion of the tantalum anode was noted at the end of the series of runs.

6.3.2.(c) General Observations.

No arcing within the dissolver bed was observed but current-voltage fluctuations occurred even when the dissolver was not tapped. Tapping was used frequently (about every 5 min.) at lower voltage gradients ($< 5V/cm.$) to ensure against a drop in current level. At higher voltage gradients, the dissolver was tapped only once every 10-15 mins. at the most as little tendency for the current to drop

was noted. Frothing of the electrolyte and bubbling of gas in the flow-circuit pipeline above the dissolver were noticed at voltage gradients higher than 5V/cm. A noise, similar to a transformer hum, was emitted by the dissolver system at these high voltage gradients.

6.4. Conclusions.

Tantalum was shown to be suitable as a material of construction for an anodic dissolver. Some improvement in the reproducibility of results was observed, particularly in the case of the $1\frac{1}{2}$ in. dia. dissolver, where even with tapping conditions during electrolytic dissolution appeared to be much more stable than was the case with the $\frac{3}{4}$ in. dia. dissolver.

Chapter 7.

Model Experiment.

Chapter 7

Model Experiment.

7.1. Introduction.

7.2. Experimental Details.

7.2.1. Apparatus.

7.2.2. Procedure.

7.3. Results and Discussion.

7.3.1. Comparison of Current Values obtained from Copper Coulometer and Ampere-hour Meter Readings.

7.3.2. Comparison of nominal and actual Distance Values.

7.3.3. Electrolyte Acidity Determinations.

7.3.4. Effect of Electrode Separation Distance.

7.3.5. Multi-cell System.

7.3.6. Potential Differences in a Multi-cell System.

7.4. Conclusions.

7.1. Introduction.

Current efficiency figures observed during experiments on the anodic dissolution of uranium from a bed composed of a large number of small uranium pellets (Chapters 5 and 6) showed quite clearly that the number of equivalents of uranium dissolved per faraday usually exceeded unity. The possibility that uranium passed into solution in the tervalent state was unlikely as uranium was previously observed to dissolve electrolytically in 6N HNO_3 with a valency of 6 (Section 5.4.2. and Appendix D). Blank runs carried out on the dissolver bed indicated that chemical dissolution could not be responsible for the increase in dissolution rate. For example, at high voltage gradients ($> 5\text{V/cm.}$) and current densities ($> 1\text{ amp/cm}^2$) when the current efficiencies were highest, chemical dissolution in 3N HNO_3 at $20\text{--}35^\circ\text{C.}$ never exceeded 10% of the weight of uranium dissolved. (The figures quoted are for the tantalum dissolver, where all the current could be assumed to pass through uranium at some stage of the dissolution process - c.f. Section 6.2.2.).

The concept of the uranium bed in the dissolver being composed of a number of individual electrolytic cells with some of the pellets acting both as the anode and the cathode to the pellets in their immediate vicinity (Section 2.2.) seemed thus to be the most likely explanation for the high current efficiency values observed. Such bipolar behaviour has been used industrially in the series system

of copper electrowinning⁽⁷⁷⁾ in which a number of copper sheets are interposed between a copper cathode and a copper anode in an electrolytic bath with the metal on each sheet dissolving from the anode side and being deposited on the cathode side. Work on stray current corrosion of a stainless steel coupon placed between two electrodes in 6N HNO_3 electrolyte was also reported⁽²⁶⁾. It showed that anodic dissolution of the coupon occurred on the side facing the cathode.

A model experiment was therefore devised to observe whether a multi-cell system was, in fact, set up when a series of uranium pellets was placed in the path of a current flowing through the electrolyte. It was also hoped that the model experiment would provide additional information on the valency of uranium (referred to earlier, Section 5.4.2. and Appendix D) and on the influence of electrode separation distance on the uranium dissolution efficiency.

7.2. Experimental Details.

7.2.1. Apparatus.

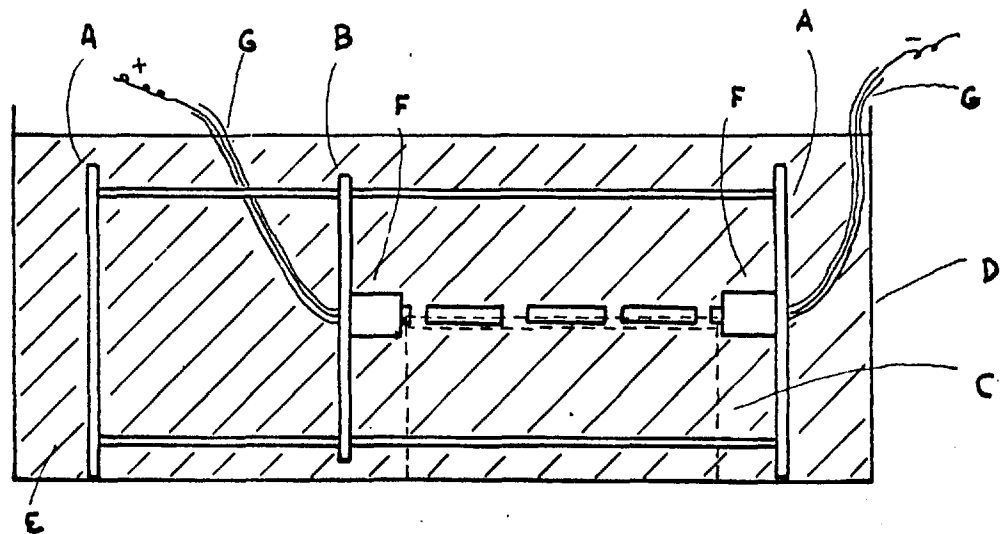
A simple stainless steel (F.D.P. alloy) framework was constructed to support a uranium anode and cathode between which varying numbers of uranium pellets could be placed (Fig.7.1.). One of the plates supporting the electrodes was movable thus allowing the distance separating the electrodes to be varied. Both connected and unconnected pellets were $\frac{3}{8}$ in. diameter x $\frac{7}{16}$ in. long. The whole model assembly was submerged in 2 l of 3N HNO_3 in a rectangular glass

tank. A polyethylene cover was fitted over the top of the tank to reduce evaporation losses. The electrolyte was stirred at a constant rate and its temperature was maintained at 18-23°C. by means of a cooling coil dipping in the electrolyte. During the course of runs carried out at high current densities, ($> 6.0 \text{ amp/cm}^2$), however, temperatures rose to as high as 35°C., the cooling coil having been inadequate to remove the heat evolved sufficiently quickly.

The uranium electrodes were connected to the d.c. supply by means of a strip of tantalum foil spotwelded on their surface. The other end of the tantalum strip was then spotwelded onto a length of brass wire to which the current leads were attached. The complete electrode assembly was inserted into a p.v.c. tube and press-fitted into the stainless steel holders on the apparatus. The p.v.c. tube was designed to act both as a sheath protecting the assembly from attack in the nitric acid electrolyte and as an insulator between the electrodes and the stainless steel framework. As the Ta - U spotwelded connections on the electrodes proved subsequently to be extremely fragile during handling, contact with the d.c. supply was maintained in the majority of runs by means of a column of mercury poured into the p.v.c. sheath.

Fig 7.1. Model Experiment

Diagram of Apparatus



Not to Scale

- | | |
|---|---|
| A Fixed Plates | D Glass Tank |
| B Movable Plate | E Nitric Acid Electrolyte |
| C Glass Support for
unconnected
Uranium Pellets | F Holders for fixed
Uranium Electrodes |
| | G PVC Sheath |

The 48A - 25V rectifier unit (Section 5.4.1.) was used as a source of d.c. supply; an added resistance being included in the circuit to control the amount of current flowing through the apparatus. A copper coulometer was used initially to measure the quantity of electricity consumed during any given run. Subsequently (Run SE 28 onwards), however, both because of ease of handling and because at high current densities the copper coulometer was subject to error (Section 7.3.), the ampere-hour meter described previously (Section 6.2.1.) was substituted as means of current measurement.

7.2.2. Procedure.

Three groups of experiments were carried out. Firstly, the dissolution efficiency of uranium was investigated at various electrode separation distances ranging from 0 - 3.5 cm. (nominal). No unconnected uranium pellets were interposed between the electrodes during this set of runs. Voltages of up to 10V were applied and currents up to 9 amp achieved.

The second group of experiments were designed to investigate the multi-cell behaviour of unconnected pellets placed between two uranium electrodes. From 1-3 unconnected pellets were interposed between the two electrodes fixed at a constant distance of 3.5 cm. (nominal) apart. Highest current and voltage values reached were 8.93 amp and 25.5V respectively.

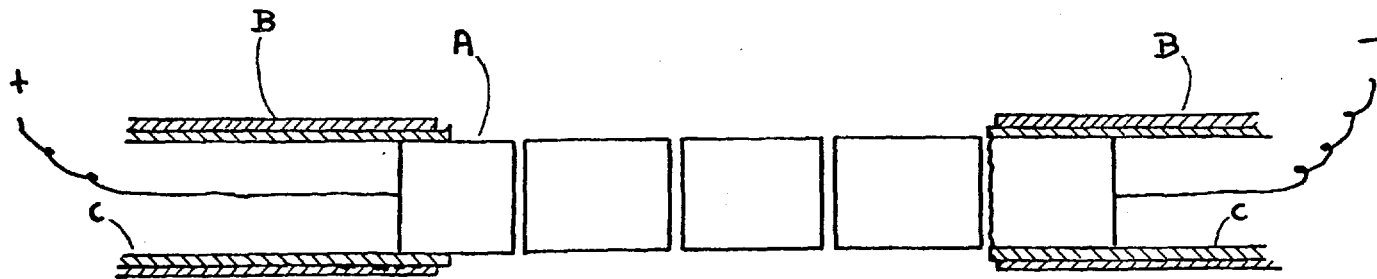
Thirdly, the effect of changing the current path on the multi-cell behaviour of 3 unconnected pellets placed between the electrodes was investigated. A change in current path was achieved by allowing the anode to protrude beyond the holder instead of being mounted flush as in the case of all other runs in this series (Fig.7.2.). Tests with currents up to 8.32 amp at 12.8V were carried out.

All uranium surfaces which were to come in contact with the electrolyte during the course of the runs were first polished using wet silicon-carbide paper in an attempt to remove as much of the surface oxide film as possible. Distances separating the pellets and the electrodes from each other were measured before the runs were started using a cathetometer. Frequent replacement of the uranium pellet forming the anode in the system was necessary as it dissolved appreciably during the course of the experiments.

Both the acidity of the 3N HNO_3 electrolyte and its uranium concentration were kept reasonably constant by periodic replacement of a part of the electrolyte with fresh 3N HNO_3 . Uranium concentration in the electrolyte ranged from 3.3 - 15.1 g U/l. Acidity and uranium determinations were carried out by methods described previously (Section 5.3.1.).

Fig. 7.2. Model Experiment

Multi-Cell Assembly - Anode Protruding



Not to Scale

A Protruding Anode

B Stainless Steel Holder

C PVC Sheath

Approximate values for the potential difference between the electrodes, the unconnected pellets and the bulk of the solution were obtained when a voltage of 10.4V was applied across an electrode system including 3 unconnected uranium pellets. The voltages were measured using stainless steel wire probes connected directly to a voltmeter.

7.3. Results and Discussion.

The effect of electrode separation distance on the amount of uranium dissolved per faraday (no unconnected pellets present) was noted in Runs SE 1-37 (Table 7.1.). Results obtained when the multi-cell concept was investigated are reported in Table 7.2. whilst data recorded during a number of preliminary runs carried out with 3 unconnected pellets in the system are given in Table 7.3.

Table 7.2. Anodic Dissolution of Uranium in Nitric Acid.

164.

Model Experiment.Two Uranium Electrodes fixed at 3.5 cm. distanceVarying numbers of Unconnected Pellets interposed.

Run No.	Duration of run, min.	V	amp	Current density, amp/cm. ²	Wt. of U dissolved, g.	Wt. U diss. F, g.	Dissol. Rate, (1) mg/min.cm. ²	Equiv. U ⁶⁺ + or - theoretical amount.
<u>One Unconnected Uranium Pellet.</u>								
SE 38	49	2.33	0.21	0.27	0.24	38.1	3.1	-0.05
39	36	2.90	0.51	0.65	0.52	45.6	9.2	+0.15
40	28	3.55	0.83	1.06	0.61	42.1	13.8	+0.06
41	26	4.35	1.24	1.58	0.96	47.7	23.5	+0.20
42	21	7.60	2.72	3.46	1.55	43.6	47.0	+0.10
43	14	13.20	5.25	6.69	1.90	41.6	86.3	+0.05
<u>Two Unconnected Uranium Pellets.</u>								
44	51	2.12	0.21	0.27	0.22	32.4	1.8	-0.19
45	47	2.79	0.61	0.77	0.83	46.6	7.5	+0.17
46	31	3.10	0.80	1.02	0.45	29.2	6.2	-0.26
47	27	3.90	1.19	1.52	1.00	50.0	15.7	+0.26
48	20	7.71	2.68	3.41	1.33	39.6	28.3	0.00
49	14	14.4	5.53	7.06	2.75	57.2	83.2	+0.43
50	10	18.9	7.83	10.0	2.57	52.8	109.0	+0.33
51	11	24.9	8.93	11.4	2.63	43.0	101.0	+0.08
<u>Three Unconnected Uranium Pellets.</u>								
52	14	12.4	6.23	7.93	4.49	82.7	102.0	+1.08
53	13	15.9	7.13	9.10	5.05	87.5	123.5	+1.20
54	12	21.0	8.15	10.4	4.86	79.9	128.8	+1.02
55	10	25.5	8.46	10.8	3.25	61.7	103.2	+0.56 (2)
<u>Three Unconnected Pellets - Connected Anode protruding.</u>								
56	56	2.08	0.20	0.25	0.34	49.3	0.97 (3)	+0.24
57	38	2.47	0.45	0.57	0.48	44.8	2.01	+0.13
58	30	3.10	0.85	1.08	0.52	32.1	2.76	-0.19
59	26	3.95	1.27	1.62	1.07	52.0	6.55	+0.31
60	23	5.60	2.62	3.33	2.05	54.7	14.2	+0.38
61	17	8.58	4.68	5.97	3.03	61.2	28.4	+0.54
62	11	12.8	8.32	10.60	4.44	78.0	64.3	+0.97

Notes: (1) Area of all anode surfaces taken.

(2) Results affected by change in shape of pellets.

(3) Figures based on total area of anodes, i.e. including circumferential area of protruding anode.

Table 7.3. Anodic Dissolution of Uranium in Nitric AcidModel Experiment - Preliminary Runs.

Run No.	Duration of run, min.	V	amp	Current density, amp/cm. ²	Wt. of U dissolved, g.	Wt. U diss. F g.	Dissol. Rate, mg/min.cm. ² (1)	Equiv. U _{vi} + or - theoretical value.
ER2	45	2.20	0.22	0.27	0.279	46.0	2.0	+0.16
ER3	41	2.70	0.45	0.57	0.537	47.3	4.2	+0.19
ER4	28	3.65	0.66	0.84	0.552	48.3	6.3	+0.22
ER5	20	6.45	2.28	2.91	1.794	63.1	28.5	+0.59
ER6	16	11.50	4.72	6.00	3.735	79.8	74.1	+1.01

Note: (1) Area of all anode surfaces taken.

The voltage-current density relationship for two uranium electrodes, at various separation distances is plotted in Fig. 7.3., whilst values for a multi-cell system are given in Fig. 7.4.

The variation of dissolution rate with current density is shown in Figs. 7.5. and 7.6. for the single cell and multi-cell systems respectively. In all cases the current density values are expressed in terms of the cross-sectional area of the electrode pellets only, whilst the dissolution rate figures are based on the total anodic area of the pellets, whether connected or unconnected.

Fig. 7.3. Anodic Dissolution of Uranium in Nitric Acid

Model Experiment - Single Cell System

Potential Difference vs. Current Density (As function of distance between electrodes)

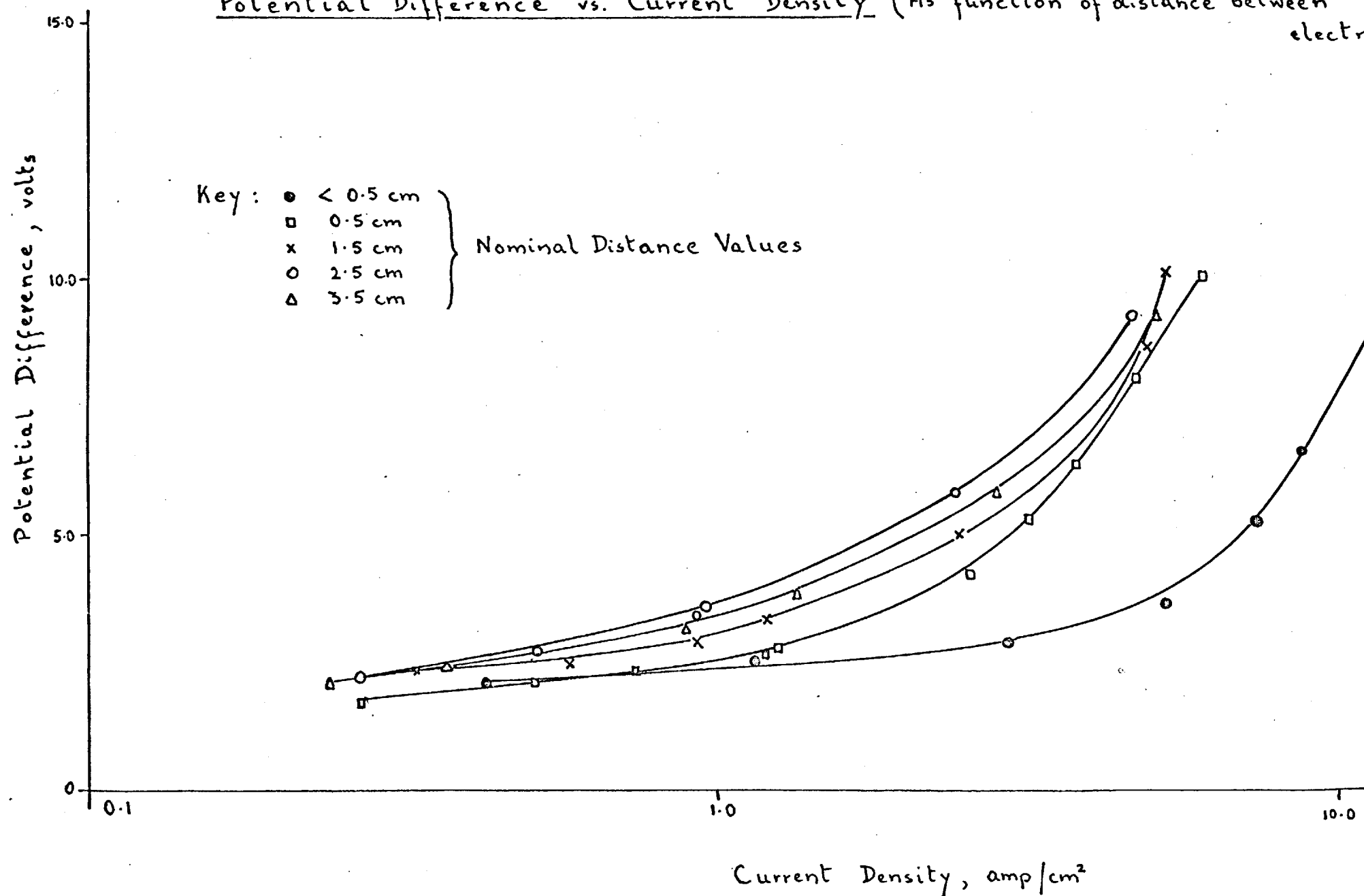


Fig. 7.4. Anodic Dissolution of Uranium in Nitric Acid

Model Experiment - Multi-Cell System

Potential Difference vs. Current Density

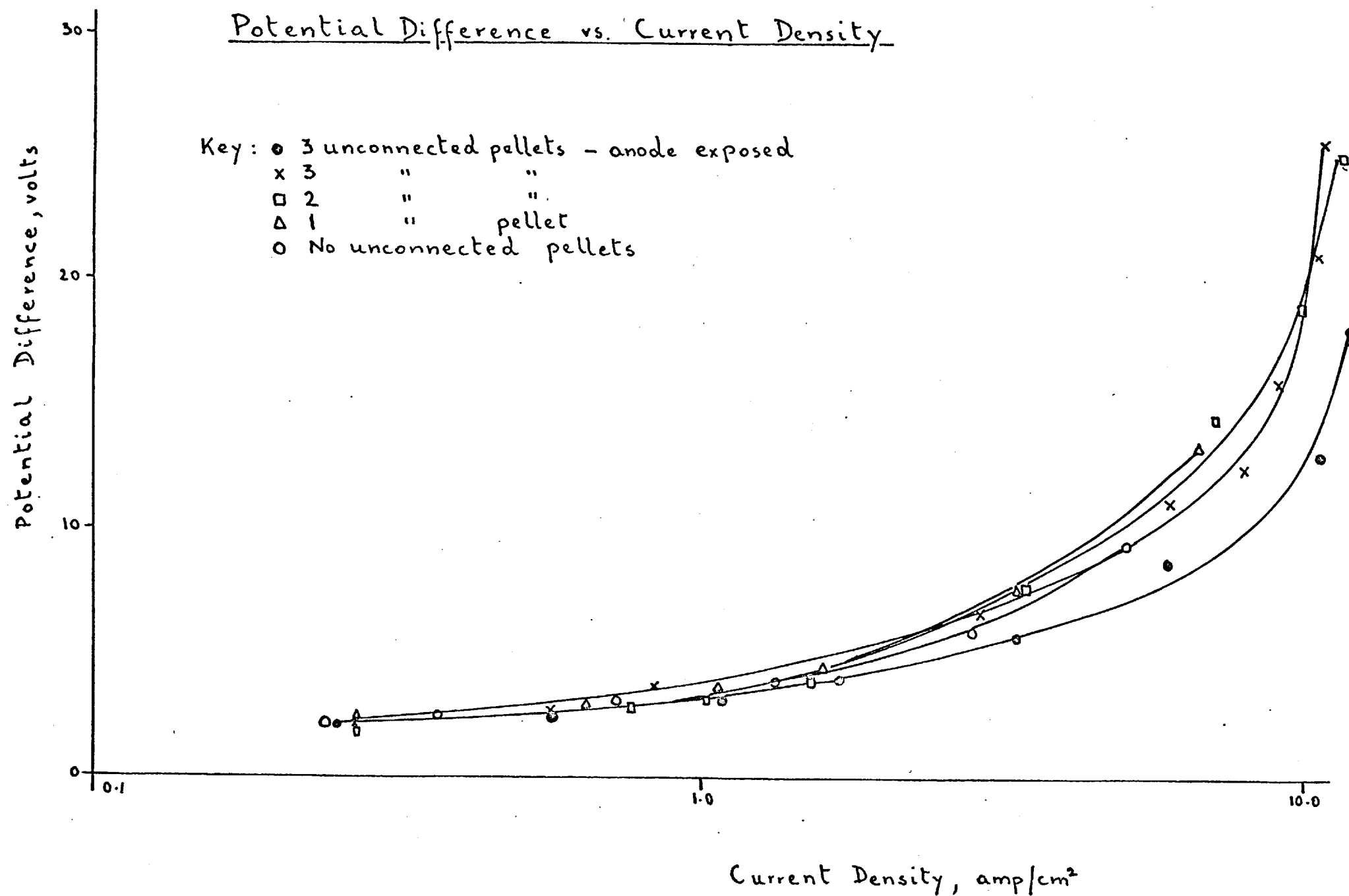


Fig. 7.5. Anodic Dissolution of Uranium in Nitric Acid

Model Experiment - Single Cell System

Dissolution Rate vs. Current Density

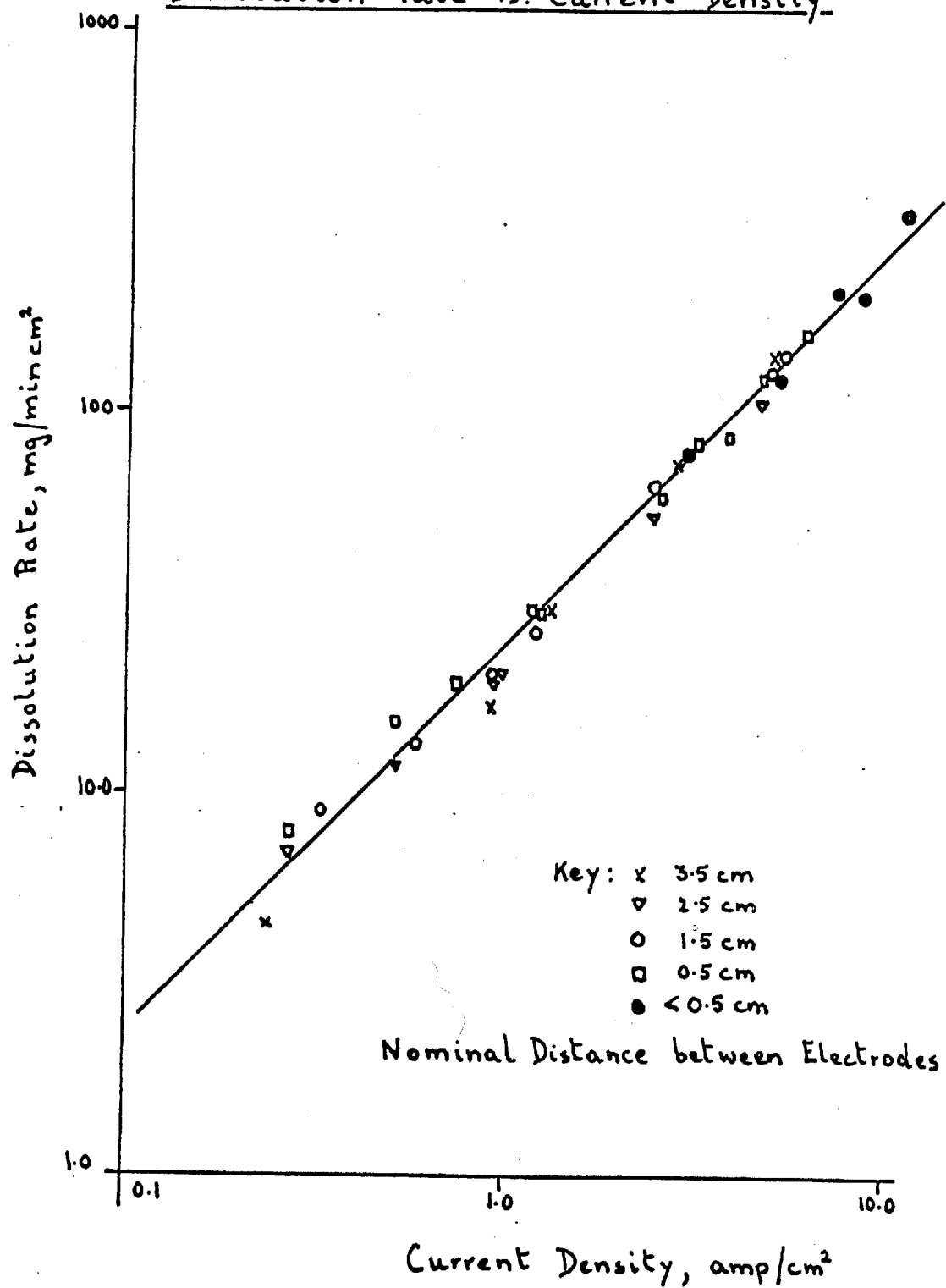
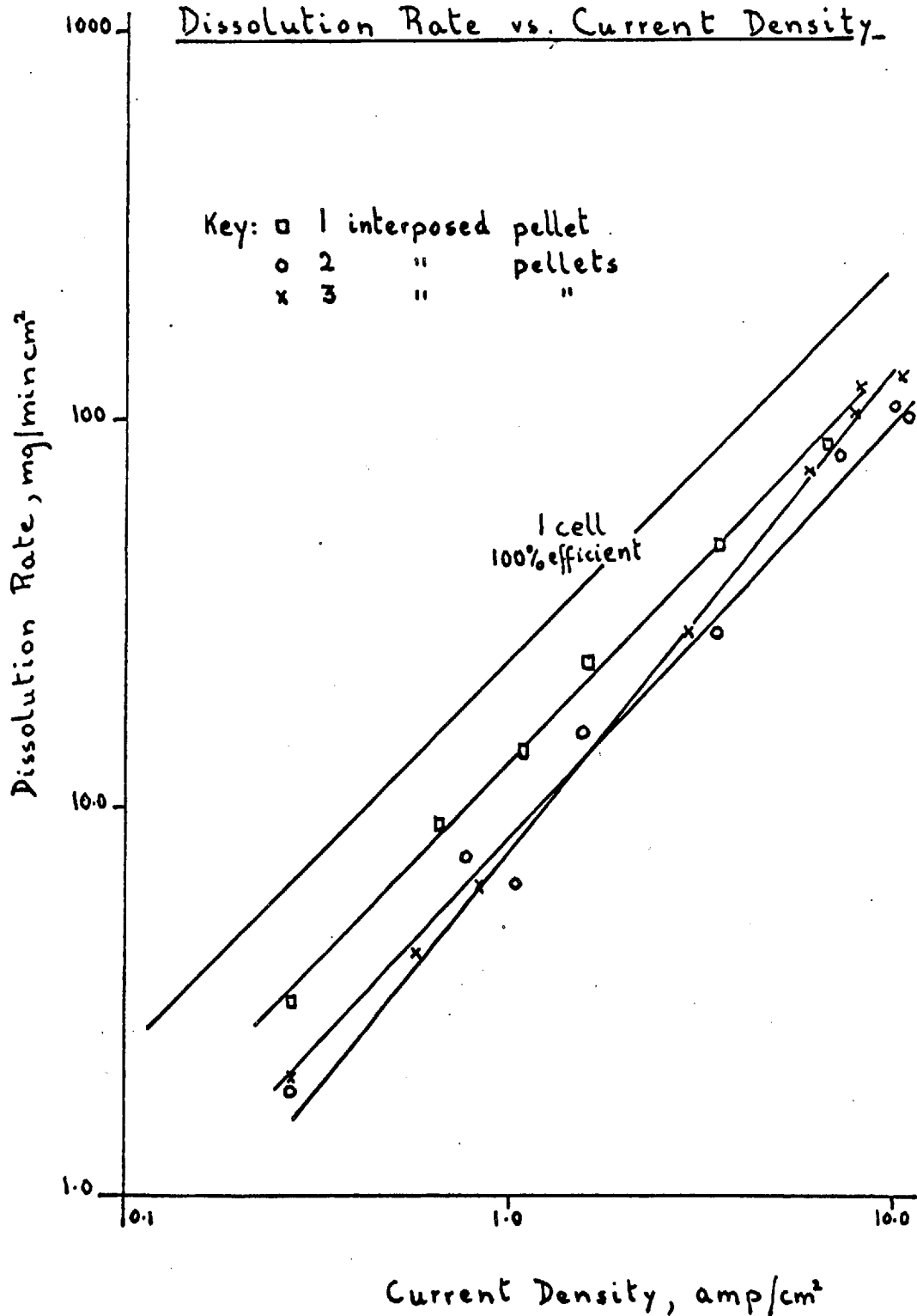


Fig. 7.6. Anodic Dissolution of Uranium in Nitric Acid

Model Experiment - Multi-Cell System

Dissolution Rate vs. Current Density



Cross-sectional areas only were considered for the anodic surfaces, as reaction on the circumference of the pellets occurred from a rather ill-defined fraction of the pellet surface. In the case where the protruding anode was used, however, (Runs SE 56-62) the circumferential area of the electrode (anode) was also taken into consideration when the total anodic surface area was calculated. (The diameter of the pellet was taken as $\frac{3}{8}$ in. = 1 cm. for the purposes of calculation).

Analytical errors were held responsible for the rather large discrepancies from the theoretical observed in the case of Runs SE 1-3. The electrolyte was not stirred during Run SE 23 and the run was repeated with stirring (Run SE 23R). No significant difference in the results obtained was observed.

7.3.1. Comparison of Current Values obtained from Copper Coulometer and Ampere-hour Meter Readings.

High current densities on the copper coulometer led to the formation of a coarse, granular deposit on the cathode which flaked off readily during handling (Section 5.4.2. and Appendix D) thus resulting in erroneous current estimations.

A value of 10 mA/cm^2 is recommended by Findlay⁽⁷⁸⁾ as being a suitable current density for the cathode of a copper coulometer. This gives a current of about 1 amp assuming a conveniently sized cathode of about 100 cm^2 is used. An increase in the capacity of

the coulometer may be obtained either by increasing the area of the cathode or connecting a number of coulometers in parallel. Either arrangement results in increased handling difficulties.

The d.c. ampere-hour meter used previously (Section 6.2.1.) was therefore connected in series with a copper coulometer during a number of runs (SE 38-43) in order to compare the current values obtained on both instruments, particularly in the lower current range. A table showing the results obtained is given (Table 7.4.).

Table 7.4. Model Experiment.

Comparison of Current Values.

Run No.	Coulombs		Amp		Diff. % on (b).
	(a)	(b)	(a)	(b)	
SE 38	593	616	0.202	0.210	-3.7
39	1074	1102	0.50	0.51	-2.5
40	1346	1401	0.80	0.83	-3.6
41	1858	1934	1.19	1.24	-3.9
42	3255	3428	2.58	2.72	-5.0
43	4041	4407	4.81	5.25	-8.3

Notes: (a) Obtained with copper coulometer.

(b) Obtained with ampere-hour meter.

These results indicate the increasing inaccuracy of the copper coulometer with rise in current at a constant copper cathode area. As the values of current obtained on both instruments in the lower current range compare fairly closely with each other, it was decided to use the ampere-hour meter only in all the later experiments.

7.3.2. Comparison of nominal and actual distance values.

Observed electrode separation distances corresponding to nominal distances quoted in Table 7.1. are given in Table 7.5. Distances measured between pellets and electrodes during the course of multi-cell experiments are given in Table 7.6., which is meant to be interpreted in conjunction with Fig. 7.7. It must be noted that all figures given (Tables 7.5. and 7.6.) refer to initial separation distance values as measured in air. These distances increased by up to 3 mm. during the course of the runs due to electrolytic dissolution of the anodic sections.

Table 7.5.Model ExperimentSingle Cell System - Distances.

Separation Distance of Electrodes (in air), cm.	
Nominal	Observed
3.5	3.840
2.5	2.540
1.5	1.704
0.5	0.576
0 - <0.5	0 - 0.204

Table 7.6.Model ExperimentMulti-Cell System - Distances.

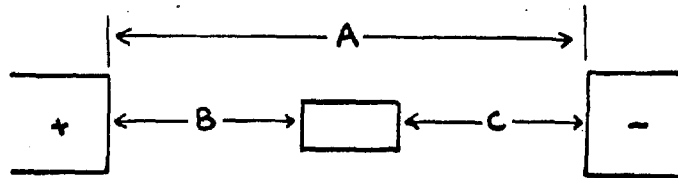
No. of unconnected pellets.	Distances, cm. (in air) ⁽¹⁾					
	A	B	C	D	E	F
1	3.926	1.410	1.420	-	-	-
2	3.864	0.510	0.614	0.544	-	-
3	3.796	0.120	0.114	0.106	0.084	-
3 (Anode exp.)	3.880	0.080	0.080	0.092	0.082	0.788

Notes: (1) Letters (A, B, C etc.) refer to distances as shown in Fig.7.7.

Fig. 7.7. Model Experiment

Multi-cell System - Distances (Table 7.6)

(a) 1 Unconnected Pellet



(b) 2 Unconnected Pellets

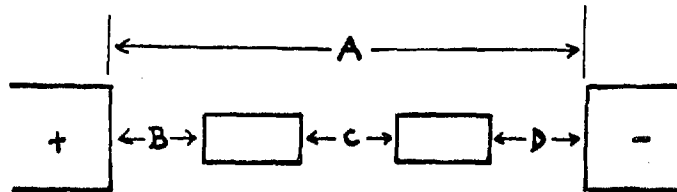
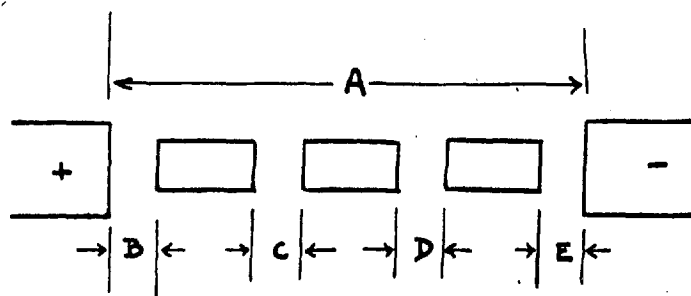
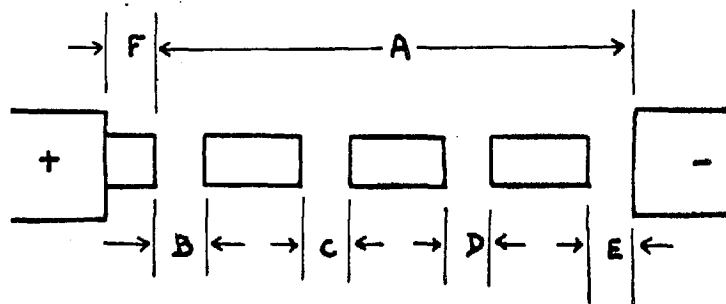


Fig. 7.7. Model Experiment (contnd.)

(c) 3 Unconnected Pellets.



(d) 3 Unconnected Pellets (Anode Protruding)



7.3.3. Electrolyte Acidity Determinations.

Results of acidity measurements (Table 7.7.) show clearly that part of the electrolyte evaporated during the runs thus raising the acidity and obscuring the quantity of nitric acid consumed by uranium dissolution. By assuming that 2 moles HNO_3 were consumed per mole uranium dissolved, however, the volume lost by evaporation can be estimated and compared with the evaporation loss found by direct volume measurement of the electrolyte remaining at the end of a set of runs.

Table 7.7. Model Experiment

Acidity Determinations.

Sample No.	Acidity as HNO_3 .
SE 13(a) ⁽¹⁾	3.61N
SE 19	3.62N
SE 20(a) ⁽¹⁾	3.41N
SE 28	3.46N

Note: (1) These samples were taken prior to Run SE 13 and SE 20 respectively.

Thus in the case of runs SE 20 - SE 28 we have :-

Weight of U dissolved = 10.6 g

$$\equiv 5.61 \text{ g HNO}_3$$

This represents a drop in normality of the acid

$$= \frac{5.61}{63}$$

$$= 0.09$$

∴ Normality, assuming no evaporation loss, of

$$\text{sample SE 28} = 3.41 - 0.09$$

$$= 3.32$$

Also final volume, assuming no evaporation loss

$$= 1.935 \text{ l.}$$

But actual normality found = 3.46 N.

$$\therefore \text{Final volume of electrolyte} = \frac{1.935 \times 3.32}{3.46} \text{ l.}$$

$$= 1.855 \text{ l.}$$

This represents a loss by evaporation of

$$1.935 - 1.855 \text{ l.}$$

$$= 80 \text{ ml.}$$

In direct volume measurements a loss of about 100 ml. was found. The assumption can thus be made that about 2 moles HNO_3 were consumed per mole uranium dissolved. Similarly, for Runs SE 13 - 19, an evaporation loss of about 50 ml. was calculated but no direct volume measurements were available for comparison.

7.3.4. Effect of Electrode Separation Distance.

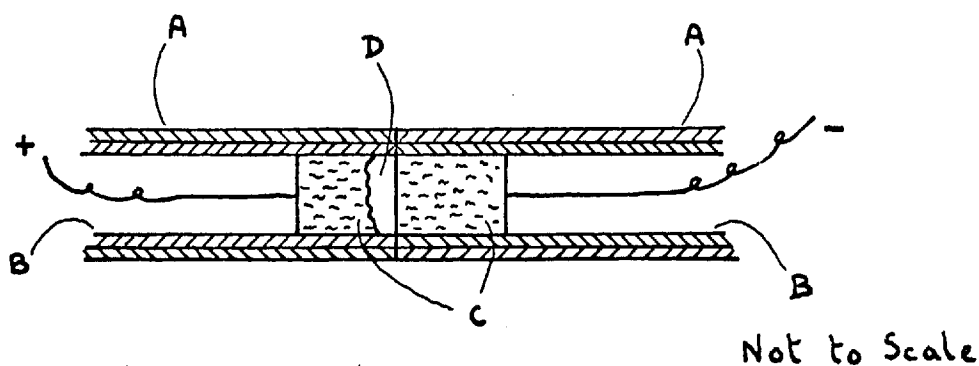
Electrode separation distance had relatively little effect on the voltage-current characteristic until the electrodes were brought close together and at distances ≤ 0.5 cm. (i.e. distances which were initially = 0 cm. and gradually increased to 0.2 - 0.3 cm. as dissolution of the anode proceeded) a marked increase in the limiting current density was observed (Fig.7.3.). Such an increase would be expected if, as in the case of stainless steel⁽²⁵⁾, the limiting current density were due to concentration polarisation at high current densities and applied potentials.

Under these conditions the rate-determining step is the transport of the dissolved uranium away from the electrode surface. Thus, when the electrodes were brought close together, the high rate of gas evolution occurring at the cathode provided an effective stirring action which resulted in an increase in the limiting current density as the dissolved uranium was swept away.

A modified arrangement was used, however, to obtain the readings at ≤ 0.5 cm. distance as cathodic gas formation during electrolysis resulted in violent current and voltage fluctuations. These were caused by pockets of gas being trapped between the anode and the cathode when flush mounted electrodes were brought close together (Fig. 7.8.). Erratic readings (Runs SE 29-32) were thus obtained and the runs were repeated using an anode mounted proud of the p.v.c. sheath (Runs SE 33-37) which allowed the gas to escape more freely into the electrolyte, thus reducing interference.

Fig. 7.8. Model Experiment

Gas Pocket Formation with Two Flush -
Mounted Electrodes Close Together.



A stainless Steel Holder

B PVC Sheath

C Uranium Electrodes

D Gas Pocket

Electrode separation distance appeared to have no effect on the efficiency of uranium dissolution, the majority of values observed falling within 10% of the theoretical amount ($39.7\text{g U}^{\text{vi}}/\text{F}$, the equivalent weight of hexavalent uranium). The figures obtained are compared with the theoretical value in Fig. 7.9. A curve obtained with the multi-cell system (3 unconnected pellets) is also included for comparison.

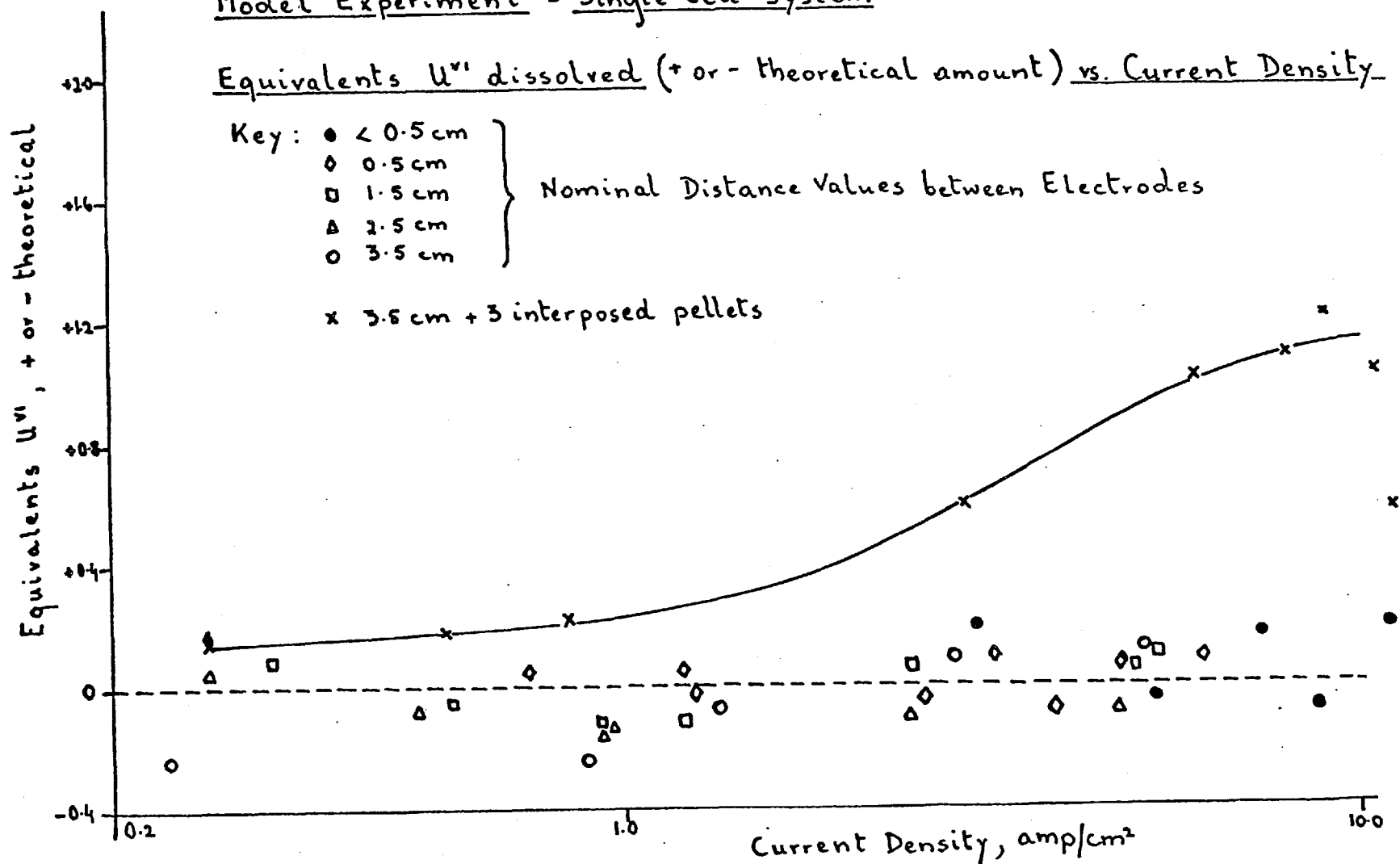
7.3.5. Multi-cell System.

Variation in the number of unconnected pellets placed between the electrodes appeared to have little influence on the voltage - current behaviour of the system (Fig.7.4.) and the curves obtained followed the graph observed when electrodes were separated by the equivalent distance, with no pellets interposed. In the case where 3 unconnected pellets were used, the separation distance between them, initially about 0.1 cm., increased to 0.2 - 0.3 cm. as the pellets dissolved. Figures giving exact sizes of gaps measured between the pellets were given earlier (Section 7.3.2.).

Fig. 7.9. Anodic Dissolution of Uranium in Nitric Acid

Model Experiment - Single Cell System

Equivalents U^{VI} dissolved (+ or - theoretical amount) vs. Current Density



The efficiency of the multi-cell behaviour of the system was influenced by two important factors:

(1) The number of pellets placed between the electrodes, and (2) the ease with which the current could by-pass the interposed pellets.

Thus, when only one pellet was interposed, no reaction appeared to take place from it until a voltage of about 13V was applied when slight signs of electrolytic activity became visible. With two interposed pellets, reaction at both became apparent at 7.5 - 8.0V, whilst when 3 pellets were inserted evidence of electrolytic attack on the two outside ones was observed at about 2.5V with the middle pellet joining in the reaction when the voltage was raised to about 10V. In all cases the distance between the connected electrodes remained the same.

Evidence of the extent to which the various arrangements of pellets took part in the overall reaction is provided by figures given in Table 7.8. Uranium dissolved in approximately equal amounts off each of the pellets in the two pellet system. When 3 pellets were interposed, 92% of the uranium lost by the unconnected pellets was contributed by the two outside ones. Efficiency of dissolution versus current density is plotted in Fig. 7.10.

The multi-cell behaviour is illustrated clearly in the case of the 3 interposed pellets which together with the uranium electrodes (connected pellets) formed a 4 cell system.

Table 7.8. Model Experiment - Multi-cell System.Dissolution of Interposed Pellets.

Run Nos.	No. of interposed pellets.	(a)	(b)
SE 38-43	1	5.78	0.33
SE 44-51	2	11.78	11.2
SE 52-55	3	17.65	44.2
SE 56-62 ^(c)	3	14.21	29.6

Notes: (a) Total weight of uranium dissolved, g.

(b) Weight dissolved off interposed pellets as % of (a).

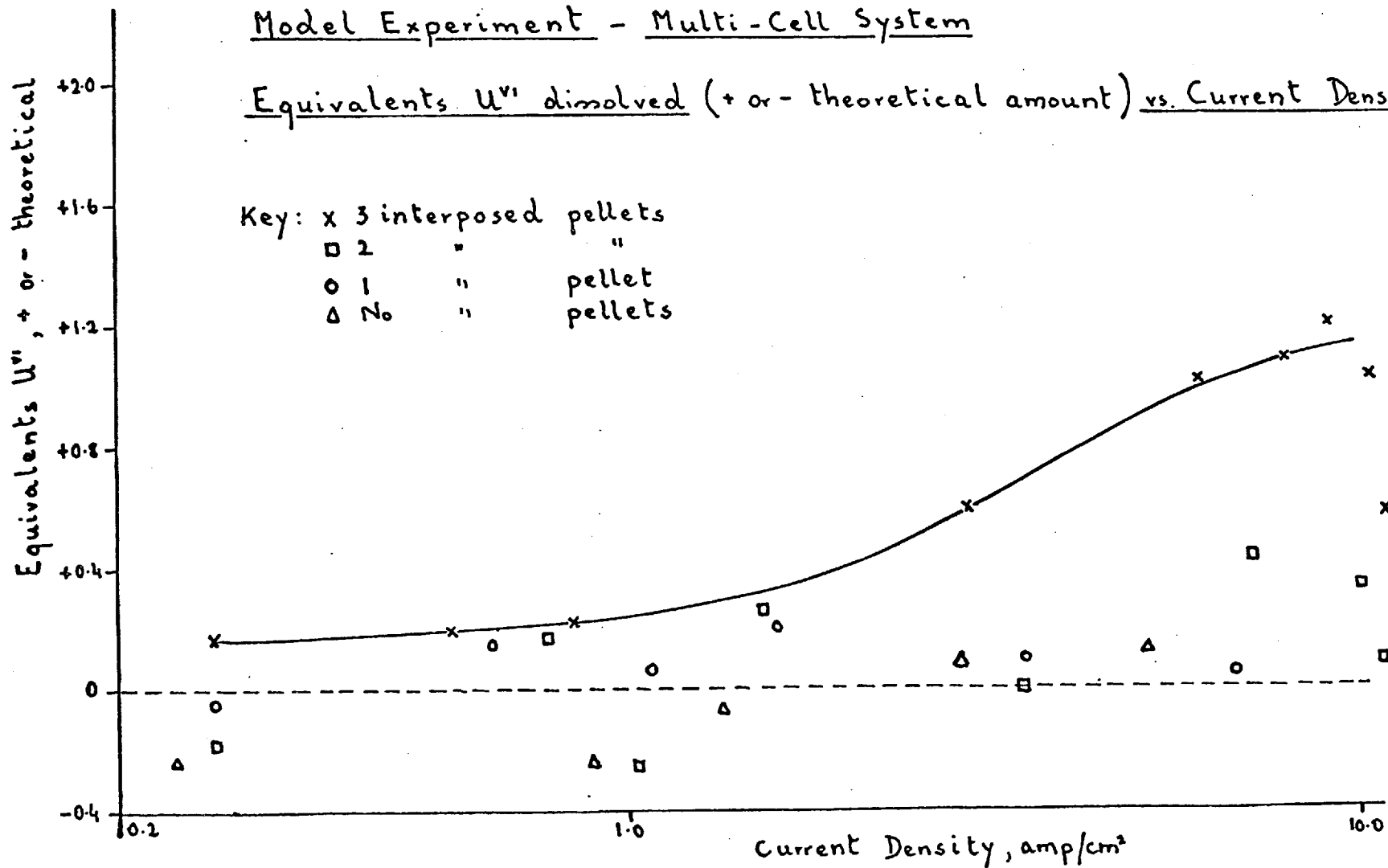
(c) Anode exposed.

Were all the current to flow through the pellets in series such a system would have resulted in 4 electrochemical equivalents of uranium dissolving per faraday. As, however a fraction of the current by-passed the interposed pellets, a dissolution efficiency of only 2 equivalents per faraday was observed, i.e. 1 equivalent in excess of the theoretical amount for one cell. Assuming that the uranium electrodes operated with 100% efficiency and would have contributed 1 equivalent/faraday, the amount dissolved off the 3 unconnected, interposed pellets which effectively formed 3 cells was therefore also 1 equivalent/faraday. An average current efficiency

Fig. 7.10. Anodic Dissolution of Uranium in Nitric Acid

Model Experiment - Multi-Cell System

Equivalents U^{VI} dissolved (+ or - theoretical amount) vs. Current Density



per cell of about 50% overall or about 30% for each of the three interposed pellets was thus obtained.

As noted above, however, 92% of the uranium which dissolved off the interposed pellets came from the outside pellets, with the middle one contributing the remaining 8%. The fraction of the current passing through each pellet can be calculated by deduction from the weights lost by the pellets, as follows:-

Average weight lost by each of the 2 outside pellets (by direct weighing, before and after Runs SE 52-55) = 3.6 g.

$$\begin{aligned} \text{This is equivalent to } & \frac{3.6 \times 26.8}{39.7} \text{ amph} \\ & = 2.43 \text{ amph} \end{aligned}$$

assuming 100% current efficiency.

Total amph passed through system during set of experiments

$$\begin{aligned} & = 6.040 \text{ amph} \\ \therefore \% \text{ current passing through outside pellets} & = \frac{2.43}{6.040} \times 100 \\ & \approx 40\% \end{aligned}$$

$$\begin{aligned} \text{Similarly, weight dissolved off middle pellet} & = 0.64 \text{ g} \\ & = \frac{0.64 \times 26.8}{39.7} \text{ amph} \end{aligned}$$

$$\begin{aligned} & = 0.43 \text{ amph} \\ \therefore \% \text{ current passing through middle pellet} & = \frac{0.43}{6.040} \times 100 \\ & \approx 7\%. \end{aligned}$$

A diagrammatic representation of current flow using the figures calculated above is shown (Fig. 7.11.). Analogous calculation in the case of 1 and 2 pellet systems show that 1% and 8.7% of the current passed through the pellets, respectively.

7.3.5. (a). Influence of Number of Interposed Pellets on Current Utilisation.

Bomar⁽²⁹⁾ has shown that in the case of a series electrolytic dissolver

$$\frac{100}{U} = 1 + \left(\frac{R_p A}{K} \right) \frac{1}{L} \quad \dots (7.1)$$

where U = current utilisation (efficiency)
per pellet, %.

R_p = polarisation resistance

A = the cross-section area of solution

K = the specific resistance

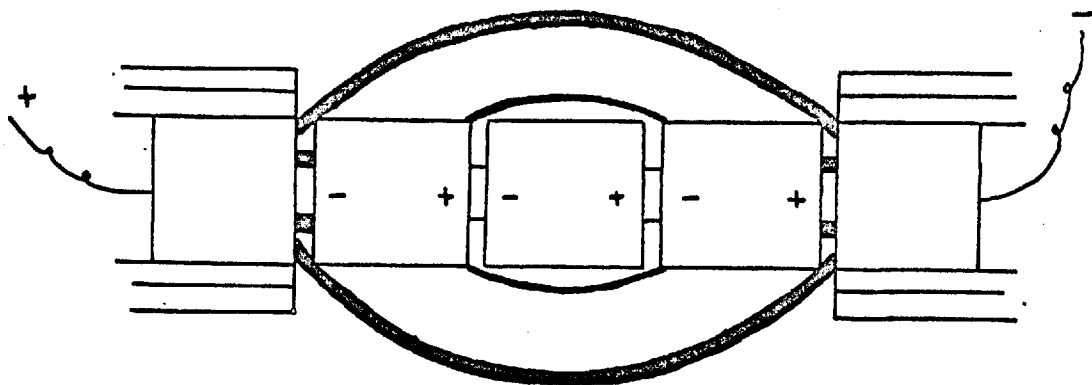
L = length of the dissolving pellet in the
direction of current flow.

A straight line was thus obtained when $\frac{100}{U}$ was plotted vs. $\frac{1}{L}$.

Fig. 7.11. Anodic Dissolution of Uranium in Nitric Acid

Model Experiment - Multi-Cell System

Diagrammatic Representation of Current
Flow (3 interposed pellets)



Scale: Approx. 2 x Full Size

Note: Thickness of Current lines drawn
approximately proportional to
% of Total Current flowing.

An attempt was therefore made to correlate values of current utilisation (U) and the total length of pellets (L'), in the direction of current flow, interposed between the electrodes. Although strict comparison between the different values of U can only be obtained when dissolution at the same current density is considered, the figures for U calculated (Table 7.9.) refer to average current utilisation values taken over the range when all the interposed pellets were involved in a given multi-cell reaction. Average current density figures in this range show only a relatively small increase (from 6.7 amp/cm.² for the 1 pellet system to 9.6 amp/cm.² for 3 pellets) and it was considered that average values of current utilisation would provide a more accurate basis of comparison than individual values obtained during the course of a given run.

Based on the form of the equation given above (Eqn. 7.1), values of $\frac{100}{U}$ were plotted on logarithmic co-ordinates against $\frac{1}{L'}$ when a straight line was obtained. (Fig.7.12.(a)). A power relationship of the form

$$\frac{100}{U} = a \left(\frac{1}{L'} \right)^n \quad \dots (7.2)$$

was thus indicated, where a and n are constants. It was considered, however, to be more representative of the physical meaning of the variables if a plot of the form

$$\frac{100}{U} = 1 + a' \left(\frac{1}{L'} \right)^{n'} \quad \dots (7.3)$$

was obtained, where a' , n' are constants (c.f. Equation 7.1)

Table 7.9. Model Experiment - Multi-Cell System.
Current Utilisation in Terms of Number
of Interposed Pellets.

Run No.	No. of inter- posed pellets.	(a) g.	(b) g.	Total Current Utilisa- tion, %.	Average Current Utilisa- tion per Pellet, U, %.	Length of pellets in current path, L', cm.
SE 43	1	1.814	0.0189	1.0	1.0	1.12
SE 48-51	2	7.590	1.3211	17.4	8.7	2.24
SE 52-55	3	8.949	7.8101	87.3	29.1	3.36

Notes: (a) Uranium dissolved, equivalent to current passed,
 assuming 100% dissolution efficiency (1 cell).

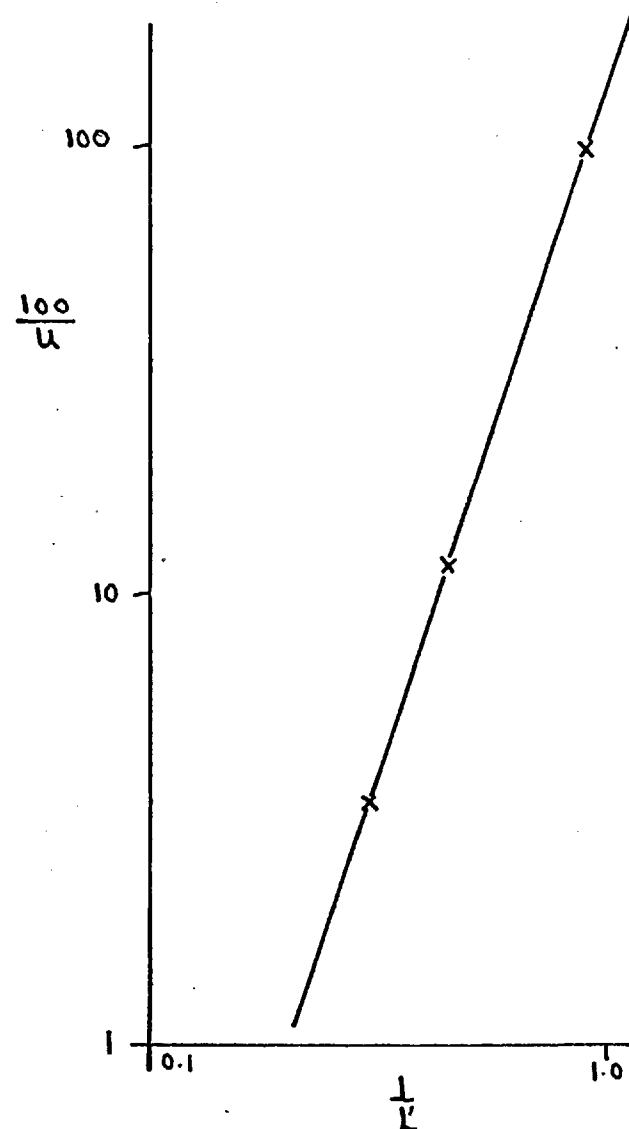
(b) Uranium lost by interposed pellets obtained by
 difference in weight of pellets before and after
 a set of runs.

Fig. 7.12. Anodic Dissolution of Uranium in Nitric Acid

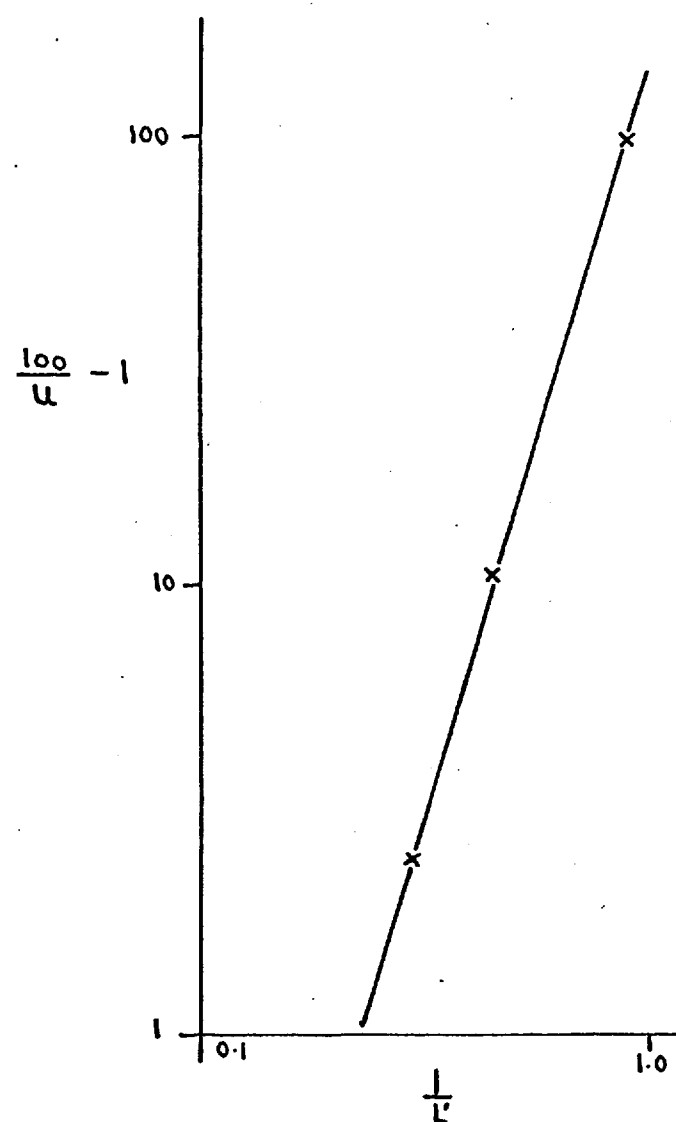
Model Experiment - MultiCell System

Current Utilization (U) vs. Total Length of Pellets in Current Path (L)

(a)



(b)



Equation 7.3. shows that $\frac{100}{U} \rightarrow 1$ as $\frac{1}{L'} \rightarrow 0$ i.e. a 100% efficient cell is indicated if the space between the electrodes (in the model experiment) is occupied almost wholly by a length of metal through which all the current would flow preferentially thus resulting in 100% current utilisation. $\frac{100}{U} - 1$ was thus plotted against $\frac{1}{L'}$ on a logarithmic scale and a straight line was again obtained (Fig.7.12.(b)) showing equation 7.3. to be a fair approximation of the relationship between U and L'. Using figures obtained from the graph (Fig.7.12.(b)) equation 7.3. becomes:-

$$\frac{100}{U} = 1 + 140 \left(\frac{1}{L'} \right)^{4.3} \quad \dots (7.4)$$

A possible explanation of the difference in relationship between U and L as observed by Bomar (Eqn. 7.1.) and U and L' as shown by equation 7.3, may be found in the difference in geometry of the two systems. Thus in the case of the model experiment, the diameter of the electrodes was the same as the diameter of the interposed pellets whilst the volume of the electrolyte surrounding the system was such as to provide a possible current path through the electrolyte whose diameter was many times (7-8) that of the pellets. It has been shown experimentally by MacMullin⁽⁷⁹⁾ that a power relationship exists between the effective width of a current path through an electrolyte and its length. Such a relationship holds for the case of parallel plane electrodes immersed in a

sufficiently large volume of electrolyte to allow for a geometrically unrestricted current path to exist between the electrodes. Assuming that the length of the interposed pellets represents an equivalent length of current path in the electrolyte, the area of that current path would be related to its length by the general relationship

$$A = b (L')^m \quad \dots (7.5)$$

where b and m are constants. Substituting for A in Equation 7.1, the general form as represented by Equation 7.3 is obtained, or, more specifically :-

$$\frac{100}{U} = 1 + c \left(\frac{R_p}{K} \right) \left(\frac{1}{L'} \right)^{n'} \quad \dots (7.6)$$

where (from Eqn.7.4)

$$\begin{aligned} c \left(\frac{R_p}{K} \right) &= 140 && \left. \begin{array}{l} \text{) constants} \\ \text{) for a} \\ \text{) given} \end{array} \right\} \\ n' &= 4.3 && \text{) system.} \end{aligned}$$

In the case of the series dissolver investigated by Bomar, the area and dimensions of the electrodes appear to be larger than those of the pellets which enabled the electrodes to "see" each other and thus provided an easier, parallel current path to the pellets, a condition which did not exist in the case of the model experiment. Also, the cross-sectional area of the solution was restricted by the size of the dissolver tube with the result that

the cross-sectional area of the current path remained independent of its length within the range of values investigated by Bomar.

7.3.5. (b) Influence of Electrode Arrangement
on Current Utilisation.

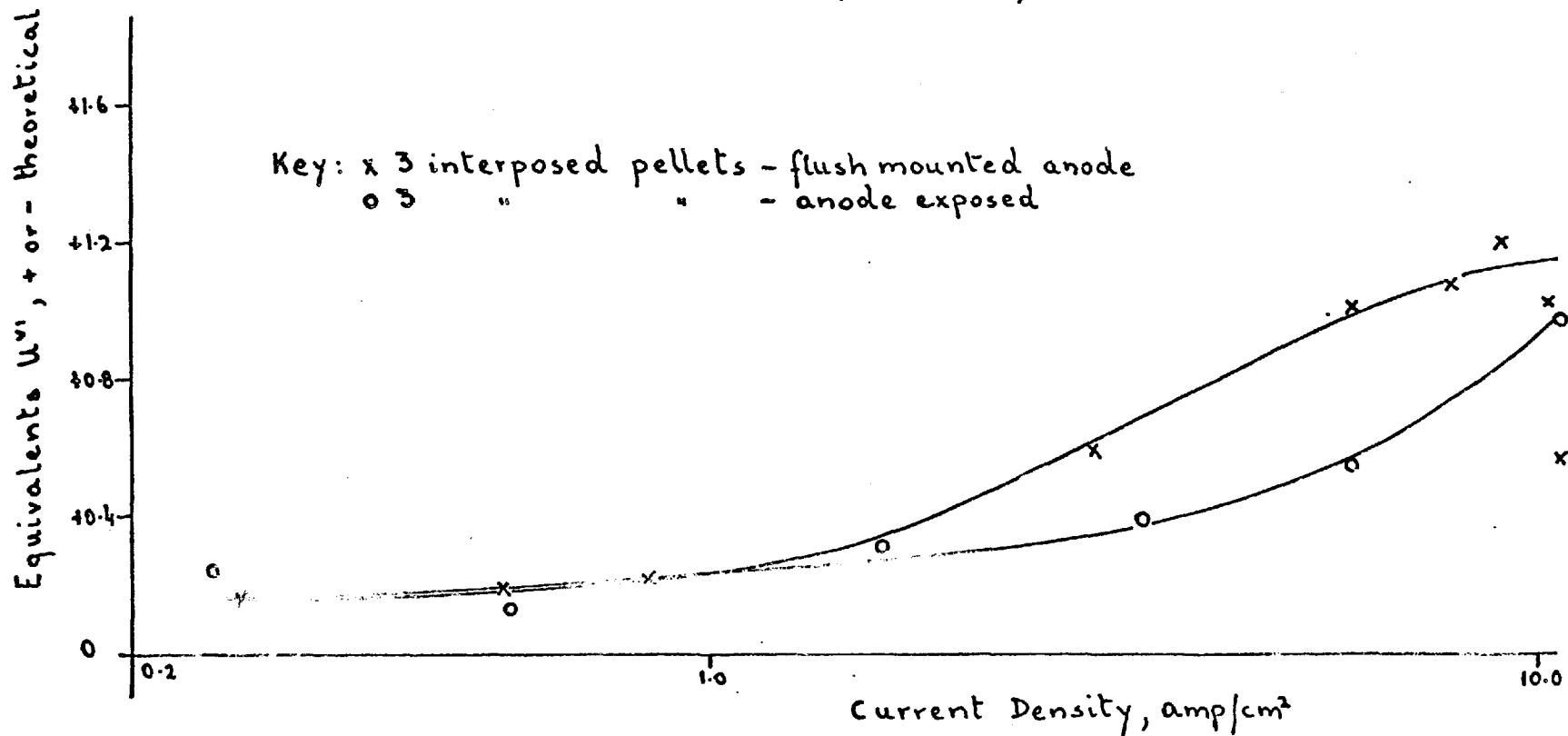
An indication of the influence of geometric arrangement of the electrodes on the current path and hence the degree of dissolution of the unconnected pellets is provided by results observed in the case of runs when the anode was allowed to protrude beyond the p.v.c. sheath (Fig. 7.2.; Runs SE 56-62). This arrangement allowed the current to flow more easily from the anode to the cathode, by-passing the interposed pellets with a consequent drop in their contribution (Table 7.8.) to the total amount of uranium dissolved. A comparison between the current efficiencies obtained with the "protruding anode" assembly and the 3 pellet system described previously is given in Fig. 7.13.

It is considered significant that the contribution (23.7%) made by the pellet nearest the protruding electrode to the amount of uranium dissolved from the interposed pellets, fell off appreciably when compared with the contribution (46%) of the equivalent pellet placed next to a flush mounted anode. This would tend to indicate that the greater portion of the current by-passed the pellet where it could do so easily, i.e. in the case of the anode,

Fig. 7.13. Anodic Dissolution of Uranium in Nitric Acid

Model Experiment - Multi-Cell System

Equivalents U^{VI} dissolved (+ or - theoretical amount) vs. Current Density
(As function of system geometry)



but not in the case of the flush-mounted cathode. Additional evidence for this behaviour was supplied by the voltages which had to be applied across the system before any reaction on a given pellet was observed. The voltage at which a reaction on the pellet nearest the anode was first noticed was almost double that at which the pellet nearest the cathode came into operation. A comparison of the extent to which the various pellets took part in the overall reaction is given in Table 7.10.

Table 7.10. Model Experiment - Multi-cell System.

Anode Protruding.

Position of pellet.	(a) V	(b) %	(c) %
next to anode	5.6	23.7	13.7
middle	8.6	7.9	5.7
next to cathode	3.1	68.4	33.2

Notes: (a) Voltage across system at which reaction first observed.

(b) U lost as % of total U loss off interposed pellets.

(c) Estimated fraction of current through pellet, %.

It must be noted that figures for the fraction of current flowing through each pellet (Table 7.10., Column (c)) are only estimates based on the total current consumed in runs during which a given pellet was observed to be reacting.

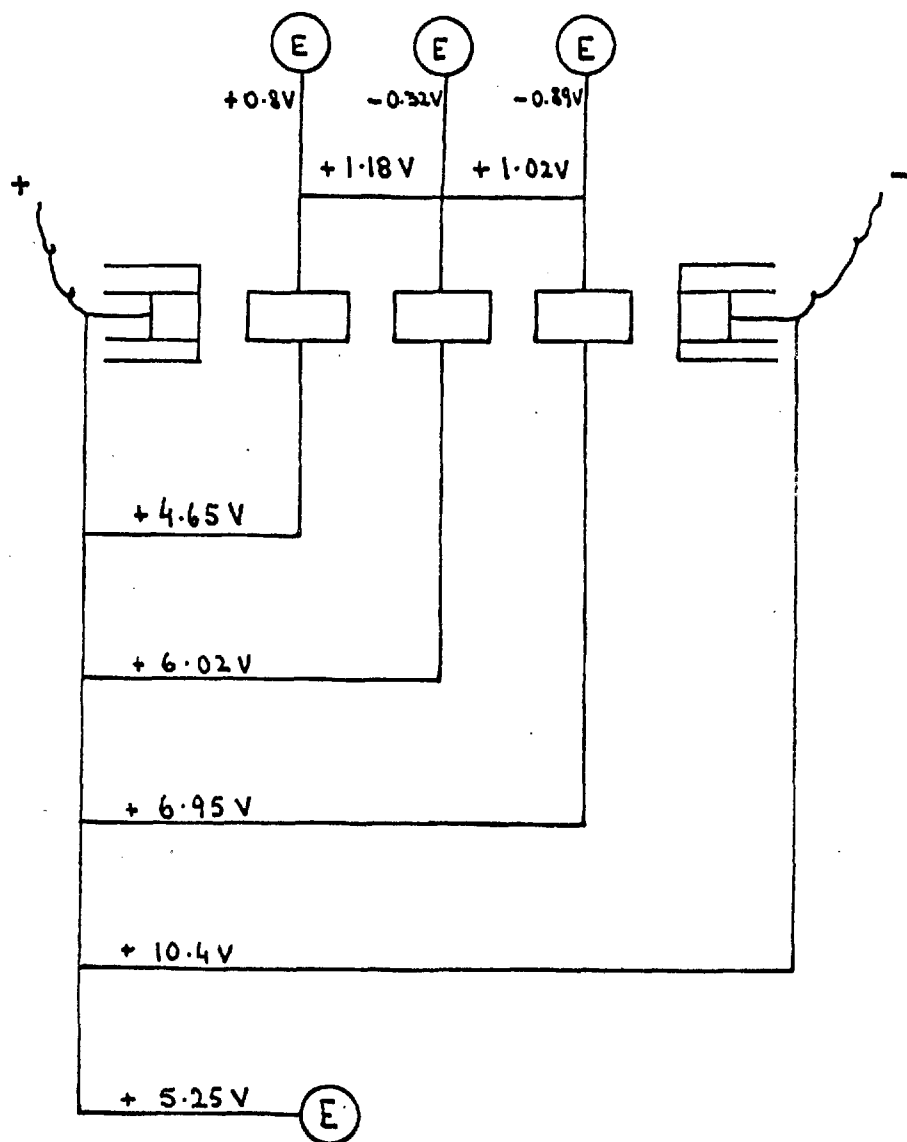
7.3.6. Potential Differences in a Multi-cell System.

Differences in potential between the anode, unconnected pellets and the electrolyte recorded during the course of an experiment carried out at the end of the preliminary runs (i.e. after Run ER 6) are shown in Fig. 7.14. All three interposed pellets were reacting electrolytically, total applied voltage across the system being 10.4 V.

The tentative nature of the experiment and the effect of the unknown factors involved (e.g. the e.m.f. of the stainless steel - electrolyte - uranium contact) precluded any but the most elementary conclusions to be drawn from the values observed. Thus a minimum potential difference of about 1 V was found between the electrolytically reacting pellets supporting the observations of Hartland ⁽¹⁸⁾, who noted that the voltage required for uranium dissolution in nitric acid (uranium anode - stainless steel cathode) was about 0.5 - 1.0 V. The pellet which showed least signs of

Fig. 7.14. Model Experiment

Potential Differences in Multi-Cell System



Note: (E) - Potential Differences measured with respect to the electrolyte

electrolytic activity (middle pellet) also showed the smallest p.d. with respect to the electrolyte. As would be expected (Ohm's Law), the magnitude of the voltage drop was higher between the points where a higher current flow was observed.

7.4. Conclusions.

Two main points were observed :

(1) Current utilisation was unaffected by the distance separating two uranium electrodes;
and (2) current utilisation depended greatly on the ease with which the current could by-pass the interposed pellets in a multi-cell system. Thus current utilisation decreased when one of the electrodes was allowed to protrude beyond its holder allowing the current to flow more easily through the electrolyte rather than through the pellets. With flush-mounted electrodes, current efficiency per pellet increased with increasing number of interposed pellets at constant electrode separation.

Chapter 8.

Discussion and Conclusions.

Chapter 8.

Discussion and Conclusions.

- 8.1. Current and Voltage Characteristics of Dissolver System.
 - 8.1.1. Cell Voltage.
 - 8.1.2. Relationship between Cell Voltage and Voltages observed during Multi-cell and Dissolver Experiments.
 - 8.1.3. Effect of Bed Size and Composition on Cell Formation.
 - 8.1.4. Polarization Resistance.
- 8.2. Dissolution Process.
 - 8.2.1. Current Density - Dissolution Rate Relationship.
 - 8.2.2. Energy Consumption.
- 8.3. Dissolution Stoichiometry.
 - 8.3.1. Uranium and Nitric Acid.
 - 8.3.2. Sludge Formation.
- 8.4. Dissolver Vessel.
 - 8.4.1. Materials of Construction.
 - 8.4.2. Scale-Up.
- 8.5. Comparison of the Tubular Dissolver with the Basket and Series (Liquid Contact) Dissolvers.
- 8.6. Conclusions and Recommendations for Future Work.

8.1. Current and Voltage Characteristics of Dissolver System.

A basic similarity in the current - voltage relationship was observed both in the case of the two dissolver systems (Figs. 5.5. and 6.1.) and the model experiment (Fig.7.4). This would be expected between the stainless steel dissolver system (Fig.5.5) and the model experiment as in both cases current could flow directly from one conducting electrode to the other and thus, under any conditions of current flow, at least one electrolytic cell was in operation. With the tantalum dissolver system metal-to-metal contact had first to be established between the conducting anode sleeve (tantalum) and the uranium bed before any cells could be formed (Section 6.1) . Data plotted in Fig. 6.1, show that this condition was achieved during the course of the runs. The similarity in curves obtained for the two dissolver systems as compared with the model experiment indicates that their electrochemical behaviour was analagous.

8.1.1. Cell Voltage.

The electrochemical behaviour of uranium is similar to that of stainless steel⁽⁵⁵⁾, a metal whose anodic potential - current density relationship in nitric acid has been derived and can be represented schematically by the general curve shown

in Fig. 8.1 (curve 1)⁽²²⁾⁽²⁵⁾. This curve follows the general pattern shown by anode potential - current density relationships for systems exhibiting anodic dissolution and anodic passivation⁽⁸⁰⁾. The rate of reduction of nitric acid (i.e. the variation of potential with current density at the cathode) is represented by Curve 2 (Fig.8.1).

The co-ordinates of the point of intersection of the two curves correspond to the corrosion (i.e. chemical dissolution) rate and corrosion potential which the metal acquires under steady state in a given set of conditions. Thus electrolytic dissolution in a dissolver involves only that part of the anodic curve (Curve 1) which lies above the point of intersection i.e. the transpassive region from a to b.

Curves 1 (region a to b) and 2 represent therefore the contribution made by the anode and cathode electrode potentials towards the overall cathodic and anodic overvoltage components of an electrolytic cell. These overvoltages are set up as a result of polarization which occurs at the metal-solution interface and may be of three kinds⁽²²⁾⁽⁸¹⁾:

Fig. 8.1. General Diagram of the Anodic and Cathodic Potential - Current Density Relationship for Stainless Steel in Nitric Acid

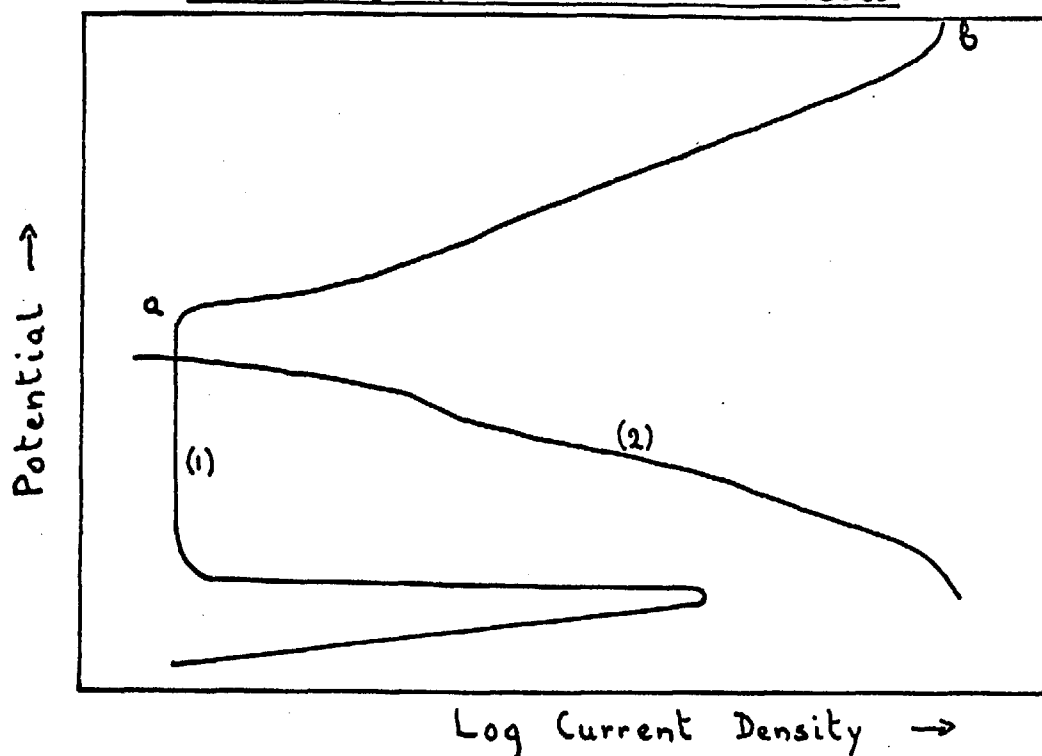
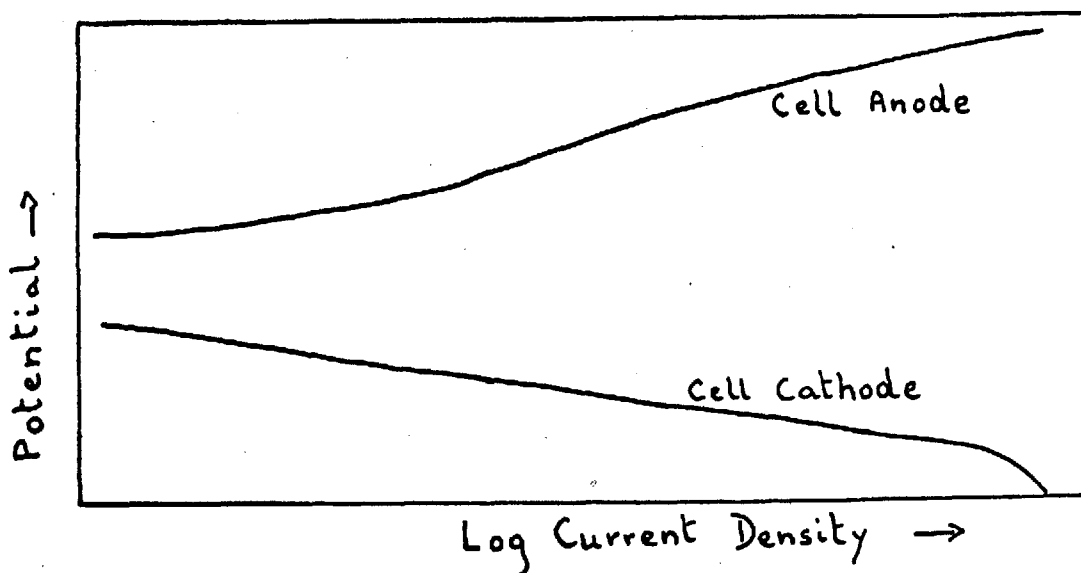


Fig. 8.2. Diagram of Polarization Components as a Function of Current Density



(i) activation overvoltage, due to a slow step in the reaction mechanism (e.g. the dissolution of the metal at the anode). Activation overvoltage varies with current in accordance with the Tafel equation:

$$\eta = a + b \log i \quad \dots (8.1)$$

where η = overvoltage

i = current

a, b = constants characteristic for each electrode process.

(ii) concentration overvoltage at an electrode results when a concentration gradient with respect to the potential - determining species is set up in a thin layer of solution immediately adjoining the metal - solution interface. Thus, in the case of anodic dissolution concentration overvoltage occurs when the thin diffusion layer at the anode contains a higher concentration of the dissolving species than the bulk of the solution. The concentration in the diffusion layer is governed by the solubility of the metal salt formed (e.g. uranyl nitrate) in the solution and as the limit of concentration is approached, the concentration gradient cannot rise any further, resulting in a limiting concentration overvoltage. This in turn leads to a limiting current density at the anode. A similar phenomenon arises at the cathode where a limiting current density is observed as the rate of diffusion of the ions through the thin layer of

solution surrounding the electrode approaches a maximum.

(iii) Ohmic overvoltage, caused by the presence on the surface of the electrode of an obstructive film e.g. oxide, insoluble salt, grease or gas.

In general, the overall cathodic (η_c) and anodic (η_a) overvoltage components are formed from overvoltages contributed by each of the above three reactions. The variation of the overall anode and cathode potentials with current density, expressed with respect to a reference electrode (e.g. the standard hydrogen electrode) may be represented schematically as shown in Fig.8.2. The difference between the anodic and cathodic components gives the voltage due to polarization in an electrolytic cell at a given current density.

The total cell voltage, V , was represented by Slansky⁽²²⁾ as follows:

$$V = (\eta_a - \eta_c) + I (R_e + R_f) \quad \dots (8.2)$$

where R_e is the resistance of the electrolyte, R_f the contact resistance (between a niobium basket and the fuel element) and I is the cell current. In the absence of a contact resistance, we have in the case of the model experiment, with no pellets interposed,

$$V = (\eta_a - \eta_c) + I R_e \quad \dots (8.3)$$

or

$$V = \eta_t + I R_e \quad \dots (8.4)$$

where $\eta_a - \eta_c = \eta_t$

Thus provided the electrolyte resistance, R_e , is known, η_t may be estimated by difference from the overall values of voltage and current which are observed in experiments with a single uranium cathode - uranium anode cell (Section 7.3.4.). The influence exerted on the value of the overall cell voltage by the $I R_e$ term (Eqn.8.4) should therefore be smallest in a cell in which, at a given current, the value of R_e is least, i.e. the electrodes are closest together. Electrolyte resistance of the cell in which the electrodes were less than 0.5 cm. apart was therefore calculated from equation 8.5 as follows:

$$R_e = \frac{Kl}{A} \quad \dots (8.5)$$

where (1) specific resistance of electrolyte, $K = 1.5 \text{ ohms}^{(65)}$

(Section 5.4.2(h)).

Note: This value may be compared with a figure of about 1.8 ohms obtained by Martin⁽¹⁷⁾ for a nitric acid -ferric nitrate electrolyte of similar concentration.

(2) Electrode separation distance, $l = 0.2 \text{ cm.}$ (Table 7.5).

(3) Width of current path, $d = \text{diameter of electrodes} = 1 \text{ cm.}$

(Section 7.3).

∴ Cross-sectional area of current path, $A = \frac{\pi d^2}{4} = 0.786 \text{ cm}^2$

Substituting in equation 8.5, we have

$$R_e = \frac{1.5 \times 0.2}{0.786}$$

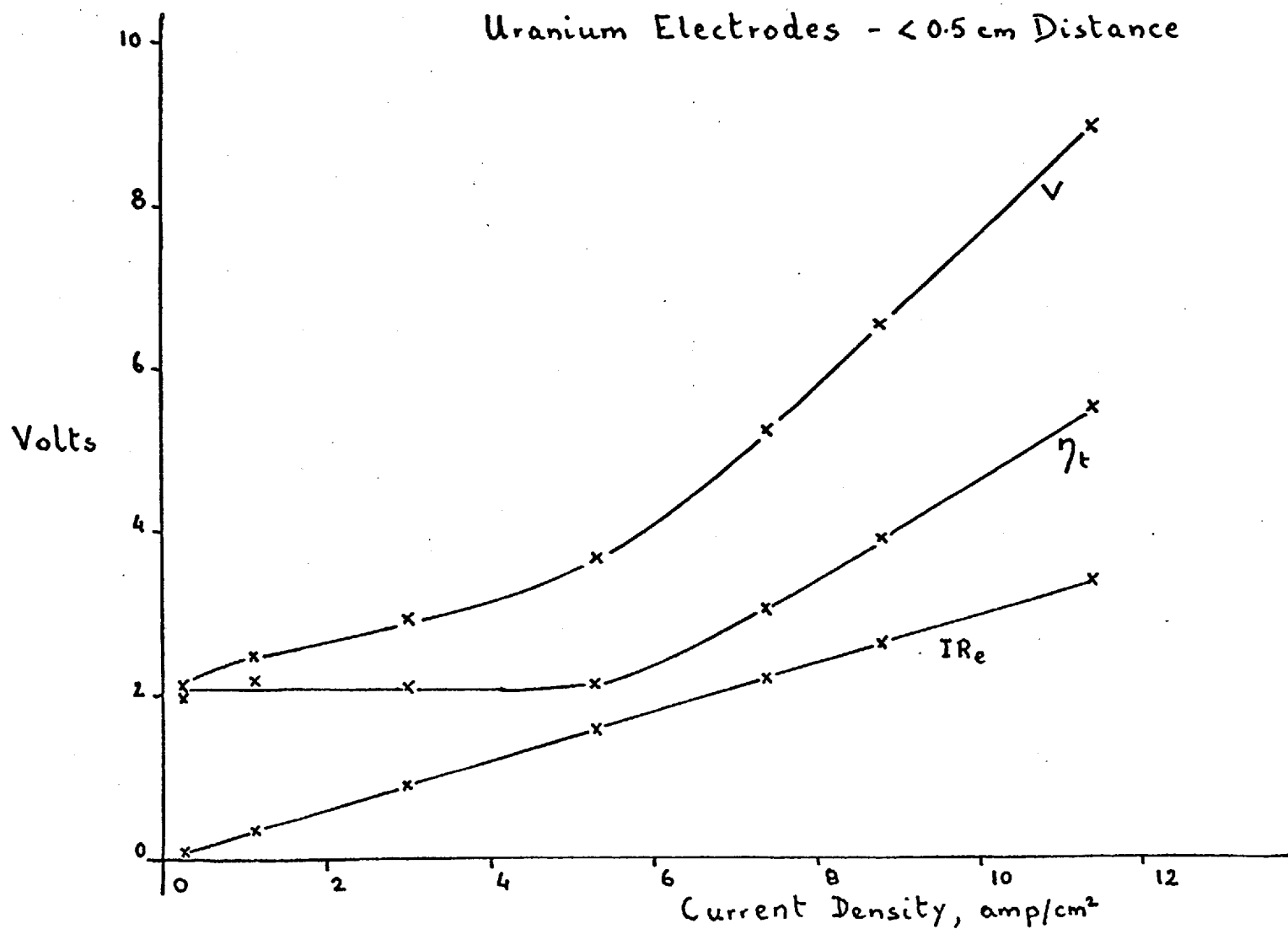
$$= 0.38 \text{ ohms.}$$

I R_e values were then calculated from figures given in Table 7.1, thus allowing η_t to be derived at various current densities.

The variation of V , η_t and I R_e with current density is plotted in Fig.8.3. Results obtained in two of the runs (SE 29 and 30) which were considered to be the least affected of the four (Runs SE 29-32) during which gas interference was observed (Section 7.3.4, Table 7.1) are also included in Fig.8.3.

The η_t (polarization component) curve in Fig.8.3. points to a change in the electrode reaction mechanism of the cell as current densities above about 6 amp/cm² are attained (c.f. Fig. 7.3). Thus the polarization voltage of the cell shows little change with current density and remains steady at about 2V until a current density of about 5-6 amp/cm² is reached indicating that the reaction at cell electrodes is largely activation controlled. At higher current densities, concentration polarization and possibly ohmic polarization due to a layer of gas bubbles on the cathode give rise to an increase in the polarization voltage which reaches a value of about 5.5 V at 10-11 amp/cm².

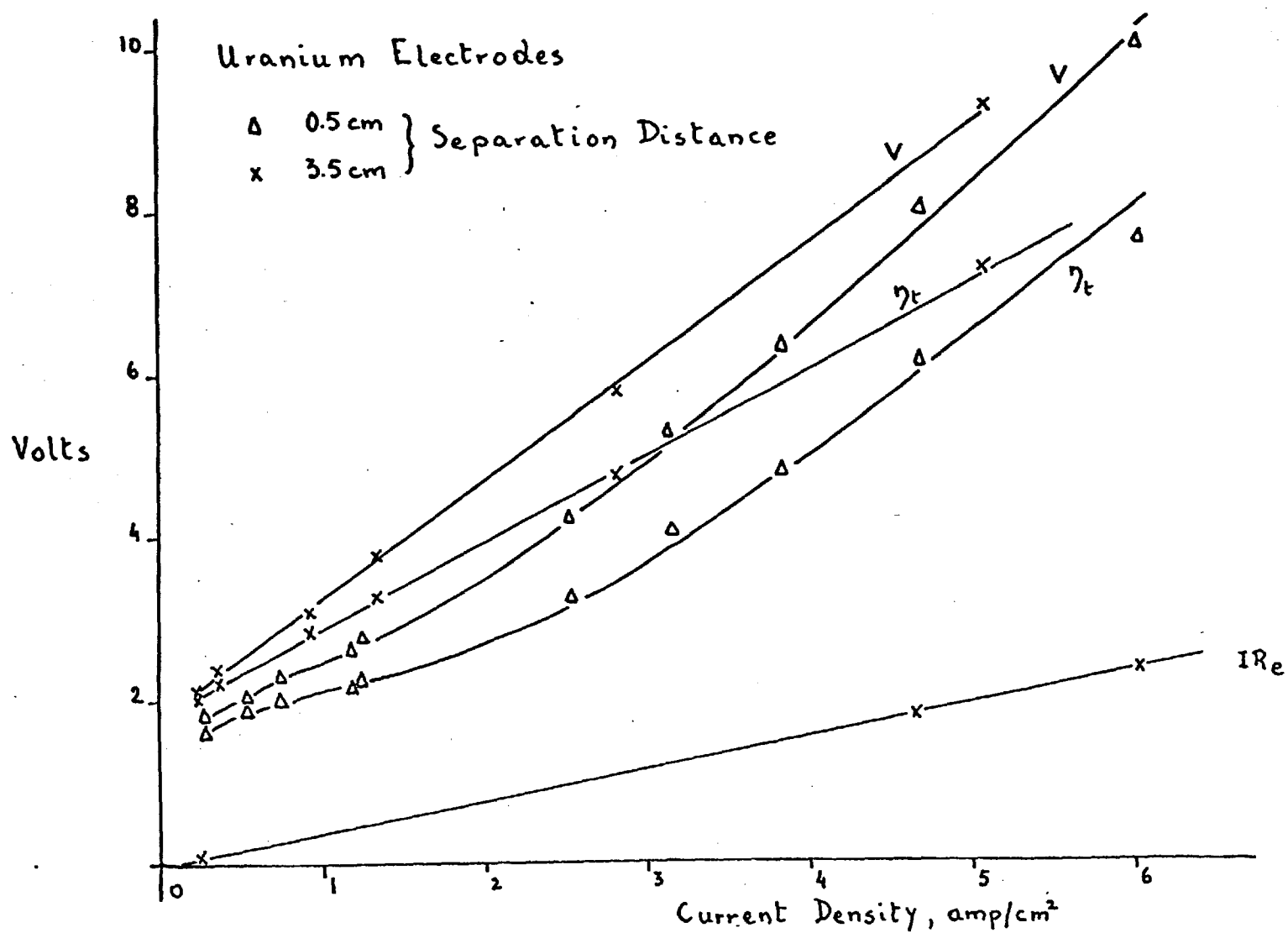
Fig. 8.3. Cell Voltage Components as Function of Current Density



A similar change in the reaction mechanism with rise in current density and overvoltage is observed during the anodic dissolution of stainless steel⁽²⁵⁾ and nichrome⁽²⁷⁾ in nitric acid - nitrate solutions and in the case of zirconium⁽⁴⁹⁾ in hydrochloric acid-methanol solutions. In all these cases the initial dissolution reaction, at low current densities, follows the Tafel equation with concentration polarization occurring at higher current densities and overvoltages, resulting ultimately in a limiting current density.

For comparison, voltage components of cells whose electrodes were separated by distances of 0.5 and 3.5 cm. (nominal) were also plotted and are shown in Fig. 8.4. Curves for the intermediate values viz. 1.5 and 2.5 cm. follow a similar pattern. If plotted, however, the curves for total cell voltage and cell polarization observed with electrodes 2.5 cm. apart, would fall above those obtained when the electrode separation distance was 3.5 cm. (c.f. Fig. 7.3). Unlike the majority of the runs which were carried out at progressively higher current densities, the experiments with electrodes 2.5 cm. apart were carried out first at a high current density which was subsequently lowered. The inversion of the current-voltage values observed could thus be due to an effect analogous to the hysteresis effect shown⁽⁸⁰⁾

Fig. 8.4. Cell Voltage Components as a Function of Current Density.



in the case of anodic dissolution under constant current density conditions.

Electrolyte resistances at various electrode separations were calculated (Eqn.8.5) and are given in Table 8.1. The values of R_e were calculated using an effective cross-sectional area of electrolyte based on the equivalent path concept developed by MacMullin⁽⁷⁹⁾ (Section 7.3.5) and actual values of electrode separation distance (Table 7.5).

Table 8.1. Resistance (R_e) of Electrolyte
between Uranium Electrodes (Model Experiment).

Distance between electrodes, cm.		z.	R_e
nominal	actual	cm.	ohms
3.5	3.8	3.6	0.56
2.5	2.5	3.0	0.53
1.5	1.7	2.6	0.48
0.5	0.57	1.4	0.56

where z = Effective Width of Path (= diameter).

Note: (1) The equivalent path concept was not used when the electrodes were < 0.5 cm. apart; the diameter of the electrolyte path was taken as equal to the diameter of the electrodes.

- (2) As the value of R_e did not vary significantly with electrode separation distance (Table 8.1), the $I R_e$ curve (Fig.8.4) was based on a constant value of $R_e = 0.5$ ohms.

A straight line plot for cell polarization (electrodes 3.5 cm. apart) which does not indicate any change in reaction at higher and lower current densities is shown by the curves in Fig.8.4. This behaviour may be compared with the marked difference in slope between the two sections of the curve observed when the electrodes were < 0.5 cm. apart (Fig.8.3), whilst the slight change in slope shown when the separation distance was 0.5 cm. marks an intermediate stage (Fig.8.4). The early rise in cell polarization and variation in polarization behaviour with distance point to the influence of ohmic overvoltage due to the formation of gas bubbles on the surface of the cathode. Thus ohmic polarization would increase if the flow of gas evolved at the cathode were less likely to be disturbed by the physical proximity of the anode.

8.1.2. Relationship between Cell Voltage and Voltages observed during Multi-cell and Dissolver Experiments.

8.1.2.(a) Multi-cell Experiments.

A test of the validity of the curves plotted in Figs.8.3. and 8.4. would be provided by a comparison of the total values

of voltage across the cells observed experimentally in the case of the multi-cell model (Chapter 7) and the total cell voltage obtained as based on values derived from those curves. Thus in the simplest case, where only one pellet was placed between the electrodes, 3.5 cm. (nominal) apart, we have (neglecting any voltage drop due to electrode connections etc.):

$$\text{Total cell voltage, } V = \eta_t + I R_e \quad \dots (8.4)$$

In the case of run SE 43 (the only run during which a reaction on the interposed pellet was observed)

$$V = 13.2 \text{ volts}$$

and η_t = total cell polarization, due to both cells
which could be formed.

$$= V - I R_e \quad \dots (8.6)$$

Now neglecting the current flowing between the electrodes via the interposed pellet which formed only a small fraction ($\approx 1\%$) of the total current (Section 7.3.5), we have

$$R_e = 0.5 \text{ ohm (Section 8.1.1.)}$$

$$I = 5.25 \text{ amp.}$$

$$\therefore I R_e = 2.6 \text{ volts.}$$

Substituting in equation (8.6),

$$\eta_t = 10.6 \text{ volts}$$

The total cell polarization η_t is, however, composed of (1) cell polarization existing on the electrodes separated by a distance of 3.5 cm. and (2) cell polarization on the anodic and cathodic surfaces of the interposed pellet. For the former, a figure of 8.9 volts at 6.69 amp/cm² is obtained by extrapolation of the appropriate curve in Fig. 8.4. For the interposed pellet, a value of 2.1 volts may be assumed at the low current density at which its cell surfaces operated.

We thus have, $\eta_t = 8.9 + 2.1 = 11.0$ volts.

This value corresponds closely with the observed figure of 10.6 volts given above. The simple relationship between the overall and individual cell voltage shown above becomes more complex when two, three or more pellets are interposed between the electrodes. With increase in number of interposed pellets the current path splits, with part of the current flowing through the pellets in series whilst the remainder bypasses the pellets and flows directly between the electrodes (Section 7.3.5). The proximity of the pellets from each other and from the electrodes affects the value of ohmic and concentration polarization and influences the fraction of the circumferential area of a given interposed pellet which may act as an electrode surface in addition to the cross-sectional area, thus affecting current density (Section 7.3).

By assuming that current flow through the metal and through the solution proceeded along independent, parallel resistance paths⁽²⁹⁾, the observed and computed voltage values could, however, be compared as follows:

Consider the case of 3 interposed pellets, at three different current densities:

- (1) High current density (Run SE.54)
- (2) Medium current density (Run SE.52)
- (3) Low current density (Run ER.6).
- (1) High current density - 10.4 amp/cm^2

We have,

Diam. of interposed pellets = 1.0 cm.

No. of electrolyte gaps between pellets = 4

Diam. of gaps = Diam. of pellets = 1.0 cm.

Assume average width of gap between pellets (which increases due to anodic dissolution) = 0.2 cm.

Specific Resistance, K (Section 8.1.1.) = 1.5 ohms

∴ Resistance of each gap (Eqn.8.5) = 0.37 ohms

Total Voltage applied = 21.0 V

Total Current flowing = 8.15 amp.

Now from previous calculations (Section 7.3.5) we know that ~40% of the current flowed through the "outside" pellets and about 7%

through the middle pellet.

∴ P.D. of two gaps between pellets and electrodes

$$= 0.4 \times 8.15 \times 2 \times 0.37$$

$$= 2.4 \text{ V}$$

P.D. of two gaps between middle pellet and "outside" pellets

$$= 0.07 \times 8.15 \times 2 \times 0.37$$

$$= 0.4 \text{ V}$$

∴ Total P.D. due to electrolyte resistance, R_e , in current path

$$\text{through pellets} = 2.4 + 0.4 = 2.8 \text{ V}$$

∴ From Eqn.(8.6), $\eta_t(\text{obs.}) = 21.0 - 2.8 = 18.2 \text{ V}$.

Two cases arise when total cell polarization, η_t , is obtained from individual cell polarization values (Section 8.1.1) :

Case (i) Assume all cells to behave according to the pattern observed for a cell whose electrodes were $< 0.5 \text{ cm.}$ apart (Fig.8.3).

Case (ii) Assume cells formed by the interposed pellets to behave as in Case (i) above with the cell formed by the electrodes behaving as one whose electrodes were 0.5 cm. apart (Fig.8.4) i.e. assuming that the gaps were bigger where anodic dissolution was greatest.

We thus have, Case (i) :

Cell polarization of electrodes operating at 10.4 amp/cm^2 (Fig.8.3)

$$= 4.9 \text{ V.}$$

Cell polarization of 3 cells, formed by the 3 interposed pellets
 $= 6.3 \text{ V.}$

(Assuming current density on interposed pellets $\approx 40\%$ of total
 current density)

$$\therefore \text{Total cell polarization, } \eta_t = 4.9 + 6.3 = 11.2 \text{ V} \\ \text{(calc.)}$$

Case (ii)

Cell polarization of electrodes at 10.4 amp/cm^2 (Fig. 8.4)

$$= 14 \text{ V (extra-} \\ \text{polated)}$$

$$\therefore \eta_t \text{ (calc.)} = 14 \text{ V} + 6.3 \text{ V}$$

$$\approx 20 \text{ V.}$$

The value of η_t observed (18.2 V) is thus considerably
 closer to the value obtained when the cell formed by the electrodes
 was assumed to operate as one whose electrode surfaces were 0.5 cm.
 apart (Case (ii) above). This suggests that the gaps between the
 electrodes and the interposed pellets nearest to them had indeed
 increased sufficiently for the disturbance caused by the evolution
 of gases at the cathode to have little influence on any tendency
 towards ohmic and concentration polarization.

Similarly, we have :

(2) Medium current density - 7.93 amp/cm^2

$$\eta_t \text{ (obs.)} = 10.2 \text{ V}$$

$$\eta_t \text{ (calc.)} = 9.7 \text{ V (Case (i))}$$

$$= 17 \text{ V (Case (ii)) (extrapolated).}$$

(3) Low current density - 6.00 amp/cm^2

This was the lowest current density at which a reaction on all 3 interposed pellets was observed. Under these conditions it may be assumed that anodic dissolution was sufficiently slow for the gaps between the pellets not to differ too much from the initial value of about 0.1 cm.

Thus we have,

$$\text{Resistance of each gap} = \frac{1}{2} \times 0.37 = 0.19 \text{ ohms}$$

$$\therefore \eta_t (\text{obs.}) = 10.6 \text{ V}$$

Also for η_t (calc.), we have :

$$\text{Case (i)} \quad \eta_t = 8.7 \text{ V}$$

$$\text{Case (ii)} \quad \eta_t = 14.2 \text{ V}$$

Thus in both the medium and lower current density ranges the observed value of η_t approximates more closely to the computed value arrived at on the basis of all the cells operating according to the pattern observed for a cell whose electrodes were $< 0.5 \text{ cm.}$ apart (Case (i)). Such a behaviour would tend to indicate that in these current density ranges the evolution of cathodic gases provided a sufficiently strong stirring action to postpone the onset of ohmic and concentration polarization.

Similar comparisons between the observed and computed η_t values may be made for both the 2 interposed pellets multi-cell system and the 3 interposed pellets multi-cell system where the anode was protruding (Runs SE.56-62).

In the

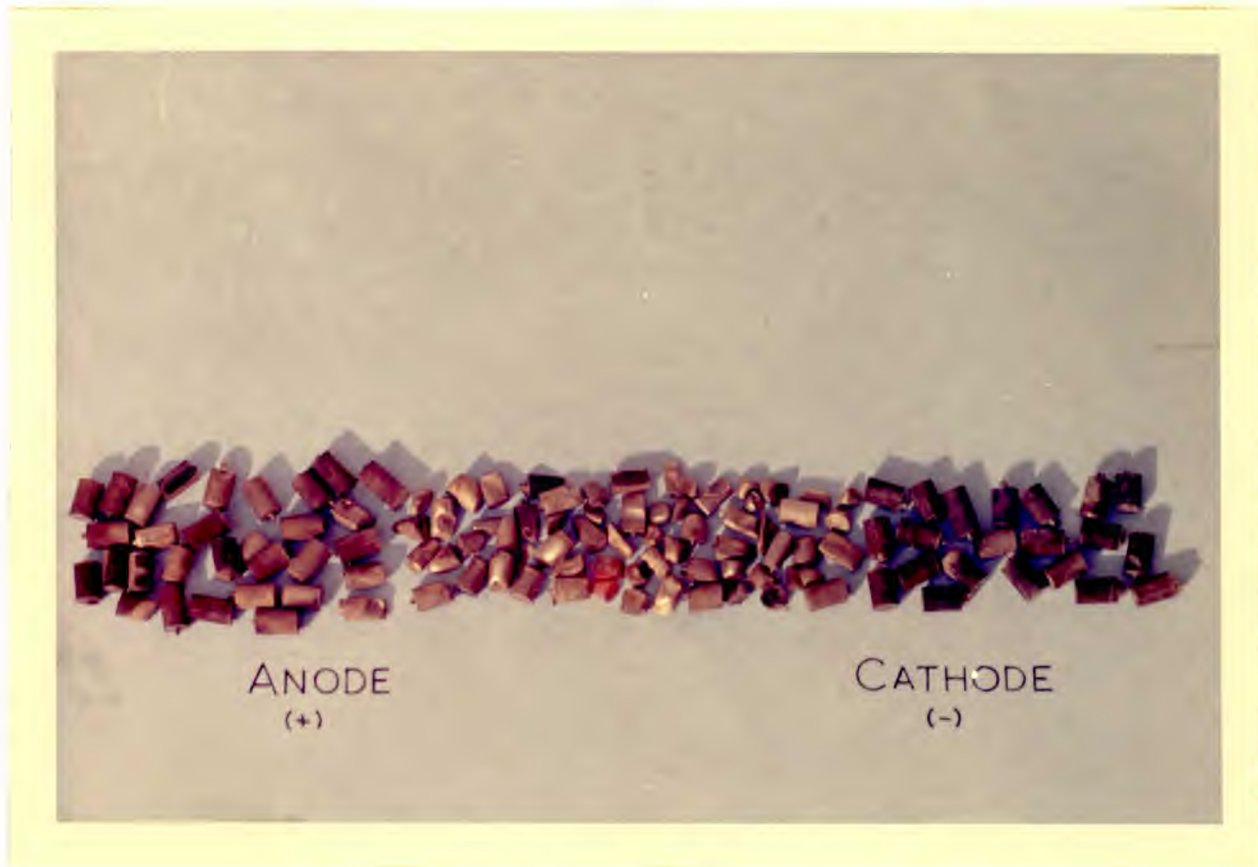
latter case, however, it must be noted that the whole of the surface of the protruding anode must be taken into consideration in calculating the current density of the cell formed by the electrodes. (Current density figures given in Table 7.2 refer to the cross-sectional area only).

8.1.2.(b) Dissolver Experiments.

No simple relationship between the individual cell polarization voltage and the overall voltages observed during dissolution runs could be established. Visual observation of the dissolver bed showed that almost all the pellets took part in the electrolytic reaction. These observations indicated that under any given conditions, a large number of cells both in series and in parallel were set up within the bed. Thus, provided the contact resistance (i.e. between the uranium bed and the anodic tantalum section) and the electrolyte resistance were taken into account, the voltage across the dissolver would be related to the number of cells formed in series between the cathodic and anodic sections of the dissolver.

Evidence of cell formation was strongest in the middle section, with little or no signs of electrolytic attack visible on the pellets contained within the cathodic portion of the dissolver.

Fig. 8.5. Appearance of Uranium Bed
after Electrolytic Dissolution.



Note: Cathodic section originally at top of a vertically
mounted dissolver.

A photograph (Fig.8.5) taken of a bed composed of No.3 size pellets and approximately 2 hours after the end of a series of runs (EDNT (E) 13-15) illustrates clearly the varying degrees of dissolution within the different sections of the dissolver; no pellets dissolved completely, however.

The bright, silvery surface shown by the pellets immediately after removal from the dissolver, gradually changed colour to a golden brown and then a dark brown as the surface became oxidised (the dark brown colour appeared after 3-4 days).

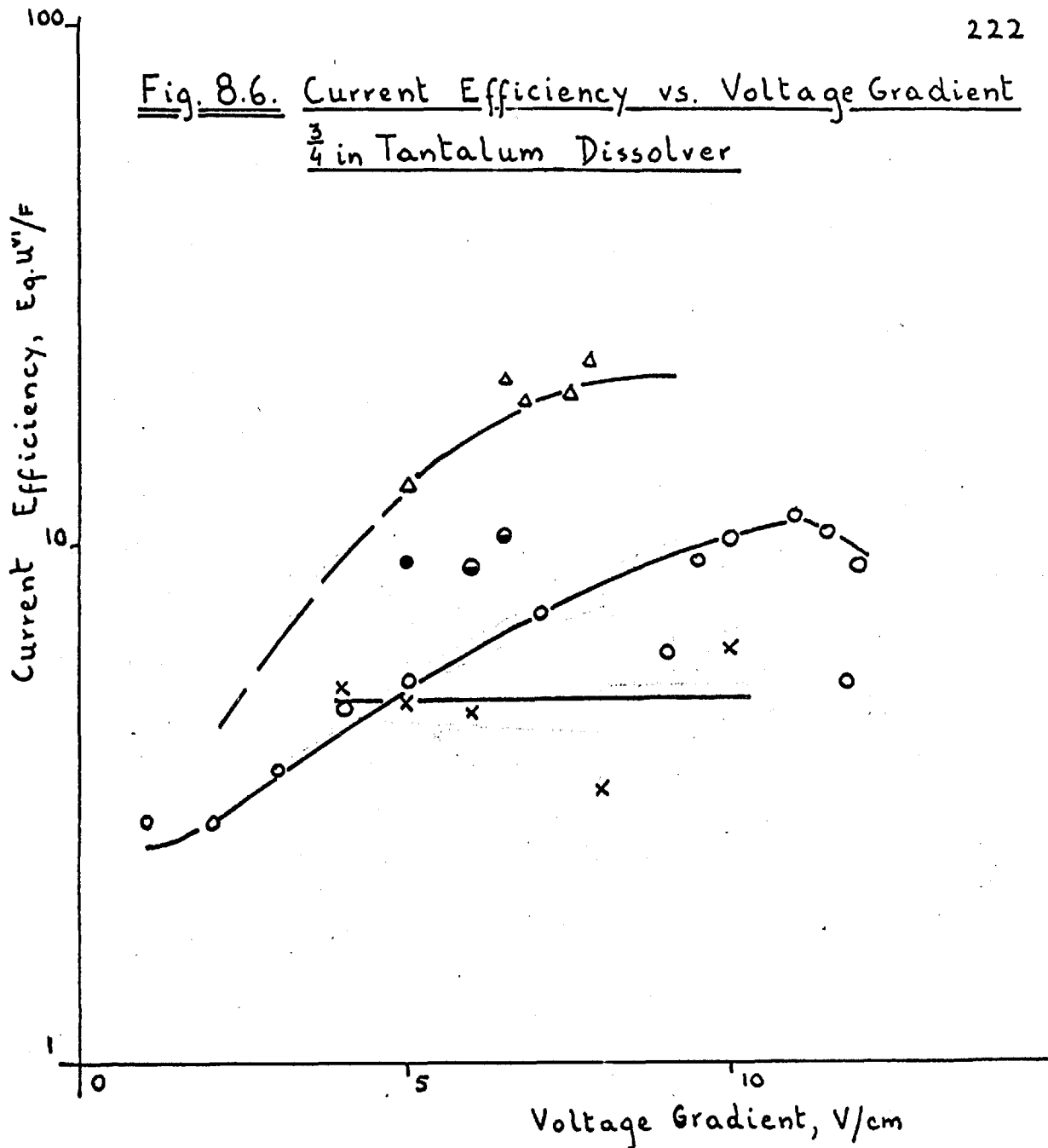
8.1.3. Effect of Bed Size and Composition on Cell Formation.

8.1.3.(a) Effect of Bed Length (Middle Section).

The overall current efficiency of the dissolver system expressed as equivalents of hexavalent uranium dissolved per faraday, bears a direct relationship to the number of cells formed and reaches a maximum which is proportional to the length of the middle section (Fig.8.6). In each case the maximum number of equivalent cells formed is doubled with doubling of the middle section length.

Most of the pellets within the dissolver system suffer electrolytic attack (Fig.8.5) and this suggests that the value for "equivalent cells" represents a larger number of cells but each operates at less than 100% efficiency.

Fig. 8.6. Current Efficiency vs. Voltage Gradient
 $\frac{3}{4}$ in Tantalum Dissolver



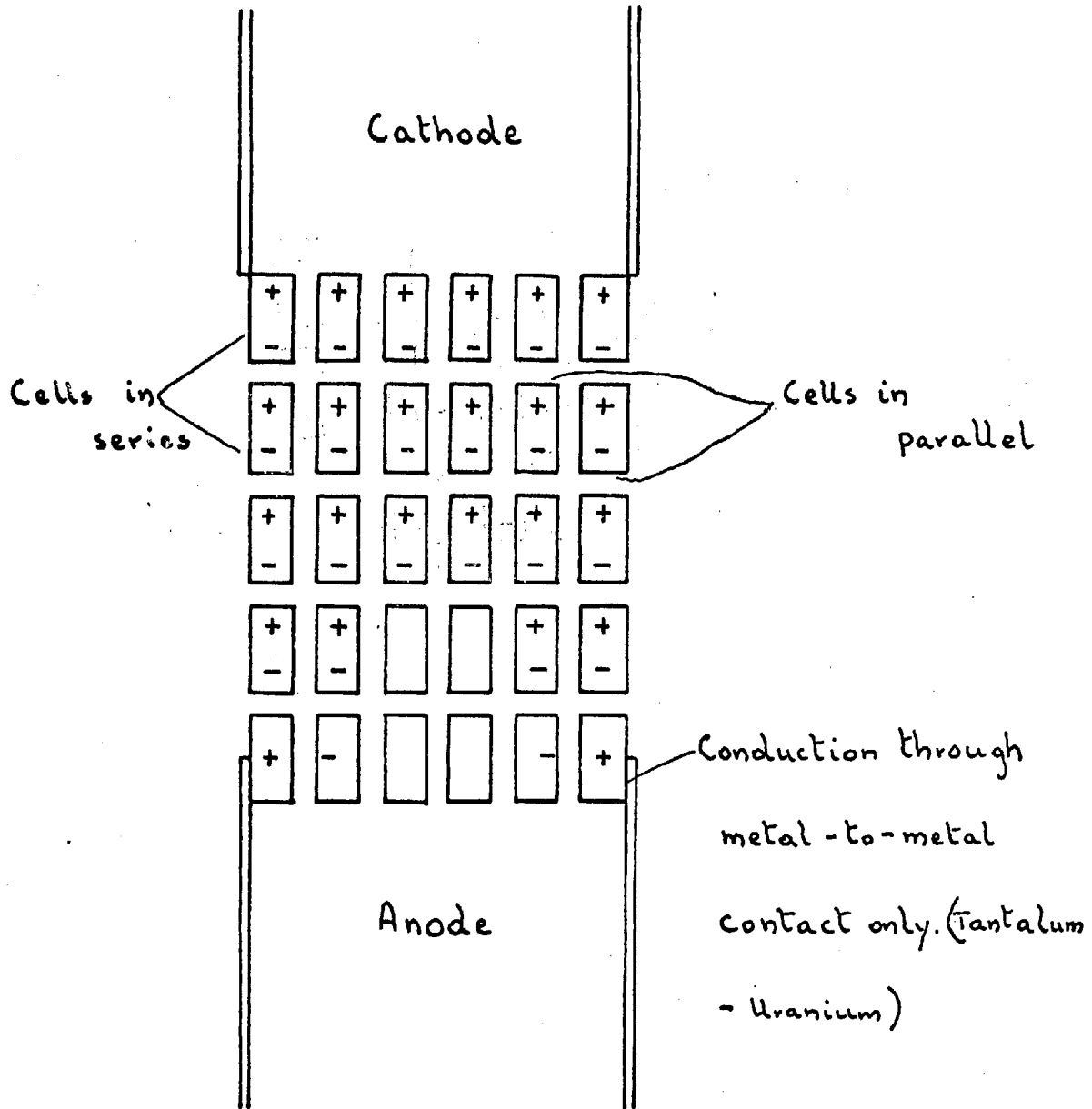
Key: x 2.5 cm Middle Section
 o 5.0 cm " "
 Δ 10.0 cm " "
 ● 5.0 cm " " (Tapping)
 ● 5.0 cm " " (Polarities Reversed)

Note: Points plotted represent average values at a given voltage gradient.

Such a system would be composed of cells operating both in series and in parallel, each at a fraction of the total observed current and each contributing towards the overall observed current efficiency figure (c.f. 4 cell model, Section 7.3.5). A simplified representation of the dissolver system described above is given in Fig.8.7. Thus an observed current efficiency of 10 may equally mean 20 such "layers" of parallel cells operating in series with 50% current efficiency or 15 "layers" in series operating with 66.7% current efficiency, assuming the applied voltage to be sufficiently high so as not to limit the number of cells which could be set up in series.

It may, therefore, be assumed that at high current densities and voltage gradients a limit on the efficiency for a given bed length and pellet size is reached when the distance between the cathodic and anodic sections of the dissolver becomes linked by a system of cells in series. It is reasonable to suppose that such a limit would be attained earlier with smaller lengths of middle section. Thus in the case of the 2.5 cm. long middle section, the current efficiency remained constant at about 5 $\text{Equiv. } U^{\text{vi}}/F$ (Fig.8.6) in the range of voltage gradients investigated (4 - 10 V/cm) showing that even at the lower end of the range a sufficiently high applied voltage was available to allow for the requisite number of cells (or cell "layers") to be established.

Fig. 8.7. Diagrammatic Representation of Cells
within a Dissolver



Not to Scale

As contact between the anodic (tantalum) section of the dissolver and the uranium bed could only be established through direct metal-to-metal contact (Section 6.1), a certain fraction of the overall voltage applied was consequently needed to overcome the contact resistance, R_c . Results of experiments with the dissolver system indicated that this resistance was unlikely to be as high as that observed under conditions more favourable to the formation of an oxide film on the uranium pellets (Table F.4, Appendix F). From a plot of the variation of total applied voltage with length of middle section at a given current density (Fig.8.8) an estimate of R_c under experimental conditions of the dissolver could be obtained as follows:

At 8.0 amp/cm^2 (Fig.8.8)

Applied Voltage, $V_1 = 60 \text{ V}$ for 5 cm. length of middle section.

" " $V_2 = 84 \text{ V}$ " 10 cm. " " " "

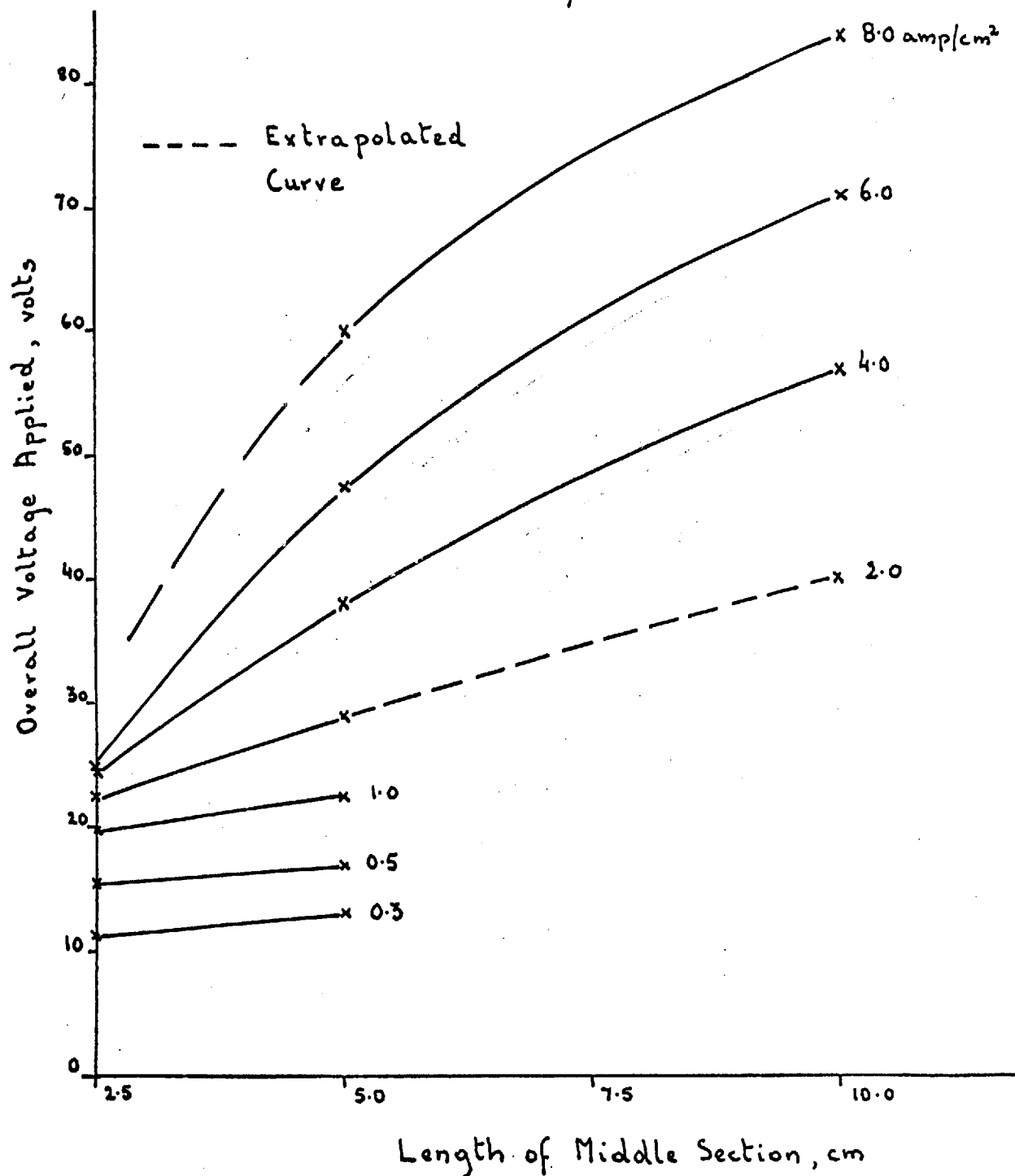
" " 5 cm. length of bed (middle section) $\approx 24 \text{ V}$

Assuming voltage drop to be uniform throughout the length of middle section;

Voltage drop due to contact resistance (anodic and cathodic)
in dissolver system

$$= 60 - 24 = 36 \text{ V}$$

Fig. 8.8. Variation of Applied Voltage with Length of Middle Section at a Given Current Density ($\frac{3}{4}$ in Dissolver)



Assuming that the anodic contact resistance, R_c , (metal-to-metal only) is mainly responsible for the observed voltage drop, we have

$$R_c = \frac{36}{8 \times 2.78} = 1.6 \text{ ohms.}$$

Similarly, R_c at other current densities may be calculated using values of voltage drop obtained both for 2.5 and 5 cm. and 5 and 10 cm. lengths of middle section. Results of these calculations are shown below (Table 8.2).

Table 8.2. Evaluation of R_c from Overall Applied Voltage Values -
 $\frac{3}{4}$ in. dia. Tantalum Dissolver.

Current Density, amp/cm. ²	Length of Middle Section, cm.			(1)	(2)	(1)	(2)
	2.5	5.0	10.0	ΔV_1 , V	R_{c1} , ohms	ΔV_2 , V	R_{c2} , ohms
	Overall Applied Voltage, V.						
0.3	11.25	13.0	-	1.75	11.4	-	-
0.5	15.5	17.0	-	1.5	10.0	-	-
1.0	19.75	22.5	-	2.75	6.1	-	-
2.0	22.75	29.0	40	6.25	3.0	11.0	3.2
4.0	24.5	38.0	57	13.5	1.0	19.0	1.7
6.0	25.0	47.5	71	22.5	0.15	23.5	1.4
8.0	-	60.0	84	-	-	24.0	1.6

Notes: (1) ΔV_1 , ΔV_2 represent differences in overall applied voltage between 2.5 and 5 cm. and 5 and 10 cm. lengths of middle section, respectively.

(2) R_{c1} , R_{c2} represent contact resistances based on ΔV_1 and ΔV_2 , respectively.

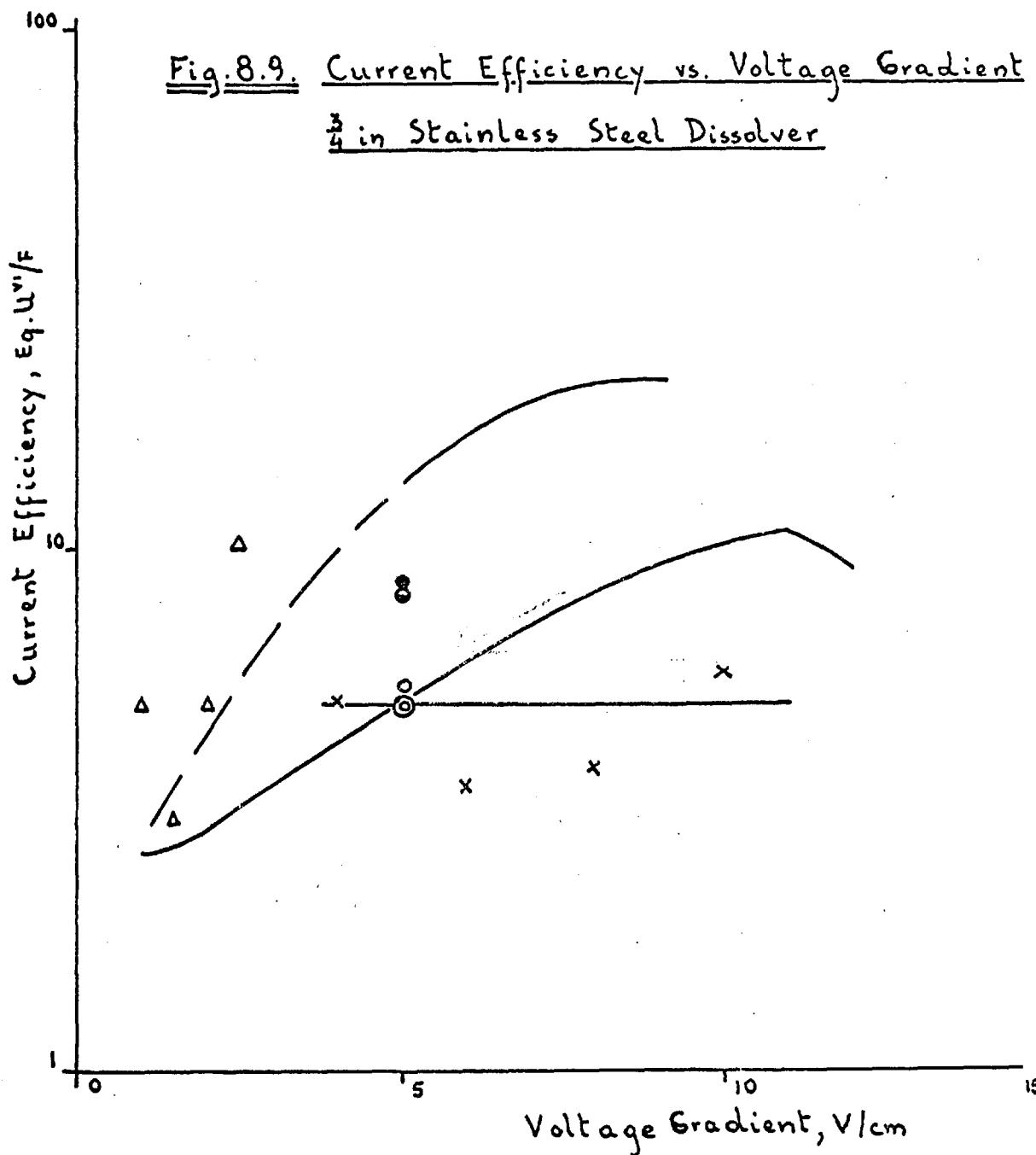
Assuming that contact resistance alone would be purely ohmic in nature, a constant value of R_c at all current densities would be expected. The observed decrease in R_c as estimated above (Table 8.2) suggests therefore that the value of R_c as calculated includes polarization resistance due to pellets contained within the anodic and cathodic sections of the dissolver. As polarization resistance of electrodes obeying the Tafel equation decreases with increase in current⁽²⁹⁾⁽⁸²⁾ (Section 8.1.4) a drop in the contact resistance, R_c , as estimated above would be shown. From values observed in the high current density region, however, a value of R_c of the order of 1-2 ohms is indicated (Table 8.2). The very low value of R_c observed when voltages across 2.5 and 5 cm. lengths of middle section at 6.0 amp/cm² were compared, is due to the large increase in current with relatively small increase in overall voltage shown in the case of dissolver experiments with 2.5 cm. long middle section (Fig.6.1). It is suspected that this disproportionate increase in current flowing was caused by shorting within the middle section through direct metal-to-metal contact between the pellets in a system undisturbed by tapping (Section 6.2.2). It must be noted that changes of about 50% in the length of bed contained within the anodic section of the dissolver (5 cm. long middle section) had no noticeable effect on the voltage-current characteristics of

the system and hence presumably on the overall value of R_c .

Higher current efficiencies observed (Fig.8.6) when the polarities of the tantalum electrodes were reversed (Section 6.2.2) may be attributed to a larger portion of the applied voltage being available for cell formation within the middle section. A lesser fraction of the overall voltage would in this case be needed to overcome the contact resistance set up by the thinner oxide film on the previously cathodic section of the dissolver.

Both a lowering of current efficiency and a rise in voltage at a given current density were noted when the level of the uranium bed fell below the level of the cathode section - e.g. in the case of Run EDNT.21 (Table 6.3) when a drop of 5 cm. was observed at the end of the experiment. A drop in current efficiency would be caused by the gradual decrease in the length of middle section available to cell formation whilst an increase in the resistance of the system would result in the absence of a pellet bed, with the current being forced to flow to the cathodic section through the electrolyte only.

No marked difference in current efficiency was observed when values obtained with the stainless steel dissolver were compared with those noted in the case of experiments using tantalum electrodes (Fig.8.9).



Key:	x	2.5 cm	Middle Section	
	o	5.0 cm	"	"
	Δ	10.0 cm	"	"
	●	5.0 cm	"	" (0.4N HNO ₃ electrolyte)
	⊖	5.0 cm	"	" (1.0N HNO ₃ ")
	⊙	5.0 cm	"	" (6.0N HNO ₃ ")

Note: (1) Curves obtained with tantalum dissolver are shown for comparison (cf. Fig. 8.6.)

(2) Points plotted represent average values.

8.1.3.(b) Effect of Bed Diameter.

As might be expected from the suggested mechanism for the dissolver (Fig.8.7), the bed of uranium pellets did not behave as an ohmic conductor when its diameter was changed. A comparison of current densities at various voltage gradients for $\frac{3}{4}$ in. and $1\frac{1}{2}$ in. dia. dissolvers at equivalent lengths of middle section is given in Table 8.3. The difference between the lengths of middle sections of the $1\frac{1}{2}$ in. dia. dissolver (9.5 cm.) and that of the $\frac{3}{4}$ in. dia. dissolver (10 cm.) is neglected for the purposes of this discussion.

Table 8.3. Current Density at various Voltage Gradients
 $\frac{3}{4}$ in. and $1\frac{1}{2}$ in. dia. Dissolvers (Fig.6.5).

Voltage Gradient, V/cm.	Current Density, amp/cm ² .		$\frac{(b)}{(a)}$
	$\frac{3}{4}$ in. (a)	$1\frac{1}{2}$ in. (b)	
4.0	2.2	0.8	0.36
5.0	3.2	1.1	0.34
6.0	4.5	1.4	0.31
7.0	6.0	1.8	0.30
8.0 ⁽¹⁾	7.5	2.2	0.29

Note: (1) Extrapolated Values.

Data reported in Table 8.3 indicate that the current flowing through the $1\frac{1}{2}$ in. dissolver approximates to that passing through a $\frac{3}{4}$ in. vessel, particularly at higher voltage gradients.

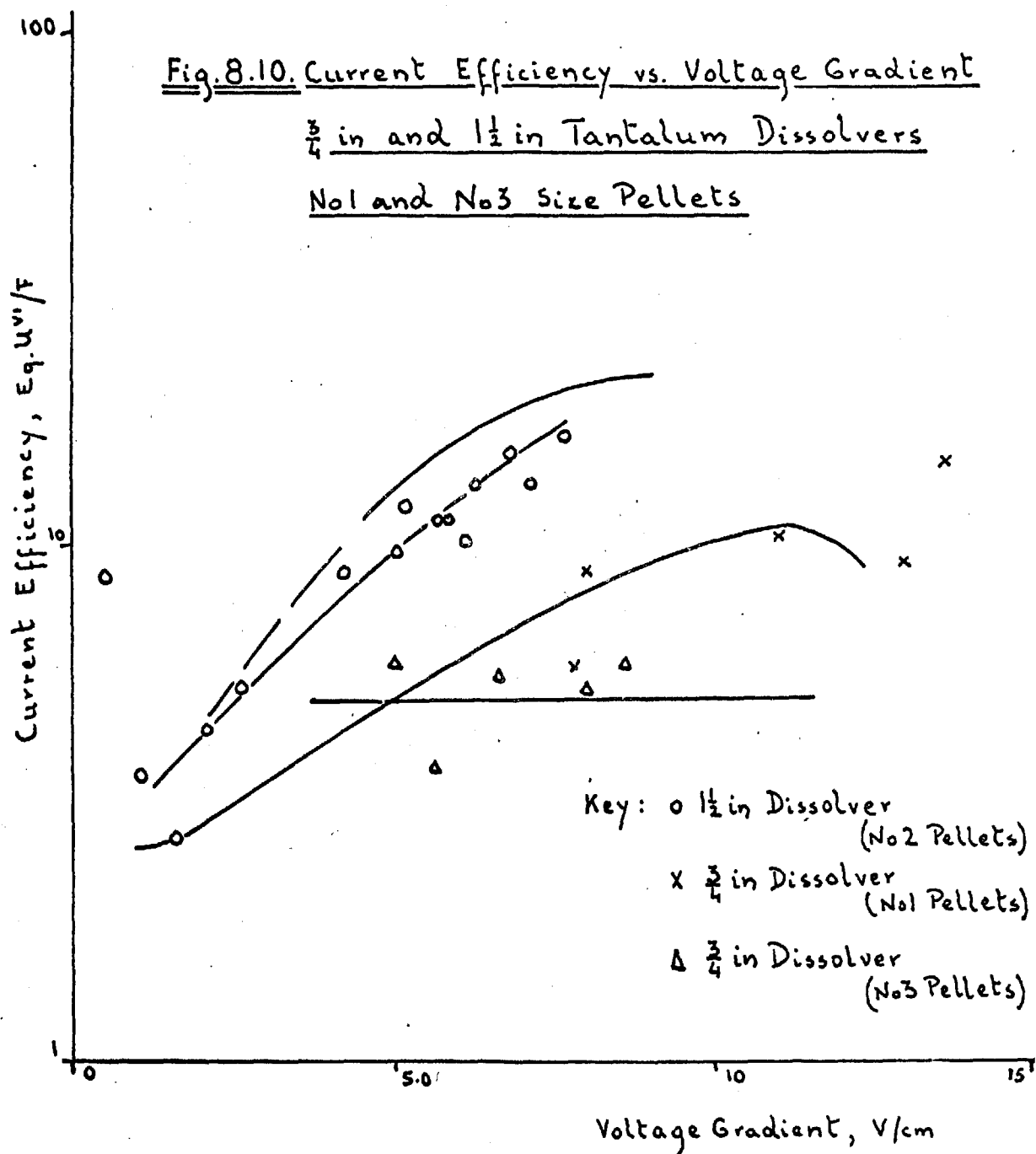
The slight increase in current at a given voltage gradient in the $1\frac{1}{2}$ in. dia. dissolver is attributed to lower overall electrolyte resistance. Thus it appears that the number of cells reacting in parallel within a given length of bed does not increase in the same proportion as the dissolver diameter and the overall resistance of the dissolver bed is governed largely by the number of cells in series, assuming the same size of pellet is used in both cases. This appears to be confirmed in Fig.8.10, where the current efficiency figures are closely similar for both dissolvers. The slightly lower current efficiency of the $1\frac{1}{2}$ in. dissolver may again be explained in terms of lower overall electrolyte resistance. Thus at a given current density,

$$\frac{R_p}{R_e} (1\frac{1}{2} \text{ in. dia. vessel}) > \frac{R_p}{R_e} (\frac{3}{4} \text{ in. dia. vessel})$$

where R_p = polarization resistance

R_e = electrolyte resistance

assuming specific resistance, K , of the electrolyte and length of middle section remain constant. Consequently the tendency for the current to flow through the electrolyte is greater in the $1\frac{1}{2}$ in. dia. vessel resulting in lower current efficiency (cf. Section 8.2.1). It must be noted, however, that the voidage, e , will decrease slightly as the diameter of the dissolver is



Note: (1) Curves obtained with $\frac{3}{4}$ in tantalum dissolver are shown for comparison (cf. Fig. 8.6.)

(2) Points plotted represent average values.

increased ($\epsilon = 36\%$ for $1\frac{1}{2}$ in. dia. dissolver, 39% for $\frac{3}{4}$ in. dia., No.2 size pellet, assumed spherical for the purpose of voidage estimation - data according to Leva⁽⁶⁰⁾) thus tending to raise the overall electrolyte resistance and counteracting the lowering of R_e due to increase in bed diameter.

It may therefore be assumed that, in the extreme case, for a given length of middle section and size of pellet, the current flowing through a dissolver will be independent of the diameter of the bed and proportional only to the magnitude of the applied voltage (or voltage gradient).

8.1.3.(c) Effect of Pellet Size.

Only a few experiments have been carried out with Size 1 and 3 pellets, but some conclusions regarding their electrolytic behaviour can be drawn on the basis of the dissolver bed envisaged (Fig.8.7) :

(1) the use of the smaller (No.1 Size) pellet will result in a higher (compared with No.2 Size) voltage gradient being needed to achieve a given current density at a constant length of middle section. This would be the result of a greater number of cells set up in series between the anodic and cathodic sections. Thus a slightly higher value of current efficiency at a given voltage gradient would also be expected;

(2) Conversely, a lower voltage gradient at a given current density and lower current efficiency at a given voltage gradient will be shown with the larger (No.3 Size) pellet.

Both effects have been observed experimentally (voltage gradient-current density relationship - Fig.6.2, variation of current efficiency with voltage gradient - Fig.8.10), although no significant difference in current efficiency values has been shown between the No.1 and No.2 Size pellets.

8.1.3.(d) Effect of Electrolyte (Nitric Acid Concentration).

Higher current efficiencies at a given voltage gradient resulted when electrolytes with acid concentrations lower than 3 N HNO_3 were used (Fig.8.9). Such an effect would be expected from a consideration of the respective conductivities at various strengths⁽⁶⁵⁾. Thus lower conductivities of 0.4 and 1.0 N HNO_3 raised the ratio of the electrolyte to polarization resistance of the system forcing more current to flow through the cells set up by the pellets and consequently increasing current efficiency. At higher acid concentrations (3 N and 6 N) the conductivity of the electrolyte rose allowing current to bypass the pellets more easily and resulting in a drop in current efficiency.

Whilst increasing the current efficiency, however, the use of low conductivity electrolytes increased the overall resistance of the dissolver system. The resistance increase led to a

significant lowering of current density at a given voltage gradient (Section 5.4.2 - Figs.5.5 and 5.7) thus decreasing the speed of dissolution.

8.1.3.(e) Effect of Electrolyte Temperature and Pressure.

The attempt made to investigate the influence of electrolyte temperature on the behaviour of the dissolver system (Section 6.2.2) was unsuccessful largely because the heat losses from the unlagged flow circuit caused too great a change in the initial temperature of the electrolyte, while the cooler proved incapable of controlling the rapid rise in temperature which occurred when dissolution at high current densities was carried out. The effect of electrolyte pressure on the electrolytic behaviour of the dissolver bed was not investigated.

8.1.3.(f) Effect of Tapping.

During the course of a run it would be expected that gaps between individual pellets within a dissolver bed would form due either to the dissolution of the uranium or bridging between pellets or both. An imposed disturbance e.g., tapping, would consequently be expected to have a beneficial effect on the bed by causing the pellets to come in closer contact again thus increasing both the current flow and current efficiency. This was confirmed experimentally during runs carried out both with and without tapping when current efficiencies (Fig.8.6) and

current densities (Fig.6.1) obtained at a given voltage gradient were compared.

Experimental evidence suggests, however, that prolonged or continuous disturbance of bed equilibrium due to tapping results in little or no improvement of the dissolver performance (Section 5.4.2). Limited use of tapping only was made therefore during the subsequent series of dissolver experiments (Sections 6.2.2.(c) and 6.3.2.(c)) when it was observed, particularly at high voltage gradients ($> 5\text{V/cm.}$), that the operation of the dissolver proceeded smoothly even in the absence of tapping. This evidence is considered important as it suggests that, at sufficiently high voltage gradients, efficient performance of the dissolver may be achieved without the use of tapping, thus minimising a serious problem in the operation of a plant-size unit. It will be noted that maintenance of adequate contact between the fuel charge and the anode basket and the subsequent need for tapping formed one of the major obstacles to the successful operation of basket-type dissolvers⁽³⁵⁾⁽³⁷⁾.

8.1.4. Polarization Resistance.

In the case where the Tafel equation (Eqn.8.1) is obeyed the polarization resistance, R_p , of an electrode varies inversely as the current density, I ⁽²⁹⁾⁽⁸²⁾. Thus we have,

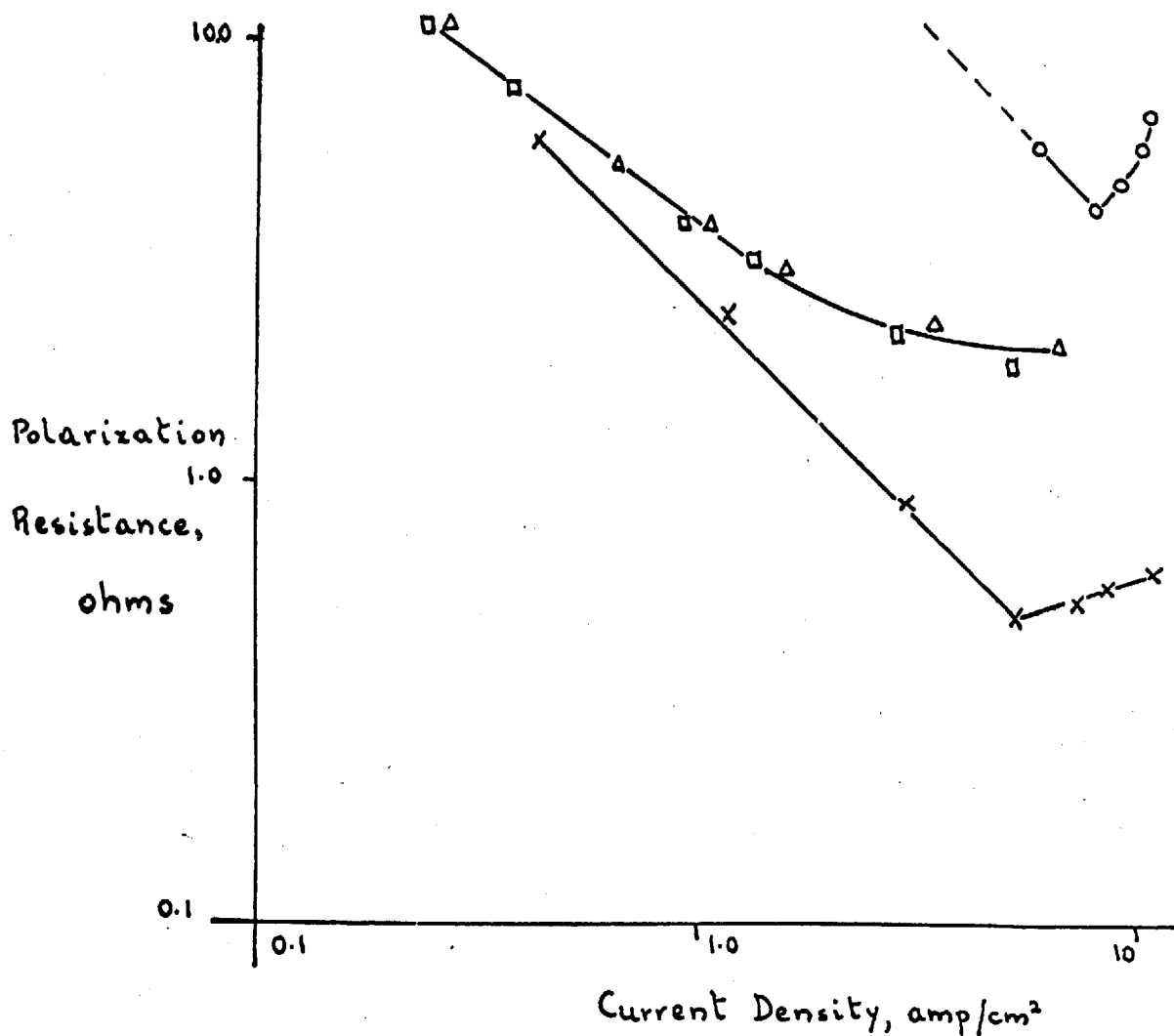
$$R_p = a I^{-b} \quad \dots (8.7)$$

where a and b are constants. A straight line will therefore be obtained when R_p vs. I is plotted on logarithmic co-ordinates. This relationship is illustrated in Fig.8.11, where cell polarization resistances obtained both in single cell and multi-cell model experiments are plotted against current density. The values of polarization resistance used in Fig.8.11 were calculated from the corresponding η_t values observed at a given current density (Sections 8.1.1. and 8.1.2). A simplified method of estimating polarization resistance was used in the case of the 3 pellet system where overall polarization resistance was obtained on the basis of the observed η_t value and an assumed 40% of the total current flowing through the cells. Only points representing values obtained when all 3 interposed pellets were reacting are plotted in Fig.8.11.

The apparent sharp rise in the value of R_p at high current densities in the 3 pellet multi-cell system shows the presence of a limiting current density⁽²⁹⁾ (at about 11 amp/cm²) which may be attributed to concentration polarization.

A less well defined limiting current density region is shown by the single cell (electrodes 0.5 cm. apart) experiment although a change in reaction mechanism is indicated by a change in slope of the curve at about 5-6 amp/cm² (cf.Fig.8.3).

Fig. 8.11. Polarization Resistance vs. Current Density
Single Cell and Multi-cell Systems
Model Experiment



Key: x Electrodes 2.05 cm apart } Single Cell
 □ Electrodes 3.5 cm " }
 ○ 3 Interposed Pellets } Multi-cell System
 Δ 1 " Pellet }

Such a lack in definition of the limiting current density region may have been caused by the physical construction of the cell (Section 7.3.4). Thus with the anode protruding beyond the rim of the holder, the dissolved uranium could stream away from the anode surface more easily, affecting concentration polarization at the anode and consequently the limiting current region of the cell as a whole.

For comparison, values of R_p obtained (1) with widely separated electrodes (single cell) and (2) with a multi-cell (1 interposed pellet) system are also shown in Fig.8.11. A change in slope indicating the onset of a limiting current density region is observed in both cases at relatively low current densities (about 2 amp/cm²). This tends to confirm the observation made earlier (Section 8.1.1) that with the electrodes widely apart, the evolution of cathodic gas had little stirring effect on the electrode-electrolyte layer interface and consequently ohmic polarization was likely to occur.

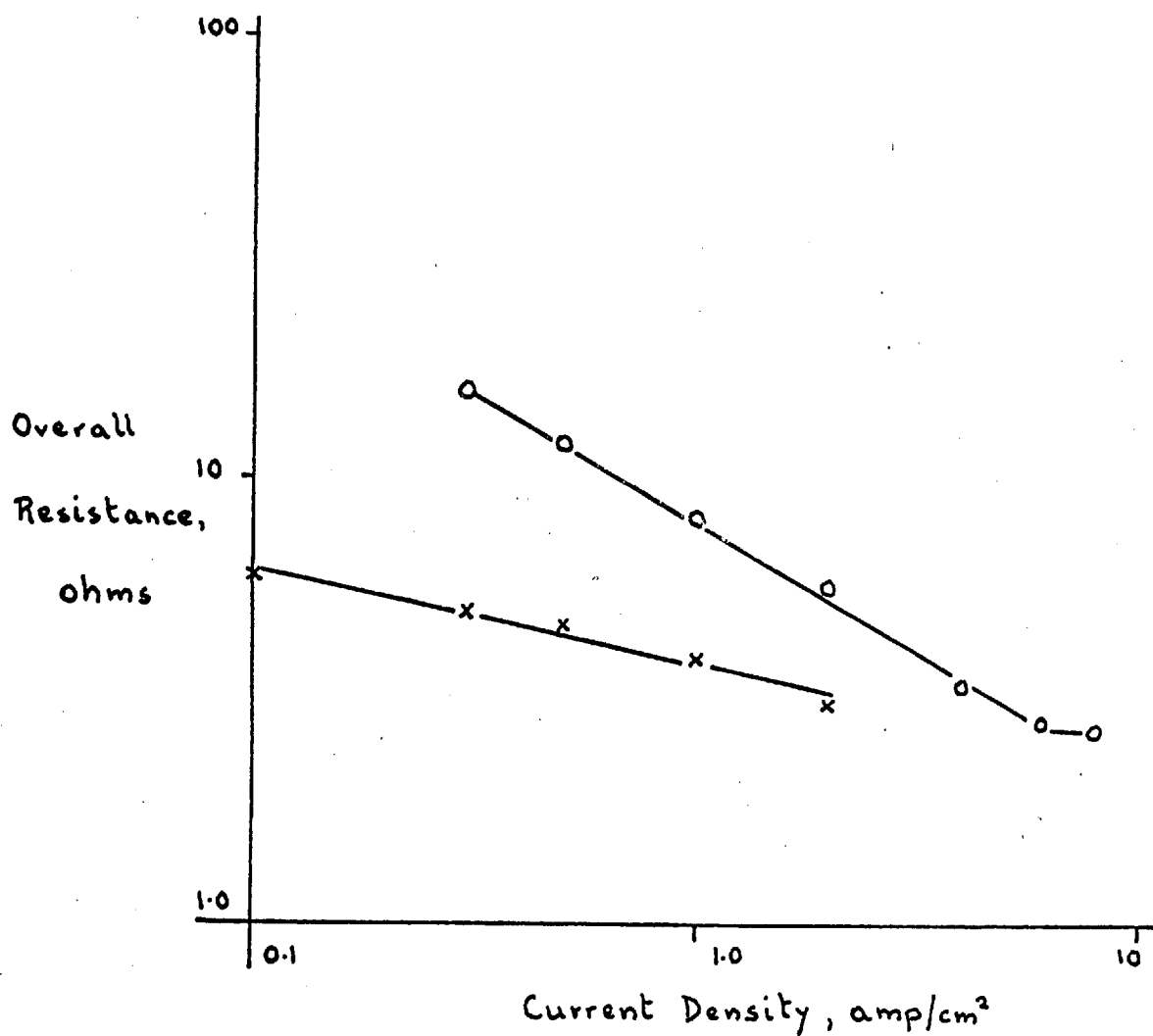
From the above arguments it follows that in a dissolver bed where the pellets are packed close together and consequently a great deal of turbulence in the electrolyte flowing across the bed may be assumed to exist, little tendency should be shown towards ohmic and concentration polarization and the onset of a

limiting current density region. Assuming that the electrolyte resistance and contact resistance (i.e. resistance between pellets and tantalum anode) of a dissolver system remain approximately constant, any variation in the polarization resistance of the cells composing the bed would be reflected by a change in the overall resistance of the system. A plot of the overall resistance against current density should therefore show any tendency towards concentration polarization and limiting current density.

Based on the steepness of the slope at high current densities of their voltage gradient - current density curves, two dissolver systems were chosen and their values of overall resistance plotted (Fig.8.12). No evidence of a limiting current density is shown in either case although a change in slope of the curve obtained with the $\frac{3}{4}$ in. dia. dissolver becomes apparent at about 6 amp/cm².

Fig. 8.12. Overall Resistance vs. Current Density.

Tantalum Dissolver



Key: O $\frac{3}{4}$ in Dissolver - 5 cm Middle Section

x $1\frac{1}{2}$ in Dissolver

8.2. Dissolution Process.

8.2.1. Current Density-Dissolution Rate Relationship.

Electrolytic dissolution is governed by Faraday's laws which may be expressed in a general form as

$$w = \frac{I t e}{F} \quad \dots (8.8)$$

where w = weight dissolved, g

I = current, amp

t = time for which the current is passed, seconds

e = equivalent weight, g

F = Faraday (96,500 coulombs).

Further, if G is the dissolution rate ($\text{mg}/\text{min}.\text{cm}^2$) and C is the current density (amp/cm^2) both G and C being based on the same area A , we have:

$$\begin{aligned} w &= \frac{C A t e}{F} \\ \text{and } G &= \frac{W \times 60 \times 1000}{A t} \\ &= \frac{60 \times 1000}{F} e C \\ &= 0.622 e C \quad \dots (8.9) \end{aligned}$$

Or, more generally,

$$G = a C \quad \dots (8.10)$$

where $a = 0.622 e$, a constant for a given ^{metal} method.

Thus for a single 100% efficient uranium cell, assuming the metal to be hexavalent

$$G = 24.7 C \quad \dots (8.11)$$

Now in each case when the experimentally observed dissolution rate is plotted against current density (Figs. 5.6, 6.3, 6.4, 6.6, 7.5 and 7.6) a curve is obtained which in its simplest form can be represented by the equation

$$G = a' C^n \quad \dots (8.12)$$

where a' , n are constants, dependent on the conditions of the experiment. Thus equation (8.12) may be taken to represent a modification of the general dissolution relationship (Eqn.8.10) applicable under conditions of multi-cell dissolution. It will be noted that from the equation of the plot for the single cell model experiment (Fig.7.5) we obtain

$$\begin{aligned} a' &= 24.5 \\ n &= 1.0 \end{aligned} \quad (\text{cf. Eqns.8.10 and 8.11}).$$

8.2.1.(a) Model Experiment - Multi-cell System.

Model experiments using the multi-cell system showed that the value of the intercept, a' , decreased and the value of n increased as more cells were formed by the addition of interposed pellets. Values of a' and n obtained from equations of lines based on figures observed during the course of multi-cell experiments (Fig.7.6) are given in Table 8.4.

Table 8.4. Multi-cell Experiment Variation
of a' and n Values (Fig.7.6).

No. of inter-posed pellets.	Total No. of cells possible.	Current Utilisation per pellet, U, % (1).	a'	n
1	2	1.0	13.0	1.04
2	3	8.7	8.5	1.09
3	4	29.1	7.7	1.25

Note: (1) Section 7.3.5.

Now in the case of the multi-cell system, the dissolution rate, G, will depend both on the weight of uranium dissolved off the connected anode and the weights contributed by the anodes from the interposed pellets. The following relationship between G and C may thus be envisaged:

$$G = 24.7 C \frac{A}{S} + 24.7 C \frac{A}{S} f \frac{R_e}{R_p} \quad \dots (8.13)$$

$\uparrow$ $\uparrow$
 Contribution Contribution of
 of connected interposed
 anode. pellets.

where A = area on which C is based

S = area on which G is based

f = factor related to number of cells operating in series

R_p = polarization resistance

R_e = electrolyte resistance, parallel to resistance of pellet system.

$\frac{R_e}{R_p}$ influences the fraction of the current which will flow through

the pellets rather than through the electrolyte, thus influencing current utilisation. Assuming that R_e remains constant for a given system, current utilisation will, therefore, increase with increase in current density as R_p decreases (Eqn.8.7).

$$\text{Now we have from Eqn.(8.7), } R_p = \alpha C^{-b} \quad \dots (8.14)$$

where α , b are constants

$$\text{also } R_e = \frac{K L}{A'} \quad \dots (8.15)$$

where, in the case of the multi-cell model,

$$L = L'$$

= total length of interposed pellets in the direction of current flow (Section 7.3.5).

A' = cross-sectional area of the electrolyte path.

$$\text{Also, } A' = \beta (L')^m \quad \dots (8.16)$$

(cf. Eqn.7.5)

where β , m are constants.

∴ Substituting for A' in Eqn.(8.15), we have

$$R_e = qK(L')^{1-m} \quad \dots (8.17)$$

where q is a constant.

From Eqns.(8.13), (8.14) and (8.17) we obtain therefore

$$G = 24.7 C \frac{A}{S} + 24.7 \frac{A}{S} f qK(L')^{1-m} \frac{C^{1+b}}{\alpha} \quad \dots (8.18)$$

Simplifying, we have

$$G = 24.7 C \frac{A}{S} + 24.7 \frac{A}{S} f K C^{1+b} \quad \dots (8.19)$$

$$\text{where } K = \frac{q K (L')^{1-m}}{\alpha} = \text{constant.}$$

Thus in the case where the contribution of the interposed pellets towards the total weight of uranium dissolved is small (1 and 2 pellet systems), the second term of Eqn.(8.19) may be neglected and the relationship between G and C will approximate to

$$G = 24.7 \frac{A}{S} C \quad \dots (8.20)$$

As the contribution of the interposed pellets increases, the influence of the second term increases and Eqn.(8.19) will tend to

$$G = 24.7 \frac{A}{S} f k C^n \quad \dots (8.21)$$

where n is a constant for a given system (Fig.7.6).

Values obtained from Fig.7.6 (Table 8.4) allow an approximation of Eqn.(8.19) to be derived which, for the multi-cell system, takes the general form (cf.Eqn.8.12)

$$G = 24.7 \frac{A}{S} C^1 + \frac{U}{100} \quad \dots (8.22)$$

where $n = 1 + \frac{U}{100}$

and U = percent current utilisation per pellet (Section 7.3.5).

8.2.1.(b) Tubular Dissolver System.

The tubular dissolver system may be regarded as one in which a large number of pellets are interposed, both in series and in parallel. From the foregoing and Eqns.(8.13) and (8.21), we obtain

$$G = 24.7 C \frac{A}{S} f \frac{R_e}{R_p} \quad \dots (8.23)$$

Now in the case of the tubular dissolver,

$$R_e = \frac{Kl}{Ae} \quad \dots (8.24)$$

where l = length of middle section.

A = cross-sectional area of the dissolver tube
(i.e. area on which C is based)

e = overall bed voidage fraction.

Substituting for R_e and R_p in Eqn.(8.23) from Eqns.(8.24) and (8.14),
we have

$$G = 24.7 \frac{A}{S} f \frac{K\ell}{Ae} \frac{C^{1+b}}{\alpha} \quad \dots (8.25)$$

$$\text{or} \quad G = 24.7 \frac{A\ell}{S} r C^n \quad \dots (8.26)$$

where r , n are constants for a given system

$$\text{and } \frac{\ell}{S} = \frac{\text{length of middle section}}{\text{surface area of all pellets in middle section}} \\ = \frac{1}{S_u}$$

where S_u = surface area of pellets in unit length of bed.

Eqn.(8.26) thus becomes

$$G = 24.7 \frac{A}{S_u} r C^n \quad \dots (8.27)$$

(cf. Eqns.8.21 and 8.12).

Experimentally observed a' and n values (Eqn.8.12) obtained
from Figs.5.6, 6.3 and 6.6 are given in Table 8.5.

Table 8.5. Tubular Dissolver.

Variation of a' and n at constant Pellet Size.

Dissolver Diam., in.	Length of middle section, cm.	Size of pellet.	a'	n	Voidage fraction, e	$\frac{1-e}{e}$
$1\frac{1}{2}$	9.5	2	3.0	1.7	0.36	1.8
$\frac{3}{4}$ (1)	5	)				
(tantalum)	10	) 2	3.0	1.4	0.39	1.6
$\frac{3}{4}$	2.5	)				
(stainless steel).	5.0	) 2	2.9	1.6	0.39	1.6
	10	)				

Note: (1) Experiments using 2.5 cm. length of middle section were not taken into consideration as there is evidence (Sections 6.2.2 (a) and 8.1.3.(a)) that the results obtained were not sufficiently representative.

Figures in Table 8.5 show that for a given pellet size, the value of a' remains constant despite variations in length of middle section and bed diameter. Thus for size 2 pellets, $a' \approx 3$.

A constant value of a' would be expected from a consideration of the group $24.7 \frac{A}{S_u}$ (Eqn.8.27) which remains a constant for a given pellet size. Substituting appropriate values of A and S_u for both the $\frac{3}{4}$ in. and $1\frac{1}{2}$ in. dissolvers (Chapters 5 and 6),

$$24.7 \frac{A}{S_u} r = 2.9 \quad \dots (8.28)$$

= a constant for size 2 pellets
(assuming $r = 1$).

Therefore, as an approximation, from Eqns.(8.8), (8.27) and (8.28),

$$a' = 24.7 \frac{A}{S_u} \quad \dots (8.29)$$

= 2.9 (for size 2 pellets).

An expression for the value of n (Eqns.8.27 and 8.12) may be derived by analogy with the multi-cell concept demonstrated in the model experiment, where experimental evidence pointed to a relationship between n and the current utilisation, U (Eqn.8.22). In the case of the tubular dissolver, current utilisation will be proportional to the relative amounts of metal and electrolyte

present in the dissolver bed. Thus

$$U \propto \frac{1-e}{e}$$

$$\text{i.e. } U = f\left(\frac{1-e}{e}\right) \quad \dots (8.30)$$

where e = voidage fraction

and f = proportionality constant.

If the analogy between the multi-cell system and the tubular dissolver holds then, for the tubular dissolver (Eqn.8.27), we have

$$n = f\left(\frac{1-e}{e}\right) \quad \dots (8.31)$$

From values quoted in Table 8.5, $f \approx 0.9 - 1.0$. As $f = 0.9$ gives the more conservative estimate of n , we have therefore

$$n = 0.9\left(\frac{1-e}{e}\right) \quad \dots (8.32)$$

The values of e chosen are those given by Leva⁽⁶⁰⁾ for smooth spherical particles, their diameter equal to the diameter of pellets used. It is considered that such an assumption is valid, pellets in the middle section losing their originally cylindrical shape as anodic dissolution proceeds. From Eqns.(8.27), (8.29) and (8.32), Equation (8.12) becomes therefore in the case of the tubular dissolver system

$$G = 24.7 \frac{A}{S_u} C^n \quad \dots (8.33)$$

$$\text{where } n = 0.9\left(\frac{1-e}{e}\right)$$

Dissolver performance may thus be assessed from Eqn.(8.33) and from a knowledge of current density, dissolver diameter and pellet size. Equation (8.33) may be expected to apply also in cases

where the specific resistance of the nitrate electrolyte, K , is similar to that of the electrolyte used (e.g. 3-6N HNO_3) and the metal to be dissolved shows a similar electrochemical behaviour to that of uranium (e.g. stainless steel or stainless steel - UO_2 cermet - Section 8.1). It would be necessary, however, to substitute an appropriate value of the equivalent weight of the metal dissolved in Eqn.(8.10) before an estimate of the value of a could be made.

The validity of Eqn.(8.33) may be tested by considering the results obtained with different size pellets (Sizes 1 and 3). Although these results are insufficient to allow for a satisfactory plot to be derived (Fig.6.4), approximate lines were drawn through the points available and values of a' and n thus obtained were then compared with those estimated from Eqns.(8.29) and (8.32). (Table 8.6).

Table 8.6. Tubular Dissolver

Variation of a' and n with varying Pellet Size.

Dissolver Diam., in.	Length of Middle Section, cm.	Size of pellet.	a'		Voidage frac- tion, e	$0.9 \left(\frac{1-e}{e} \right)$	n
			observed	calc. (1)			
$\frac{3}{4}$	5	1	1.1	1.3	0.36	1.6	1.5
$\frac{3}{4}$	5	3	6.1	6.3	0.47	1.0	1.1

Note: (1) Values of S_u - Section 6.2.2.(d).

Values observed for other sizes of pellets tend thus to be in general agreement with those predicted from Eqn.(8.33).

8.2.2. Energy Consumption.

8.2.2.(a) Model Experiment.

As would be expected, energy consumption expressed in terms of watt-hours consumed per gram of uranium dissolved, was least when the gap of electrolyte separating the electrodes of a given cell was smallest (Fig.8.13). Similarly, energy consumption fell with increase in the number of interposed pellets (cf. increase in current utilisation - Section 7.3.5) and at 8 amp/cm^2 an energy consumption of 4 Wh/g was observed for the 3 pellet multi-cell system compared with about 3.5 Wh/g for a single cell with electrodes $< 0.5 \text{ cm.}$ apart. Consumption rose sharply when (a) the electrodes of a cell system were widely apart (1 pellet multi-cell system and 3.5 cm. separation) thus allowing ohmic polarization to occur and (b) at high current densities ($> 8 \text{ amp/cm}^2$), the limiting current region was approached (2 and 3 pellet systems).

8.2.2.(b) Tubular Dissolver System.

Nearly all the experiments involving the tubular dissolver system fell below the limiting current density region whilst closely packed pellets in the dissolver bed prevented the onset of ohmic polarization (Section 8.1.4).

A variation in energy consumption of $3 \pm 1 \text{ Wh/g}$ was observed (Fig.8.14) over the whole current density range ($0.2 - 8 \text{ amp/cm}^2$) investigated; the increase in energy needed to overcome the electrolyte resistance being counterbalanced by a decrease in polarization resistance of the system. As a conservative estimate,

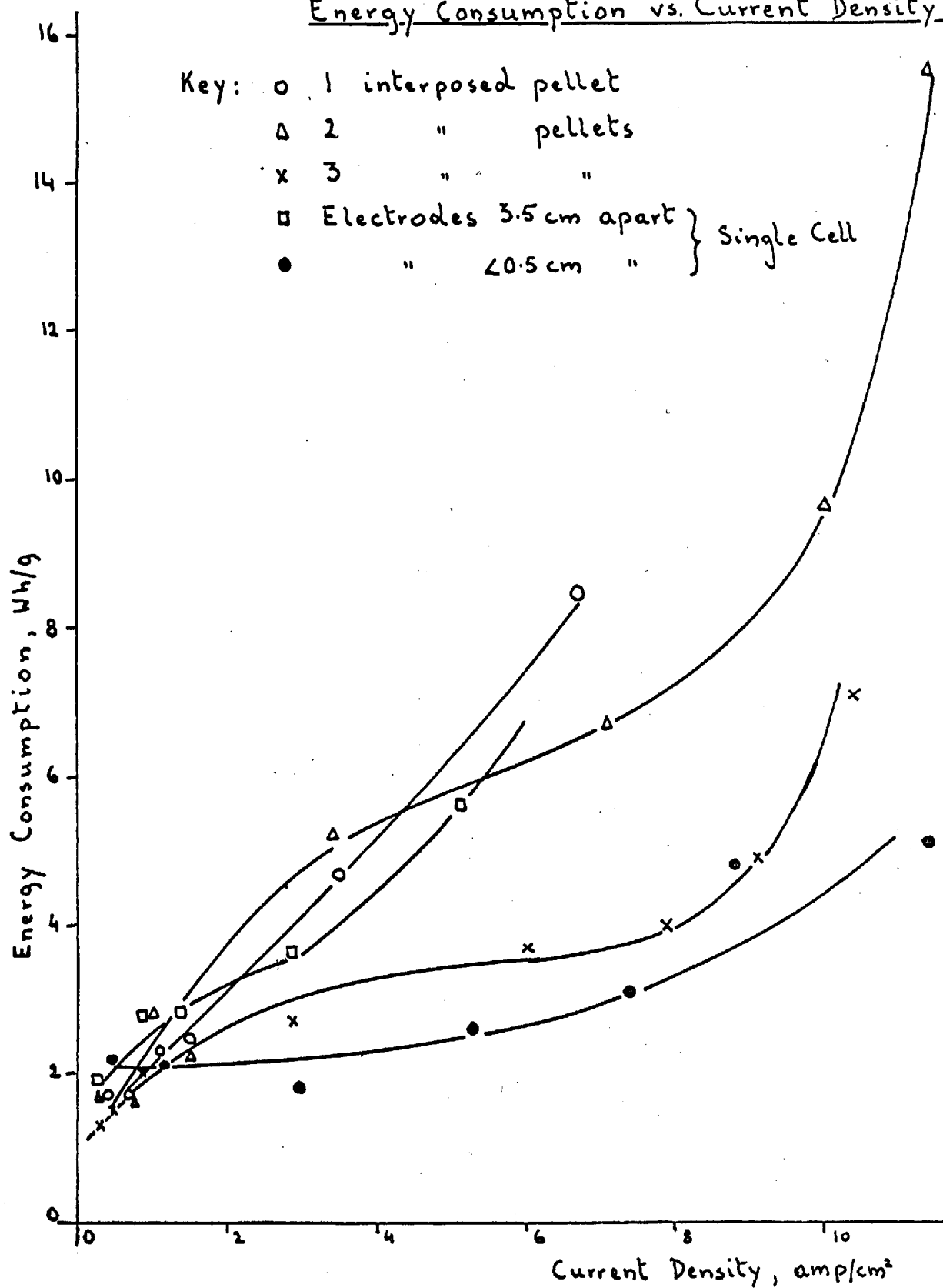
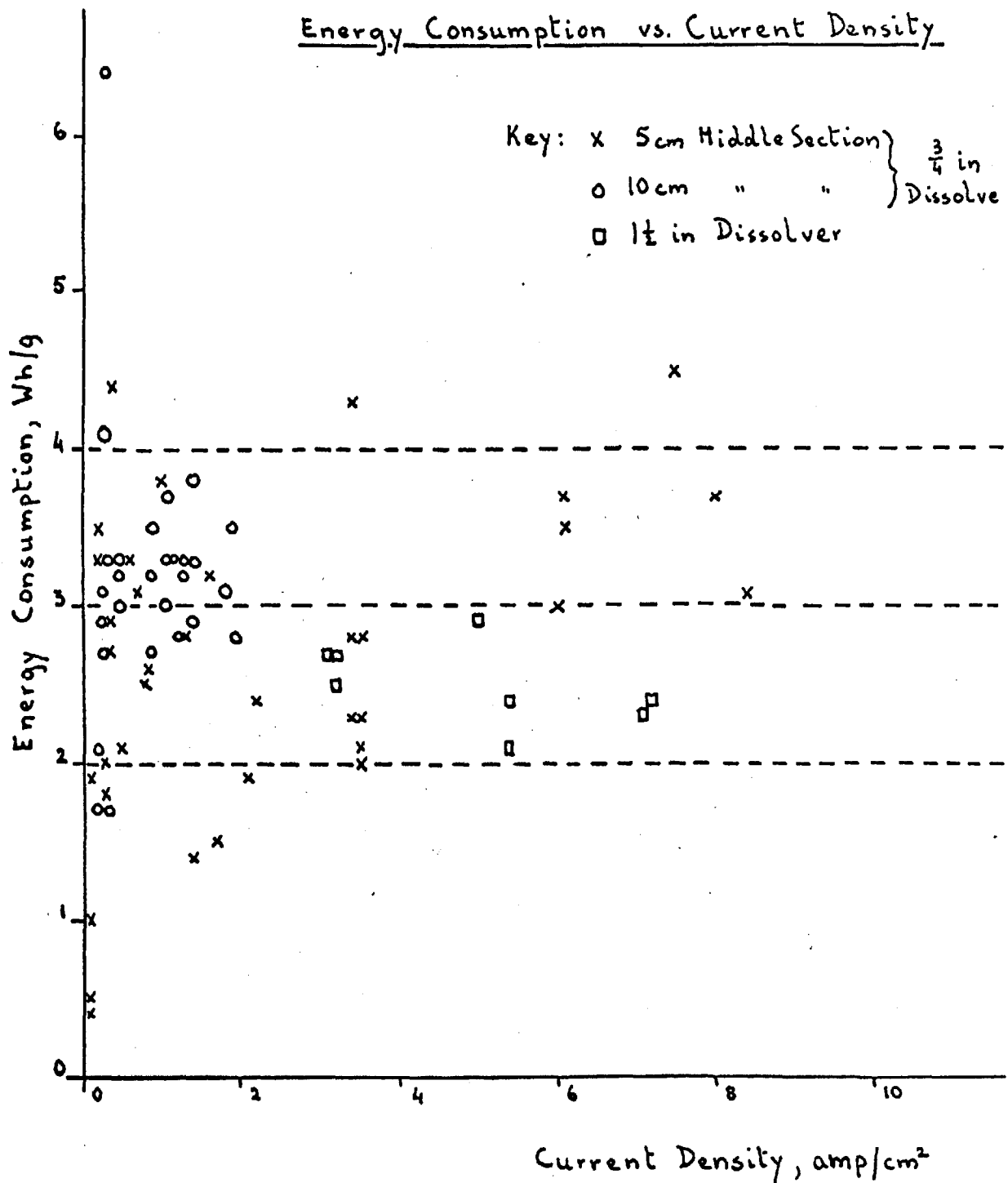
Fig. 8.13. Model ExperimentEnergy Consumption vs. Current Density

Fig. 8.14. Tantalum Dissolver

a figure of 5 Wh consumed per gram of uranium dissolved may be taken to represent the energy consumption in a tubular dissolver. At 2d/kWh⁽⁸³⁾ the cost of electrical energy required to dissolve 1 tonne of uranium becomes therefore,

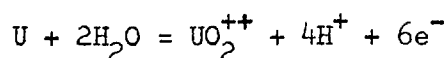
$$\begin{aligned}\text{Cost} &= \frac{5 \times 1000 \times 1000 \times 2}{1000 \times 240} \\ &= £42/\text{tonne}.\end{aligned}$$

This compares favourably with the estimate by Hall and Logsdail⁽⁸³⁾ for cermet dissolution (£55/tonne of cermet) in a basket-type dissolver.

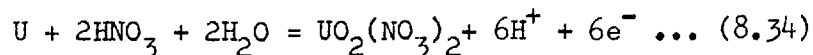
8.3. Dissolution Stoichiometry.

8.3.1. Uranium and Nitric Acid.

Only the presence of hexavalent uranium ions was noted during the course of dissolution experiments (Sections 5.4.2.(f), 7.3.4, Appendix D). It may be assumed, therefore, that the overall electrochemical reaction at the anode was of the form⁽⁸⁴⁾⁽⁸⁵⁾

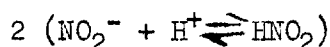
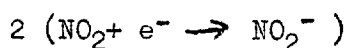
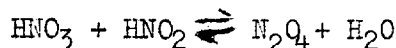


Or, in the presence of nitric acid,

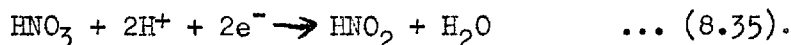


As gas evolution at the anode was negligible (Section 5.4.2.(g)) indicating an absence of purely chemical dissolution, it can be assumed that formation of uranyl nitrate is 100% efficient with respect to nitric acid consumption, i.e. 1 mole of uranium combines with 2 moles of nitric acid to form 1 mole of uranyl nitrate (Eqn.8.34).

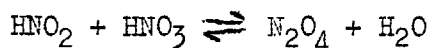
Simultaneously, however, a reduction of nitric acid takes place at the cathode. On stainless steel surfaces this reaction is considered by some authors⁽²²⁾⁽⁸⁶⁾ to be analogous to that which occurs on a platinum electrode viz.



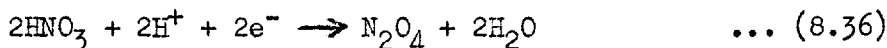
Giving an overall reaction



At high nitrate and hydrogen ion concentrations the nitrous acid decomposes giving,

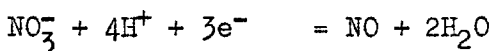
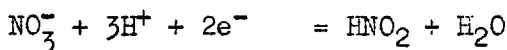
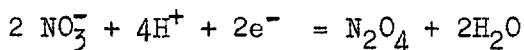


which combined with Eqn.(8.35) leads to the overall cathodic reaction

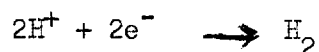
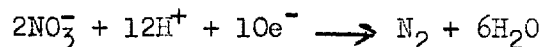
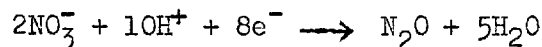
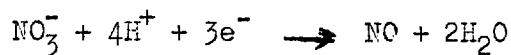


Theoretical considerations led McIntosh and Evans⁽⁸⁷⁾ to

postulate the following reactions on a stainless steel cathode in nitric acid:



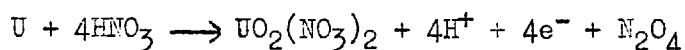
On a tantalum surface in 1M nitric acid cathodic reduction was said⁽⁴⁷⁾ to occur as follows:



Thus in all cases the electrolytic reduction of nitric acid results predominantly in a mixture of nitrogen oxides being evolved at the cathode. Less than 2% hydrogen was observed in the off-gas from the tantalum cathode⁽⁴⁷⁾, corresponding closely with the amount found when a stainless steel cathode was used (Section 5.4.2.(g)). It may therefore be assumed that the cathodic reduction of nitric acid is relatively independent of the nature of the cathode material and consequently a similar set of reactions may be expected to occur on a uranium cathode. Similar quantities of gas were evolved off both the stainless steel and uranium cathodes (110-150 ml/amph at 20-25°C. - Section 5.4.2.(g)) and off the tantalum cathode⁽⁴⁷⁾ (30-150 ml/amph at 50°C.).

Expressed stoichiometrically, the observed rate of gas evolution (both stainless steel and uranium cathodes) was 18-24 l/mole of uranium dissolved (Section 5.4.2.(g)). Thus approximately 1 mole of gas (22.4 l at STP) is evolved per mole of uranium dissolved. Now from the reactions given above, for each mole of gas formed,

1-2 moles (depending on the oxide formed) of nitric acid are reduced. By combination with Eqn.(8.34) we have, therefore, that for each mole of uranium dissolved, three to four moles of nitric acid are consumed (cf. 4-4.4 moles of nitric acid/mole of metal obtained by Slansky⁽²²⁾) resulting in the production of one mole of uranyl nitrate and one mole of gas. For example from Eqns.(8.34) and (8.36),



As gas evolution did not appear to vary greatly over the whole range of cathodic current densities investigated (0.25-0.7 amp/cm²) it may be assumed that the dissolution stoichiometry is independent of current density. Slansky⁽²²⁾ observed this and also found that the stoichiometry was dependent on hydrogen ion concentration; higher nitric acid consumption being observed at higher concentrations (4 moles/mole at 1M HNO₃, 4.4 moles/mole at 5M HNO₃). Although sufficient results are not available to confirm this in the present work, it may be noted that the consumption of 6N HNO₃ is significantly higher than the average obtained using 3N HNO₃ (Section 5.4.2.(b) - Table 5.6).

Provided an efficient off-gas recovery system is used, however, or a sufficient volume of oxygen-rich electrolyte is present to absorb the gases formed, the net consumption of nitric acid will approximate to the stoichiometric quantity of 2 moles of nitric acid per mole of uranium dissolved (Section 5.4.2.(b)). Under those

circumstances, electrolytic dissolution resembles fumeless (chemical) dissolution (Section 5.3.2.(a) - Eqn.5.4).

8.3.2. Sludge Formation.

Only very small quantities of finely particulate sludge were formed during dissolution of uranium when tantalum electrodes were used. The sludge formed was black in colour and remained suspended in the electrolyte settling gradually if the solution was allowed to stand undisturbed for longer than about 3 days. Based upon figures observed for stainless steel electrodes (Section 5.4.2.(e)), dissolution of about 1 kg U led to the formation of 1 g of sludge. Visual evidence would indicate that use of tantalum electrodes does not increase the rate of sludge production.

The physical appearance of the sludge supports the earlier suggestion (Section 5.4.2.(e)) that it results largely from the uranium impurities (e.g. C, Si). The amount of sludge formed will thus be a function of the metal composing the dissolver charge and higher quantities of sludge might therefore be expected when stainless steel or stainless steel - UO_2 cermet is dissolved.

It has been suggested,⁽²²⁾ however, that the amount of sludge formed also depends on the process conditions (e.g. temperature, current density, acidity). Consequently it should be possible to reduce sludge formation by a suitable choice of conditions for a given process.

8.4. Dissolver Vessel.

8.4.1. Materials of Construction.

Both the metal used for the cylindrical electrodes and the insulation material must be resistant to chemical and electrolytic attack by the electrolyte and capable of maintaining both their corrosion resistance and mechanical strength under conditions of intense irradiation. Tantalum, chosen originally for its resistance to electrolytic attack (Section 6.1), is considered suitable for the construction of the metallic sections of an industrial dissolver vessel. Choice of an insulator was more difficult because the majority of plastic materials are damaged under irradiation⁽²⁴⁾⁽⁸⁸⁾ (this is particularly true of p.t.f.e. - used throughout this work).

8.4.1.(a) Tantalum.

(i) Pitting.

The presence of "craters", observed on the surface of the anodic tantalum section (Sections 6.2.2.(b) and 6.3.2.(b)), was also noted by workers investigating the performance of a niobium basket dissolver⁽³⁷⁾. This effect was attributed to the high contact temperatures which can be developed between the charge and the anode basket (or, in the case of the tubular dissolver, between the uranium bed and the anode section) leading to poor

electrical contact, oxidation and subsequent melting of the oxide on the valve metal surface. Thus the following relationship between the maximum contact temperature ($^{\circ}\text{K}$), T , and the contact potential (volts), V_c , has been quoted⁽³⁷⁾ :

$$T^2 = T_o^2 + 10^7 V_c^2 \quad \dots (8.37)$$

where T_o = temperature of massive metal, $^{\circ}\text{K}$.

From Eqn.(8.37) it can be seen that even at very low contact potentials (0.7V), very high contact temperature may occur (about 2000°C . - m.pt. Ta_2O_5 - 1870°C .⁽⁸⁹⁾) leading to pitting and erosion of the tantalum surface.

Visual examination of the surfaces of the dissolver tubes showed, however, that far fewer pitting marks were present in the case of the $1\frac{1}{2}$ in. dia. dissolver than in the case of the smaller $\frac{3}{4}$ in. dia. vessel. As the maximum voltages applied were approximately the same (about 70V) in both cases, the smaller incidence of pitting in the wider vessel may be attributed to the higher contact force exerted by the greater weight of the uranium bed (2-2.5 kg vs. 0.6-0.7 kg) and the consequent improvement in contact between the uranium and the tantalum. Thus a lowering of contact resistance with increase in contact force was observed when electrical contact between stainless steel and niobium was investigated⁽³⁷⁾. It may therefore be assumed that the problem of pitting will be reduced provided a sufficient weight of charge is present in the dissolver.

(ii) Hydrogen Embrittlement.

Although both tantalum and niobium are subject to hydrogen embrittlement⁽²³⁾⁽⁴⁷⁾⁽⁹⁰⁾, extensive tests have shown that neither metal suffers from it under cathodic conditions in nitric acid⁽²³⁾⁽⁴⁷⁾. Lack of hydrogen embrittlement may also be regarded as auxiliary evidence that hydrogen forms only a small fraction of the cathode gas given off during the electrolytic decomposition of nitric acid.

(iii) Effect of Radiation on Overvoltage.

Photoconduction on irradiation with ultra-violet light or soft X-rays has been observed with a tantalum anode in solution⁽⁹¹⁾. Even at an applied voltage of 140V, however, the photocurrent measured amounted to less than 100 μ A.

An electrolytic cell with both niobium and tantalum electrodes (10M nitric acid electrolyte) was tested in a radiation field of 10^7 rep/hr.⁽⁴⁷⁾. At an applied voltage of 18V no increase in the steady diffusion current (0.2 mA) was observed during exposures of up to 10^9 rep. It may be expected, therefore, that the overvoltage of tantalum will not be affected significantly by the high radiation fields obtaining in a plant-scale dissolver under process conditions.

8.4.1.(b) Insulating Material.

Of all the plastic materials investigated for their stability to radiation in dissolver product solutions⁽²⁴⁾⁽²⁶⁾⁽²⁹⁾ only a

polyethylene type plastic⁽²⁴⁾ and a glass fabric-silicone resin⁽²⁹⁾ were found to withstand dose rates of up to 4×10^6 R/hour to a total dose of 10^9 R. A useful life dose of up to 10,000 Mrad has been quoted for a glass fabric-silicone resin, whilst the life dose of polyethylene was placed at 2000 Mrad⁽⁸⁸⁾. Alumina also proved to be satisfactory under testing, but it is considered that a plastic type material would be preferable due to its ease of fabrication.

The glass fabric-silicone resin appears to be the more suitable insulating material and at an estimated dose rate of 1 Mrad/hour would be expected to remain serviceable for about 1 year of operation under dissolver plant conditions.

8.4.2. Scale-Up.

8.4.2.(a) Size of Dissolver.

(i) Length of Middle Section and Voltage Gradient.

The total overall voltage which may be applied across the middle section of a dissolver is governed primarily by the over-voltage of the tantalum electrodes and should therefore not exceed 180V if the electrolytic inertness of the tantalum anode is to be preserved (Section 6.1.). Allowing for a margin of safety, an overall potential of 140V has been chosen as the operational value.

A voltage gradient of 8V/cm. appears to be the minimum at which maximum current efficiency, particularly in the case of the $1\frac{1}{2}$ in. dia. dissolver, is attained (Figs. 8.6 and 8.10). Based

on 8V/cm. a length of middle section of about 18 cm. (approx. 7 in.) is obtained. Allowing for a 10 cm. length of bed charge in each of the electrodes, the overall length of bed in the dissolver is about 38 cm. (approx. 15 in.).

(ii) Diameter and Current Density.

The diameter of the dissolver vessel is limited by the criticality consideration and will be taken as 2.5 in. (6.3 cm.) (Chapter 3) giving a cross-sectional area of 31.2 cm^2 .

From data obtained with the $\frac{3}{4}$ in. dia. dissolver we see that at a constant voltage gradient of 8V/cm. the current increases by about 8.5 amp with a 5 cm. increase in length of middle section (5 and 10 cm. middle sections - Fig. 6.1). Assuming that a similar increase in current will occur when the length of middle section is increased by a further 7.5 cm., we obtain for a $\frac{3}{4}$ in. dia. dissolver and 8V/cm. voltage gradient.

Current flowing - 10 cm. middle section = 21 amp (Fig. 6.1)

" " - 17.5 cm. " " ≈ 30 amp (estimated).

At 8V/cm. an increase of about 20% in the current flowing occurs when the bed diameter is doubled from $\frac{3}{4}$ in. to $1\frac{1}{2}$ in. (Fig. 6.5 and Table 8.3).

Thus current flowing through an equivalent $1\frac{1}{2}$ in. dia. dissolver (17.5 cm. middle section) = $30 \times 1.2 = 36$ amp.

Assuming that an increase of 10% in the current occurs when the dissolver diameter is raised from $1\frac{1}{2}$ to $2\frac{1}{2}$ in., then:

Current flowing through $2\frac{1}{2}$ in. dia. dissolver $\approx$ 40 amp.
(8V/cm., 17.5 cm. middle section).

8.4.2.(b).Performance of Dissolver.

(i) Throughput and Material Balance.

Assuming bed charge to be composed of fuel pieces which approximate to No.3 Size pellets ($\frac{1}{4}$ in. dia. x $\frac{3}{8}$ in. long) :

$$\frac{D_P}{D_T} = \frac{0.25}{2.5} = 0.1$$

where D_P = diameter of particle

D_T = diameter of dissolver tube.

Voidage fraction, $e = 0.37$

(according to Leva⁽⁶⁰⁾, for smooth, uniform spherical particles).

$$\therefore \frac{0.9(1 - e)}{e} = 1.5 \quad (\text{Eqn.8.32}).$$

Surface area of pellets per unit length of bed charge, S_u ,

$$= \frac{11 \times 31.2}{2.8} = 123 \text{ cm}^2/\text{cm}.$$

$\therefore$ From Eqn.(8.33) :

$$\begin{aligned} \text{Dissolution Rate, } G &= 24.7 \times \frac{31.2}{123} \times (1.25)^{1.5} \\ &= 8.8 \text{ mg/min.cm}^2 \end{aligned}$$

$\therefore$ Throughput of dissolver for a 17.5 cm. length of middle section,

$$\begin{aligned} &= \frac{8.8 \times 123 \times 17.5 \times 60}{1000 \times 1000} \\ &= 1.14 \text{ kg U/hr.} \end{aligned}$$

Which is equivalent to 8.2 tonne U/year (300 days).

It must be noted that the estimated throughput quoted above is based on the performance of the dissolver operating at (a) fairly low electrolyte temperatures (25-40°C.) maintained during the course of the experiments and (b) in the absence of a radiation field. Published evidence suggests that higher electrolyte temperatures would improve the performance. Thus a temperature range of 60-70°C. was recommended for the anodic dissolution of stainless steel⁽²⁴⁾⁽²⁵⁾ in nitric acid whilst a marked rise in the dissolution rate of a uranium anode was observed with increase in temperature (from 37.5 to 90°C.) of the electrolyte (5N H₂SO₄)⁽⁹²⁾.

Data on the effect of irradiation are somewhat contradictory. Thus no increase in the chemical dissolution rate of irradiated uranium in 4M H₂SO₄ as compared with unirradiated samples was observed by Swanson⁽⁹³⁾ whilst noble metal fission products were suspected of contributing to an increased corrosion rate of irradiated uranium noted by other workers⁽⁹²⁾. Electron bombardment lowered the anodic and cathodic overvoltages of certain metals⁽⁹⁴⁾ e.g. Zr, Ti (cf. effect on tantalum - Section 8.4.1.(a)) but it is not expected that a marked change in the performance of the dissolver will result when irradiated fuel pieces are processed.

Now, expressing the throughput in moles :

$$\text{Throughput/hour} = 4.8 \text{ g moles U/hr.}$$

Assuming no off-gas recovery and 4 g moles of nitric acid consumed per g mole uranium dissolved (Section 8.3.1.), we have :

$$\text{Acid required/hour} = 19.2 \text{ g moles HNO}_3/\text{hr.}$$

$$\approx 6.4 \text{ } 3\text{N HNO}_3/\text{hr.}$$

We also have as products, 4.8 g moles $\text{U O}_2(\text{NO}_3)_2$ per hour (i.e. 1.89 kg/hr.) and 4.8 g moles gas/hr. (at S.T.P.) (i.e. 108 l/hr.).

(ii) Energy Consumption and Heat Evolution.

From data in Section 8.4.2., we have:

$$\text{Power Input of Dissolver} = \frac{140 \times 40}{1000} = 5.6 \text{ kWh/hr.}$$

$$\therefore \text{Energy Consumption} = \frac{5.6}{1.14} = 5 \text{ Wh/g U dissolved}$$

i.e. the cost of electrical energy required for dissolution is of the same order (£40-£45 per tonne of uranium) as that calculated earlier (Section 8.2.2.(b)) in the case of the pilot plant dissolver.

Now, assuming the total power input to be converted into heat, we have :

$$\begin{aligned} \text{Heat Output of Dissolver} &= 5.6 \times 860 = 4820 \text{ kcal/hr.} \\ &(\text{Electrical}) \end{aligned}$$

Calculations carried out by Slansky et. al.⁽²²⁾ in the case of the electrolytic dissolution of stainless steel and Chittenden⁽⁹⁵⁾ in the case of uranium have shown that the ratio of chemical to electrical heat liberated is of the order of 1:3.

$$\therefore \text{Heat Output of Dissolver} \approx 1600 \text{ kcal/hour} \\ (\text{Chemical})$$

$$\begin{aligned} \therefore \text{Total Heat Output (Chemical + Electrical)} \\ = 6420 \text{ kcal/hour.} \end{aligned}$$

(iii) Electrolyte Flow Rate and Pressure Drop.

Under steady state conditions, the total heat output of the dissolver would have to be removed by the circulating electrolyte. Allowing for a 10°C . rise in the temperature of the electrolyte, we have

$$\text{Electrolyte Flow Rate} = \frac{6500}{0.81 \times 10} = 800 \text{ kg/hour}$$

where the specific heat of the electrolyte is taken as the specific heat of 3 N HNO_3 = 0.81⁽⁹⁶⁾.

Taking the S.G. of the electrolyte (3N HNO_3 + 80 g U/l) as 1.2⁽⁹⁷⁾, we have

$$\begin{aligned} \text{Superficial Velocity of Electrolyte} &= \frac{800 \times 1000}{1.2 \times 3600 \times 31.2} \\ &= 5.9 \text{ cm/s (0.2 ft/s).} \end{aligned}$$

Pressure drop per foot-length of dissolver charge may be estimated from equations tested previously (Section 4.2). Thus :

(a) On the basis of Leva's equation (Eqn.4.12)

$$\frac{\Delta P}{L} = \frac{3.50 G^{1.9} \mu^{0.1} (1-e)^{1.1}}{D_P^{1.1} \phi_s^{1.1} \rho_F g_c e^3}$$

where, using the symbols as defined in Section 4.2., we have for

No.3 Size pellets and 3N HNO_3 electrolyte,

D_P = diameter of the equivalent-volume sphere
(Leva⁽⁹⁸⁾)

$$= 0.33 \text{ in.}$$

$$\phi_s = 0.85 \text{ (Leva⁽⁹⁸⁾)}$$

$$e = 0.34 \text{ (Leva⁽⁶⁰⁾)}$$

(assuming originally a bed of smooth, uniform cylinders and $D_P = 0.25 \text{ in.}$)

$$\mu_{250} = 1.1 \text{ cP}^{(99)}$$

$$L = 1 \text{ ft.}$$

Substituting for the appropriate values in Eqn.(4.12) :

$$\begin{aligned} \Delta_P &= 106 \text{ lb/ft.}^2 \\ &= 0.74 \text{ lb/in.}^2 \text{ per foot-length of dissolver} \\ &\quad \text{charge.} \end{aligned}$$

(b) On the basis of the correlation developed by Chennakesavan and Laddha (Eqn.4.10)

$$\frac{\Delta H_B e^4}{\Delta H_T} = 24.8 \left[\left(\frac{D_T}{D_P} \right) (1.5) (1-e) \lambda + 1 \right] - 22.3$$

Using the symbols as defined in Section 4.2. and substituting for values characteristic of the packing, electrolyte and proposed dissolver size, we obtain

$$\begin{aligned} \Delta H_B &= 2.64 \text{ ft. of electrolyte} \\ &= 3.16 \text{ ft. of water} \\ &= 1.37 \text{ lb/in.}^2 \text{ per foot-length of charge.} \end{aligned}$$

Now in the case of the $1\frac{1}{2}$ in. dia. dissolver (nearest in size to the dimensions of the proposed plant-scale vessel), using Size 2 pellets, the observed pressure drop compares as follows with values calculated from Eqns.(4.10) and (4.12) (Table 8.7) :

Table 8.7. Comparison of Observed (Typical Values) and Calculated Pressure Drop Values.

$1\frac{1}{2}$ in. dia. Dissolver - No.2 Size Pellets.

Overall length of bed, in.	Flow rate $\bar{V}$ /min.	Δp obs. lb/in. ² per foot.	Δp_1 lb/in. ² per foot.	Δp_2 lb/in. ² per foot.
9	8.5	2.7	5.8	9.2
	11.0	4.0	9.8	14.6

Note: Δp_1 - Pressure Drop from Eqn.(4.12).

Δp_2 - Pressure Drop from Eqn.(4.10).

Thus the correlation of Chennakesavan and Laddha (Eqn.4.10) which was derived largely on the basis of spherical packings⁽⁵⁷⁾ appears to break down when cylindrical particles are considered. Both estimated values, however, are higher than the observed value suggesting that a certain amount of channeling might have occurred within the dissolver bed, an effect which would tend to lower the observed pressure drop.

As a conservative estimate, therefore, a pressure drop of 1 lb/in.² per foot-length of dissolver charge may be taken in the case of the proposed plant-scale dissolver, giving an overall value of 1.25 lb/in.² for the pressure drop across the length of bed considered (Section 8.4.2.(a)).

A summary of the performance and characteristics of the dissolver is given in Table 8.8.

Table 8.8. Anodic Dissolution of Uranium in Nitric Acid.
Summary of Proposed Plant-Size Dissolver
Characteristics and Performance.

Length of Middle Section	17.5 cm.
Overall Length of Dissolver Bed	37.5 cm.(approx.)
Diameter (internal)	6.3 cm.(2.5 in.)
Overall Voltage Applied	140V
Current (d.c.)	40 amp
Voltage Gradient	8 V/cm.
Current Density	1.25 amp/cm ²
Power Input/hour	5.6 kWh
Heat Evolved/hour	6420 kcal
Electrolyte Flow Rate/hour	800 kg
Pressure Drop/foot length of bed	1 lb/in. ²
Material Balance (Hourly Basis)	
Reactants In	Products Out
1.14 kg U	1.89 kg $\text{UO}_2(\text{NO}_3)_2$
6.4 lb 3N HNO_3	108 lb gas at S.T.P.

8.5. Comparison of the Tubular Dissolver with the Basket
and Series (Liquid Contact) Dissolvers.

Both the tubular dissolver investigated here and the series dissolver developed by Bomar⁽³⁰⁾ operate on the principle of allowing current to flow through a number of fuel pieces interposed between the electrodes. As the current flows from piece to piece,

a number of cells are set up in series allowing a current efficiency greater than 1 equivalent per faraday to be achieved.

Whilst direct metal-to-metal contact was used to convey current to the bed in the tubular dissolver, Bomar sought to obviate the problem of contact resistance by using a platinum anode to convey the current to the electrolyte and hence to the interposed fuel pieces. The use of platinum, however, results in the evolution of oxygen at the anode, a characteristic considered undesirable in view of the presence of hydrogen in the off-gas (Section 8.3.1).

In the case of the basket dissolvers investigated, both on laboratory⁽³³⁾⁽³⁶⁾⁽³⁸⁾ and on semi-plant scale⁽³⁵⁾⁽³⁷⁾⁽⁴⁰⁾, the fuel charge behaved as part of the anode with the current flowing from it and through a layer of electrolyte to the cathode. Current efficiencies greater than 1 equivalent per faraday could thus not be achieved as in effect only a one cell system was in operation.

In order to obviate the problem of contact resistance, the basket dissolver system was adapted to the liquid contact method⁽³⁷⁾⁽⁴¹⁾⁽⁴²⁾. As the fuel pieces forming the dissolver charge were joined together, however, the charge was equivalent to one large, interposed block of metal (cf. model experiment, one interposed pellet - Section 7.3.5) dissolving only on the side facing the cathode. Again current efficiencies greater than 1 equivalent per faraday could not be achieved.

The basket type dissolver (a one cell system) resulted in a low voltage - high current unit particularly when large throughputs were desired. The tubular and series dissolvers on the other hand required a relatively high voltage - low current power supply. In general the latter system is preferable as it obviates the disadvantages of a high current-low voltage supply, e.g. the need for heavy bus-bars and water-cooled conductors.

8.6. Conclusions and Recommendations for Future Work.

It has been shown that a bed of metal pellets may be dissolved electrolytically in a vessel of critically safe dimensions, using nitric acid as the electrolyte. The dissolver system operates on a basis of multi-cell formation thereby allowing current efficiencies many times greater than 100% to be achieved.

Although natural uranium was the only metal whose anodic behaviour was investigated, it is considered that the electrolytic dissolver developed may be used equally successfully to process other metals of importance in the nuclear fuel programme e.g. uranium alloys, stainless steel and stainless steel - WO_2 cermets. It is not regarded, however, as a method suitable for the processing of zirconium or zirconium alloys as large amounts of ZrO_2 produced as a result of the anodic disintegration of zirconium in nitric acid would tend to block the dissolver bed. In the latter case alternative electrolytes (e.g. HCl - methanol) may have to be used.

It is considered that the system investigated is sufficiently simple and reliable to be adapted for continuous, remote control operation. Suitable materials of construction exist which would allow the dissolver vessel a limited but sufficiently long period of operation under conditions of intense radiation.

The physico-chemical behaviour and mode of operation of the dissolver could be elucidated further by the following investigations :

- (i) a detailed investigation of the overvoltage - current density behaviour of any given metal whose electrolytic dissolution is considered. This would allow for a better estimate of the optimum current density of dissolution and electrolyte temperature to be made;
- (ii) the influence of irradiation (both γ and fission product) on the electrode potential and hence the anodic dissolution characteristics of the metal.
- (iii) an extension of the model multi-cell experiment by using greater numbers of interposed pellets and a study of the current path, current utilisation and cell formation within the tubular dissolver by using a two-dimensional model of the dissolver bed.

It is expected that the use of such models would allow a more precise evaluation of the constants involved in the dissolution equations linking current density and dissolution rate (Section 8.2.1). Allied to these investigations, a qualitative study of

bed behaviour may also be made by using a transparent tube to enclose the middle section thus allowing phenomena such as flashing and electrolyte flow patterns during dissolution to be observed.

Chapter 9.

Design Suggestions for a Plant-Size Dissolver.

Chapter 9.

Design Suggestions for a Plant-Size Dissolver.

9.1. Introduction.

9.2 Description of Equipment.

9.2.1. Dissolver Vessel.

9.2.2. General.

9.3. Annular Dissolver.

9.1. Introduction.

The simple tubular dissolver (Fig.5.1.) proved satisfactory as a laboratory-scale, batch dissolution unit. Although such a unit could be developed into a plant-size dissolver ($2\frac{1}{2}$ in. I.D., flanged joints throughout, insulator covered metal middle section) it would suffer from serious disadvantages viz. (1) difficulty of removal and replacement in the flow circuit by remote control, and (2) the danger of an integral section of the dissolver flow circuit (i.e. the dissolver vessel itself) being at a relatively high potential (140V) with respect to the rest of the system. Thus even if the dissolver vessel were insulated from the remainder of the flow circuit by means of suitable gaskets inserted at the flanged joints, failure of such insulation could result in electrification of the whole dissolution system.

To overcome these disadvantages a modified design is outlined which could fulfill better the requirements of a remotely controlled, continuously operating plant-size unit (Chapters 1 and 3).

9.2. Description of Equipment.

9.2.1. Dissolver Vessel.

The presence of plastic insulating materials in the construction of the dissolver limits the life of a unit to a period of about 1 year (Section 8.4.1.). It is considered, therefore, that ease of removal and replacement of the dissolver unit is of great importance

in the design of a remotely controlled vessel.

A dissolver consisting, in effect, of two vessels is proposed. An inner vessel (Fig.9.1) forms the dissolver proper and consists of both an anodic and a cathodic section separated by a length of plastic insulating material (middle section). This inner vessel is held vertically inside an outer, all-metal shell (Fig.9.2.) to which all the supply and take-off lines necessary for operating the dissolver are connected (e.g. electrolyte inlet and outlet, fuel charge chute). The inner dissolver vessel may therefore be removed for replacement or inspection without disturbing the rest of the dissolution circuit and the outer shell which forms an integral part with the dissolver circuit remains electrically neutral.

9.2.1.(a) Inner Vessel.

The inner part of the dissolver (Fig.9.1.) consists basically of a tantalum tube covered both on the inside and on the outside with a layer of glass-fibre silicone resin. One end of the tube (lower) is closed by means of a perforated tantalum base-plate, also covered with insulating material. A tantalum cover is attached to the upper end of the tube. Rings fixed to the cover allow the whole assembly to be withdrawn from the dissolver circuit when necessary. A section of the tube at the upper end of the dissolver is cut away in order to allow for fuel pieces and electrolyte flow to enter the dissolver.

Fig. 9.1. Proposed Plant-Size Dissolver - Inner Vessel

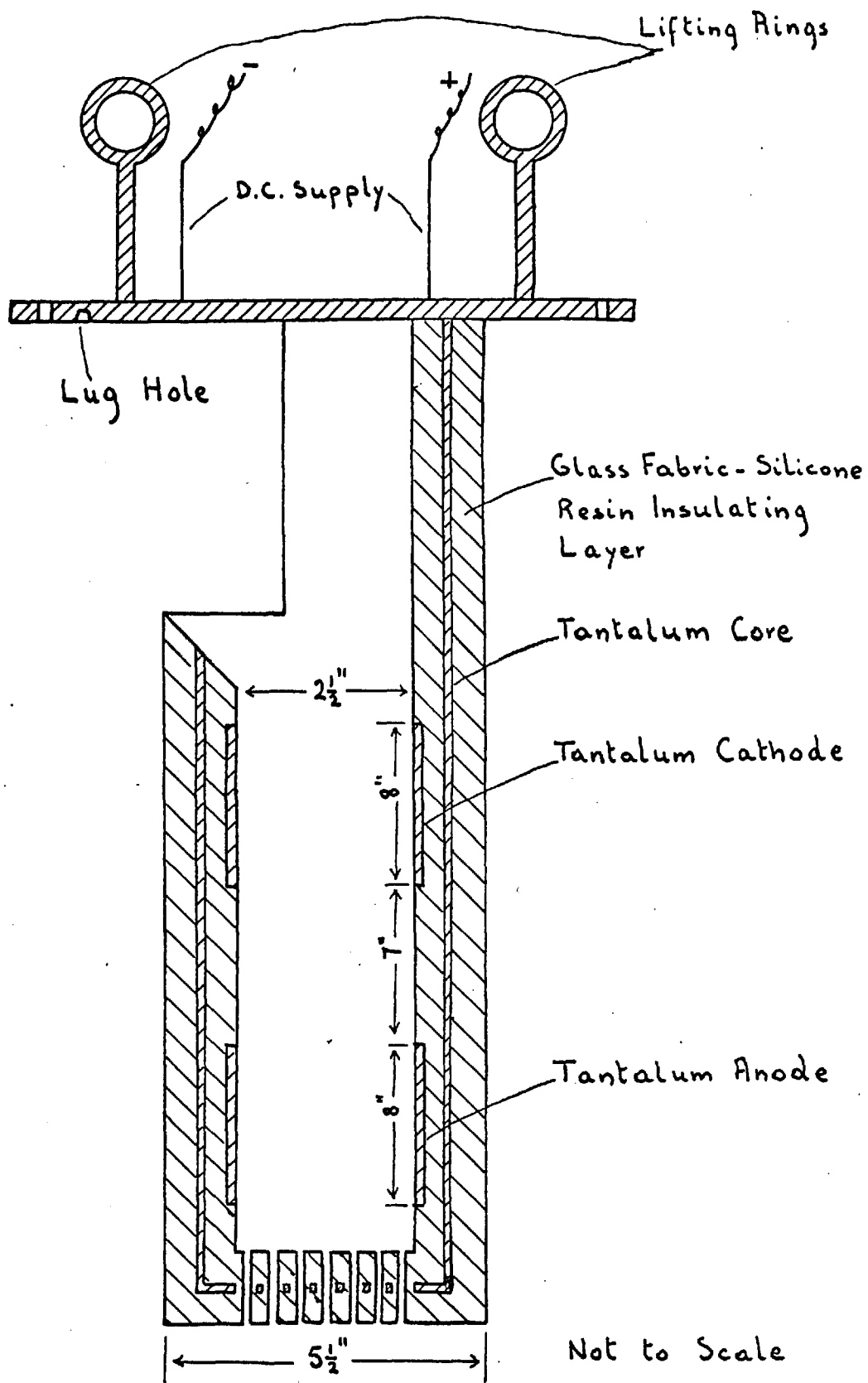
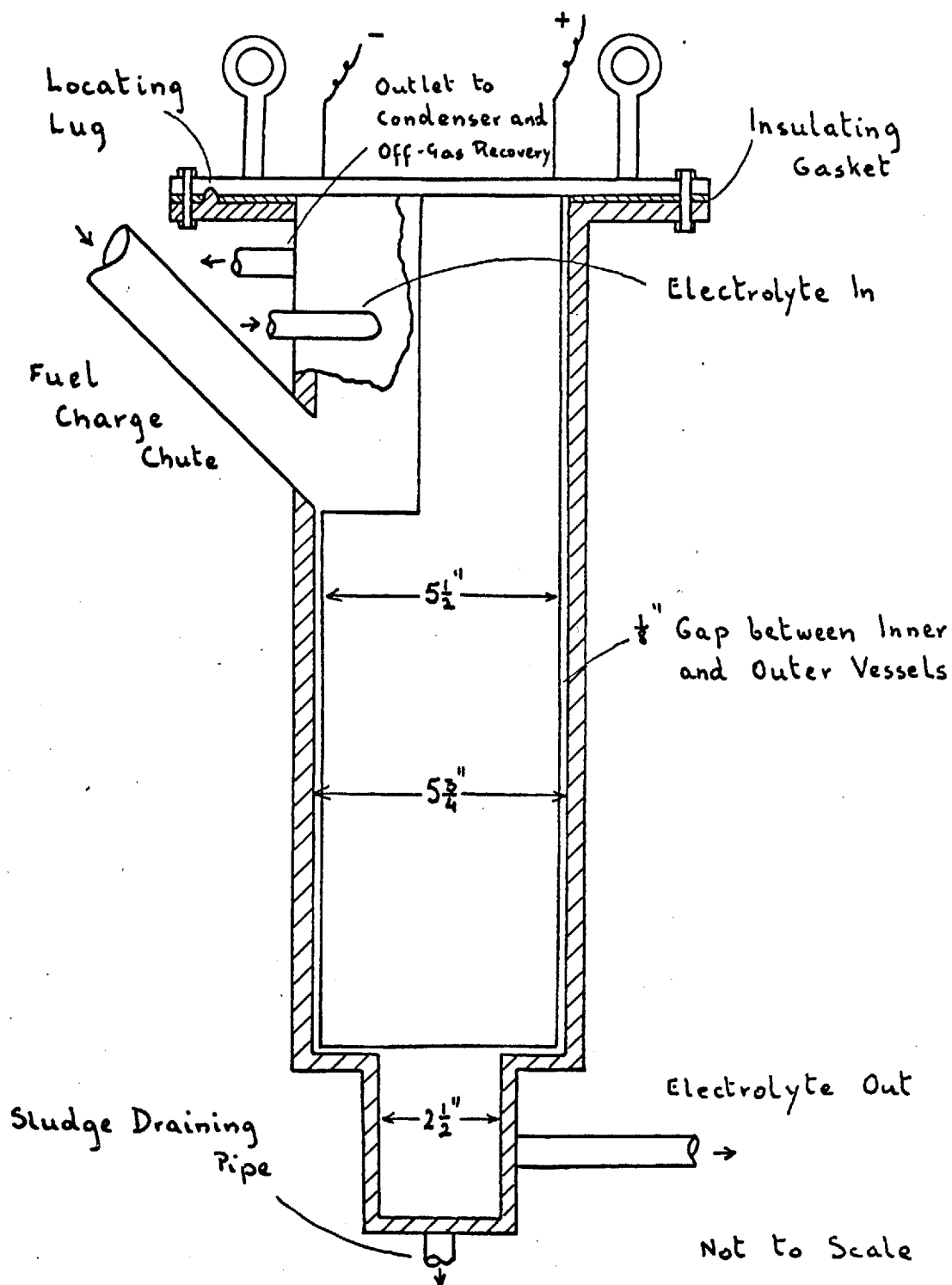


Fig. 9.2. Proposed Plant-Size Dissolver - Outer Vessel
(Inner Vessel Outlined in Position)



Electric current is conveyed to the fuel charge within the dissolver by means of two tantalum rings (one anodic, one cathodic) set into the layer of insulating material on the inside of the dissolver vessel. These rings are separated in a vertical plane by a length of insulating material which forms the middle section within which most of the electrolytic dissolution of the fuel occurs. The tantalum electrodes are connected to the source of d.c. power by means of leads set into the plastic insulating layer (detail not shown in Fig.9.1.) and passing straight through the dissolver cover. In order to prevent the lead connected to the lower (anodic) sleeve from touching the upper (cathodic) sleeve it is suggested that the lead to the anode be set into the insulating layer covering the outside of the tantalum tube.

The principal dimensions and characteristics of the proposed (inner) dissolver vessel are given below:

Table 9.1. Dimensions and Characteristics of Proposed Dissolver.
(Inner Vessel).

Materials of Construction: Metal	Tantalum
Insulator	Glass fabric-silicone resin.
I.D. of dissolver	2 $\frac{1}{2}$ in.
I.D. of tantalum tube	3 $\frac{3}{4}$ in.
Thickness of insulating layer at either side of tantalum tube	$\frac{5}{8}$ in.
Metal thickness: (a) tantalum tube, conducting sleeves and base plate	$\frac{1}{4}$ in.
(b) cover plate	$\frac{1}{2}$ in.

Table 9.1. - contd.

Length of Middle Section	7 in. (17.5 cm. - Section 8.4.2.).
Length of each of the conducting sleeves	8 in.
Overall length of fuel charge	2-2 ¹ / ₂ ft.
Pressure drop due to fuel charge at an electrolyte flow rate of 800 kg/hour	2-2 ¹ / ₂ lb/in. ² (estimated - Section 8.4.2.).

Note: A greater length than that originally suggested (4 in. = 10 cm. - Section 8.4.2.) is proposed in order to minimise still further any contact resistance effects.

9.2.1.(b) Outer Vessel.

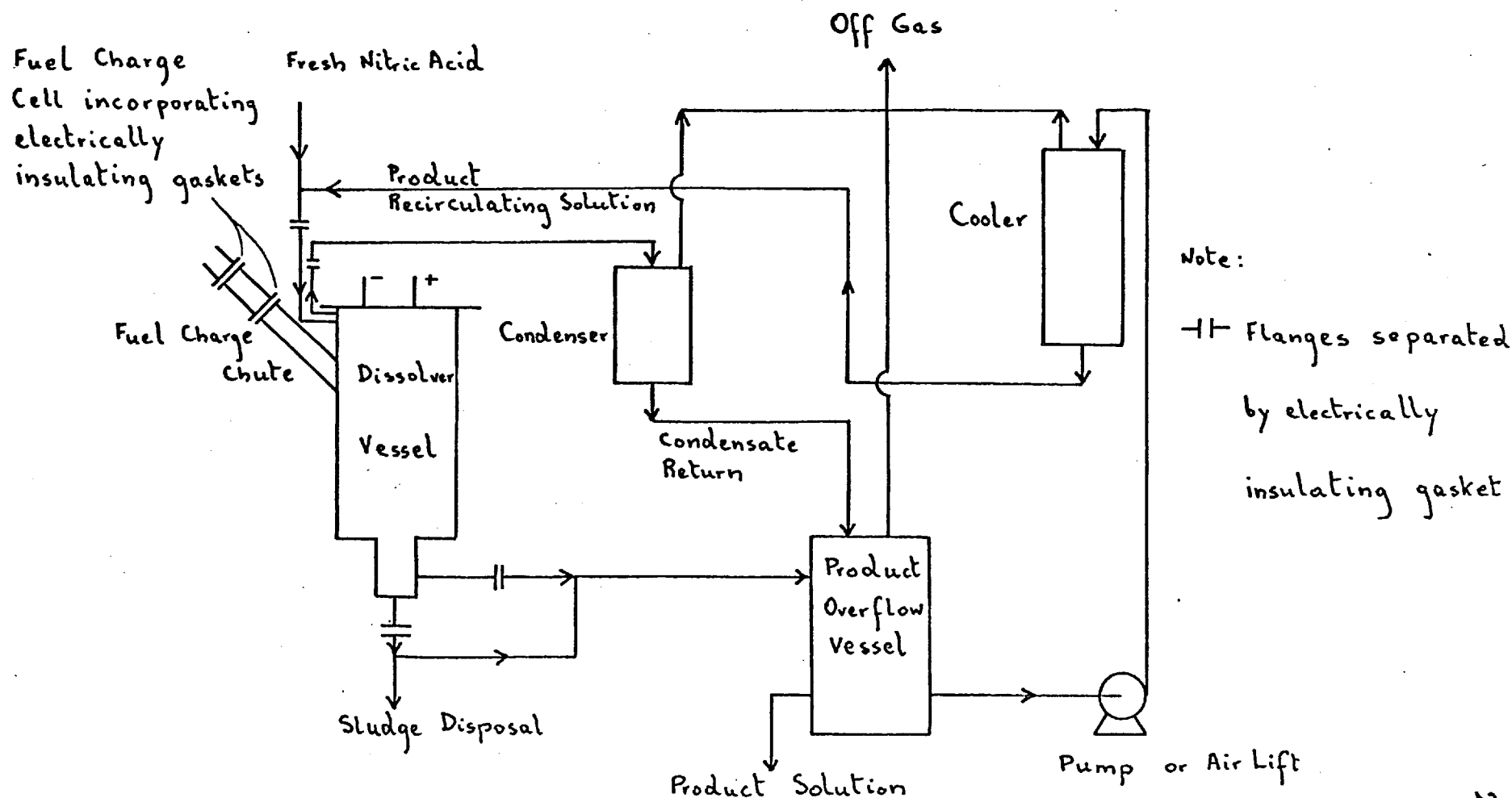
The outer part of the dissolver (Fig.9.2.) consists of a cylindrical tantalum shell enclosing the inner vessel, allowing for an overall clearance of $\frac{1}{4}$ in. ($\frac{1}{8}$ in. either side). A narrower tantalum tube, 2¹/₂ in. I.D. (to ensure critically safe conditions⁽⁸⁾) is attached to the lower end of the shell immediately below the inner vessel. The electrolyte outlet pipe is fixed radially to it in such a way that part of the 2¹/₂ in. tube serves as a trap for the sludge formed during fuel dissolution and for any small, undissolved particles of the fuel charge which may fall through the perforated base plate. Any accumulated sludge can then be cleared away through a pipe attached to the bottom of the 2¹/₂ in. section.

A tantalum flange equipped with asymmetrically spaced locating lugs is fixed to the upper end of the dissolver shell. These lugs fit into corresponding lug holes in the cover plate of the inner vessel in such a way that the inner part of the dissolver may be inserted correctly into the shell in one position only. Such an arrangement ensures that the cut-away section of the inner vessel always faces the fuel and electrolyte inlet lines which are attached to the upper section of the dissolver shell. An electrically insulating gasket between the cover plate and flange and insulating washers on bolts help to prevent any direct electrical contact between the outer and inner vessels.

9.2.2. General.

The proposed dissolver assembly is incorporated in a flow circuit shown in Fig.9.3. To afford full protection from stray current corrosion, tantalum is suggested as material of construction for all lines connected directly to the dissolver assembly. Published evidence shows⁽²⁶⁾ that no stray currents are likely in pipes connected to such lines via electrically insulating gaskets. Depending on the temperature of the electrolyte, suitable grades of stainless steel (Type 347, Carpenter-20 at low electrolyte temperatures) or titanium (electrolyte at boiling point) could then be used for the construction of the remainder of the dissolver circuit⁽²⁶⁾.

Fig.9.3. Proposed Plant-Size Dissolver - Flow Circuit Arrangement



9.2.2.(a) Tapping.

No special provisions are made in the proposed dissolver design for the installation of a tapping mechanism as it is considered that the high voltage applied and the large contact area between the fuel charge and the tantalum electrodes will ensure a steady current flow. In addition, the periodic discharge of fresh fuel pieces into the dissolver should provide a sufficient jarring effect on the system to help re-establish efficient contact if necessary.

9.2.2.(b) Safety.

A fixed voltage d.c. supply is suggested in order to prevent any accidental rise in potential from exceeding the overvoltage of tantalum. Trip fuses should be provided to cut off the d.c. supply when (i) the current exceeds a pre-determined value (e.g. 50% above the estimated design figure of 40 amp - Section 8.4.2.); (ii) the electrolyte flow is interrupted, e.g. through pump failure.

9.3. Annular Dissolver.

Criticality data on annular vessels suggest⁽⁸⁾ that comparatively large size safe geometry equipment may be constructed using such an arrangement. Thus, assuming a layer of cadmium plating on the inside of the annulus and a core of water or other hydrogen-rich material as moderator, an annular vessel with an internal diameter of 25 in. and an external diameter of 30 in. (and of infinite length)

may be constructed giving a cross-sectional area of annulus approximately 44 times greater than the cross-sectional area of a $2\frac{1}{2}$ in. dia. pipe. If the inner pipe of such an annular system were made the anode (say) and the outside pipe the cathode, then with the annular space packed with fuel pieces, an electrolytic (multi-cell) dissolver would result whose volumetric capacity could be much greater than that of a $2\frac{1}{2}$ in. dia. tubular dissolver.

It is considered, however, that a number of scoping experiments would have to be carried out first in order to determine the operational characteristics of such a system before any design suggestions could be made. On the basis of comparison with the tubular dissolver the following points may, however, be made:

(1) assuming tantalum as the material of construction, the maximum voltage between the inner and outer pipes of the dissolver is limited to about 140V;

(2) the maximum current flowing at that voltage is limited mainly by the resistance of the cells set up in series;

(3) even at fairly short pipe lengths (e.g. 3 ft.) the current density of the system would be low due to the very large surface area of the electrodes resulting in high polarization resistance of the cells (Section 8.1.4.). As the resistance of the electrolyte would be low (large cross-sectional area of current flow), the current would tend to by-pass the fuel pieces resulting in lower current efficiencies and dissolution rates.

Appendix A.Electrode Potential Measurements.

Table A 1 : 3N HNO_3 .

Table A 2 : 6N HNO_3 .

Table A 3 : 9N HNO_3 .

Table A 4 : Cu-CuSO₄ Electrode.

Potential vs. Time Measurements for Uranium
in Nitric Acid.

Table A 1 : 3 N HNO₃

Experiment	I		III		IV		V	
Electrode Type	1		1		1		2	
Temperature, °C	22		19		19		25	
Electrolyte	Fresh 3N nitric acid		Same as used in Expt. I		Same as used in Expt. III		Fresh 3N nitric acid	
	Time	EMF mV	Time	EMF mV	Time	EMF mV	Time	EMF mV
	1'00"	+74	1'00"	+16	0'20"	+ 56	0'05"	+ 60
	2'30"	+85	2'00"	0	0'50"	+ 70	0'20"	+ 98
	4'00"	+86	3'00"	-11	1'40"	+151	0'50"	+187
	5'30"	+85	4'00"	-10	2'00"	+166	1'35"	+235
	7'00"	+70	5'00"	-11	3'00"	+153	2'35"	+267
	8'00"	+35	6'00"	- 9	4'00"	+213	3'00"	+285
	11'00"	-51	7'00"	-19	5'00"	+239	4'00"	+288
	11'30"	-74	8'00"	-21	6'00"	+295	5'00"	+288
	13'00"	-109	9'00"	-23	7'00"	+292	6'00"	+288
	14'00"	-126	10'00"	-17	8'00"	+302	7'00"	+288
	15'00"	-140			9'00"	+317	8'00"	+288
	16'00"	-139			10'00"	+317		
	17'00"	-142						
	18'00"	-133						
	19'00"	-125						
	20'00"	-105						

Table A2 : 6N HNO₃.

Experiment	VI	VII	VIII
Electrode Type	2	2	2
Temperature, °C	25	25	25
Electrolyte	Fresh 6N nitric acid.	Same as used in Expt. VI.	Fresh 6N nitric acid.
	Time, EMF, mV	Time EMF, mV	Time. EMF, mV
	0'20" +355	0'15" +380	0'20" +370
	1'00" +385	0'45" +395	0'45" +392
	1'30" +395	1'00" +400	1'00" +400
	2'00" +405	1'30" +406	1'30" +410
	2'30" +420	2'00" +413	2'20" +425
	3'00" +430	3'30" +430	3'00" +428
	4'00" +433	4'00" +433	4'00" +430
	5'00" +433	5'00" +433	5'00" +431
	6'00" +433	6'00" +432	6'00" +431
	7'00" +433	7'00" +432	7'00" +429
	8'00" +433	8'00" +432	8'00" +429

Table A3 : 9N HNO₃.

291.

Experiment	IX		X		XI		XII	
Electrode Type	2		2		2		2	
Temperature, °C.	25		25		25		25	
Electrolyte	Fresh 9N nitric acid.		Same as used in Expt. IX		Fresh 9N nitric acid.		Same as used in Expt. XI.	
	Time	EMF mV	Time	EMF mV	Time	EMF mV	Time	EMF mV
	0'25"	+415	0'10"	+440	0'20"	+455	0'15"	+420
	0'45"	+458	0'25"	+460	0'45"	+483	0'45"	+446
	1'00"	+475	0'45"	+488	1'00"	+485	1'00"	+460
	1'30"	+481	1'00"	+487	1'30"	+485	1'30"	+475
	2'00"	+484	1'30"	+486	2'00"	+484	2'00"	+480
	3'00"	+485	2'00"	+487	3'00"	+483	3'00"	+482
	4'00"	+485	3'00"	+486	4'00"	+481	4'00"	+482
	5'00"	+483	4'00"	+484	5'00"	+481	5'00"	+480
	6'00"	+482	5'00"	+482	6'00"	+480	6'00"	+480
	7'00"	+482	6'00"	+482	7'00"	+480	7'00"	+481
	8'00"	+480	7'00"	+481	8'00"	+479	8'00"	+481
			8'00"	+480				

Table A4 : Test of Potentiometer Circuit

using Cu-CuSO₄ electrode,
E = 0.318 volts at 25°C. (54)

	Check I	Check II	Check III
	Before start of experiments.	Before start of experiments.	At end of experiments.
Temperature,	22°C.	23°C.	23°C.
E, volts.	0.323	0.328	0.318
	0.321	0.328	0.319
	0.322		0.320

Note: (1) All readings of E.M.F. in Tables A1, A2 and A3 are given with respect to a 1N KCl calomel electrode.

(2) Readings of E.M.F. in Table A4 are given with respect to the standard hydrogen electrode.

(3) The potential of the normal calomel electrode was in all cases taken as 0.281 V at 25°C. (51)

Appendix B.

Pressure Drop Test Data and Calculations.

B.1. Test Data.

Tables B.1.1. and B.1.2.

B.2. Specimen Calculations.

Nomenclature.

D_p	-	diameter of particle, ft.
D_T, d	-	diameter of tube, ft.
e	-	overall bed voidage fraction, dimensionless.
G	-	mass rate of flow, lb/sec.
G_m	-	mass rate of flow, lb/hr.ft. ²
g	-	gravitational constant, ft/sec. ²
g_c	-	gravitational constant, ft/hr. ²
ΔH_B	-	pressure drop in packed tube, ft.
ΔH_T	-	pressure drop in empty tube, ft.
L, ℓ	-	bed height, ft.
Δp	-	pressure drop in packed tube, lb/ft. ²
R	-	shear stress in fluid at boundary surface, lb/ft.sec. ²
u	-	fluid velocity, ft/sec.
μ	-	fluid viscosity, lb/ft.sec.
μ_m	-	fluid viscosity, lb/ft.hr.
ρ, ρ_F	-	fluid density, lb/ft. ³

B.1. Tables B.1.1. and B.1.2.

Readings of pressure drop, at various rates of flow in $\frac{3}{4}$ in. diameter and $1\frac{1}{2}$ in. diameter dissolver tubes. Packing dimensions as specified in Table B.1.1. and B.1.2. below.

Table B.1.1. $\frac{3}{4}$ in. diameter tube

Packing Size.	Packing Height	Flow Rate, ℓ /min.	Pressure Drop, cm.Hg.
Run 1. 5-7 mm. glass beads.	6 in.	- (1)	-
		4.5	0.3
		9.9	1.6
		10.5	1.8
		10.7	1.9
		11.0	2.0
		12.0	2.4
		13.0	3.0
		13.5	3.4
		13.8	3.6
		15.0	4.4
		3.6	7.4
		5.0	14.4
		8.0	33.6
		11.1	57.0
		Run 2.	
		3.5	5.6
		4.7	11.2
		5.9	18.0
		6.8	23.6
		7.5	28.4
		9.0	38.0
		10.4	52.6

(1) Tube empty except for stainless steel gauze support.

Table B.1.1. (continued).

	Packing Size.	Packing Height	Flow Rate, ℓ./min.	Pressure Drop, cm.Hg.
Run 3.	5-7 mm. glass beads.	6 in.	2.9	4.6
			3.5	6.5
			4.2	9.6
			5.1	13.4
			5.7	16.7
			6.7	23.0
			8.0	33.0
			8.7	37.4
			9.8	43.6
			10.4	57.0
Run 4.		3 in.	3.6	2.4
			4.0	4.0
			5.8	8.8
			6.7	12.4
			7.9	16.0
			9.4	22.6
			10.1	26.6
			11.1	31.6
			12.2	36.0
Run 5.			13.0	39.6
			3.2	1.8
			3.5	3.0
			3.9	4.0
			5.2	7.0
			6.2	10.4
			7.4	14.4
			8.7	20.4
			9.9	24.0
			10.5	28.2
Run 6.	$\frac{3}{8}$ in. diam meter por- celain spheres.	6 in.	11.4	32.6
			12.8	40.4
			3.1	0.4
			4.5	2.0
			5.2	3.0
			7.7	7.0
			9.1	10.8
			10.7	13.8
			11.6	16.6
			12.5	19.4
			13.3	22.6

Table B.1.1.1 (continued).

	Packing Size.	Packing Height.	Flow Rate, ℓ /min.	Pressure Drop, cm.Hg.	
Run 7.				4.8	2.8
				5.9	4.6
				7.4	7.0
				8.4	9.0
				9.4	11.0
				10.5	14.4
				11.1	15.6
				11.8	17.0
				12.0	18.4
				13.0	23.0
				13.5	23.6
				1.8	0.2
				6.0	2.6
Run 8.			3 in.	8.7	5.4
				10.0	7.0
				11.6	9.6
				12.0	11.0
				13.3	13.4
				14.0	15.0
				4.6	1.5
Run 9.	3 in. 8 diameter porcelain spheres.		3 in.	7.1	3.6
				8.0	5.0
				9.7	7.0
				11.1	8.6
				12.0	10.6
				12.5	12.2
				13.3	13.4
				14.0	15.0

Table B.1.2.
 $1\frac{1}{2}$ in. diameter tube.

	Packing Size	Packing Height.	Flow Rate, %/min.	Pressure Drop cm. Hg.
Run 1.	5-7 mm. glass beads.	6 in.	2.8	1.0
			4.1	2.4
			5.9	4.0
			7.1	5.0
			8.1	7.0
			9.5	9.6
			10.4	11.0
			10.9	12.0
			12.2	14.0
			13.3	16.6
			15.0	22.0
			15.4	22.4
			15.4	22.0
			14.8	21.0
Run 2.			14.3	19.0
			13.0	17.0
			12.5	16.0
			11.5	13.0
			9.7	10.0
			9.1	9.0
			7.5	6.4
			5.7	3.6
			4.1	2.4
			2.8	1.0
Run 3.		3 in.	14.3	13.5
			13.0	12.0
			12.5	11.0
			12.0	10.4
			11.1	8.0
			10.2	7.0
			9.1	5.6
			8.8	5.0
			7.1	3.4
			6.25	2.4
			5.0	1.4
			3.0	0.4

Table B.1.2. (continued)

	Packing Size.	Packing Height.	Flow Rate, $\ell/\text{min.}$	Pressure Drop, cm.Hg.
Run 4.			2.4	0.2
			3.9	1.0
			5.3	2.2
			6.8	3.0
			7.8	4.4
			9.1	5.8
			10.4	7.0
			10.7	7.6
			11.3	8.6
			12.5	10.4
			13.0	11.0
			15.0	14.6
Run 5.	$\frac{3}{8}$ in. dia- meter por- celain spheres.	6 in.	14.3	10.4
			13.6	9.6
			12.0	8.0
			11.1	7.0
			10.3	6.0
			9.4	4.4
			8.5	3.4
			6.4	2.0
			5.2	1.0
Run 6.			3.4	0.4
			2.0	0.5
			3.5	1.0
			5.1	1.4
			6.3	2.0
			7.7	3.0
			8.8	3.8
			9.7	4.6
			11.1	6.0
			12.0	7.6
			12.5	8.0
			13.0	9.0
Run 7.		3 in.	14.6	10.4
			14.3	7.0
			12.8	6.0
			12.0	5.0
			10.4	3.6
			7.5	2.0
			6.5	1.4
			3.8	0.4

Table B.1.2. (continued).

300.

	Packing Size.	Packing Height.	Flow Rate Q /min.	Pressure Drop cm.Hg.
Run 8.	$\frac{3}{8}$ in. dia- meter por- celain spheres.	3 in.	4.5	0.5
			5.7	1.0
			7.1	1.6
			8.3	2.4
			9.8	3.0
			11.6	4.0
			12.5	5.0
			13.3	5.6
			15.0	7.0
Run 9.	$\frac{1}{2}$ in. dia- meter por- celain spheres.	6 in.	15.8	8.0
			14.6	7.0
			13.0	5.0
			10.9	4.0
			9.5	2.6
			7.7	1.6
			6.7	1.0
			4.1	0.2
			4.3	0.6
Run 10.			7.7	1.6
			9.1	2.4
			10.2	3.4
			11.8	4.2
			13.0	5.0
			13.9	6.4
			15.8	7.6
			16.6	8.0
Run 11.		3 in.	16.2	6.6
			14.0	5.4
			12.5	4.0
			10.5	2.6
			7.1	1.0
Run 12.	$\frac{1}{2}$ in. dia- meter por- celain spheres.	3 in.	5.2	0.4
			4.3	0.1
			5.8	0.6
			7.2	1.3
			11.1	3.0
			12.2	4.0
			14.6	5.6
			16.2	6.6

B.2. Specimen Calculations:

(a) Using Equation developed by Chennakesavan and Laddha⁽⁵⁷⁾ we have

$$\frac{\Delta H_B e^4}{\Delta H_T} = 24.8 \left[\left(\frac{D_T}{D_P} \right) (1.5)(1-e) + 1 \right] - 22.3 \quad \dots (4.10)$$

(See Ch.4.2)

Consider a flow rate of 6 l/min., $1\frac{1}{2}$ inch diameter tube, 5-7 mm. diameter glass beads.

Under those conditions, we have:

$$e = 0.39 \text{ and } e^4 = 0.0231.$$

$$\frac{D_T}{D_P} = 6.1$$

H_T = pressure drop in empty tube

$$= 4 \left(\frac{R}{\rho u^2} \right) \frac{\ell u^2}{dg} \quad \dots (i)$$

$$\text{Cross-sectional Area of tube} = \frac{\pi}{4} \times \frac{3}{2} \times \frac{3}{2} \times \frac{1}{144} \text{ ft.}^2$$

$$= 0.0123 \text{ ft.}^2$$

$$\therefore \text{Velocity, } u = \frac{6 \times 0.22 \times 10}{62.5 \times 60 \times 0.0123} \text{ ft./sec.}$$

$$= 0.286 \text{ ft/sec.}$$

$$d = \frac{1.5}{12} \text{ ft.}$$

$$g = 32.2 \text{ ft/sec.}^2$$

$$\ell = 1 \text{ ft.}$$

The dimensionless friction factor, $\frac{R}{\rho u^2}$, is obtained from the Reynolds number and "absolute roughness"⁽¹⁰⁰⁾ as follows:

$$Re = \frac{4G}{\pi \mu d} \quad \dots (ii)$$

$$\begin{aligned} \text{Mass rate of flow, } G &= \frac{6 \times 0.22 \times 10}{60} \text{ lb/sec.} \\ &= 0.22 \text{ lb/sec.} \end{aligned}$$

$$\begin{aligned} \text{Viscosity of water, } \mu_{25^\circ\text{C.}} &= 0.93 \text{ cp} \\ &= 0.93 \times .000672 \text{ lb/ft. sec.} \\ &= 0.000625 \text{ lb/ft. sec.} \end{aligned}$$

∴ Substituting in (ii), we have

$$\begin{aligned} Re &= \frac{4 \times 0.22 \times 12}{\pi \times 0.000625 \times 1.5} \\ &= 3.58 \times 10^3 \end{aligned}$$

The "absolute roughness" for pipe is 0.00015

$$\begin{aligned} \therefore \text{"Relative roughness"} &= \frac{e}{d} = \frac{0.00015}{1.5} \\ &= 0.0001 \end{aligned}$$

where e = absolute roughness

d = diameter of pipe, inches.

Using the above calculated values of Re and $\frac{e}{d}$, we obtain⁽¹⁰¹⁾

$$\frac{R}{\rho u^2} = 0.0054$$

Substituting in (i),

$$\begin{aligned} \Delta H_T &= \frac{4 \times 0.0054 \times 1 \times (0.286)^2 \times 12}{1.5 \times 32.2} \\ &= 0.00044 \text{ ft. (water).} \end{aligned}$$

Re-arranging eqn. 4.10, we obtain

$$\Delta H_B = \frac{\Delta H_T}{e} \left\{ 24.8 \left[\left(\frac{D_T}{D_P} \right) (1.5)(1-e) + 1 \right] - 22.3 \right\}$$

Substituting values calculated,

$$\begin{aligned}\Delta H_B &= \frac{0.00044}{0.0231} \left\{ 24.8 \left[(6.1)(1.5)(1-0.39) + 1 \right] - 22.3 \right\} \\ &= 2.69 \text{ ft. (water)} \\ &= 6.0 \text{ cm. (mercury)}\end{aligned}$$

This compares with a pressure drop of 6.4 cm. Hg. observed experimentally.

(b) Using Equation developed by Leva⁽⁵⁸⁾

$$\Delta p = \frac{3.50 G_m^{1.9} \mu_m^{0.1} (1-e)^{1.1}}{D_P^{1.1} \rho_F g_c e^3} \text{ lb/ft.}^2 \quad \dots (4.12)$$

for each foot length of bed.

Note: Some of the symbols have been given additional suffixes in order to distinguish them from similar symbols used in the previous section.

$$\begin{aligned}\text{Mass rate of flow, } G_m &= \frac{6 \times 0.22 \times 10 \times 60}{.0123} \text{ lb/hr.ft.}^2 \\ &= 64,300 \text{ lb/hr.ft.}^2\end{aligned}$$

Using again a flow rate of 6 l/min., $1\frac{1}{2}$ inch diameter tube, 5-7 diameter glass beads, we have

$$\begin{aligned}G_m^{1.9} &= (64,300)^{1.9} \text{ lb/hr.ft.}^2 \\ &= 1.37 \times 10^9 \text{ lb/hr.ft.}^2\end{aligned}$$

Viscosity of water at 25°C., $\mu_m = 2.25 \text{ lb/ft.hr.}$

$$\begin{aligned}\mu_m^{0.1} &= (2.25)^{0.1} \\ &= 1.085 \text{ lb/hr.ft.}\end{aligned}$$

Voidage fraction, $e = 0.39$

$$\therefore e^3 = 0.059$$

$$\text{and } (1-e)^{1.1} = 0.58$$

Particle diameter, $D_p = 6 \text{ mm.}$

$$= 0.0205 \text{ ft.}$$

$$\therefore (D_p)^{1.1} = 0.01393 \text{ ft.}$$

Gravitational constant, $g_c = 4.17 \times 10^8 \text{ ft/hr.}^2$

Substituting in Eqn. 4.12, we have

$$\begin{aligned} \Delta p &= \frac{3.50 \times 1.37 \times 10^9 \times 1.085 \times 0.58 \text{ lb/ft.}^2}{0.01393 \times 62.5 \times 4.17 \times 10^8 \times 0.059} \\ &= 141 \text{ lb/ft.}^2 \\ &= 5.1 \text{ cm. (mercury)} \end{aligned}$$

This again is compared to an experimental value of 6.4 cm.Hg.

Using appropriate figures for flow rate, particle and tube diameter, other values of pressure drop were thus calculated, using both the Leva and Chennakesavan equations.

Appendix C.Analytical Methods.

C.1. Uranium Analysis - thiocyanate method.

C.2. Uranium Analysis - the tetrapropyl-ammonium
uranyl trinitrate complex method.

C.3. Determination of Acidity in the presence of the Uranyl Ion.

C.1. Colorimetric Determination of Uranium with Thiocyanate.

Both the general method of analysis and the preparation of the necessary reagents were carried out as described by Currah and Beamish⁽⁶¹⁾. A modification to the analytical procedure was introduced, however, to compensate for the alkaline nature of the sodium bicarbonate electrolyte. In this case aliquots of the electrolyte, ranging in volume from 0.25-2.0 ml. depending on the uranium concentration, were first neutralised with a few drops of 6N HNO_3 . The resulting solution was then heated to boiling in order to expel the carbon dioxide and cooled. The corresponding amounts of reagents were added to develop the thiocyanate-uranyl complex colouration and the solution was made up to 50 ml. in a standard flask with distilled water.

Aliquots of standard uranium solutions were treated similarly to compensate for the presence of sodium ion. 1 ml. of saturated sodium bicarbonate solution was added to 1 ml. of the standard solution which was then treated as described above in the case of the electrolyte aliquots. Using a Unicam SP 500 spectrophotometer and 1 cm. cells, maximum absorbency for the complex was obtained at 335m μ . (As opposed to 365 m μ as used in the original method). A standard curve was then plotted from which the concentrations of uranium in the electrolyte were deduced.

C.2. Colorimetric Determination of Uranium using the Tetrapropylammonium-Uranyl Trinitrate Complex.

The method described by Maeck et al⁽⁶⁴⁾ was followed with the exception that both the quantities of sample taken for analysis and the volumes of reagents used were doubled in order to allow for a sufficient volume of the organic phase to be available to fill 1 cm. cells in the absence of a Teflon spacer.

C.3. Acidity Determination in the Presence of Uranium.

C.3.1. Principle of Method.

Uranium was complexed by the addition of potassium oxalate and the free acid titrated with standard alkali using a pH meter. A pH curve was drawn and the end point read off the graph.

C.3.2. Reagents.

20% Potassium Oxalate, pH 7.

N/10 Sodium Hydroxide.

C.3.3. Method.

A suitable aliquot of the electrolyte was pipetted into the pH meter cell or a suitable beaker and 10 ml. 20% potassium oxalate were added. The solution was made up to 50-60 ml. with distilled water, stirred and the pH noted. Aliquots of the standard alkali were added with stirring, the pH of the resultant solution being noted after each addition. A pH-titration curve was constructed in the usual way and the end-point read off. The normality of the acid solution was then calculated as follows:

$$\text{Normality of Acid} = \frac{\text{Titration(ml.)} \times N \text{ NaOH}}{\text{Aliquot of electrolyte (ml.)}}$$

Appendix D.

Determination of the Valency of Uranium.

D.1. Apparatus and Experimental Procedure.

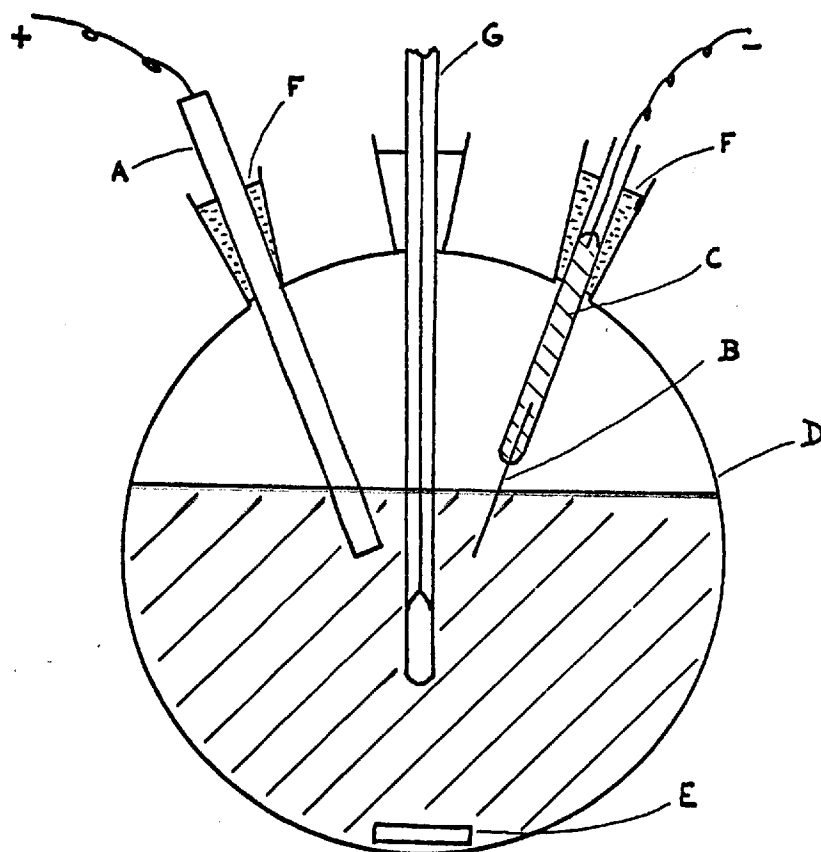
D.2. Results.

D.1. Apparatus and Experimental Procedure.

A diagram of the apparatus used is given in Figure D.1. A three-necked 750 ml. flask was filled initially with electrolyte consisting of 500 ml. 6N nitric acid and containing no dissolved uranium. The electrolyte was not renewed during subsequent runs, however, and these were thus carried out with a certain concentration of uranium already present at the beginning of a run. Samples of electrolyte were taken at the end of each run for uranium analysis, but no fresh acid was added to compensate for the amount of solution withdrawn. Analyses for the uranium content were carried out using the method of Maeck et al⁽⁶⁴⁾.

A $\frac{3}{8}$ in. diameter uranium rod was used as the anode. Electrical contact between it and the source of d.c. power was maintained, as described previously (Section 4.1.2., Type 2 electrode). The lower part of the electrode was not grooved, however, and no Araldite coating was applied to it. The cathode was made up of a length of 16 s.w.g. stainless steel wire, sealed into a glass tube which was filled with mercury to provide contact with the rest of the circuit. No special cleaning or electropolishing of the electrodes was carried out prior to their usage. D.C. power was supplied by a battery charger and a copper coulometer was included in the circuit to measure the current. Additional variation of current density on the anode was achieved by changing the depth of immersion of the

Fig. D.1. Anodic Dissolution of Uranium in Nitric Acid
Valency Determination Apparatus



- A. Uranium Anode
- B. Stainless Steel Cathode
- C. Mercury Pool serving as Electrical Contact
- D. Three-necked, 750 ml Flask
- E. Magnetic Stirrer
- F. Rubber Sleeves
- G. Thermometer (Glass Cone and Socket)

uranium anode in the electrolyte. An independent check on the uranium dissolved during electrolysis was provided by weighing the anode before and after each run.

Although temperature was not controlled, it remained in the range 25-30°C. during the course of the runs. A vent was cut into the stopper holding the thermometer to allow for the escape of gases evolved from the cathode during electrolysis. Stirring of the electrolyte was provided by means of a magnetic stirrer.

D.2. Results.

Results of runs and figures of valency obtained from them are given in Table D.1. Close correspondence between figures of uranium dissolved as determined by direct weighing and analysis was obtained in all cases. The rather low figure observed for the valency of uranium in Run 3 was directly due to the coarse, granular nature of the copper deposit on the coulometer cathode resulting from the high current density in that run. Some of the copper deposited was consequently lost despite careful handling, leading to an inflated value of the equivalent weight of uranium as calculated.

No formation of a green colouration, which would be indicative of the presence of U^{iv} ion, was observed at either of the electrodes during the course of electrolysis.

Table D.1. Determination of Uranium Valency during Electrolytic Dissolution
in 6N Nitric Acid.

Run No.	Duration, min.	V	A	Average C.D. (2) at Anode, amp/cm ²	Weight of Cu deposited, g.	Coulombs	Weight of (1) U dissolved, g.		Weight of U dissolved/F, g.	Valency of U.	Depth of Anode immersion, cm.
							(a)	(b)			
1	43	6.5	1.3- 1.7	0.45	1.4849	4514	1.92	1.89	40.6	5.88	1
2	41	6.5	0.9- 1.5	0.15	0.8404	2554	1.08	1.07	40.4	5.92	2
3	20	12	3.4- 4.0	1.04	1.5979	4858	2.10	2.08	41.7	5.74	1

Notes: (1) Weights given in column (a) were obtained by direct weighing whilst those in column (b) were determined analytically.

(2) Current density values calculated on the basis of current figures obtained from the coulometer.

Appendix E.

Gas Evolution during Electrolysis.

E.1. Apparatus and Experimental Procedure.

E.2. Results.

E.1. Apparatus and Experimental Procedure.

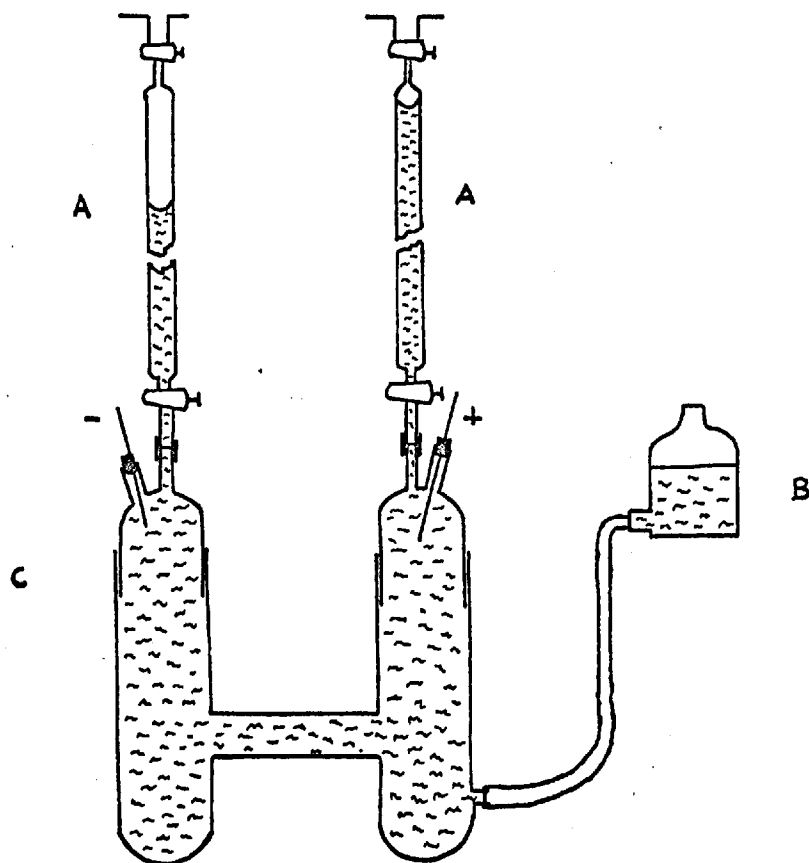
A diagram of the apparatus used is given in Figure E.1. A glass, H-shaped electrolytic cell allowed the gases evolved at the electrodes to be collected separately in 100 ml. gas burettes. The whole apparatus was filled with 3N nitric acid which served as the electrolyte. Initial uranium concentration in the electrolyte was zero, but as the nitric acid was not renewed with every run, uranium content of the electrolyte rose gradually. A uranium rod formed the anode throughout the series of runs but both 16 s.w.g. stainless steel wire and uranium cathodes were used. Details of the electrode construction were given previously (Appendix D, Section D.1.). D.C. power was supplied from a battery charger and the gases evolved at the electrodes were collected by downward displacement of the electrolyte in the gas burettes. In each case the run was stopped when the gas burette above one of the electrodes (invariably the cathode) became full of gas. The duration of the experiments was noted and in the case of two of them (Runs 3 and 4) the hydrogen content of the gas collected above the cathode determined by gas chromatography.

E.2. Results.

Full results of the experiments carried out and the gas evolution rates calculated from them are given in Tables E.1. and E.2.

Fig. E.1. Anodic Dissolution of Uranium in Nitric Acid

Off Gas Collection Apparatus



A Gas Burettes (100 cc)

B Levelling Flask

C H-Cell

Not to Scale

Table E.1. Anodic Dissolution of Uranium in Nitric Acid.Gas Evolution during Electrolysis.

Run No.	Duration of run, min.	V	A	Current Density amp/cm ²		Electrode Material.		Volume of gases ⁽¹⁾ collected, ml.		Gas Evolution Rate, ml/amph (cathode).	Temp., °C.
				anode	cathode	anode	cathode	anode	cathode		
1	100 ⁽³⁾	12	1.1	0.3	0.9	U	S.S.	0.5	100	55 ⁽²⁾	20
2	66	12	0.8	0.2	0.7	U	S.S.	1.0	100	114	23-26
3	53	12	0.8	0.2	0.7	U	S.S.	0.5	100	142	24
4	52	12	0.9	0.2	0.7	U	S.S.	0.5	100	128	24
5	53	12	1.0	0.25	0.25	U	U	<0.5	100	114 ⁽²⁾	21
6	37	12	1.1	0.3	0.3	U	U	<0.5	100	147	22

Notes: (1) Volume measured at room temperature and pressure. No correction applied for vapour pressure of the electrolyte.

(2) Fresh (3N nitric acid) electrolyte used in these runs - all other runs carried out using electrolyte remaining from the previous experiment.

(3) This figure is an estimate as Run 1 was only in the nature of a pilot experiment.

Table E.2. Anodic Dissolution of Uranium in Nitric Acid.

Estimation of the volume of gas evolved per mole of Uranium dissolved.

Run No.	amph	Weight of U dissolved, g ⁽²⁾	Vol. of gas evolved per mole of U dissolved ⁽¹⁾ .
1	1.83	2.73	8.7 ⁽³⁾
2	0.88	1.31	18.2
3	0.71	1.06	22.5
4	0.78	1.16	20.5
5	0.88	1.31	18.2
6	0.68	1.02	23.6

Notes: (1) 1/mole.

(2) Calculated on the basis of the electrochemical equivalent of uranium = 40 g.

(3) See Note 3, Table E.1.

The volume of gas evolved at the anode has been disregarded for the purpose of calculating gas evolution rates and all figures given in Tables E.1. and E.2. are based on volumes evolved at the cathode. The hydrogen content of the cathode gas was determined on a trial basis in the case of Run 3, and found to be between 1-2%. A more precise determination in the case of Run 4 gave a figure of 1.67%.

Current density values were based on the estimated surface area of the part of the electrode which was immersed in the electrolyte.

Although Run 1 was only a trial experiment and its length of duration was not noted very accurately, this inaccuracy is insufficiently large to be wholly responsible for the rather low gas evolution rate observed in the case of that run. It must thus be assumed that absorption of the more soluble oxides of nitrogen in the fresh electrolyte occurred, leading to a progressive saturation of the electrolyte and an apparent increase in gas evolution rate during subsequent runs.

The difference in behaviour of fresh electrolyte with respect to gas evolution observed in the case of Runs 1 and 5 may be explained in terms of differences of cathode material and cathode current density leading to a change in off-gas composition. Thus a preponderance of the more soluble oxides of nitrogen, e.g., NO_2 or possibly N_2O , would lead to higher absorption in the case of gases coming off the stainless steel cathode than one would obtain were the gases coming off the uranium cathode (Run 5) richer in a less soluble gas, e.g., NO . Whatever the cathode material, the mixture of gases given off was colourless and did not ignite. The gases given off at the uranium cathode, however, formed brown fumes of NO_2 on contact with air thus indicating that NO constituted a significant portion of the mixture as originally evolved. This qualitative evidence gives additional support to the assumption that NO was the predominant gas given off at a uranium cathode as

no brown fumes were observed when gases evolved at a stainless steel cathode were mixed with the atmosphere.

It was noticed that the rate of gas evolution during the course of a run was not constant but increased as the experiment proceeded. A similar effect was observed by Clark and Peterson⁽⁴³⁾ who investigated gas evolution behaviour during the electrolytic disintegration of Zircaloy-2 in nitric acid.

Appendix F.

Measurements of Resistance

F.1.1. Results.

Tables F.1., F.2., F.3., F.4.

F.1.2. Specimen Calculation.

F1.1. Results.Table F.1. Resistance Measurements on Bed of dry Uranium Pellets.Tubular Dissolver - Stainless Steel Electrodes.

B_c cm.	B_m cm.	B_t cm.	V	mA	Ω	Remarks.
0 ⁽¹⁾	5	10	6 12	10 10-20	600 800	Attacked U pellets, washed and dried. Battery charger.
0 ⁽¹⁾	5	10	6	4-5	1330	Fresh U pellets (i.e. unattacked).
0 ⁽¹⁾	5	10	12	5-10	1600	Battery charger
5	5	15	6	10-15	530	as source of
5	5	15	12	15-40	440	current.
7.5	10	22.5	6	50-60	109	
7.5	10	22.5	12	100-120	109	
7.5	10	22.5	5	30	167	Fresh U pellets.
			10	70	143	
			15	120	125	25V 50A.
			20	180	111	Rectifier as
			25	240	104	source of current.

Notes: (1) Uranium bed just touching cathode section.

B_c , B_m , B_t refer to lengths of bed in cathode
and middle sections and the total length respectively.
Length of bed in anode section was constant at about
5 cm.

Table F.2. Resistance Measurements on Bed of Moist Uranium Pellets.Tubular Dissolver - Stainless Steel Electrodes.

V	Time after drainage, min.									
	8		15		30		45		Overnight	
	mA	Ω	mA	Ω	mA	Ω	mA	Ω	mA	Ω
5	50	100	5	1000	2.2	2300	1.2	4170	0.9	5550
10	150	67	15	670	6	1670	3	3330	5	2000
15	225	67	30	500	13	1150	5.5	2730	20	750
20	250	80	50	400	22	910	8	2500	30	660
25	200	125	60	420	45	560	15	1670	20	1250

Details of Bed : $B_c = 7.5$ cm.) where B_c , B_m , B_t refer to
 $B_m = 10$ cm.) respective bed length sections
 $B_t = 22.5$ cm.) defined in Table F.1., and B_a
 $B_a = 5$ cm.) refers to the length of bed
 within the anode section.

Original Electrolyte flowing through bed — 3N nitric acid containing 17.0-17.5 gU/l.

Table F.3. Measurement of Electrolyte Resistance under Flow Conditions.

Tubular Dissolver - Stainless Steel Electrodes.

V	Nominal composition of Nitric Acid Electrolyte.							
	0.4N 2.2 gU/l		1.0N 5.4 gU/l		3.0N 13.4 gU/l		3.0N ⁽¹⁾ 13.4 gU/l	
	A	Ω	A	Ω	A	Ω	A	Ω
5	0.06	83	0.16	31	0.33	15	0.33	15
10	0.18	56	0.45	22	0.90	11	0.87	11
15	0.31	48	0.74	20	1.55	10	1.53	10
20	0.43	47	1.05	19	2.10	10	2.10	10
25	0.56	45	1.35	19	2.72	9	2.70	9

Bed Details : Bed Packing - 5.7 mm. dia. glass beads
(15 cm. total length)

Length of Middle Section - 5 cm.

Range of Flow Rate - 7.3-8.0 l/min.

Range of Pressure
across Bed - 5.2-5.5 p.s.i.g.

Notes: (1) Flow Rate in this experiment was dropped to 6.0 l/min.
to observe whether any change in resistance occurred.

Table F.4. Resistance of Uranium Bed (Water as Circulating Liquid). $\frac{3}{4}$ in. dia. Tubular Dissolver - Tantalum Electrodes.

Expt. No.	V		mA		Conduc- tance of circ. water, μ mhos	Overall resist- ance of system, R, ohms		Resis- tance of bed, r, ohms
	a.c.	d.c.	a.c.	d.c.		a.c.	d.c.	
1	23.3	27.0	103	24	-	226	1150	
2	23.2	26.7	73	17	-	318	1570	
3	23.3	26.7	65	16	-	359	1670	
4	23.5	-	46	-	440	512	-	620
5	23.2	26.8	45	11	460	517	2440	636
6	23.0	-	42	-	430	548	-	670
7	22.8	-	40	-	410	570	-	685

Notes: Length of Middle Section : 5 cm.Lengths of Anodic and
Cathodic Sections : 10 cm. each.

Conductivity Cell Constant: 1.4

Temperature Range : 20-22°C.

F.1.2. Specimen Calculation of Resistance (Table F.4.).

Taking a.c. current-voltage values and basing the resistance of uranium bed on the length of the middle section, the resistance figures, r, were calculated as follows:

Taking the last set of figures in Table F.4. we have,

$$\text{Conductance of water} = 410 \text{ } \mu\text{mhos}$$

$$\therefore \text{Conductivity of water} = 410 \times 1.4 \text{ } \mu\text{mhos/cm.}$$

$$= 574 \text{ } \mu\text{mhos/cm.}$$

$$\therefore \text{Resistivity of water} = 1745 \text{ ohms/cm.}$$

$$\therefore \text{Resistance of water across length of}$$

$$\text{middle section} = 1745 \times \frac{5.0}{2.78} \text{ ohms}$$

$$= 3140 \text{ ohms}$$

$$= r_w \text{ (say)}$$

Now,

$$\frac{1}{R} = \frac{1}{r} + \frac{1}{r_w}$$

$$\therefore \frac{1}{r} = \frac{1}{R} - \frac{1}{r_w}$$

$$= \frac{1}{570} - \frac{1}{3140}$$

$$= .00146$$

$$\therefore r = 685 \text{ ohms.}$$

The above calculations do not take into account the bed voidage fraction, e . Thus if an approximate value of $e = 0.4$ is assumed, the overall resistance of the water across the middle section increases by a factor of 2.5 and the resistance of the metal (U pellets) part of the bed approximates to the overall observed resistance values i.e. 500-600 ohms.

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<u>Code Letters</u>	<u>Company</u>
D.P.	E.I. du Pont de Nemours & Co.
I.D.O.	Phillips Petroleum Co.

E.g. - Full Title of Report:

Meyer, L.H. & Occhipinti, E.S., Reprocessing of Power Reactor Fuels, Seventh Quarterly Progress Report, E.I. du Pont de Nemours & Co., U.S.A.E.C. Report DP-421, Sept. 1959.

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