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Chemical Separations Processes
for Plutonium and Uranium

AEC Research and Development Report

PROCESSING OF POWER REACTOR FUELS

SIXTEENTH QUARTERLY PROGRESS REPORT

JULY 1 TO OCTOBER 1, 1961

Compiled by
F. G. Rust

Separations Engineering Division

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(TID-4500, 17th Ed.)

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Compiled by

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Work done by

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ABSTRACT

In the semiworks dissolver, average currents were about 2000 amp during dissolution of stainless steel and about 1200 amp during dissolution of Zircaloy. These currents were obtained when the current was transferred to a fuel assembly by direct contact with the columbium basket. High dissolution rates are anticipated when the dissolver is modified so that the electrolyte makes the only electrical contact with the charge. Laboratory experiments were made to determine the important characteristics of this type of dissolver.

High corrosion rates of stainless steel equipment by boiling nitric acid - stainless steel solutions (under evaporator conditions) is caused by Cr^{+6}.

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INTRODUCTION

Work continues on methods for the dissolution of the principal types of spent fuels from nuclear reactors. Electrolytic dissolution in nitric acid has been shown to be feasible on a laboratory scale for stainless steel, Zircaloy, aluminum, stainless steel - uranium oxide cermets, graphite, and uranium-molybdenum alloy(1-5). The nitric acid electrolyte is compatible with conventional materials of construction and with existing processes for radiochemical separation. For this technique to be practical on a plant scale, a method had to be demonstrated to transfer large amounts of current to the fuel assemblies. In previous work, mock fuel assemblies were placed in an anodic basket of columbium, and the current flowed from the basket to the fuel charge through the points of contact. The concluding tests using this technique are described in this report. Work was initiated on a "liquid contact" method in which the assemblies are suspended in nitric acid between a platinum anode and columbium cathode and the current is transferred through the acid instead of through a metal contact. A platinum anode was used previously in the ICPP "series dissolver" concept to transfer current through an electrolyte to dissolve pieces of metal(6).

Nitric acid solutions containing dissolved stainless steel can be corrosive to stainless steel equipment. Most of the corrosion is caused by the presence of Cr^{+6}(7). Corrosion is not a problem in an electrolytic dissolver because the solution is kept below the boiling point. The objective of corrosion work in the laboratory has been to decrease the corrosion rate in evaporators. The present approach has been to eliminate corrosion by chemically reducing the Cr^{+6} to the noncorrosive Cr^{+3}(8)

SUMMARY

The capacity to dissolve stainless steel and Zircaloy assemblies in the metal contact dissolver was limited by an insulating layer of oxide that formed at the point of contact between the fuel and the anode basket. The contact resistance increased with time to give an equivalent reduction in dissolving rate. The automatic striker was somewhat effective in re-establishing contact. An average current of 2000 amp for stainless steel and 1200 amp for Zircaloy appeared to be the limit that could be obtained in the 5 by 12-inch basket in the semiworks dissolver. These currents were obtained at 15 v; higher voltage caused anode damage. Since about 34,000 amp would be required to dissolve the stainless cladding in Yankee assemblies at a rate equivalent to 1 tonne of uranium per day, 17 such baskets would be needed for that processing rate.

High dissolution rates cause damage at the points where the charge touches the anode basket. Laboratory tests show that these points of contact are heated, sometimes to melting, and that the high temperature causes oxidation of both the columbium anode basket and the stainless steel charge. Good contact was obtained in laboratory tests by limiting the current to 120 amp/kg of charge weight, but for sustained operation a limitation to less than 60 amp/kg must be applied to prevent oxidation of the points of contact.

The heat damage and current limits imposed by the direct passage of current between charge and anode basket (metal contact dissolver) can be avoided by using the nitric acid electrolyte to pass current between both electrodes and the charge ("liquid contact" dissolver). The parameters affecting the efficiency of a liquid contact dissolver were explored prior to modifying the 5000-amp unit at the Semiworks. The measurements that were made and equations that permit calculation of the resistance introduced by anode baskets, small electrodes, and cylindrical configurations of electrode are presented in the Appendix.

An irradiated blanket rod of Zircaloy-2-clad uranium oxide was dissolved electrolytically in a small, direct contact dissolver. Uranium loss to the sludge was negligible. Dissolution of the irradiated rod was no different from previous dissolutions of unirradiated rods.

High corrosion of stainless steel by nitric acid - stainless steel solutions during evaporation is caused by the Cr^{+6} and is independent of nitric acid concentration (3 to 12M) except as the acid concentration affects the Cr^{+6} concentration. The Cr^{+6} is formed by the oxidation of Cr^{+3} by boiling nitric acid.

DISCUSSION

SEMIWORKS

The tests in the 5000-amp dissolver with a 5 by 12-inch basket were designed to determine the highest practical rates of dissolution under conditions in which the current is transferred to the charge solely by metallic contact with the columbium anode basket. In order to minimize damage to the basket in the first series of tests, the potential was limited to 15 v. Short (2 ft long) fuel assemblies were used so that all contacts with the anode basket would be immersed in the nitric acid electrolyte. The mock fuel assemblies, made of 1/4-inch-diameter, type 304 stainless steel pipe, were charged to the basket in one case so that one 6 by 14-tube array rested on the bottom in a vertical position, and in the second case so that one 6 by 6-tube array rested on the bottom in a horizontal position and five similar arrays were stacked above it. The fuel charge in each case weighed about 70 lb, and a columbium weight of 95 lb was placed on the fuel charge in sliding contact with the wall of the basket. The weight served to simulate the weight of uranium in actual fuel assemblies and permitted current to enter at the top of the charge.

Operation was satisfactory with both the horizontal and the vertical charges provided the columbium weight was placed on the charge. Good electrical contact was obtained with the striker on a 30-sec cycle. There was no indication of arcing or overheating. The vertical charge was 97% dissolved (as shown in Figure 1) at an average rate of 2000 amp; the horizontal charge was 93% dissolved at an average rate of 1600 amp. The current had decreased to less than 400 amp when the runs were terminated. The operating characteristics of the runs are shown in Figure 2. The current supplied to the vertical charge was briefly increased by 35% in the middle of the run by increasing the potential from 15 to 30 v, but there was evidence of overheating at the area of contact between the weight and the basket even though this area was submerged. Removal of the columbium weight decreased the dissolution rate by a factor of ten. The decreased dissolution rate was caused by loss of the top contacts and by effectively decreasing the contact force that held the charge in contact with the anode basket.

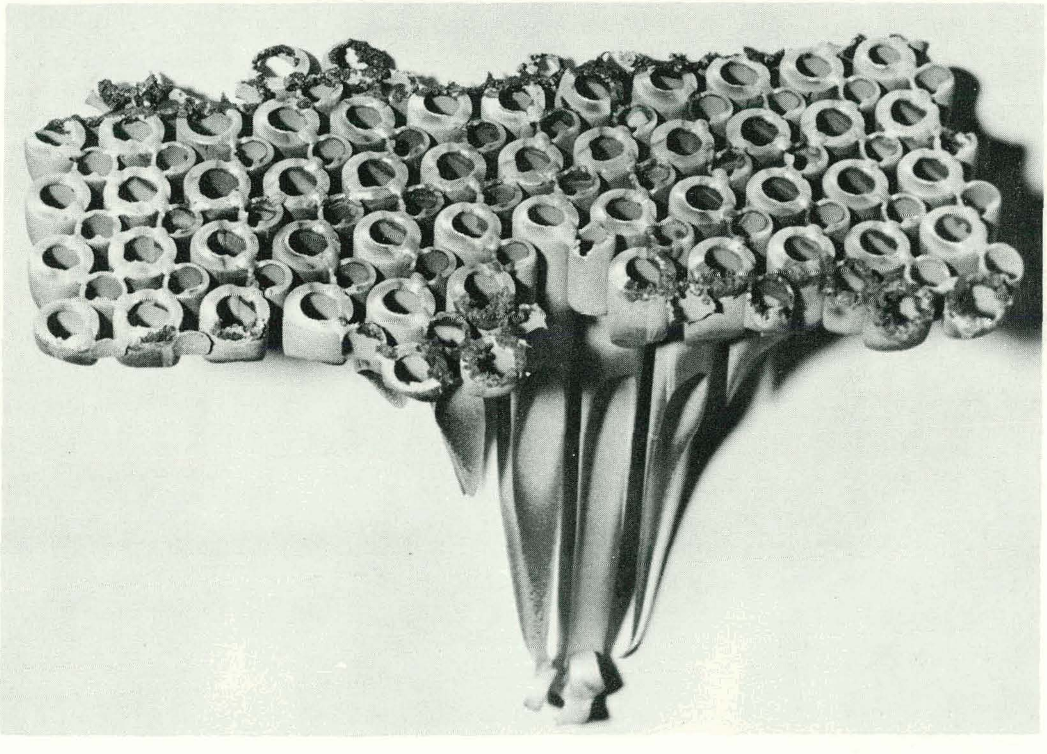
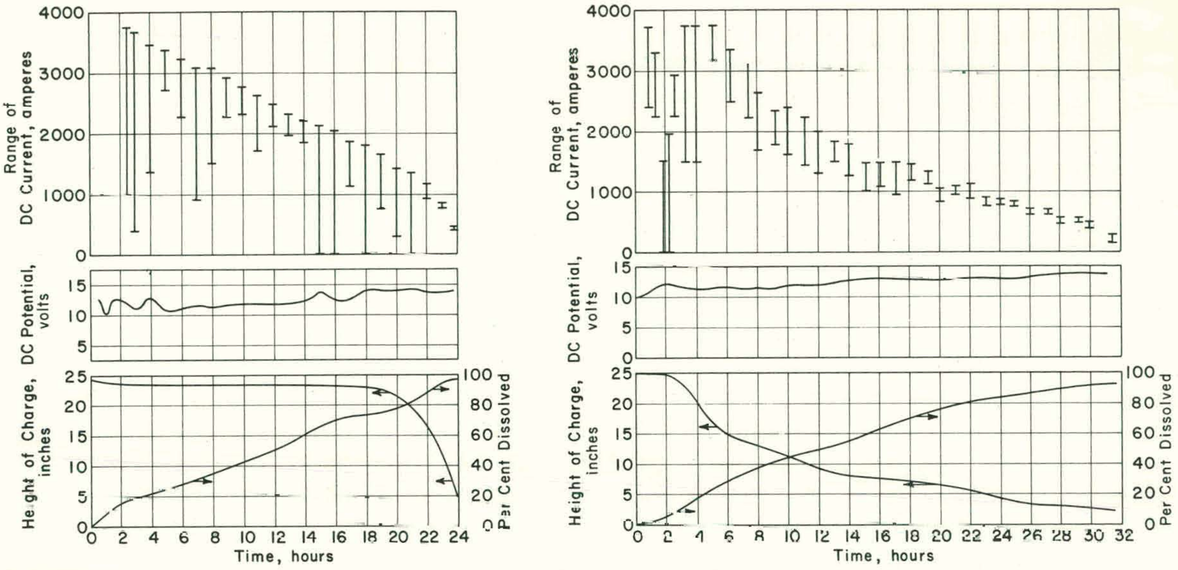


FIG. 1 VERTICAL CHARGE AFTER DISSOLUTION



a. Vertical Fuel Tubes
Single 70-lb Assembly

b. Horizontal Fuel Tubes
Six 12-lb Assemblies, Stacked

FIG. 2 OPERATING CHARACTERISTICS DURING ELECTROLYTIC DISSOLUTION

The highest average current attained without damage to the anode basket was 2000 amp for stainless steel (1.2 kg of stainless steel dissolved per hour). The average current for Zircaloy is 1200 amp (1.2 kg of Zircaloy dissolved per hour). Scrap and heels from Zircaloy dissolution did not dissolve readily upon the addition of a new charge. Assuming a ratio of uranium to cladding of 3 to 1 in a typical power fuel, a rate of 20 kg of cladding per hour would be required to process one tonne of uranium in a 16.5-hour day. For a nominal "one-tonne-per day" dissolver, 17 baskets would be required.

LABORATORY

ELECTROLYTIC DISSOLUTION BY DIRECT CONTACT

Experience with the 5000-amp semiworks dissolver has shown that at high dissolution rates the points of contact between the charge and anode basket heat up, melt, and oxidize. The result of this heating is poor electrical contact and erosion of the columbium basket. A laboratory study has been made of contacts in order to determine operating conditions that permit high dissolution rates without damage to the anode basket.

The voltage drop across points of contact between stainless steel and columbium immersed in nitric acid has been measured as a function of current. No current will flow until the contact potential reaches 0.25 to 0.35 v; this voltage is probably required to break down the layer of oxide between the contacts. Once the oxide has been broken down, the potential can be reduced without loss of contact.

Llewellyn-Jones has developed an equation[9] that relates contact potential to the maximum temperature in a contact.

$$T^2 = T_o^2 + 10^7 V_c^2$$

where
T = maximum temperature of contact, °K
T_o = temperature of massive metal, °K
V_c = contact potential

This relationship is not affected directly by either current or contact force. The equation was developed and verified for contact between pure metals in a vacuum. Although neither of these conditions is met by the stainless steel - columbium contact, experimental observations are consistent with the Llewellyn-Jones equation.

Columbium oxidizes when it is heated in a point of electrical contact. Columbium held at 250°C for 2 hr in air forms an oxide layer 10^{-4} cm thick[10]; the oxide is about as thick as the oxide film that is formed anodically[11]. The rate of oxidation of columbium increases with temperature; therefore, high contact potentials would lead to high contact temperatures, rapid formation of an oxide coating, and deterioration of the electrical contact. Formation of iron oxide is thought to be more severe and probably creates an equivalent or greater resistance.

The electrical contact between columbium and stainless steel immersed in nitric acid was observed at various contact potentials (Table I). The temperatures are calculated from the Llewellyn-Jones equation. In all cases, the actual point of contact was enveloped in a bubble about 1/8 inch in diameter. The pits in the columbium (Table I, column 4) are probably formed by oxidation of the columbium and subsequent melting of the oxide (melting point of Cb_2O_5 is 1500°C). The size of the pits probably depends on the contact force, which was 0.2 kg for this experiment. At all voltages, a burned spot was observed on the stainless steel contact.

TABLE I

Observations of Columbium - Stainless Steel Contacts Immersed in 6M HNO_3

Contact Potential, v	Calc Temp, °C	Observations		Duration of Contact
		During Contact	Damage to Cb	
0.31	800	Bubble	None	No change in 2 hrs
0.37	950	Bubble	Discoloration	Voltage tripled in 32 minutes
0.45	1200	Small orange glow	5-mil-dia pit	-----
0.70	2000	Large white glow	30-mil-dia pit	Lost contact after several seconds

Damage to the columbium anode can be avoided by keeping the maximum temperature in a point of contact down to 300°C. By the Llewellyn-Jones equation, 300°C corresponds to a contact potential of 0.15 v (measured directly across the contacts); but, flow of current cannot be initiated at 0.15 v because of the insulating layer of oxide that covers anodized columbium. Electrical contact can be established by increasing the contact potential to about 0.30 v and then decreasing the contact potential to 0.15 v.

The effect of force on an electrical contact was determined by measuring the current at constant voltage as a function of contact force (Figure 3).

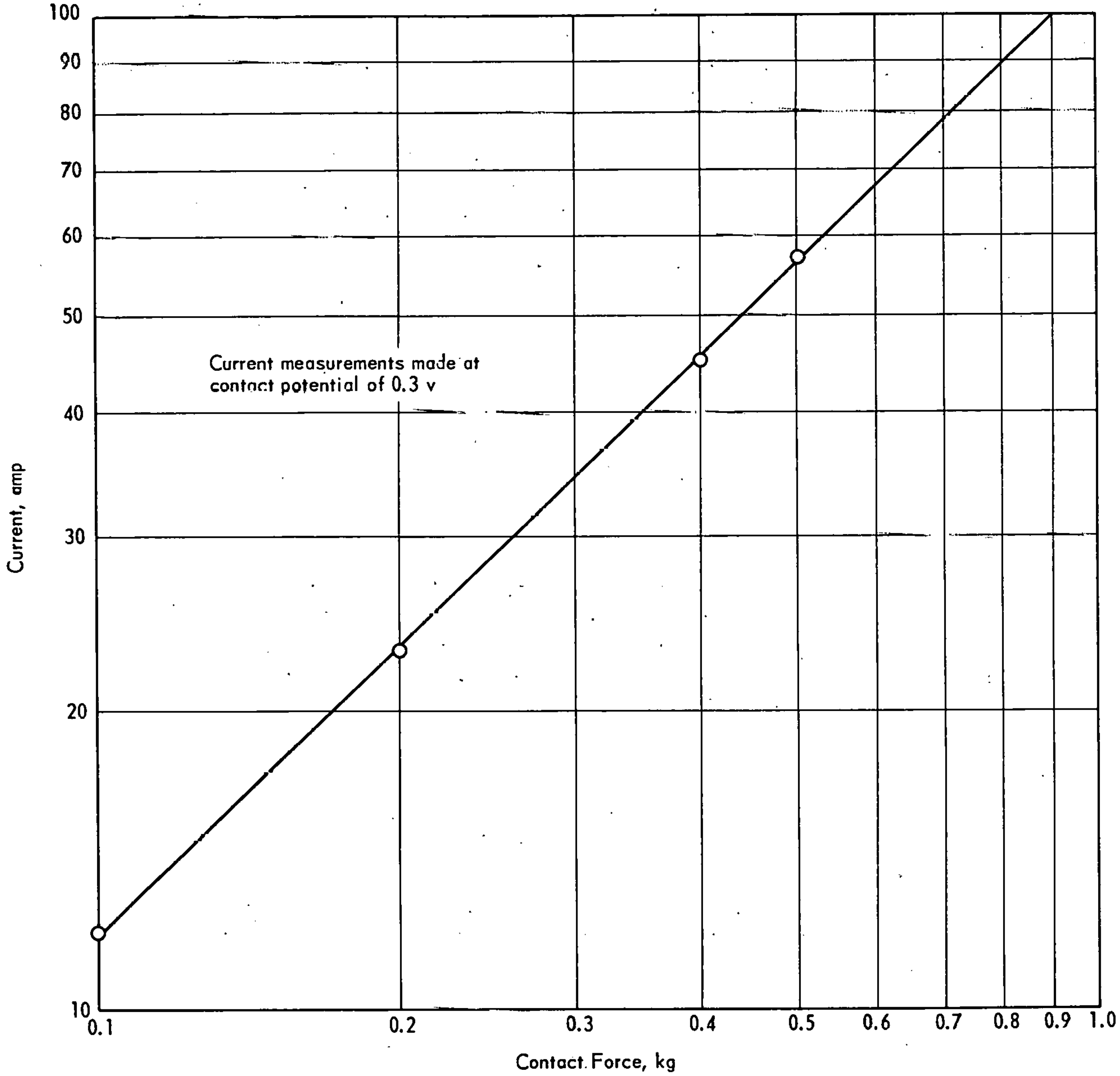


FIG. 3 CURRENT VS. CONTACT FORCE

The lowest potential at which good contact can be established, 0.3 v, was chosen for the constant potential of the contact. At this potential the current was found to be directly proportional to contact force. In a large electrolytic dissolver in which it is not practical to measure either contact temperature or contact potential, the contact temperature can be controlled by the ratio of current to contact force. Good electrical contact can be established by limiting the current to 120 amp for every kilogram of charge weight (0.3 v contact potential), but during sustained operation the current must be limited to less than 60 amp/kg of charge weight (0.15 v) to prevent damage to the columbium.

Higher dissolution rates might be realized without anode damage in a direct contact dissolver by replacing the pure columbium with an alloy. Alloys of columbium with 5% of either molybdenum or vanadium are five times as resistant to oxidation as columbium(12).

LIQUID CONTACT DISSOLVER

Many of the problems associated with metal-to-metal contact can be avoided by using the nitric acid electrolyte to make electrical contact between the anode and the charge. A dissolver that uses the liquid contact principle must be arranged so that the charge, which does not touch either electrode, presents a more attractive path to the current than does the nitric acid. Under such conditions, anodic dissolution will occur on the side of the charge facing the cathode.

Large currents will flow from an electrode to an electrolyte only if an electrochemical reaction takes place. Platinum is used as an anode cladding because it is the only material that is not damaged during anodic reaction in nitric acid(13). The anodic reaction produces oxygen on the surface of the platinum. Oxides of nitrogen are produced at the columbium cathode.

In order for current to flow through the charge, the potential drop between the electrolyte touching the two extremes of the charge must exceed the combined anodic and cathodic reaction potentials of the charge. The resistance of the charge is negligible. Combined anodic and cathodic reaction potentials were determined by measuring the current at several different potentials for a cell that had charge material for both anode and cathode. The straight line portion of the plot of potential vs. current was extrapolated back to the reaction potential, the potential at which no current flowed (see Table II).

TABLE II

Reaction Potentials

Material	Reaction Potential, v
Stainless steel	1.1
Aluminum	1.95
Zirconium	~3.5
Pt-Cb electrodes	2.8

In laboratory experiments to examine the feasibility of the liquid contact dissolver, a platinum anode and a columbium cathode were placed parallel to each other and 35 cm apart in a large glass vessel containing 4M HNO_3 at 27°C. A rod of stainless steel, 33 cm long and with a transverse cross-sectional area equal to about 1% of the area of either electrode, was placed perpendicularly between the electrodes with a clearance of 1 cm at each end. Calculations indicated that approximately 90% of the total cell current would be conducted by the stainless steel. The calculations were confirmed by tests with cell potentials of 10 to 20 v and with currents of 2.5 to 10 amp; the mass of steel that dissolved in the tests was equivalent to between 85 and 90% of the total current. When the cross-sectional area of the steel was reduced to 1/2% of that of the platinum anode between 75 and 80% of the current was still conducted by the steel. The results were not affected by changes in anode current density between 0.3 and 3 amp/cm^2. These laboratory tests demonstrated that the major portion of the cell current effectively dissolves the steel even when the steel occupies a very small portion of the space between the electrodes.

The best design for a liquid contact electrolytic dissolver is one that minimizes the distance between charge and electrodes and maximizes the areas of contact and the distance between electrodes. The electrode compartment of the proposed semiworks dissolver (Figure 4) is a box

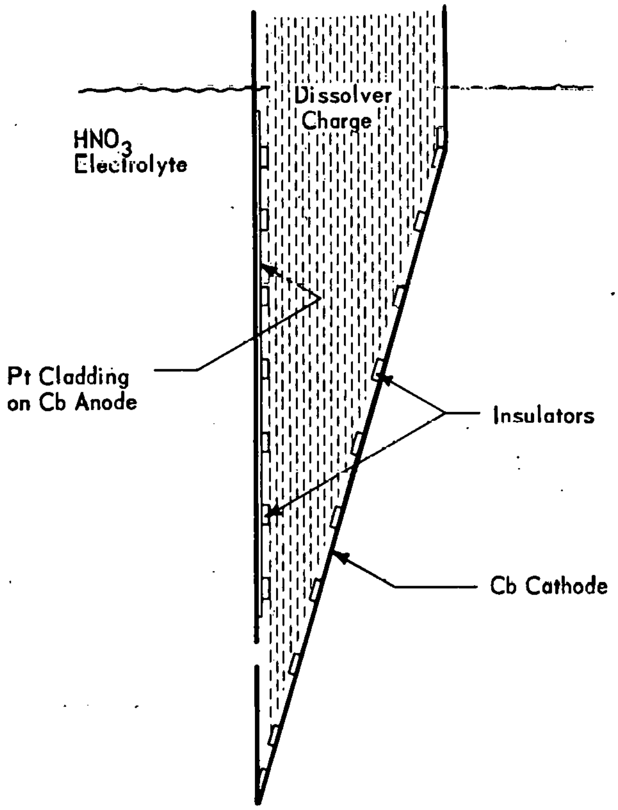


FIG. 4 PROPOSED DESIGN OF THE ELECTRODES FOR LIQUID CONTACT DISSOLVER

with electrodes on opposite sides. The walls connecting the electrodes are made of insulating material. The cathode is sloped so that it extends from the liquid level down under the anode. The charge is vertical and rests on thin strips of insulation on the sloped cathode. The anode also has strips of insulation on it to prevent the charge from making direct contact with the anode. Dissolution occurs on the side of the charge that faces the cathode (the bottom). The charge falls as it dissolves and stays close to the cathode. Therefore the gap between the charge and the electrodes remains constant throughout the dissolution.

To eliminate costly rectifying equipment, alternating current was briefly investigated as a source of power for the liquid contact dissolver. The charge that was suspended between two platinum electrodes dissolved satisfactorily. However, the 60-cps alternating current caused some dissolution of the platinum electrodes. Other work(14) has shown that at high frequencies, 5 kc, no dissolution of the platinum occurs.

DISSOLUTION OF IRRADIATED ZIRCALOY-2

A Zircaloy-2-clad UO_2 pin that would normally be used in the blanket of the Shippingport Atomic Power Station (PWR) and that had been irradiated to 5000 MWD/T in the Materials Testing Reactor was dissolved anodically at rates that showed that irradiation had no effect on the rate of disintegration of the Zircaloy. The 200-g pin was nominally 10 inches long and 411 mils in diameter. The cladding was 27 mils thick, and the total Zircaloy-2 in the cladding and end plugs was 34 g. The pin was cut into two 5-inch lengths, so as to be completely immersed in the electrolyte, and the sections were disintegrated electrolytically in 10M HNO_3. Of the 60% of the cladding that was disintegrated, 85% of the zirconium formed insoluble ZrO_2. The loss of uranium to the sludge after rinsing was about 0.1%, which is satisfactorily low. This small loss may have resulted from incomplete washing of the sludge. The current utilization for the disintegration of the remaining Zircaloy scrap was between 0.9 and 1.1 g/amp-hr (the same as for unirradiated Zircaloy).

CORROSION

Boiling solutions of nitric acid containing dissolved stainless steel are corrosive to metallic stainless steel. The corrosion is caused by the combined action of Cr^{+6} and nitric acid(7,8). Corrosion is not a problem during the electrolytic dissolution of stainless steel in nitric acid because the temperature is kept below 90°C and because corrosive Cr^{+6} is reduced by the large quantities of nitrogen oxides generated at the cathode. Corrosion is a serious problem during evaporation because the temperature is higher and the reducing oxides of nitrogen are soon lost from the boiling solution.

A method of analysis has been developed(8) for Cr^{+6} and acid in the presence of high concentrations of dissolved stainless steel. Analysis has shown that the Cr^{+6} concentration and instantaneous corrosion rate change during a standard 48-hr test. As is described in the following paragraphs, the change in Cr^{+6} concentration is caused by: (1) the oxidation of Cr^{+3} to corrosive Cr^{+6} by boiling nitric acid and (2) by reduction of Cr^{+6} to Cr^{+3} by the oxides of nitrogen that are produced by the corrosion of stainless steel. After about 100 hr, both reaction rates are constant and an equilibrium is established. At equilibrium conditions the concentration of Cr^{+6} and the corrosion rate are constant.

Cr^{+3} is slowly oxidized to Cr^{+6} by boiling nitric acid. In limited tests chromic nitrate was dissolved in nitric acid and refluxed in a clean glass system with no corrosion coupon present. The oxidation rate is shown in Figure 5 as a function of nitrate concentration.

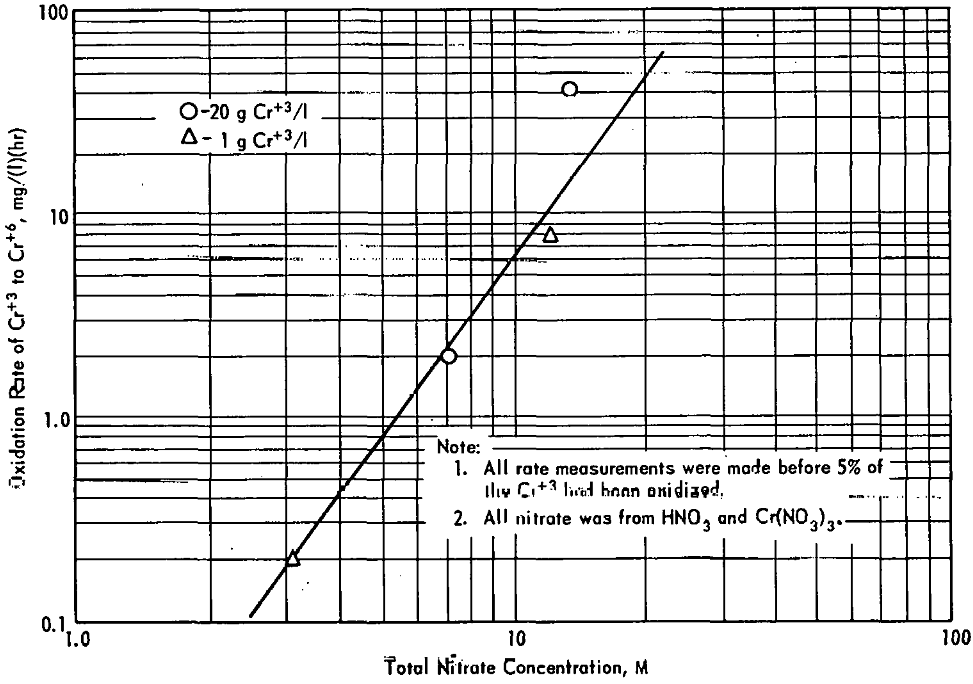


FIG. 5 RATE OF OXIDATION OF Cr^{+3} TO Cr^{+6} BY BOILING HNO_3

During corrosion tests the nitric acid oxidation of Cr^{+3} to Cr^{+6} is limited by the corrosion products of stainless steel. Corrosion by HNO_3-Cr^{+6} produces nitrous acid and oxides of nitrogen that reduce Cr^{+6} to Cr^{+3} (Figure 6). By this reduction some of the Cr^{+6} in a highly corrosive solution is reduced to the inactive Cr^{+3} and the corrosion rate is decreased. Figure 7 is a comparison of the corrosion rate and Cr^{+6} concentration of three boiling solutions: one of them originally contained 6 g Cr^{+6}/l (from sodium dichromate) in 10M HNO_3, the second solution contained 31 g/l of dissolved stainless steel (6 g Cr/l),

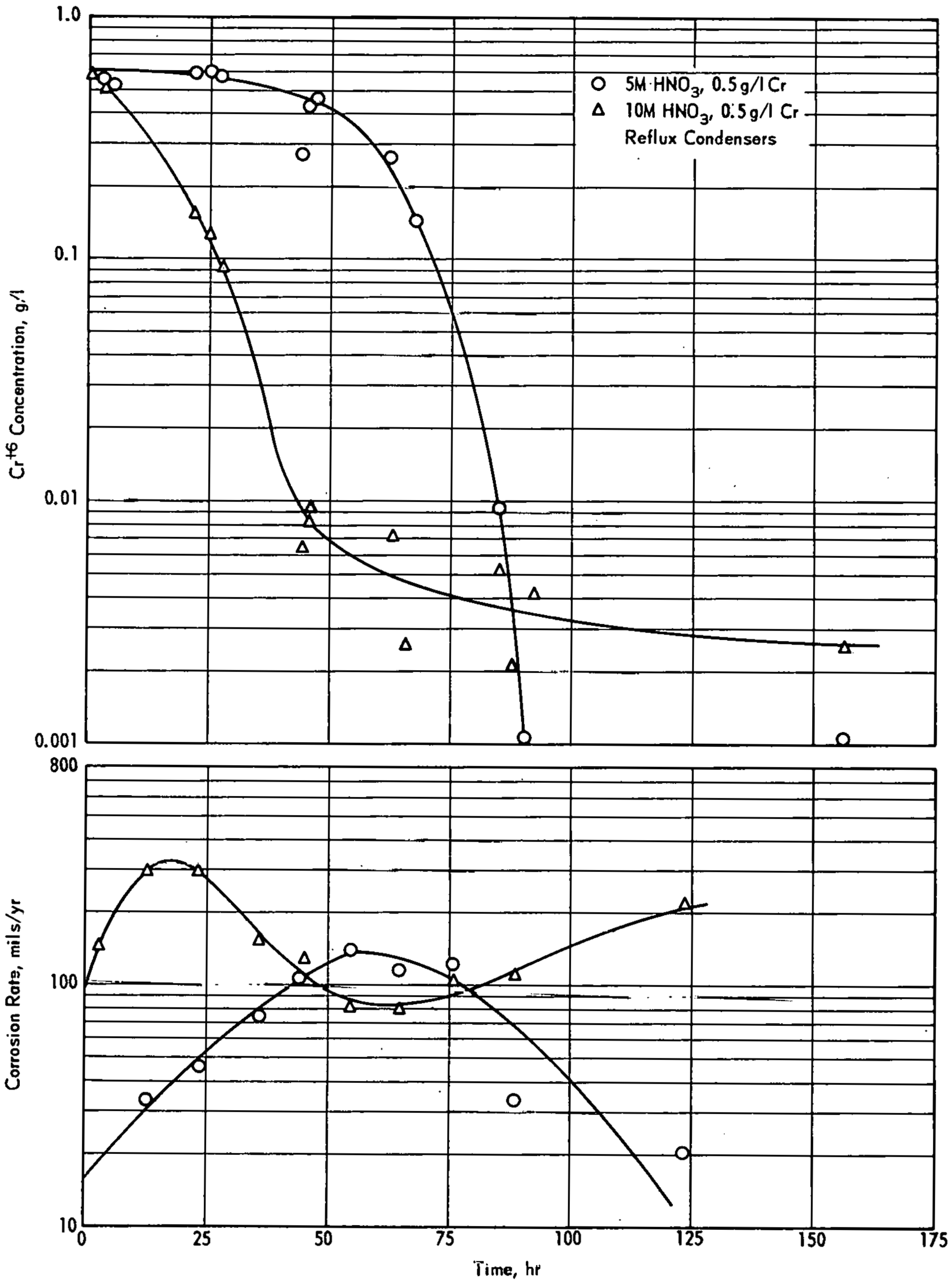


FIG. 6 REDUCTION OF Cr^{+6} AS THE RESULT OF THE CORROSION PROCESS

and the third solution was the same as the second except that it had a cold finger condenser, whereas the first two solutions had reflux condensers. After the solutions were boiled for about 100 hr an equilibrium was reached in the solutions. The corrosion rates were found to be higher in the tests with the reflux condensers because they are open to the atmosphere and oxides of nitrogen can be swept out of the system. Removal of the corrosion coupons eliminates the protection of the nitrogen oxides, and oxidation to Cr^{+6} continues unchecked.

The Cr^{+6} concentration and the corrosion rate of stainless steel were measured in various solutions of boiling nitric acid and Cr^{+6}. After 50 to 100 hr, equilibrium was reached at which neither the Cr^{+6} concentration nor the corrosion rate changed significantly. At this steady state a solution of dissolved stainless steel in nitric acid corroded type 304L stainless steel at about the same rate as a nitric acid solution containing the same concentration of Cr^{+6} (Figure 7). The corrosion rate at steady state has been plotted against Cr^{+6} concentration at equilibrium (Figure 8). From this plot it can be seen that acid concentrations over the range of 5 to 12M have little effect on corrosion rates. The major effect of acid is its effect on the rate of oxidation of Cr^{+3} to Cr^{+6}. Acid concentration affects the concentration of Cr^{+6} at steady state rather than the corrosion rate. In a similar manner the type of condenser affects the final Cr^{+6} concentration, through retention of nitrogen oxides, rather than the corrosion rate.

Corrosion is caused by Cr^{+6} and nitric acid. Chemical reduction of the Cr^{+6} to Cr^{+3} would reduce the corrosion rate. The copious quantities of mixed nitrogen oxides generated during electrolytic dissolution of stainless steel reduce all the Cr^{+6} in the electrolyte. In previous laboratory tests(8), nitrous oxide (N_2O) was found to have no effect and nitric oxide (NO) was found to reduce corrosion by a factor of eight. In recent experiments nitrogen dioxide (NO_2) was found to have no effect on the Cr^{+6} concentration or corrosion rate in a boiling solution of 6M HNO_3 - 30 g/l of stainless steel. Poor gas utilization was probably the reason that the sparging of nitrogen oxides failed to inhibit Cr^{+6} corrosion in the laboratory tests. Finely divided solid reductants are now being investigated. Nitric acid oxidizes the dispersed reductant and generates oxides of nitrogen throughout the solution.

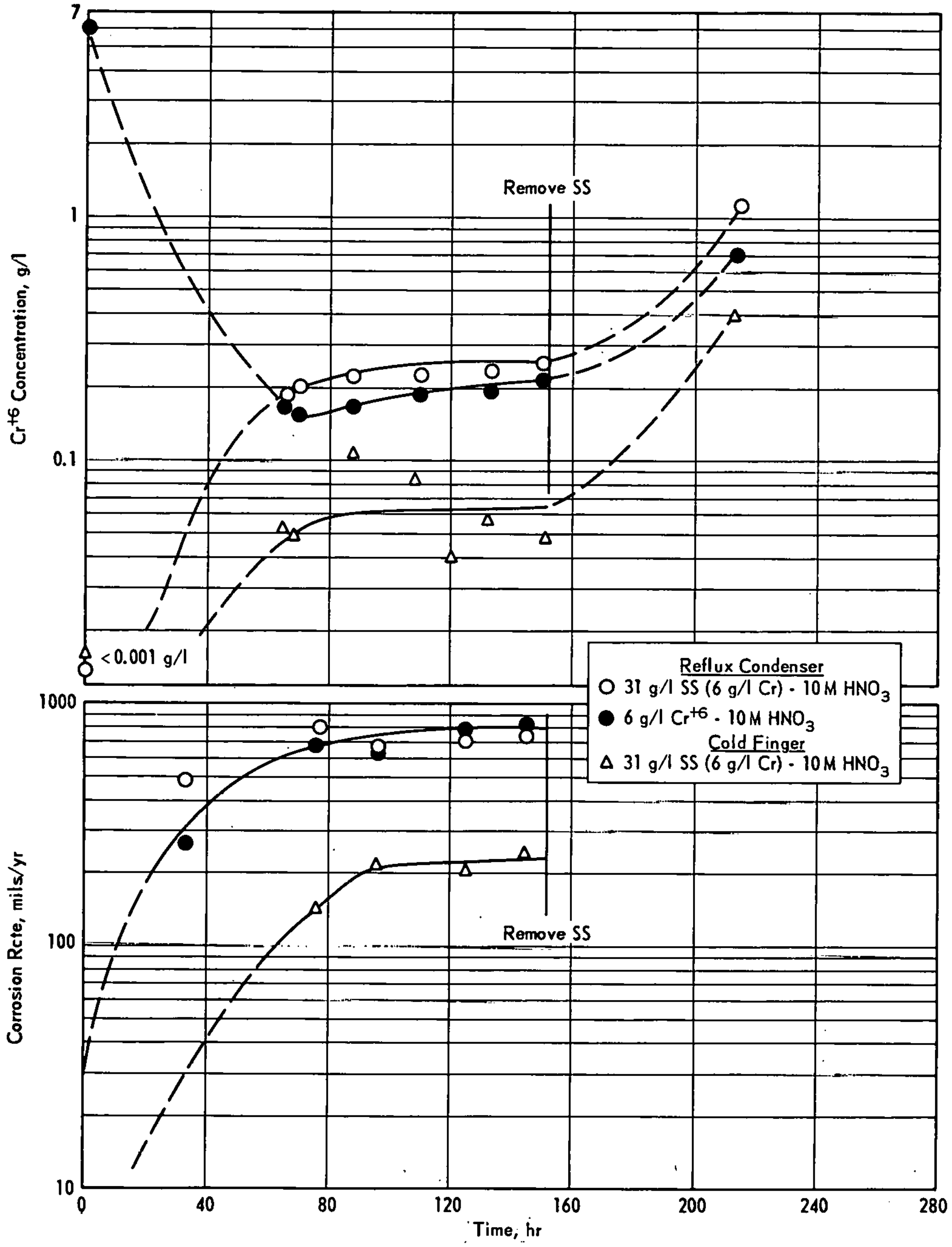


FIG. 7 RATE OF CORROSION OF TYPE 304L STAINLESS STEEL IN BOILING HNO_3 CONTAINING Cr^{+6} OR DISSOLVED STAINLESS STEEL

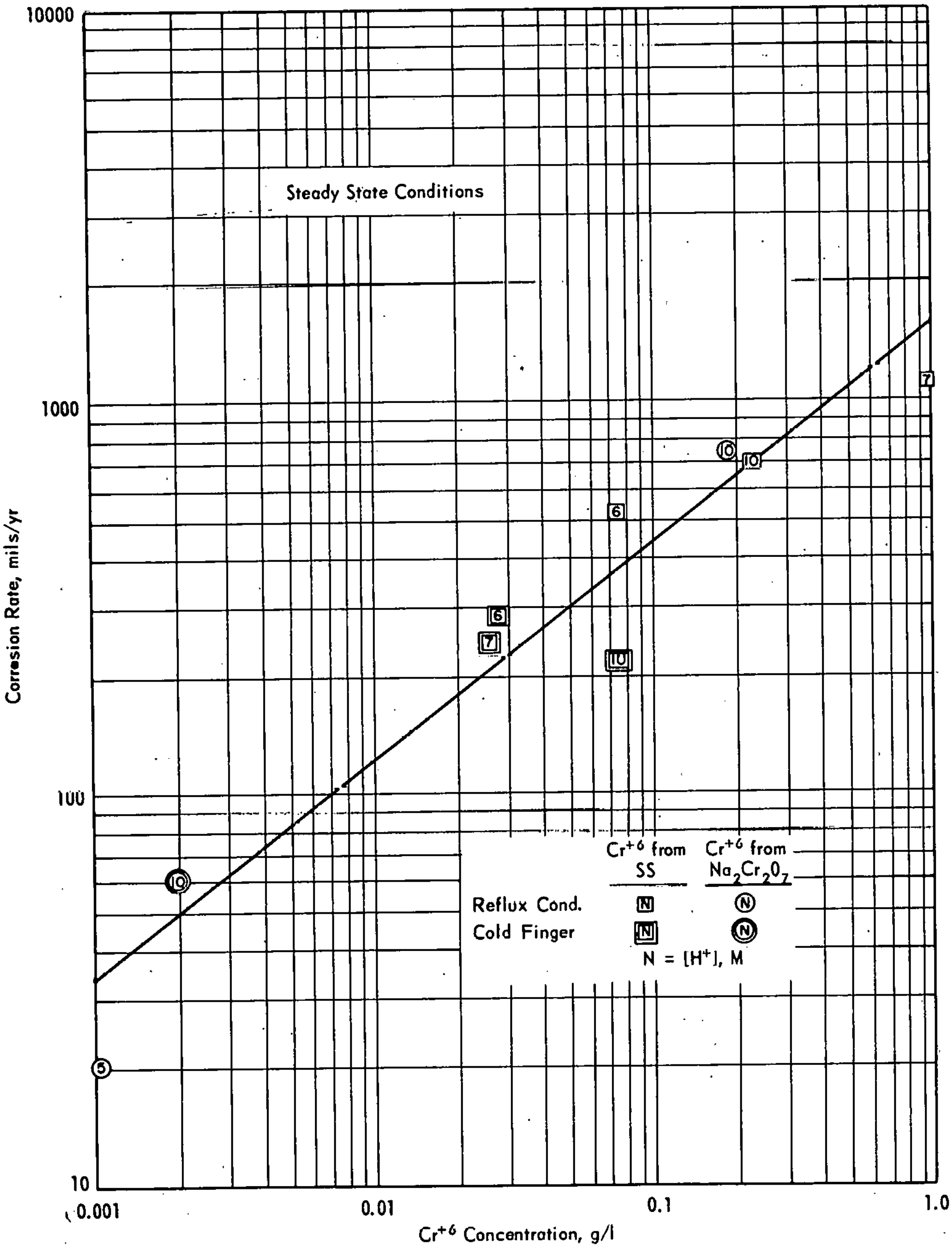


FIG. 8 RATE OF CORROSION OF TYPE 304L STAINLESS STEEL BY BOILING HNO_3 - Cr^{+6} SOLUTIONS

APPENDIX

RESISTANCE CALCULATIONS

Modifications to both liquid contact and direct contact dissolvers can be evaluated by use of equations for calculating electrical resistance. The simplest case is the calculation of the resistance of an electrolyte of uniform cross section between two parallel electrodes.

$$R = \frac{\rho_L}{A_s}$$

where

R = electrical resistance

ρ = electrical resistivity

L = distance between electrodes

A_s = area of solution normal to current path

The electrical resistance of a cell will be increased by inserting a diaphragm with a hole in it between the electrodes of the cell. The additional resistance imposed by the hole is generally called a constriction resistance. For the purpose of calculation, the resistance of a constriction can be considered to be the resistance of a disc with the diameter of the hole and a length equal to the radius of the hole. The resistance of the rest of the electrolyte is calculated as though there were no diaphragm except that the thickness of the above disc, the radius of the hole, is subtracted from the distance between electrodes. If the diaphragm has significant thickness, then this thickness is added to the length of the constriction resistance. The total resistance of a cell that contains a thick diaphragm with a hole in it is:

$$R = \underset{\text{constriction resistance}}{\frac{\rho r_H}{A_H}} + \underset{\text{diaphragm resistance}}{\frac{\rho t}{A_H}} + \underset{\text{effective resistance of rest of cell}}{\frac{\rho L_e}{A_s}}$$

Since

$$L_e = L - r_H - t$$

then

$$R/\rho = \frac{(L - r_H - t)}{A_s} + \frac{(r_H + t)}{A_H}$$

where

R = total resistance of cell

ρ = electrical resistivity of the electrolyte

L = distance between electrodes

L_e = effective length of electrolyte between electrodes

t = thickness of diaphragm

r_H = radius of the hole

A_H = area of the hole

A_s = area of the solution normal to current path

The electrical resistance of the hole (in the above expression) was determined experimentally by subtracting the resistance of the cell without a diaphragm from the resistance of the same cell with a diaphragm. The measured resistance of a cell without a diaphragm, R_c, was substituted for the calculated cell resistance term ρ_L/A_s in the above equation.

$$R = \frac{\rho r_H}{A_H} + \frac{\rho t}{A_H} + R_c - \frac{\rho r_H}{A_s} - \frac{\rho t}{A_s}$$

Simplifying:

$$R/\rho = \frac{R_c}{\rho} + \left(r_H + t\right)\left(\frac{1}{A_H} - \frac{1}{A_s}\right)$$

The measured and calculated values for resistance are tabulated in Table III.

TABLE III

Resistance of a Cell Containing a Diaphragm with a Hole

Electrolyte: 6.0M HNO_3

ρ_{18^oC} = 1.3 ohm-cm

t = 0.15 cm

L = 5.6 cm

							R/ρ	
r_H, cm	Temp, °C	ρ, ohm-cm	R, ohms	R_c/ρ, cm^{-1}	A_H, cm^2	A_s, cm^2	Calc, cm^{-1}	Obs, cm^{-1}
0.825	36	1.03	0.57	0.215	2.13	38.4	0.59	0.55
0.55	27.5	1.13	0.96	0.215	0.95	38.4	0.935	0.85
0.30	22.	1.22	2.33	0.193	0.28	35.2	1.77	1.91
0.22	21.4	1.22	3.15	0.193	0.16	35.2	2.51	2.58

A diaphragm with more than one hole in it has a lower electrical resistance than a diaphragm containing a single hole of the same area. The mathematical expression for the resistance of a cell that contains a diaphragm with n uniformly distributed holes in it is:

$$R/\rho = \frac{(L - r_H - t)}{A_s} + \frac{(r_H + t)}{nA_H}$$

where

n = number of holes

This relationship was substantiated by measuring the resistance of two arrays of holes: (1) 10 holes of 0.77-cm diameter on 2.4-cm centers and (2) 40 holes of the same diameter on 1.2-cm centers. The results are in Table IV.

An electrode that is smaller than the cross-sectional area of the electrolyte increases the resistance of a cell. The resistance caused by the small electrode is half of the resistance of a hole in a diaphragm. For the experiments tabulated in Tables V and VI, one electrode is small and the other electrode fills the entire cross section of the electrolyte. The equation for a cell with electrodes of different sizes is:

$$R/\rho = \frac{L - 0.5r_H}{A_s} + \frac{0.5r_H}{A_H}$$

where

r_H = radius or narrowest dimension of a small electrode

A_H = area of small electrode

The equation for the resistance of a solution was applied to cylindrical electrolytic dissolvers. Experimental measurements were made for the case where the anode is small compared to the cathode that surrounds it.

$$R = \rho \frac{r}{A}$$

$$dR = \rho \frac{dr}{2\pi hr}$$

$$\int_o^R dR = \frac{\rho}{2\pi h} \int_{r_a}^{r_c} \frac{dr}{r}$$

$$R = \frac{\rho}{2\pi h} \ln \frac{r_c}{r_a}$$

where

r_c = radius of cathode

r_a = radius of anode

h = length of electrodes

TABLE IV

Resistance of Arrays of Holes

Electrolyte: 4M HNO_3
Diaphragm thickness negligible

No. Holes	r_H, cm	Temp, °C	ρ, ohm-cm	L, cm	A_S, cm^2	A_H, cm^2	R/ρ Calc, cm^{-1}	R/ρ Obs, cm^{-1}
10	0.385	26	1.21	3.8	56.2	0.465	0.144	0.149
40	0.385	26	1.21	3.8	56.2	0.465	0.0816	0.083

TABLE V

Resistance of a Cell with One Electrode Smaller than the Cross-Sectional Area of the Cell

Run	Shape of Electrode	r_H, cm	A_H, cm^2	A_S, cm^2	L, cm.	R/ρ Calc, cm^{-1}	R/ρ Obs, cm^{-1}
H	Circle	0.55	0.95	9.08	4.2	0.721	0.69
B	Circle	0.55	0.95	9.08	2.4	0.534	0.60
E	Circle	0.55	0.95	9.08	4.7	0.776	0.82
D	Circle	0.55	0.95	484	2.3	0.293	0.39
F	Circle	0.55	0.95	484	4.7	0.388	0.43
A	Circle	0.55	0.95	5.72	2.4	0.660	0.62
C	Circle	2.48	6.15	9.08	2.5	0.341	0.30
G	Circle	2.48	6.15	9.08	4.7	0.583	0.53
1	Rectangle	0.16	1.59	18.0	1.1	0.107	0.11
2	Rectangle	0.75	3.82	25.0	0.75	0.112	0.10

TABLE VI

Calculated and Measured Resistances of a Cylindrical Dissolver

r_a, cm	r_c, cm	h, cm	ρ, ohm-cm	R_{cal}, ohms	R_{obs}, ohm
0.159	8.0	7.7	1.3	0.105	0.10
0.635	8.0	7.7	1.3	0.062	0.064
1.27	8.0	7.7	1.3	0.049	0.055
0.477	10.8	5.6	1.09	0.100	0.099
0.635	10.8	5.6	1.09	0.088	0.094

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