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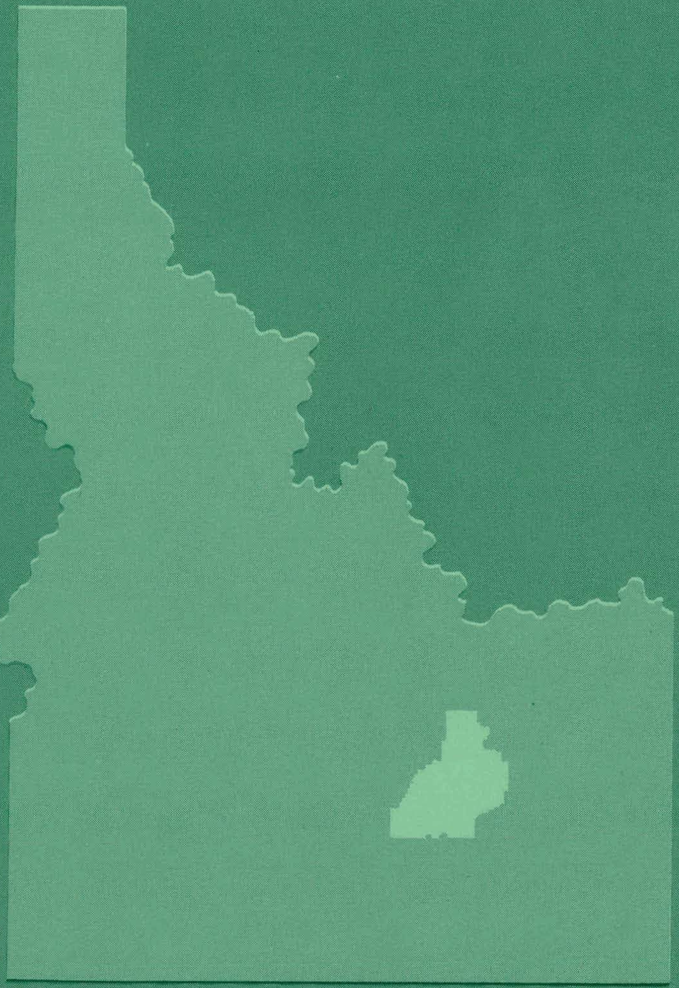
ELECTROLYTIC DISSOLUTION OF NUCLEAR FUELS

Part I. Zirconium in HCl-Methanol

J. R. Aylward
E. M. Whitener
H. T. Hahn

December 29, 1961



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Part I. Zirconium in HCl-Methanol

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Atomic Energy Division
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ELECTROLYTIC DISSOLUTION OF NUCLEAR FUELS
Part I. Zirconium in HCl-Methanol

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ABSTRACT

The electrolytic dissolution of zirconium in HCl-methanol was studied as a function of potential, solution composition, and temperature. The dissolution is characterized by two regions. At high potentials the zirconium is electropolished and complete dissolution is achieved. At low potentials the current is an exponential function of the potential (Tafel behavior). In this region a small amount of finely divided α-zirconium which is insoluble in HCl-methanol separates from the bulk metal.

The energy of activation for the corrosion reaction (0.0 volt) is 16.5 Kcal/mole; in the electropolishing region (1.0 volt) the activation energy is 7.7 Kcal/mole.

A broad solvent capability for metallic reactor fuels is offered by the HCl-methanol medium since, in addition to zirconium, stainless steel is also dissolved electrolytically while uranium and aluminum dissolve chemically. Other process implications are discussed.

ELECTROLYTIC DISSOLUTION OF NUCLEAR FUELS
Part I. Zirconium in HCl-Methanol

J. R. Aylward, E. M. Whitener, H. T. Hahn

I. SUMMARY

Present aqueous chemical processing of zirconium reactor fuel elements is complicated by the presence of fluoride ion required to effect dissolution. Use of aqueous nitrate or chloride solutions has not been promising; even electrolytic dissolution of zirconium alloys in these media is incomplete and results in the production of relatively large amounts of potentially uranium-bearing solids. As an alternative to aqueous media, organic solvents were considered as electrolytic dissolution media and solutions of hydrogen chloride in methanol selected.

Potential-current density relationships were determined for zirconium metal in solutions of up to 13M hydrogen chloride in methanol. These data were used to define the factors affecting the dissolution, the reactions taking place, and their mechanisms. The results of this investigation may be summarized as follows:

1. At low overvoltage values, both the anodic and cathodic reactions are activation controlled. The reaction rates in this region are independent of HCl concentration.
2. Dissolution in the overvoltage range 0 to +0.4 volt is accompanied by the separation of finely divided alpha-zirconium from the electrode. The amount of residue decreases with increasing overvoltage, with no residue formed at high anodic overvoltages.
3. At high anodic overvoltages, where complete dissolution is attained, the current density is independent of potential. This limiting current density decreases with increasing hydrogen chloride concentration and here the rate is controlled by mass transport.
4. The energy of activation for the corrosion reaction (0.0 volt) is 16.5 Kcal/mole; the electropolishing reaction (1.0 volt) has an activation energy of 7.7 Kcal/mole.

5. The data support the hypothesis that in the activation controlled region the rate-determining step is electron transfer. In the electropolishing region the controlling step is the dissolution of a film, possibly $ZrCl_4$.

6. The rate of dissolution or current density for a zirconium electrode in HCl-methanol solution is given by:

$$I = \frac{\exp\left[20.09 - \frac{8294}{T} + \frac{\eta}{5.03 \times 10^{-4}T - 0.0988}\right] - \exp\left[20.09 - \frac{(8294 + 4350\,\eta)}{T}\right]}{1 + C^{0.469}\exp\left[6.07 - \frac{4430}{T} + \frac{\eta}{5.03 \times 10^{-4}T - 0.0988}\right]}.$$

where η = overvoltage (-0.5 to 12.0 volts)

T = temperature (273 to 323°K)

C = HCl concentration (1.5 to 13<u>M</u>).

7. In limited tests, stainless steel, iron, nickel, and chromium were found to dissolve electrolytically while aluminum and uranium dissolved chemically in HCl-methanol with no evidence, at feasible rates, of solids formation.

II. INTRODUCTION

The dissolution of reactor fuel elements containing zirconium as the major constituent can be carried out successfully in hydrofluoric acid or hydrofluoric-nitric acid mixtures. Systems containing fluoride ion, however, present problems in the solvent extraction and waste storage phases of fuel element reprocessing. It was the purpose of the present work to attempt the dissolution of zirconium in other media in the hope of finding a more attractive process. It was also desired to find a system which would be suitable for the dissolution of other fuel element materials (stainless steel and aluminum alloys).

The above requirements suggested an investigation of electrolytic dissolution since the application of electric potential may serve to remove protective films which impede normal chemical action. Although both stainless steel and aluminum can be dissolved electrolytically in aqueous nitric acid, zirconium dissolution is incomplete, resulting in the production of relatively large amounts of potentially uranium-bearing solids. Similarly, scoping experiments in aqueous chloride solutions were disappointing in that approximately 15 per cent of the zirconium remained as an undissolved sludge irrespective of the pH, temperature, or current density employed. These unsatisfactory results led to the consideration of the non-aqueous chloride solutions, and a review of zirconium chemistry in various organic solvents resulted in the choice of HCl-methanol as the dissolving medium.

Potentiostatic determinations of the potential-current density relationships for zirconium in HCl-methanol solutions were undertaken to define the factors affecting the dissolution, the reactions taking place, and their mechanisms.

III. EXPERIMENTAL

The cell and electrode design used in this work is shown in Fig. 1. Vacuum annealed reactor grade zirconium rod was machined to fit tightly in the Teflon holder so that one square centimeter of electrode surface would be exposed to the solution. A 12-gauge copper wire was inserted into a nipple on the zirconium and crimped. In all cases the resistance from the electrode surface to the end of the copper lead was less than 0.002 ohm. A stainless steel screw mechanism facilitated removal of the zirconium from the Teflon holder upon completion of an experiment. The holder was cut with a 19/38 standard taper (₸) and provided with stainless steel hooks to give a leak-proof fit in the polished ₸ 19/22 glass joint of the cell. The counter electrode was machined from Hastelloy C to fit the other ₸ 19/22 polished glass joint and a tapered Teflon sleeve used to prevent leaking. A solution bridge with a Luggin capillary connected the cell to a saturated calomel reference electrode (S.C.E.). The absence of IR drop error and shielding effects with this capillary was confirmed by the use of interrupter techniques.

The solutions were freshly prepared by saturating absolute methyl alcohol with anhydrous hydrogen chloride gas at 15°C and diluting this

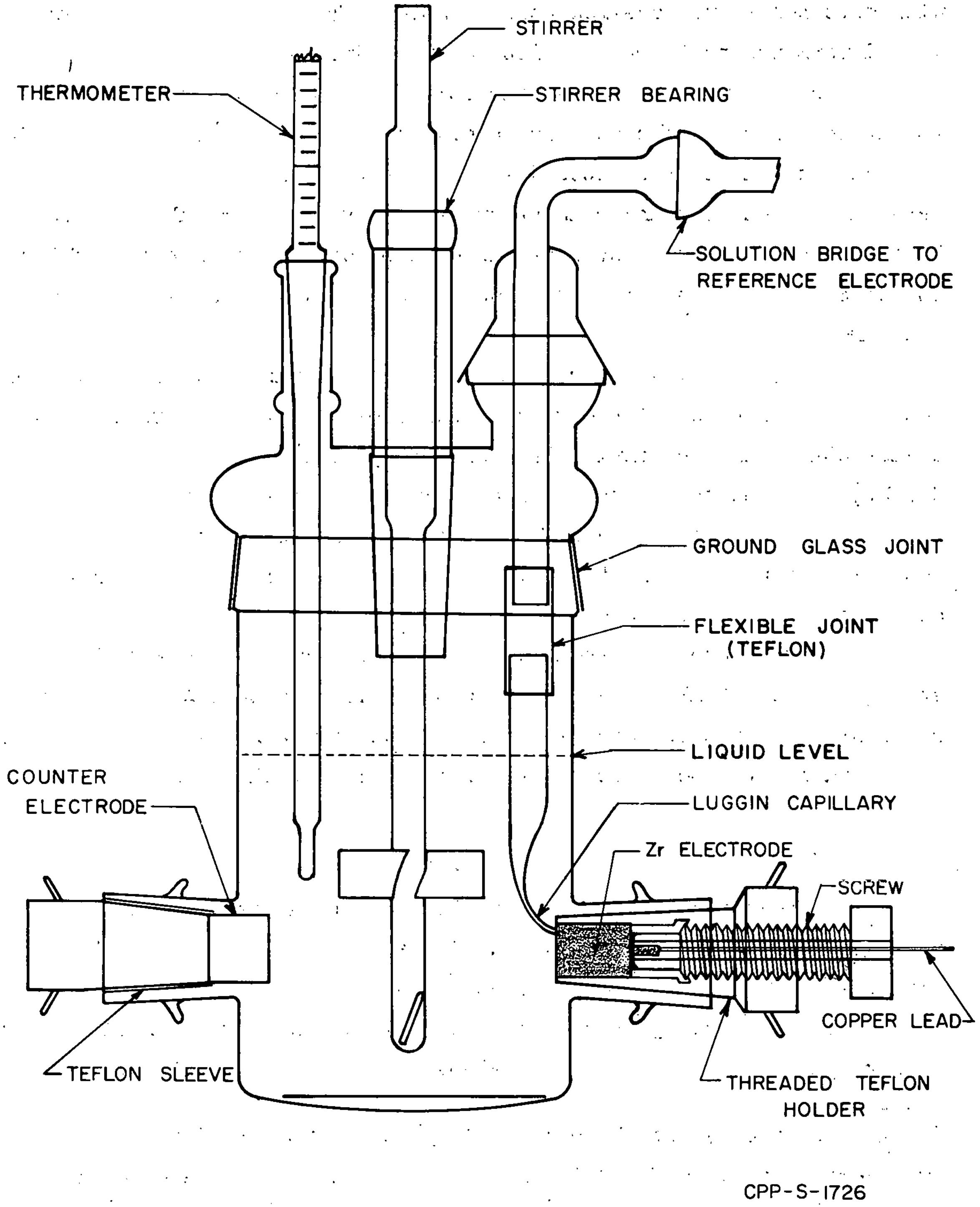

Figure 1
Electrolysis Cell

with methanol to the desired concentration. The solution concentrations were determined by titration with sodium hydroxide.

During a given experiment the solution temperature was controlled to within ± 1°C and the stirring speed maintained at 140 ± 10 rpm. Prior to each experiment, the exposed surface of the zirconium electrode was refaced by machining under an argon atmosphere. The resulting work-hardened surface was removed by dissolution at a high current density in an HCl-methanol solution of the same concentration as used in the ensuing experiment.

An electronically controlled potentiostat* was used to obtain the potential-current density curves. Measurements were initiated at the steady state mixed potential (approximately -0.54 v with respect to the S.C.E.). The potential was increased in 50 mv increments to +1.0 volt, then decreased stepwise back to the steady state mixed potential. The cathodic potential-current density curve was measured after completion of the anodic measurements.

This procedure was repeated three times for each run and the current at a given potential found to be reproducible to within ± 10 per cent. Duplicate experiments were also carried out for each temperature and HCl concentration to check the overall reliability of the data.

IV. RESULTS

The anodic and cathodic overvoltage**-current density relationships for a zirconium electrode in HCl-methanol solutions are shown in Fig. 2 as a function of HCl concentration.

At low overvoltage values a Tafel relationship*** is obtained indicating that both the anodic and cathodic reactions are activation

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* A block diagram of the circuit is given on page 23.

** Overvoltage is defined in this case as the difference between the potential at any current density and the steady state mixed potential. It is, as usual, positive for the anode and negative for the cathode.

*** The overvoltage η follows an equation of the form $\eta = a + b \log I$ where a and b are constants and I is the current density.

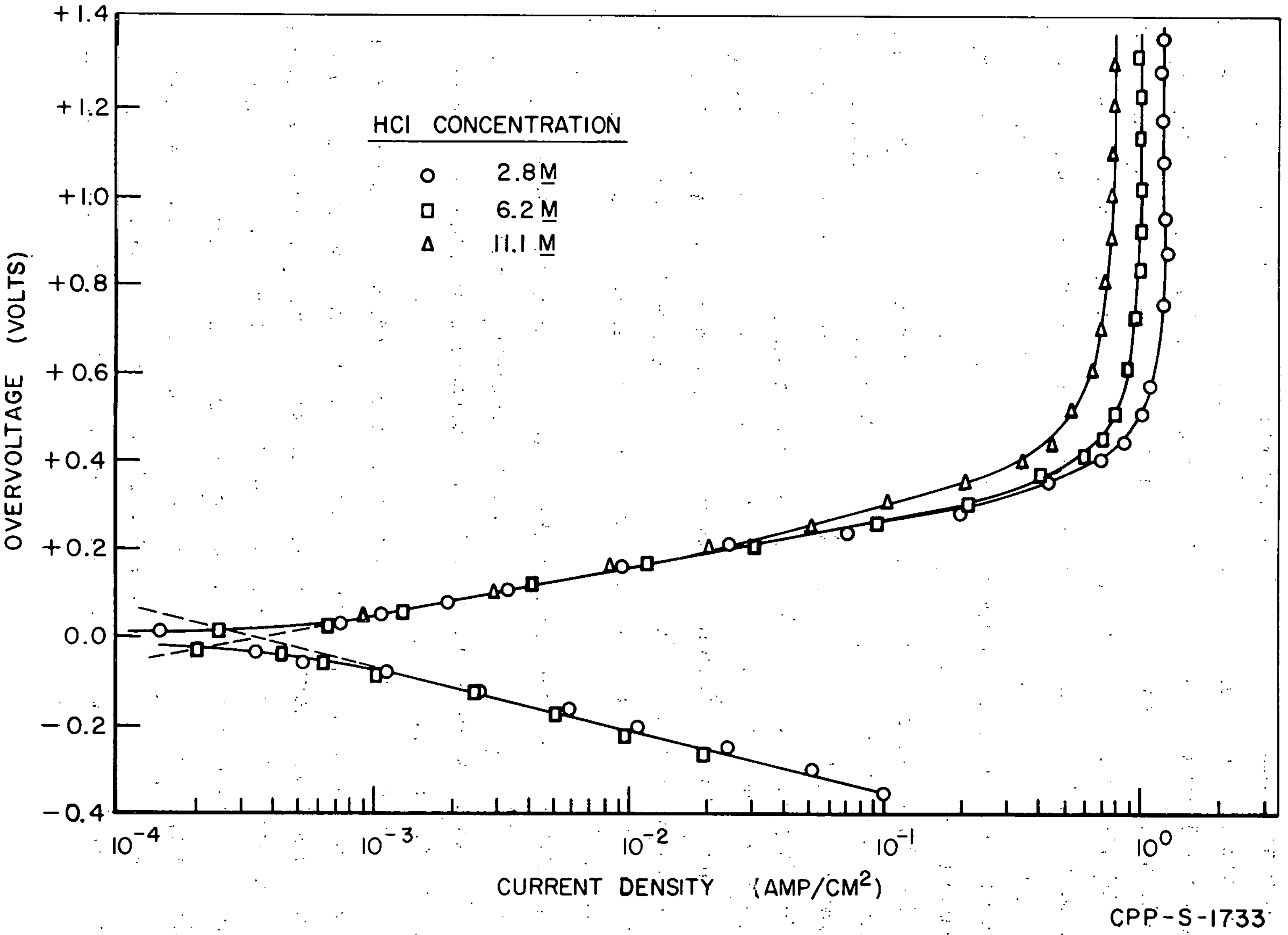


Figure 2

Overvoltage at a Zirconium Electrode as a Function of
HCl Concentration at 20°C

controlled. It can be seen that the reaction rates in this region are independent of HCl concentration. The rate of "chemical" dissolution, or the corrosion rate as given by the intersection of the Tafel lines extrapolated to zero overvoltage, is also independent of HCl concentration within the limits of reproducibility (3 to 5 x 10^{-4} amp/cm^2). The reproducibility of the steady state mixed potential (-0.54 volt vs the S.C.E. for 6.0M HCl) was in the order of ± 10 mv. Because of this, it was difficult to determine with any accuracy the variation of the steady state mixed potential as a function of solution composition. However, there appeared to be a trend toward more positive values with increasing HCl concentration ($\approx$30 mv in going from 1M to 10M HCl).

Zirconium dissolution in the overvoltage range from zero to approximately +0.4 volt results in an etched surface and is accompanied by the separation of a finely divided black residue from the electrode. This residue is pyrophoric and gives an x-ray pattern corresponding to α-zirconium. The relative amount of residue decreases with increasing overvoltage, finally becoming zero at high anodic overvoltages. The particulate zirconium residue is also quite passive in HCl-methanol solutions in contrast to bulk zirconium which corrodes at a rate of 3.4 x 10^{-4} amp/cm^2.

At high anodic overvoltages the current density is independent of potential. This limiting current density decreases with increasing HCl concentration. Also, in this region the zirconium is electropolished and complete dissolution attained.

As shown in Fig. 3, the anodic behavior of zirconium in more dilute HCl-methanol solutions (< 1.5M) is different in that the limiting current density is not well defined and its value at constant overvoltage decreases with decreasing HCl concentration. In this case the surface at high overvoltages is etched (as opposed to electropolished) but the overall surface is brighter than the etched surface obtained at low overvoltages.

A comparison of the different surface features obtained under the various dissolution conditions mentioned above is shown in Fig. 4. In

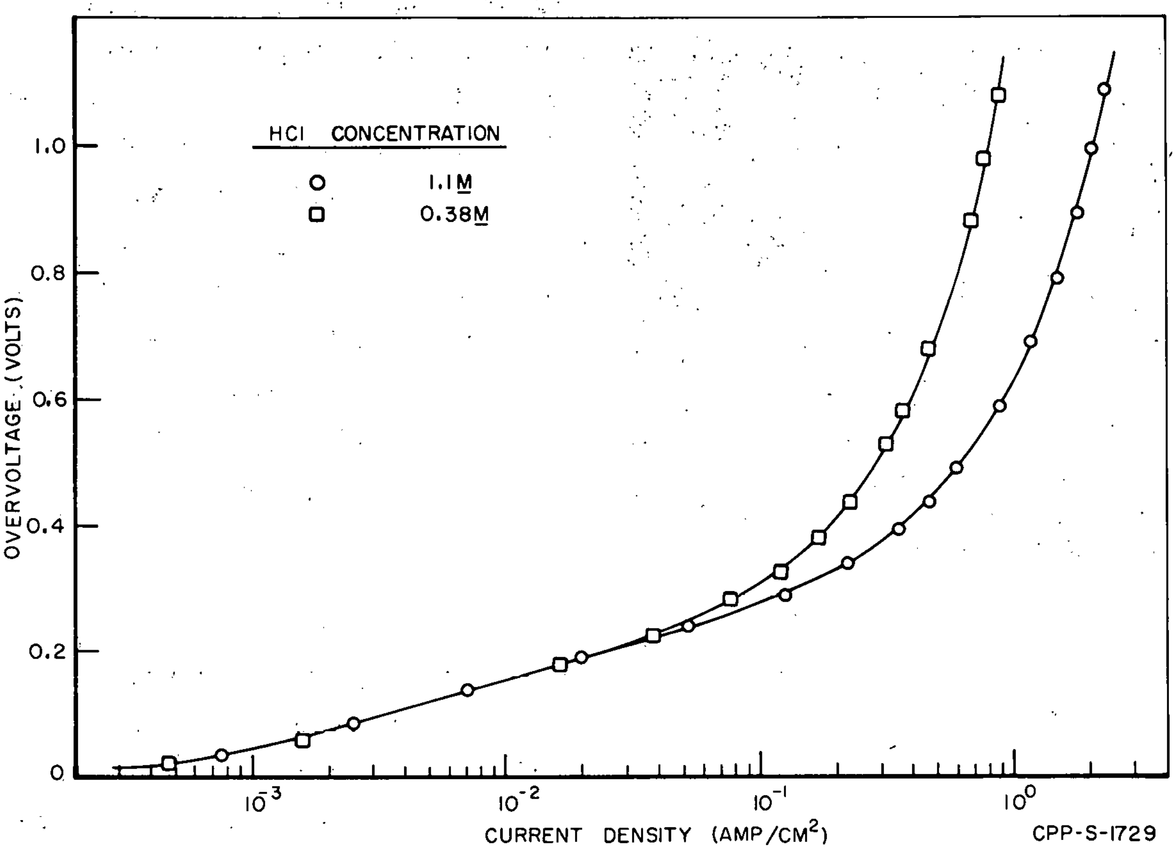


Figure 3

Anodic Overvoltage of a Zirconium Electrode in Dilute HCl-Methanol Solutions at 20°C

A and B of Fig. 4 the effect can be seen of a higher dissolution rate at the electrode boundary. This is due to the presence of a considerable product concentration gradient which plays a predominant role in controlling the reaction rate in the limiting current density region. The fact that the gradient is larger at the electrode edge results in a higher dissolution rate at this point. In the region where the reaction is activation-controlled, an even dissolution rate is observed over the whole surface (electrode C of Fig. 4). Schlieren photographs of the metal-solution interface under conditions corresponding to A, B and C of Fig. 4 are shown in Figs. 5A, B and C, respectively. The light areas

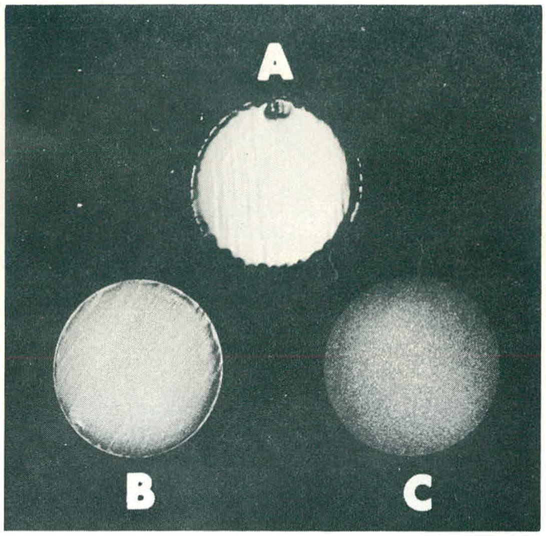


Figure 4

Electrode Surface Obtained Under Various Dissolution Conditions:

A - 6.0$\underline{M}$ HCl, +0.8 v overvoltage, $\approx$1 amp/cm^2

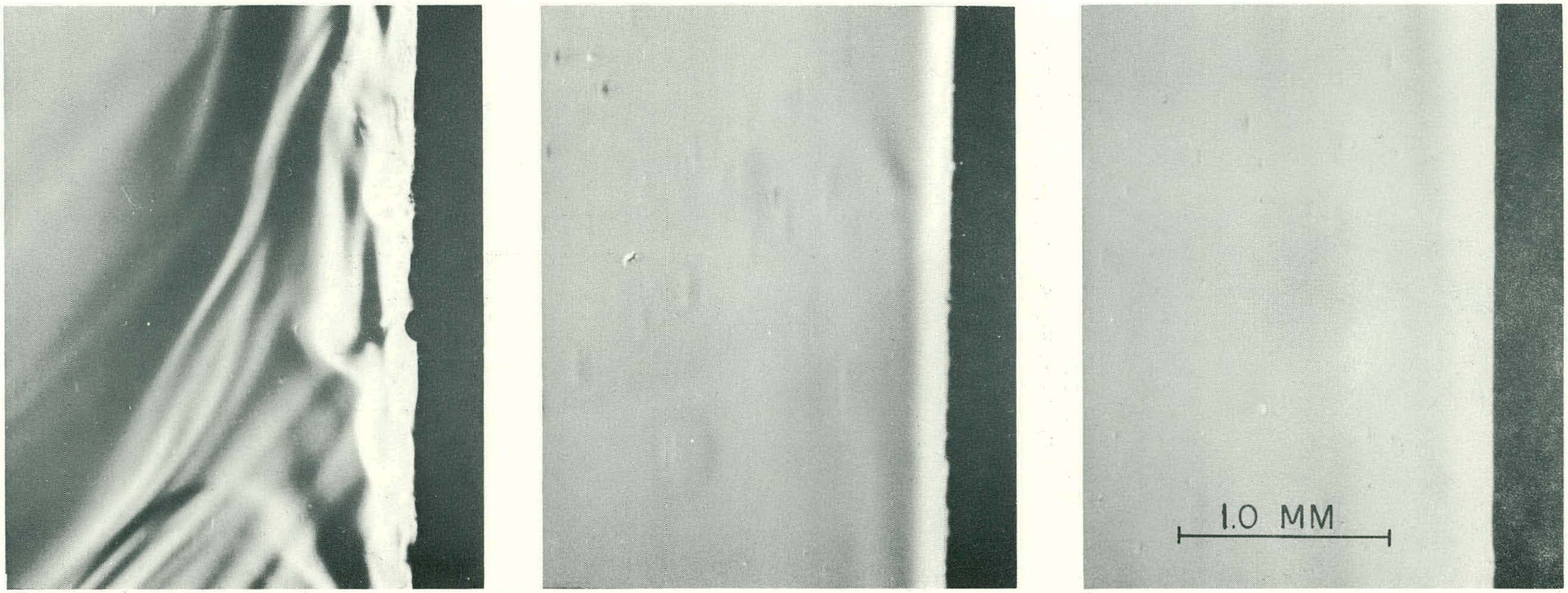
B - 1.0$\underline{M}$ HCl, +0.8 v overvoltage, $\approx$1 amp/cm^2

C - 6.0$\underline{M}$ HCl, +0.3 v overvoltage, $\approx$100 ma/cm^2

represent regions of higher refractive index (dissolution product concentration). In A of Fig. 5, the streaming off of the viscous layer is characteristic of electropolishing, while in B a quiescent concentration gradient typical of concentration polarization is evident. Both A and B were taken at the same current density (1 amp/cm^2). Fig. 5C obtained at approximately 100 ma/cm^2 (activation controlled region) shows no significant concentration gradient.

The effect of HCl concentration on the limiting current density at an overvoltage of 1.0 volt is shown in Fig. 6. The concentration range for electropolishing is characterized by a negative slope and non-electropolishing by a positive slope.

Figure 9 shows the effect of temperature on the anodic overvoltage curves in 6.0$\underline{M}$ HCl-methanol. From these data the energy of activation was found at overvoltages of zero and 1.0 volt (corresponding to the corrosion and electropolishing reactions,respectively). This is shown in the Arrhenius plots of Figs. 7 and 8. At an overvoltage of 0.0 volt the energy of activation for the corrosion reaction is 16.5 Kcal/mole, and in the electropolishing region at 1.0 volt it is 7.7 Kcal/mole. The low energy of reaction obtained for the electropolishing region is compatible with a mass transport controlled mechanism.



A
6.0M HCl, 1 amp/cm^2

B
1.0M HCl, 1 amp/cm^2

C
6.0M HCl, 100 ma/cm^2

Figure 5

Schlieren Photographs of Metal-Solution Interface During Dissolution in HCl-Methanol

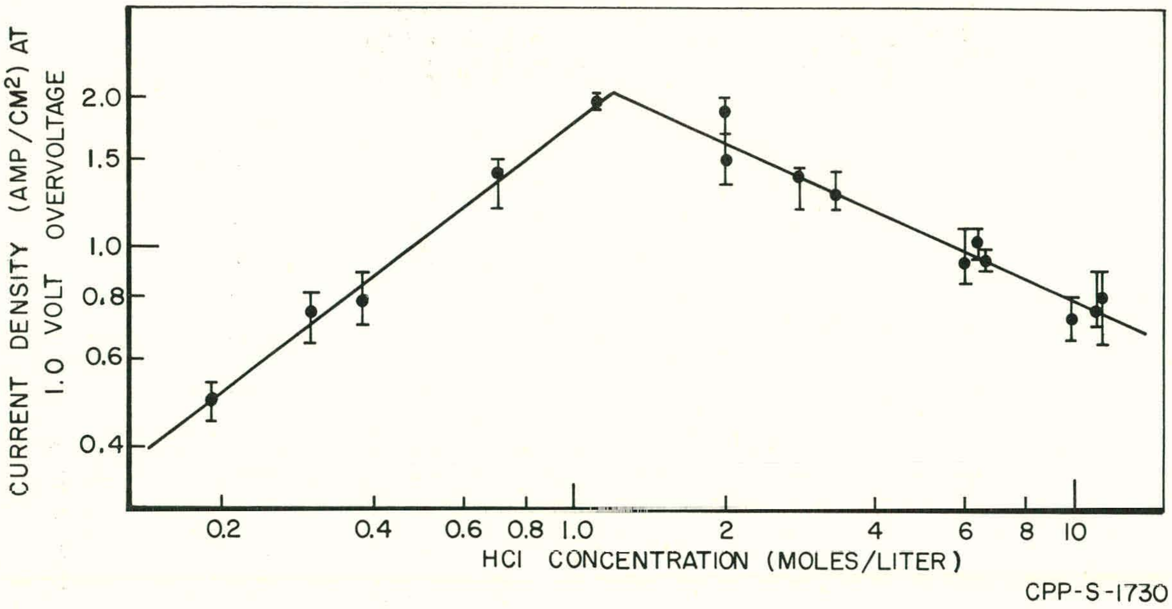
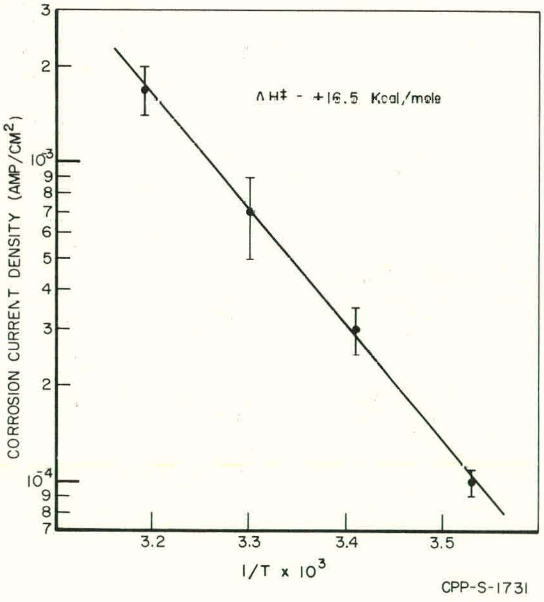


Figure 6

Effect of HCl Concentration on Limiting Current Density at 1.0 Volt Overvoltage (20°C)



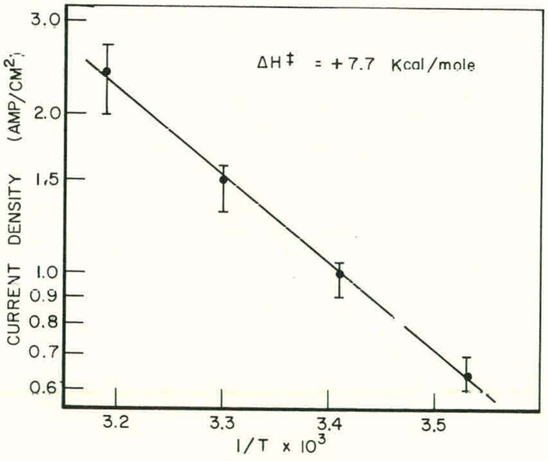


Figure 7

Arrhenius Plot for the Reaction at an Overvoltage of Zero Volt

Figure 8

Arrhenius Plot for the Reaction at an Overvoltage of 1.0 Volt

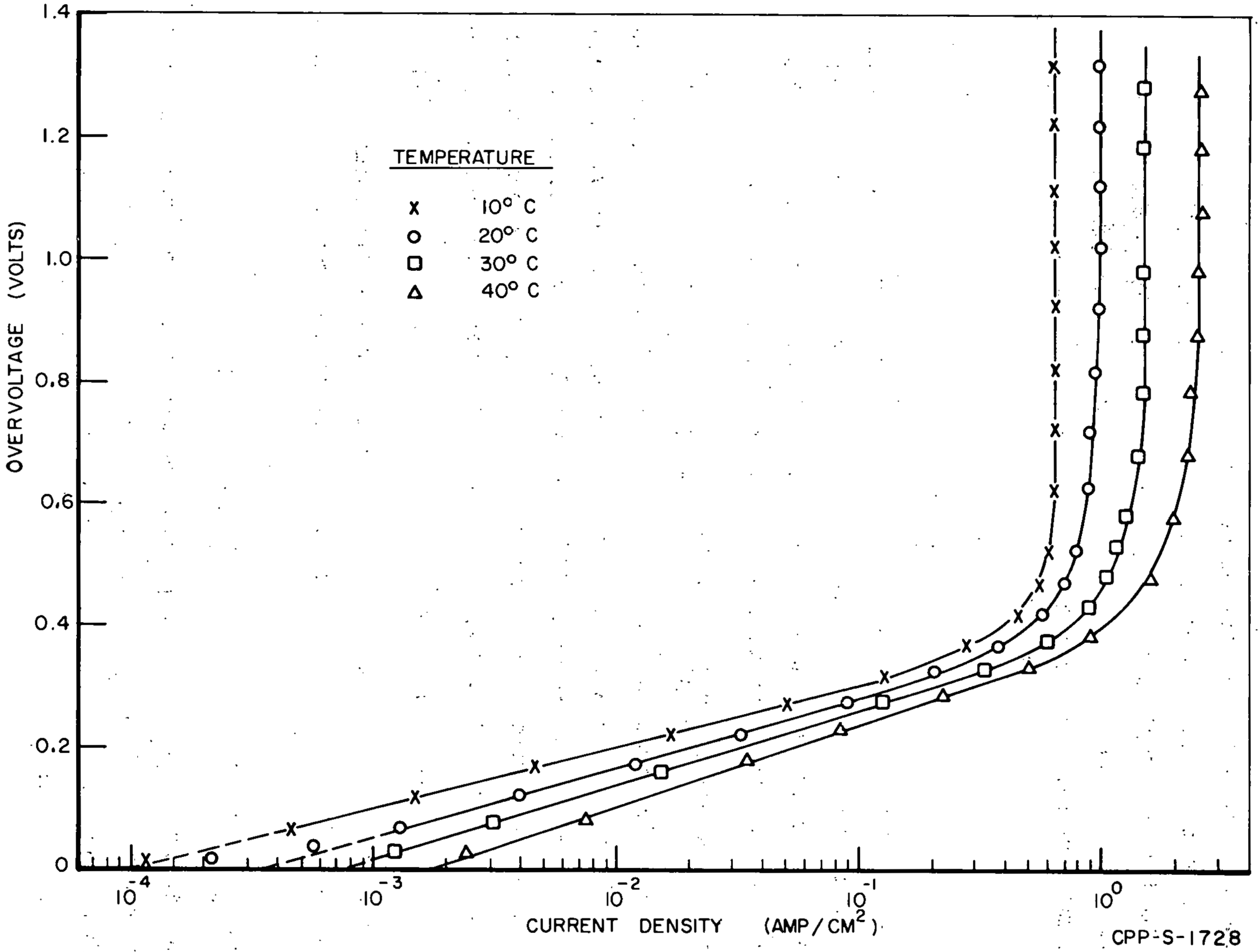


Figure 9

The Effect of Temperature on the Anodic Overvoltage of Zirconium in 6.0M HCl-Methanol

Miscellaneous Experiments. Although no attempt was made to determine the solubility of zirconium in HCl-methanol, it was observed that this solubility exceeded 2.8M. Concentration of the zirconium-HCl-methanol solutions by evaporation produced a glass.

In limited tests of other reactor metals aluminum and uranium were found to dissolve rapidly by chemical means in HCl-methanol. In the same medium stainless steel and its major components, iron, nickel and chromium, were dissolved electrolytically at feasible rates (> 0.5 amp/cm^2).

V. DISCUSSION

When zirconium is placed in an HCl-methanol solution, dissolution of the metal takes place at a very slow rate to give as products hydrogen gas and a mixture of the various chlorozirconium methoxides. This overall reaction is shown in (1) where x has values from 0 to 4.

$$Zr + (4-x)HCl + xCH_3OH \longrightarrow ZrCl_{(4-x)}(OCH_3)_x + 2H_2. \qquad (1)$$

Evidence for this reaction is supported by the identical optical spectra of dissolver solutions and solutions prepared by adding zirconium tetrachloride to methanol. Reaction (1) is believed to take place in two principal steps. First, zirconium reacts with hydrogen chloride to form zirconium tetrachloride and hydrogen gas at the metal-solution interface.

$$Zr + 4HCl \longrightarrow ZrCl_4 + 2H_2. \qquad (2)$$

The next step (3) takes place primarily in the bulk of the solution (at HCl concentration > 1M) and so has little, if any, effect on the dissolution rate.

$$ZrCl_4 + xCH_3OH \overset{K_x}{\rightleftharpoons} ZrCl_{(4-x)}(OCH_3)_x + xHCl. \qquad (3)$$

The equilibrium constants K_x for the above reaction were determined by Simmons and Hansen(1) ($pK_1 = 1.62$, $pK_2 = 5.18$, $pK_3 = 10.4$, $pK_4 = 18.2$). From these data it is obvious that $ZrCl_4$ and $ZrCl_3OCH_3$ are the main species in solution.

For the purpose of this discussion it is convenient to divide reaction (2) into two half-reactions, one representing an oxidation (4) and the other a reduction (5) (anodic and cathodic reactions),

$$Zr + 4Cl^{-} \longrightarrow ZrCl_4 + 4e \tag{4}$$

$$4H^{+} + 4e \longrightarrow 2H_2. \tag{5}$$

If zirconium is made the anode of an electrolytic cell in which HCl-methanol is the electrolyte, reaction (4) predominates; if it is the cathode, reaction (5) takes place at a faster rate. In reaction (4) it is not to be construed that the reactive species is the chloride ion as such because molecular HCl is present at a higher concentration and may serve just as well. However, if the ionization equilibration ($H^{+} + Cl^{-} \rightleftharpoons HCl$) is rapid, the two would be kinetically equivalent.

When reactions (4) and (5) are activation controlled, their respective rates i_a and i_c are given by:

$$i_a = i_o' \exp\left(\frac{1}{b_a}\eta\right) \tag{6}$$

and

$$i_c = i_o' \exp\left(-\frac{1}{b_c}\eta\right), \tag{7}$$

where η is the overvoltage, b_a and b_c constants characteristic of the reaction mechanism and i_o' the reaction rate at zero overvoltage. At zero overvoltage the anodic (4) and cathodic (5) rates are equal, and, therefore, i_o' is the corrosion or chemical dissolution rate (reaction (2)). The cell current density, I, will be given by the difference in the rates of reaction (4) and (5). Thus,

$$I = i_a - i_c = i_o'\left[\exp\left(\frac{1}{b_a}\eta\right) - \exp\left(-\frac{1}{b_c}\eta\right)\right] . \tag{8}$$

This particular form of the equation gives negative values for the cell current when zirconium is the cell cathode and positive when it is the anode.*

Under circumstances where a limiting current density is observed, e.g., in the electropolishing region, it can be shown(2,3) that the equation expressing the current density as a function of overvoltage

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* In Fig. 2 this sign convention is disregarded.

takes the form

$$I = \frac{i_a - i_c}{1 + i_a/i_\ell} = \frac{i_0'\left[\exp\left(\frac{1}{b_a}\eta\right) - \exp\left(-\frac{1}{b_c}\eta\right)\right]}{1 + i_0'/i_\ell \ \exp\left(\frac{1}{b_a}\eta\right)} \qquad (9)$$

where i_ℓ is the limiting current density. Equation (9) can be simplified considerably for certain overvoltage ranges. For example, when η is more negative than about -0.05 volt, $i_a \ll i_c$ and i_ℓ so that (9) reduces to

$$I = i_c = i_0' \exp\left(-\frac{1}{b_c}\eta\right) \qquad (10)$$

or

$$\eta = 2.30\ b_c \ \log i_0' - 2.30\ b_c \ \log I. \qquad (11)$$

Likewise, if $\eta < +0.05$ volt and i_a/i_ℓ can be neglected then $i_c \ll i_a$ and equation (9) simplifies to

$$I = i_a = i_0' \exp\left(\frac{1}{b_a}\eta\right) \qquad (12)$$

or

$$\eta = -2.30\ b_a \ \log i_0' + 2.30\ b_a \ \log I. \qquad (13)$$

Finally when $i_a/i_\ell > 1$ then $I \longrightarrow i_\ell$. Under conditions where equations (11) or (13) are valid, a plot of overvoltage η versus log I gives a straight line from which the Tafel slope ($-2.30\ b_c$ or $2.30\ b_a$) and the intercept i_0' can be determined.

Since the value of the Tafel slope depends on the type of reaction step that is rate-determining, it is one of the important criteria used in establishing the reaction mechanism. From electrode kinetic theory b_a is given by

$$b_a = \frac{\gamma RT}{\beta nF}, \qquad (14)$$

where γ is the stoichiometric number*, β the symmetry factor**, n the

---

* The number of times the rate-determining step must take place during one act of the overall process.

** For the symmetrical energy barriers normally encountered $\beta = 0.5$.

number of electrons transferred during one act of the overall process (equal to four from reaction (4)) and the other terms have their usual significance. The stoichiometric number calculated from the average experimental anodic Tafel slope ($2.3\ b_a = 0.115 \pm 0.005$ volt) and equation (14) is 3.96 ± 0.16. From this it can be concluded that the rate-determining step in the activation controlled region for the anodic process represented by equation (4) must take place four times for each act of the overall reaction. However, the behavior of the corrosion rate and the steady state mixed potential with changing HCl concentration can not easily be associated with any simple sequence of reaction steps for the overall process. The change in the steady state mixed potential of approximately 30 mv in going from 1M to 10M HCl is not of real significance because of the possible changes in the liquid junction potential (HCl-methanol || KCl aqueous) with HCl concentration. Unfortunately, the Ag, Ag_2Cl_2 electrode was found to be unsuitable as a reference in concentrated HCl-methanol because of the high solubility of Ag_2Cl_2.

The lack of dependence of the corrosion rate on HCl concentration can possibly be explained by assuming complete coverage of the zirconium surface with specifically adsorbed Cl^-. This adsorption step could be rapid at the potentials and HCl concentrations involved.$^{(4)}$ The next step would then result in the formation of a positively charged zirconium chloride species which could react further with chloride ion or methanol in the double layer to form a soluble product. Thus, the reaction may be divided into three parts:

$$M\text{-}Zr + pCl^- \longrightarrow M\text{-}ZrCl_p^{-p} \qquad (15a)$$

$$M\text{-}ZrCl_p^{-p} \longrightarrow M\text{-}ZrCl_p^{+(4-p)} + 4e \qquad (15b)$$

$$M\text{-}ZrCl_p^{+(4-p)} + (4-p)Cl^- \longrightarrow M + ZrCl_4. \qquad (15c)$$

The stoichiometric number of four indicates that the rate-determining step may be associated with the formation of the zirconium chloride species of (15b).

Under conditions of electropolishing, it is generally believed that a solid film is formed on the metal surface which in the steady state is dissolving as fast as it is formed.(5,6) The rate-determining step is the "physical" dissolution of this film and is, therefore, independent of electrode potential. Increasing the potential merely increases the steady state film thickness. Since the film is the controlling factor in the dissolution, the differing rates of removal of cations from the metal lattice due to their special positions within the lattice are no longer of significance. On the other hand, in the non-electropolishing region, preferential attack at grain boundaries, etc., results in etching and the separation of small bits of metal from the surface. Fedot'ev and Grilikhes(6) attribute electropolishing to the formation of oxide films rather than salt films. This may be true for the most part in aqueous systems but we do not believe it to be the general case in non-aqueous solutions. It is difficult to see how increasing the HCl concentration would decrease the dissolution rate of an oxide film (see Fig. 2) but this effect is conceivable if the film were a chloride of zirconium.

At low HCl concentrations and high current densities the transport of HCl to the electrode surface becomes rate-determining (concentration polarization) and the value of the limiting current density decreases as the HCl concentration is decreased (see Fig. 3). Under these conditions the electrode surface can not be completely covered with adsorbed Cl^- so that it becomes possible for the solvent (methanol) to play a direct part in the dissolution mechanism with the resulting formation of chlorozirconium methoxides at the metal-solution interface. This, combined with the fact that the rate of transport of Cl^- to the metal surface would increase with increasing potential (in the absence of supporting electrolyte), may explain the ill-defined limiting current density observed at low HCl concentrations.

VI. PROCESS IMPLICATIONS

It was shown previously that the rate of zirconium dissolution in HCl-methanol is a function of overvoltage, temperature, and HCl concentration. From the data in Figs. 6, 7 and 8 the corrosion rate i_0 and the limiting current density i_ℓ (both in amp/cm^2) can be expressed in terms of HCl concentration C and absolute temperature T as follows:

$$i'_o = \exp\left[20.09 - \Delta H_o^\ddagger/RT\right] \qquad (16)$$

$$i_\ell = C^{-0.469}\left[\exp 14.02 - \Delta H_\ell^\ddagger/RT\right] \qquad (17)$$

where $\Delta H_o^\ddagger = 16.5$ Kcal/mole is the energy of activation for the corrosion reaction (2) and $\Delta H_\ell^\ddagger = 7.7$ Kcal/mole is the activation energy for the electropolishing process. Substituting equations (16) and (17) into (9) results in:

$$I = \frac{\exp\,(20.09 - 8294/T + \eta/b_a) - \exp\,(20.09 - 8294/T - \eta/b_c)}{1 + C^{0.469}\exp\,(6.07 - 4430/T + \eta/b_a)}. \qquad (18)$$

The experimental anodic Tafel slopes were found to differ slightly from the temperature dependence shown in equation (14). This is probably due to changes in the symmetry factor β with temperature. The data were best fitted by the empirical formula:

$$b_a = 5.03 \times 10^{-4}T - 0.0988. \qquad (19)$$

The cathodic slope was determined only at 293°K. These data combined with (18) and (19) yield the current density I at a zirconium electrode in HCl-methanol solutions as a function of overvoltage (-0.5 to +2.0 volts), HCl concentration (1.5 to 13M) and temperature (273 to 323°K):

$$I = \frac{\exp\left[20.09 - \frac{8294}{T} + \frac{\eta}{5.03 \times 10^{-4}T - 0.0988}\right] - \exp\left[20.09 - \frac{(8294 + 4350\,\eta)}{T}\right]}{1 + C^{0.469}\exp\left[6.07 - \frac{4430}{T} + \frac{\eta}{5.03 \times 10^{-4}T - 0.0988}\right]}. \qquad (20)$$

Equation (20) reduces to more simple forms in some overvoltage ranges. For example, if (20) is rewritten as

$$I = \frac{A - B}{D} \qquad (21)$$

the following simplifications are possible. When η is more negative than about -0.05 volt, $A \cong 0$ and $D = 1$ so that $I = -B$. The negative sign indicates that the zirconium is the cell cathode, a case which is only of theoretical interest. If η is $> +0.05$ but $< +0.3$ volt, then $B \cong 0$ and $D \cong 1$ so that $I = A$. For values of η above +0.6 volt, $B = 0$ and $D \gg 1$ so that $I = A/D \cong i_l$. This is the electropolishing region where the current density is independent of overvoltage. In this case the desired dissolution rate must be obtained by controlling the variables of temperature and HCl concentration. The current density as a function of these two parameters is given by (17) and is rewritten below with the proper numerical constants.

$$i_l = C^{-0.469} \exp\left[14.02 - 3864/T\right]. \tag{22}$$

Since the reaction rate in the electropolishing region is essentially mass transport controlled, a considerable concentration gradient is present in the solution next to the electrode. Stirring reduces the gradient thickness thereby increasing the dissolution rate. The type and rate of solution flow next to the dissolving metal depends to such a great extent on dissolver geometry that it was felt a quantitative study of dissolution rates vs stirring speed on a laboratory scale would be of little use. This solution flow factor must, therefore, be considered in applying equation (22) to other dissolver systems.

It has been shown that the dissolution of zirconium in HCl-methanol at an overvoltage of less than approximately +0.5 volt is accompanied by the separation of some finely divided metal particles from the bulk zirconium. This residue is completely insoluble in HCl-methanol and the amount formed decreases with increasing overvoltage. Only in the electropolishing region is complete dissolution obtained. Therefore, in order to avoid possible uranium loss from the undissolved material it would be necessary to carry out the dissolution entirely within the electropolishing region.* This starts at an overvoltage of approximately

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* The nature of the overvoltage-current density curves necessitates use of a constant voltage or very low impedance power supply to maintain stable operation in the electropolishing region.

+0.5 volt, but limited operation down to +0.4 volt would not be detrimental. The upper limit of overvoltage for the electropolishing region has not been sharply defined but appears to be about +2 volts. Operation up to +3 volts has been maintained for short periods of time, but the onset of gas evolution at high overvoltages tends to break up the concentration gradient and produces instability of the limiting current density. Beyond the limiting current density for zirconium dissolution, evolution of chlorine gas is encountered with a resultant decrease in current efficiency for the dissolution process. Complete dissolution may also be possible under these conditions but experimental difficulties discouraged study in this region.

The complete dissolution of zirconium fuel elements with a complex geometry presents some problems in that the potential across the metal-solution interface at all points must be within the electropolishing region. Although the useful range between minimum and maximum potential over the surface is relatively large for this system (1.5 volt), the ten-fold higher resistance of the electrolyte* compared to aqueous solutions of similar concentration counteracts this advantage somewhat. In other words, a system with excellent throwing power is needed to completely dissolve complex elements. The requirements for good throwing power are (1) high polarization (limiting current density is ideal) and (2) low solution resistance. Only the first of the above requirements is met for HCl-methanol solutions, the result being a system with only medium throwing power. An alternative to improve the potential distribution over an element surface would be to modify the element and/or dissolver geometry. For example, it may be possible in some cases to reduce a complex fuel element to a more simple shape by a cutting or crushing operation.

Operation of a large scale dissolver entirely within the electropolishing region may be impossible to achieve when dealing with fuel elements of complex geometries. A separate treatment for the small

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* This high electrolyte resistance will also create a heat dissipation problem.

amount of undissolved residue (about 1 per cent) might then be necessary. For example, dissolution in a small amount of hydrofluoric acid is rapid and complete. However, since the precipitate is α-zirconium and not zirconium oxide, uranium inclusion may be minimal, and it may be possible to discard the precipitate without further treatment.

Other materials that can be dissolved in HCl-methanol are iron, nickel, chromium, or their alloys (stainless steel), aluminum and uranium. In some cases dissolution proceeds at a sufficient rate without an external current, e.g., aluminum and uranium. Although there was a limited number of dissolution experiments carried out with the above materials, no evidence of incomplete dissolution was observed as with zirconium at low overvoltages.

Uranium dioxide is not dissolved by HCl-methanol solutions, so that the decladding of UO_2-type elements is possible. This was demonstrated in the laboratory by dissolving a zirconium clad fuel pin containing UO_2 pellets. No uranium could be detected in the dissolver solution, and subsequent treatment of the remaining solids with nitric acid resulted in the complete separation of uranium from zirconium. The aqueous uranium nitrate solution obtained by this procedure lends itself well to treatment by existing solvent extraction methods.

Another feature of process significance is the larger zirconium capacity of the HCl-methanol system relative to aqueous fluoride solutions. The greater solution stability offers greater flexibility in both chemical separation and waste storage aspects. In the latter case final storage as a glass may be possible.

Although there are some major problems to be solved or investigated in developing the HCl-methanol system into a process, e.g., radiation stability, equipment development, and uranium separation, the ability of this solvent to dissolve a large number of reactor fuel metals and its relatively high metal capacity suggest further research to define its capabilities.

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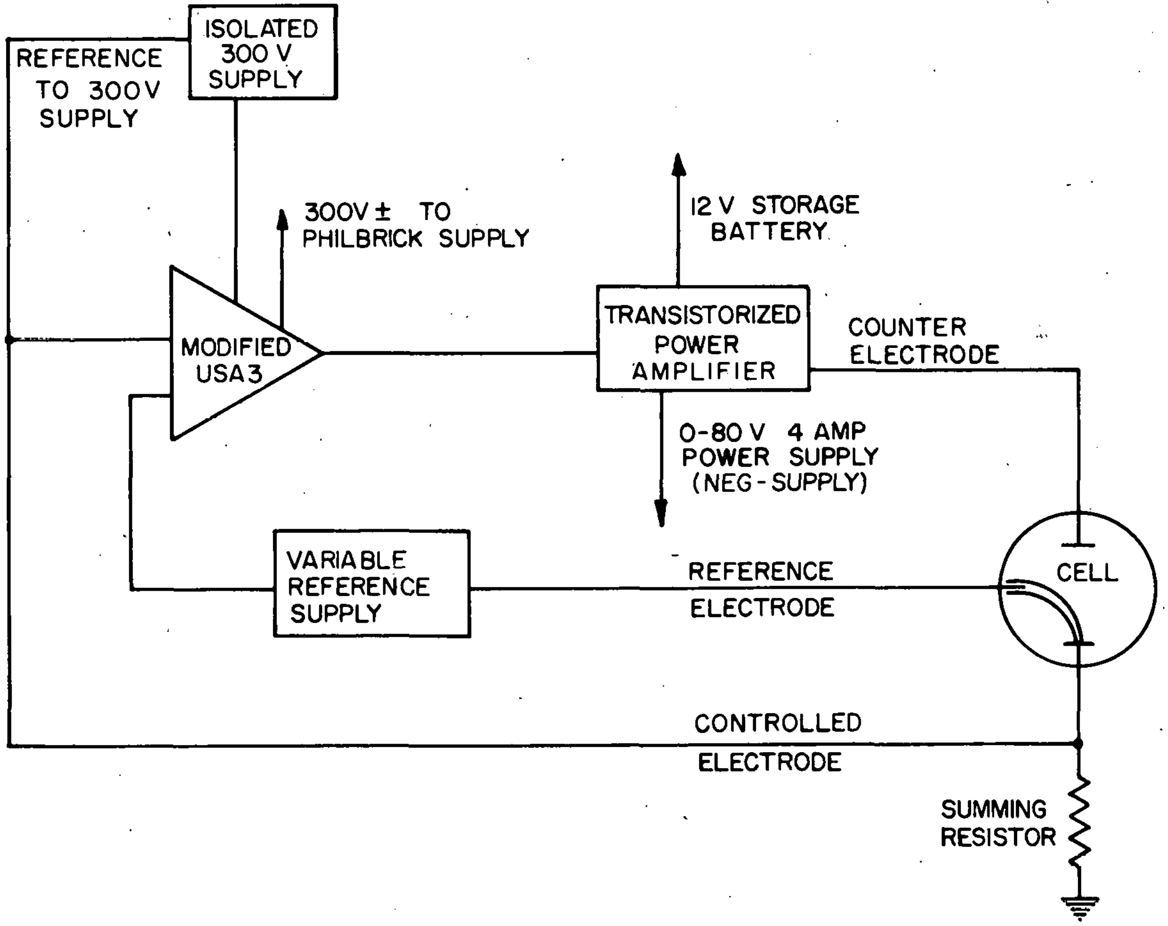

Schematic Diagram of Potentiostat

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