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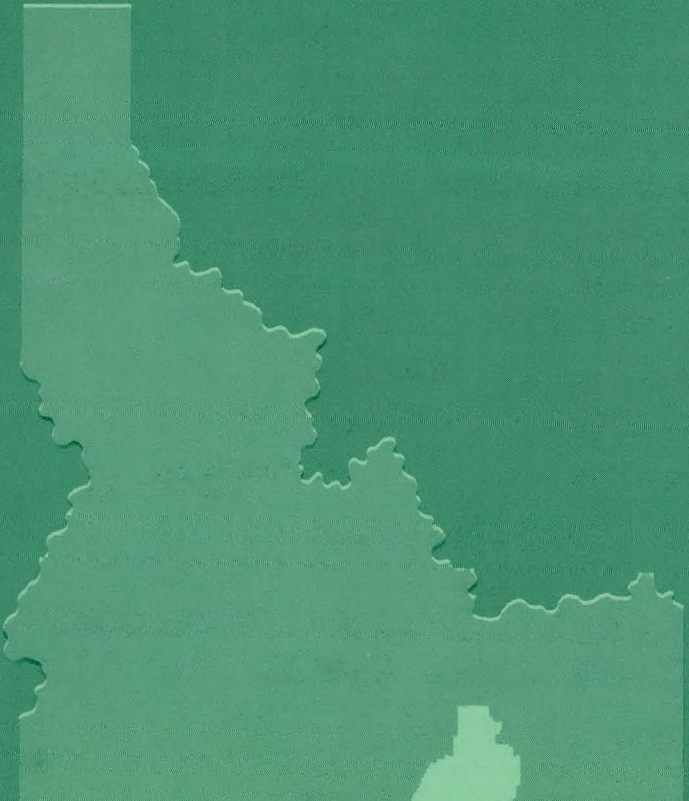
# STAINLESS STEEL WASTES. II. CO-REMOVAL OF FISSION PRODUCTS IN THE ELECTROLYTIC SEPARATION OF IRON, CHROMIUM, AND NICKEL AT A DROPPING MERCURY ELECTRODE

K. T. Faler
D. R. Anderson

March 2, 1961



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K. T. Faler
D. R. Anderson

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# STAINLESS STEEL WASTES. II. CO-REMOVAL OF FISSION PRODUCTS IN THE ELECTROLYTIC SEPARATION OF IRON, CHROMIUM, AND NICKEL AT A DROPPING MERCURY ELECTRODE

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## ABSTRACT

A study has been made of the removal rates of cesium, barium, strontium, yttrium, cerium, ruthenium, and zirconium as a function of electrode potential at a dropping mercury cathode. Removal was studied in sulfate solutions containing varying concentrations of iron, chromium, nickel, chloride, and acid. Results indicated that iron, chromium, and nickel can be removed from acidic sulfate solutions with good separation from all fission product ions studied except zirconium and possibly ruthenium. Polarographic half-wave potential data were obtained and tabulated together with minimum removal potentials for the fission product ions. A description of the mercury drop-washing polarographic cell used for studying removal of tracer amounts of radioisotopes is presented.

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# STAINLESS STEEL WASTES. II. CO-REMOVAL OF FISSION PRODUCTS IN THE ELECTROLYTIC SEPARATION OF IRON, CHROMIUM, AND NICKEL AT A DROPPING MERCURY ELECTRODE

by

K. T. Faler
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## I. SUMMARY

As part of a study of the possibility of developing a mercury cathode separation process in which iron, nickel, and chromium would be removed from a nuclear fuel element reprocessing waste solution, a polarographic investigation of the behavior of important fission products has been carried out. Data obtained include ordinary polarograms of fission-product elements in sulfate solutions and removal rates as a function of applied potential for tracer-concentration radioisotopes. The latter study was carried out using the mercury drop-washing technique developed by Love(5), in which rates were determined by gamma-ray counting of mercury samples rather than measuring current flow.

Results of the study showed that iron, nickel, and chromium can be removed from an acidic sulfate solution at potentials of -2.0 volts or less with respect to a saturated calomel electrode. The minimum potential for reduction and removal of a fission ion was found to be -1.8 volts for ruthenium and zirconium; however, zirconium was found to be co-removed with the steel-alloy ions during their reduction at very low potentials. The mechanism for this co-removal is not apparent. Minimum potentials for reduction of other ions were found to be -2.1 volts for cesium, -2.2 for strontium, -1.9 for barium, -2.0 for yttrium, and -2.5 for cerium. No significant amount of co-removal of tracer ions was observed except in the case of zirconium during electrolytic reduction of iron, nickel, and chromium from a simulated sulfate waste solution of about 0.1<u>M</u> metal ion concentration.

Inasmuch as zirconium is not an exceptionally important heat-producing fission product, or hazardous from the health-physics standpoint after about two years, and since the separated steel-alloy metals would doubtless contain sufficient $Co^{60}$ to prevent complete decontamination of the alloy metals by this method, a satisfactory separation of bulk metals from most fission products can be accomplished by electrolytic reduction.

# II. INTRODUCTION

Chemical reprocessing of nuclear reactor fuel elements which contain stainless steel structural components results in waste solutions containing iron, chromium, and nickel together with high concentrations of radioactive fission products. Long-term storage or disposal of this material would be greatly simplified if the steel-alloy material could be separated from most of the fission product activity and treated separately.

An interesting and straightforward method of separation appears to be the electrolytic reduction of $Fe^{+3}$, $Cr^{+3}$, and $Ni^{+2}$ to the metallic state under such conditions that fission product ions remain in solution. By using an electrolytic cell with a circulating mercury cathode, the reduced metals could be removed from the cell and separated from the cathode. A method survey and preliminary examination of the technical feasibility of such a process have been carried out(1). The encouraging results of that study prompted the present investigation of the behavior of important fission product ions at a mercury cathode during the reduction of stainless-steel alloy ions. A similar study in which mercury cathode electrolysis is used as a means of separation of homogeneous reactor fuel is being carried out at Oak Ridge National Laboratory(2).

Electrolytic reduction is the principal method by which ions are removed from solution at a mercury cathode. Standard potentials for reduction to the metallic state are between -0.25 and -1.0 volt vs normal hydrogen electrode for iron, chromium, and nickel; while potentials of important fission products such as cesium, cerium, promethium, strontium, and yttrium are between -2.4 and -2.9 volts. It is this wide separation in reduction potentials which makes an electrolytic separation procedure appear attractive.

Two other mechanisms by which fission product ions might be removed from solution at a mercury cathode are adsorption at the mercury surface and co-removal during reduction of the steel-alloy ions. Adsorption might be direct, involving anionic complexes or colloidal particles, or it might be simple entrainment of ions in an occluded aqueous phase. Co-removal might also involve physical trapping at the site of amalgam formation or chemical reaction with the reduced iron, chromium, or nickel metallic or intermediate species.

The purpose of this study is to elucidate the behavior of fission product ions with respect to these various removal mechanisms in a solution typical of possible process wastes.

# III. THEORY

Ions are reduced at a mercury cathode by receiving electrons from the cathode surface according to the equation

$$M^{+n} + ne^- \longrightarrow M \qquad (1)$$

where $M^{+n}$ is the ionic species of charge n, $e^-$ is the electron, and M the reduced species. Where the reduced species combines with the mercury, the equation becomes

$$M^{+n} + ne^- + Hg \longrightarrow M(Hg) \qquad (2)$$

where M(Hg) represents the mercury phase containing the reduced species. When the reduced species is a mercury-soluble metal, M(Hg) represents the amalgam formed in the reaction.

The potential of the mercury electrode at which a reversible reaction takes place is given by the Nernst equation

$$E = E_a^o - \frac{0.059}{n} \log \frac{A_a}{A_s A_{Hg}} \qquad (3)$$

where $A_s$, $A_a$, and $A_{Hg}$ are the thermodynamic activities of $M^{+n}$ ions in solution, metal in the mercury phase, and mercury in the mercury phase, respectively.

$E_a^o$ is the standard reduction potential of metal in the mercury phase against the reference electrode; that is,

$$E_a^o = E_m^o + \frac{0.059}{n} \log \frac{a_{sat}}{a_{Hg\ sat}} \qquad (4)$$

where $E_m^o$ is the ordinary standard potential of the cell,

$$\text{reference electrode} \left| M^{+n}(a=1) \right| M_{solid}$$

The normal hydrogen electrode oxidation potential is +0.246 volt vs the saturated calomel electrode and is expressed as a negative value by polarographic convention. $E_s$ is the potential associated with the reversible formation of an M(Hg) phase and is given by

$$E_s = - \frac{\Delta G}{nf} \qquad (5)$$

where G is the free energy change in the reaction

$$xM + yHg = M_xHg_y \qquad (6)$$

In the saturated mercury phase, the activity is $a_{sat}$ and the activity of the mercury is $a_{Hg\ sat}$.

Using a dropping mercury electrode, the magnitude of the current flowing through the cell is controlled by concentration polarization in the region surrounding the drop. Concentrations vary as the surface of the drop grows and reduction proceeds, so concentration values refer to the average concentration during the lifetime of the drop. The concentration of reduced metal in the mercury phase is considered to be that concentration near the surface of the electrode. The potential which is characteristic of the reduction of a particular species is that potential at which the current increase reaches one-half of its fully polarized value with respect to the species. This point is called the half-wave potential. It is designated by $E_{1/2}$ and is a constant characteristic of the ionic species and supporting electrolyte.

The thermodynamic significance of the half-wave potential has been investigated by Heyrovsky and Ilkovic(3). When appropriate simplifying assumptions are made(4), their equation becomes

$$E_{1/2} = E_m^o + E_s + \frac{0.059}{n} \log a_{sat} \qquad (7)$$

for the reversible formation of an amalgam or dissolved non-metallic substance.

Where the reduced species forms a suspension of solid in the mercury phase, $E_s = 0$. The equation for the formation of a solid suspension becomes

$$E_{1/2} = E_m^o + \frac{0.059}{n} \log a_{\frac{s}{2}} \qquad (8)$$

When the electrode reaction consists of the reversible reduction of an ionic species to a lower oxidation state which does not enter the mercury phase, the electrode acts simply as a "noble" electrode at whose surface the reaction takes place. The half-wave potential in this case is(4)

$$E_{1/2} = E_m^o - \frac{0.059}{n} \log \frac{f_{red}}{f_{ox}} \left(\frac{D_{ox}}{D_{red}}\right)^{1/2} \qquad (9)$$

where $f_{red}$ and $f_{ox}$ are the activity coefficients of the reduced and the oxidized species, and $D_{ox}$ and $D_{red}$ are the diffusion coefficients of the ions in the aqueous solution. The stepwise reduction of an ionic species thus results in a current-voltage curve consisting of multiple "waves" representing the different reduction steps.

When the species undergoing reduction is a complex rather than a simple ion, an additional term is introduced into Equation (7) which involves the dissociation constant of the complex species and the activities of the complex and its dissociation products. The existence of a complex rather than a simple ion usually results in a shift of $E_{1/2}$ to a more negative value.

The foregoing discussion applies only to reversible electrode reactions. In the case of irreversible electrode processes, these equations do not apply, $E_{1/2}$ being generally shifted to a larger negative value.

## IV. PROCEDURE

The first phase of the laboratory investigation involved a study of the polarographic behavior of iron, chromium, and nickel in dilute sulfate solution to determine potentials at which removal of these metals would occur. Then, to study systematically the reduction behavior of each fission product of interest, the following stepwise procedure was used:

1. Determination of the polarographic current vs voltage curve for the fission product ion in dilute neutral and/or slightly acidic solution containing an appropriate supporting electrolyte. This determination allowed comparison with published results when available and also demonstrated the reduction behavior of the ion under the simplest possible conditions.

2. Determination of the removal rate of the radioactive fission product ions at tracer concentrations as a function of applied potential from a solution of supporting electrolyte equivalent to that of Step 1. Comparison of this curve with that from Step 1 revealed any differences in behavior between macro concentrations and tracer concentrations.

3. Determination of a removal rate vs potential for the radioactive ions at tracer concentration from a dilute solution of ferric, chromic, and nickelous sulfates in sulfuric acid. Comparison with the curve from Step 2 indicated removal rate effects caused by the presence of iron, chromium, or nickel in solution or their reduction at the mercury cathode.

4. Determination of the rate of removal of the ions at tracer concentrations from a sulfate solution containing iron, chromium, and nickel at concentrations typical of nuclear reactor fuel reprocessing wastes. This curve revealed any removal of the fission product ions by co-removal with the iron, nickel, or chromium in a solution of practical interest.

5. Determination of the effect of added carrier ions on the removal rate at a fixed potential. Addition of carrier to a tracer-containing solution should not affect the rate of removal of radioactive material, for, although the ions reduced per unit time should increase in proportion to their concentration, the fraction which is radioactive decreases in proportion to concentration and thus should be removed at a constant rate. This step acted as a check on instrument behavior, experimental reproducibility, and rapid exchange between radioactive and carrier atoms. Stepwise addition of foreign ions would be expected to cause a decrease in removal rate by furnishing competition for cathodic electrons and by electrode depolarization.

## V. EXPERIMENTAL EQUIPMENT AND METHODS

The development of a polarographic cell for the separation of radioisotopes has been described by Love(5). In this cell the mercury drop falls from the cathode into a layer of $CCl_4$. The drop passes through the inert liquid where the aqueous material adsorbed by it is washed off and returns to the aqueous layer above. The mercury collects above a stopcock through which it may be removed.

A similar cell was constructed for use in this study. A diagram of the cell is shown in Fig. 1. The cathode cell was separated from the saturated calomel reference electrode by a sintered glass disk and an agar plug. A constant-pressure-head-device(6) insured a constant rate of flow of mercury at all times. The inert layer was $CCl_4$ diluted with heptane to a density only slightly greater than that of the aqueous layer. The cell was dry filmed when using zirconium solutions to avoid adsorption.

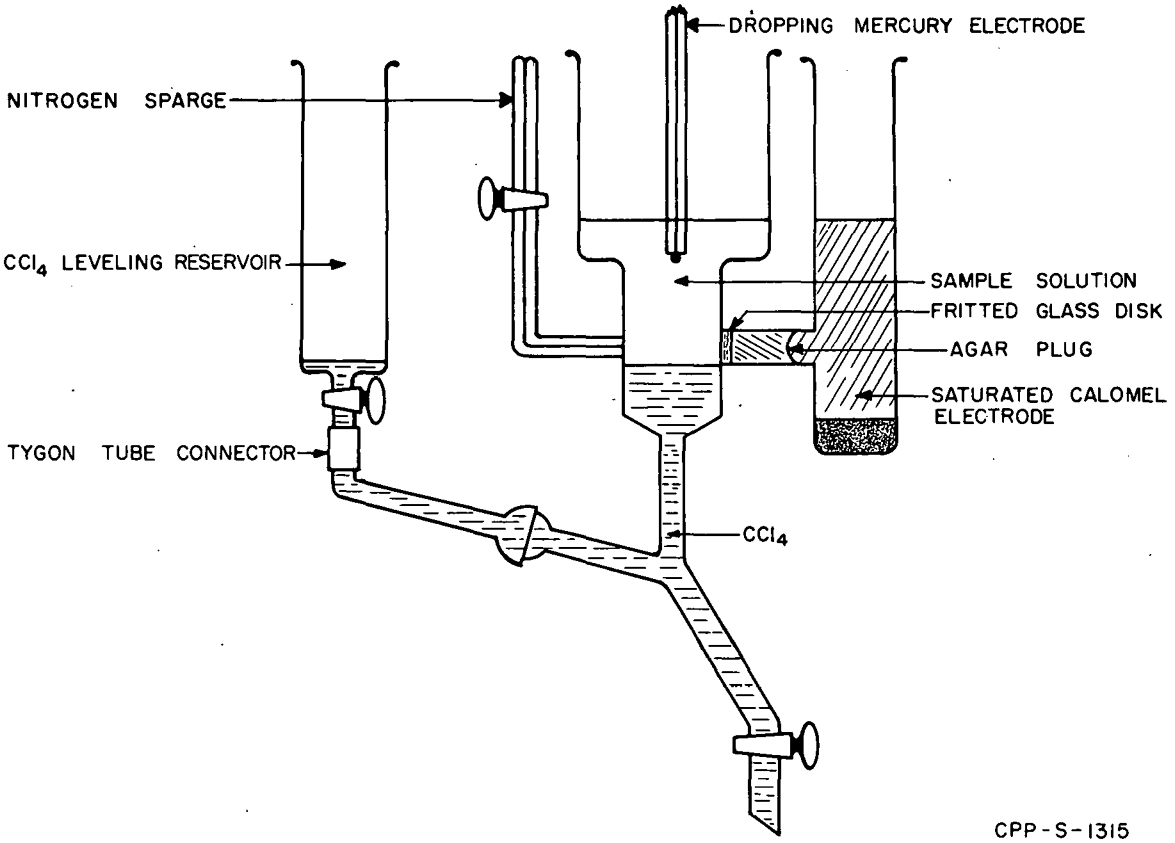

Fig. 1 - Polarographic Cell for Studying Inclusion of Fission Products in Mercury During Electrolysis of Stainless Steel Wastes

Interfacial tension caused holdup of small mercury drops at the surface of the inert layer, which was partly overcome by the addition of a small amount of commercial detergent to the aqueous phase. The detergent caused no detectable adverse effect in the polarograms.

With a conventional flat-faced capillary tube it was found that, under conditions which resulted in hydrogen evolution at the cathode, the gas sometimes collected over an appreciable part of the mercury surface. This phenomenon prevented ions from reaching part of the drop and produced erratic results. This effect was almost completely eliminated by using a capillary tube ground to a pencil-like point which sloped to the edges of the capillary opening. The gas bubbles rose to the surface of the liquid as soon as they formed, instead of collecting at the flat surface of the capillary.

Most of the studies were carried out with a saturated calomel electrode which was 0.246 volt negative with respect to the normal hydrogen electrode. In those studies where it was desirable to eliminate chloride completely from the solution, a mercury-mercurous sulfate-saturated $K_2SO_4$ reference electrode was used which was 0.40 volt positive with respect to the saturated calomel electrode. All results, however, were corrected and reported with respect to the saturated calomel electrode, designated as S.C.E.

The polarograph used was a Leeds and Northrup Electro-Chemograph, Type E. Oxygen was removed from the solution before each polarogram by sparging with suitably purified tank nitrogen.

All radioisotopes used in the study were obtained from Oak Ridge National Laboratory and were converted to the chemical form desired.

Mercury samples were collected for periods of 1 or 2 minutes, and excess $CCl_4$-heptane was drawn off by vacuum into a solvent trap. A study of washing methods showed that additional washing with inert organic solvents did not remove any appreciable further amount of adsorbed aqueous material, and thus no further wash step was employed.

The radioactive isotope content of the mercury was measured by gamma-ray counting the samples in a well-type NaI(Tl) crystal scintillation counter with associated scaler and power supply. Samples of equal volume were used in each experiment; therefore, no sample self-absorption or geometry corrections were necessary. $Cs^{137}$ and $Ru^{106}$ samples were allowed to stand until their daughters had grown to equilibrium concentrations prior to counting. The largest uncertainty in the sample measurement was introduced through difficulty in quantitatively collecting and washing the accumulated mercury drops.

Each fission product was studied in a solution which is designated as being of "polarographic composition". This type of solution is one of iron, chromium, and nickel sulfates in sulfuric acid in which the concentration of each of these components gives an optimum polarographic current-voltage curve.

Studies were also carried out in a solution designated as being of "waste composition". This was a solution containing ferric, nickelous, and chromic ions in concentrations expected to be typical of stainless steel fuel element reprocessing waste solutions. The compositions of the experimental solutions are shown in Table 1.

## TABLE 1

## SOLUTION COMPOSITIONS

| Component | Molar Concentration<br>Polarographic Composition | Waste Composition |
|---|---|---|
| $Fe^{+3}$ | 0.001 | 0.10 |
| $Cr^{+3}$ | 0.002 | 0.02 |
| $Ni^{+2}$ | 0.001 | 0.01 |
| $H_2SO_4$ | 0.0005 | 0.50 |
| $K_2SO_4$ | 0.05 | 0.00 |
| Fission Product | Carrier free | Carrier free |

# VI. EXPERIMENTAL RESULTS AND DISCUSSION

## A. Hydrogen

The potential at which hydrogen ions are reduced is considerably more negative than that of the reversible hydrogen electrode. The magnitude of this overvoltage depends on the nature of the electrode surface and on the supporting electrolyte. At a mercury electrode, the overvoltage is about -1.4 volts vs S.C.E. In this study, $E_{1/2}$ for the hydrogen ion was about -1.55 volts, as shown in Fig. 2 where the hydrogen reduction wave is clearly shown following the nickel wave.

## B. Steel-Alloy Ions

The polarogram of nickel in sulfuric acid is shown in Fig. 2. Nickel is reduced directly from $Ni^{+2}$ to the metal at a half-wave potential of -1.03 volts. The measured potential indicates that the reaction is irreversible, since the reversible potential is -0.50 volt. Pavlick(7) has noted that at increased temperature $E_{1/2}$ becomes more positive rapidly and the reaction becomes more nearly reversible.

Chromium is reduced in two separate steps, as shown in Fig. 3. The first wave is clearly defined; the second one, with an $E_{1/2}$ of about -1.5 volts, merges with the hydrogen wave. The electrode reactions of chromium have recently been investigated in this laboratory(8).

The reduction of ferric ion to the ferrous form takes place at a potential which is positive with respect to the calomel electrode, and thus was not observed. Ferrous ion is irreversibly reduced to the metal at $E_{1/2}$ = -1.49 volts. This reduction is also far from the reversible potential of -0.69 volt. Like the reduction of chromous ion, the ferrous reduction curve merges smoothly with that of hydrogen to form an apparently single wave, as shown in Fig. 4.

The steel-alloy ions $Fe^{+3}$, $Cr^{+3}$, and $Ni^{+2}$ are all reduced at potentials considerably more negative than the equilibrium reaction potential. However, the solubility of these metals in mercury is very slight, e.g., that of iron is $10^{-17}$ weight per cent. Therefore, the shift in potential due to free energy of solution is obviously negligible, and the reversible half-wave potential should be nearly equal to the standard reduction potential. However, the reduction of substances which do not dissolve in mercury at a mercury electrode is generally irreversible, and this is the case for iron, chromium, and nickel. It is the irreversibility of these reactions which tends to make the half-wave values more negative than the equations for the reversible reactions predict. Even though the most negative half-wave potentials are for iron and chromium (both about -1.49 volts), the minimum reduction voltages vs the S.C.E. were observed to be -1.2 volts for $5 \times 10^{-4}$M ferric sulfate and -1.3 volts for $1 \times 10^{-3}$M chromic sulfate. Removal of iron, chromium, and nickel would then take place to some extent even at these low voltages.

## C. Cesium

Alkali metals form amalgams very readily, contributing about +1 volt to the half-wave potential from the amalgam formation reaction; that is, $E_s$ is about +1 volt. Thus, the $E_m^o$ value for cesium is -3.17 volts and the observed $E_{1/2}$ value in this study is -2.16 volts, as seen in Fig. 5. Lithium chloride was used in this study to avoid interference from potassium ions which are reduced at a lower potential. Fig. 5 shows that $E_{min}$ is -2.1 volts and that cesium reduction is preceded by a well-developed hydrogen wave.

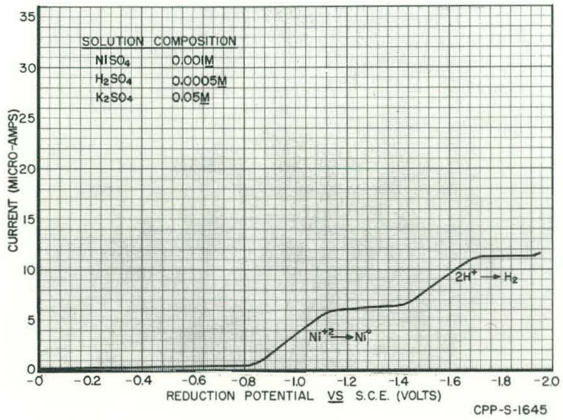

FIGURE 2

Polarographic Reduction of Nickel in Acid Solution at 25°C

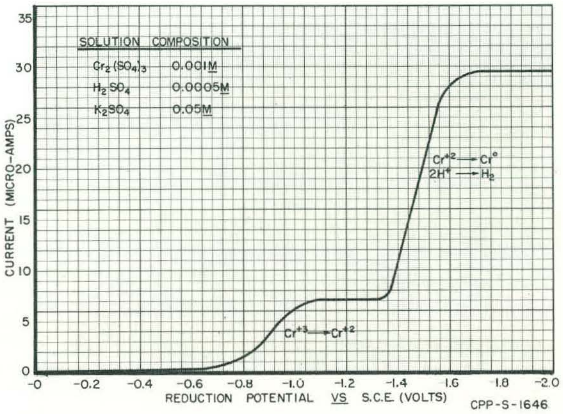

FIGURE 3

Polarographic Reduction of Chromium in Acid Solution at 25°C

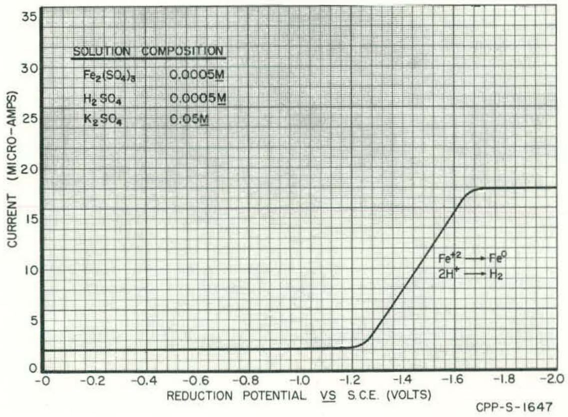

FIGURE 4

Polarographic Reduction of Iron in Acid Solution at 25°C

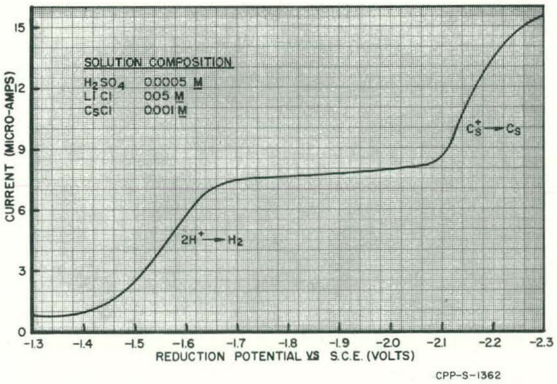

FIGURE 5

Polarographic Reduction of Cesium in Acid Solution at 25°C

Using tracer $Cs^{137}$, reduction rate curves were obtained as a function of applied potential in a solution containing only added supporting electrolyte and also in a solution of "polarographic composition". The curves were identical, and the curve for the latter solution is shown in Fig. 6. No detectable activity was recorded below -1.9 volts, and the curve indicated that the only mechanism by which cesium is removed from solution is through reduction to the metal and formation of a cesium amalgam.

The removal rate was next measured in a solution of "waste composition" as a function of potential. The upper limit of the measurement was -1.6 volts because cathode "streaming" became excessive above this point. Throughout this region no significant removal of cesium was detected, and it was concluded that none was co-removed during reduction of the steel-alloy ions, all of which were removed below this potential.

As was anticipated, addition of carrier cesium to the $Cs^{137}$ supporting electrolyte solution at a constant potential of -2.30 volts did not alter the $Cs^{137}$ removal rate. Addition of foreign ions also showed the predicted results, i.e., little effect up to concentrations of foreign ions near 0.01M, and then a rapid decrease in rate at higher concentrations.

It appears that under the conditions of this study, $Cs^{137}$ is removed from solution only by ordinary reduction to the metal and not by co-removal with steel-alloy ions.

D. Barium

Barium 137 is produced as a daughter of $Cs^{137}$, so it was studied in the same set of experiments. The total radioactive content of the mercury samples obtained in the cesium study was counted during decay, and the resulting curves were resolved into their two components. A polarogram of barium in lithium chloride is shown in Fig. 7. Hydrochloric acid was the acid used due to the limited solubility of barium sulfate. The observed $E_{1/2}$ was -1.99 volts, and the $E_{min}$ was -1.9 for the $10^{-4}$M barium solution.

Results of the measurement of the removal rate of barium tracer from a "polarographic composition" solution are shown in Fig. 8. The points are rather scattered, due to the complexity of counting and decay curve resolution, but it may be concluded that the curve is nearly the same as that shown in Fig. 7.

E. Strontium

Fig. 9 shows the polarogram of strontium in acid solution. Similar to the behavior of barium, a large $E_s$ value reduced $E_{1/2}$ to -2.15 volts even though $E_m^o$ = -3.14 volts. An ordinary, well-developed wave was obtained for the reduction of strontium following the usual hydrogen wave.

The behavior of $Sr^{85}$ was investigated in a solution of lithium chloride and sulfuric acid identical to that used in Step 1. Strontium 85 was substituted for $Sr^{90}$ to avoid the presence of relatively long-lived $Y^{90}$ daughter. The results of the tracer study were checked qualitatively with $Sr^{90}$-$Y^{90}$, however, and were found to be in good agreement.

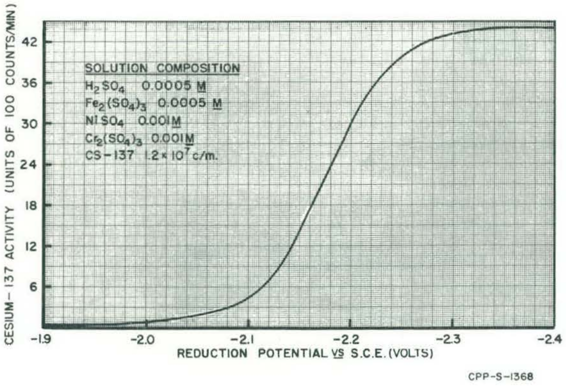

FIGURE 6

Polarographic Reduction of Cesium 137 in Acidic, Alloy Metal Ion Solution

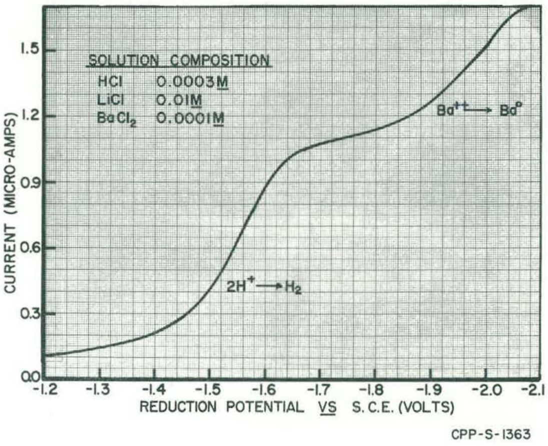

FIGURE 7

Polarographic Reduction of Barium in Acid Solution

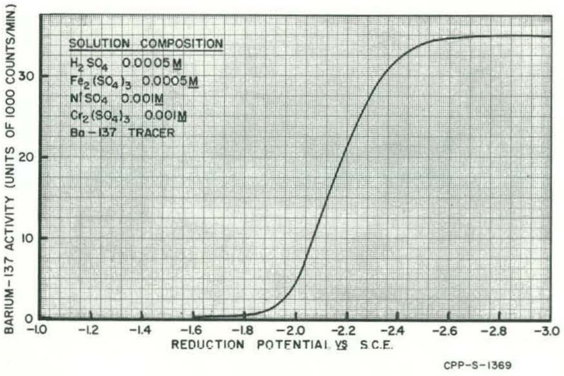

FIGURE 8

Polarographic Reduction of Barium 137 in Equilibrium with Cesium 137 in Acidic, Alloy Metal Ion Solution

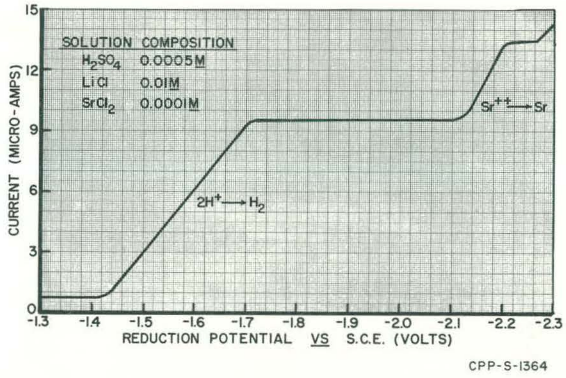

FIGURE 9

Polarographic Reduction of Strontium in Acidic, Alloy Metal Ion Solution

The surprising results of Step 2 showed that $Sr^{85}$ removal did not follow an ordinary reduction curve similar to strontium behavior at macro concentrations, but rather exhibited a linear rate increase starting at -2.2 volts. This phenomenon was also found to be identical in a solution of lithium chloride alone. The linear rate increase is evidently due, then, not to acidity or the presence of other ions, but to a phenomenon associated with the presence of strontium at tracer concentration. Since Fig. 10 shows no strontium reduction below -2.1 volts, the tracer studies indicated only that the electrode did not become polarized with respect to strontium at tracer concentration even at -3.0 volts.

At "waste composition", the removal of $Sr^{85}$ was studied up to the experimental maximum potential of -1.8 volts, and no appreciable strontium was removed.

Stepwise addition of carrier strontium to the tracer solution showed no effect on removal rate at the chosen potential, -2.80 volts. Addition of nickelous sulfate stepwise, however, caused an immediate gradual rate reduction, followed by a rapid decrease above $10^{-3}\underline{M}$ nickelous sulfate. A limited investigation of $Sr^{90}$ indicated that there was no difference in behavior not attributable to the presence of the $Y^{90}$ daughter.

From these results it was concluded that $Sr^{90}$ was not removed from any of the solutions studied below about -2 volts, under any of the experimental conditions.

## F. Yttrium

Yttrium 90 is not sufficiently long-lived to warrant a full study. It was, however, desirable to investigate its properties to an extent which would prevent confusion in interpretation of the $Sr^{90}$ data. For this reason its polarogram in acid solution is shown in Fig. 11. This stepwise reduction has been observed by many other investigators. It is believed that the first wave represents reduction of $Y^{+3}$ to at least $Y^{+2}$, but there is considerable uncertainty as to the nature of the anomolous second wave. In any event, the reduction curve is sufficiently similar to that of the strontium to make separation of the two impossible. In the tracer studies, $Sr^{90}$-$Y^{90}$ showed the same behavior as $Sr^{85}$, except that removal began at a slightly lower potential; this is expected, since yttrium reduction begins near -1.8 volts for the first step and -2.0 volts for the second.

## G. Cerium

In the presence of $1 \times 10^{-3}\underline{M}$ lithium chloride and using $1.0 \times 10^{-4}\underline{M}$ ceric nitrate, no half-wave potential for cerium was obtained, as shown in Fig. 12. In a similar solution made acidic to $5 \times 10^{-4}\underline{M}$ sulfuric acid, a wave was observed (Fig. 13), but its true shape was masked by the appearance of a large polarographic "maximum" which could not be suppressed by the usual method of adding surface-active agents. From the appearance of the curve in Fig. 13, however, the $E_{1/2}$ value is probably near -1.95 volts, in close agreement with the value of -1.97 volts reported by Noddack and Bruckl(9) for $0.01\underline{M}$ ceric sulfate with no supporting electrolyte.

It was found that tracer removal rate was even more anomalous. Removal from "polarographic composition" solutions showed a gradual increase in rate represented in Fig. 14, starting at about -2.5 volts with no maximum value up to the -3.0 volt limit of the measurement.

Cerium removal from solutions of "waste composition" was found to be negligible up to the -1.8 volts experimental limit, as in previous cases. Addition of carrier cerium had no effect on the removal rate of cerium, and the stepwise addition of foreign ions caused a gradual reduction in the rate of removal of cerium at -2.8 volts.

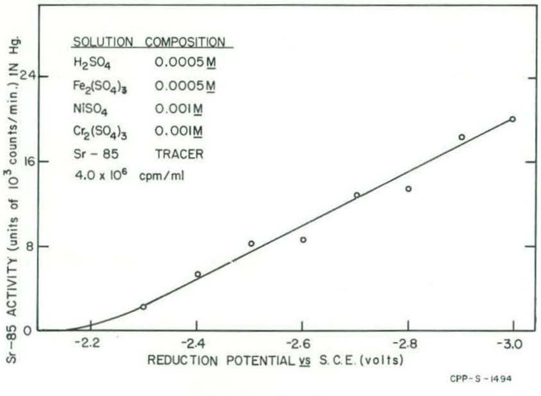

FIGURE 10

Polarographic Reduction of Strontium 85 in Acidic, Alloy Metal Ion Solution

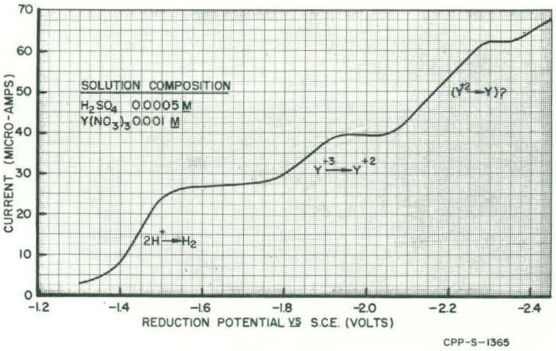

FIGURE 11

Polarographic Reduction of Yttrium in Acid Solution

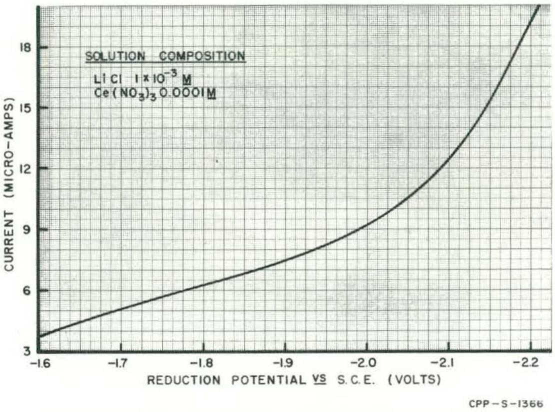

FIGURE 12

Polarographic Reduction of Cerium in Neutral Solution

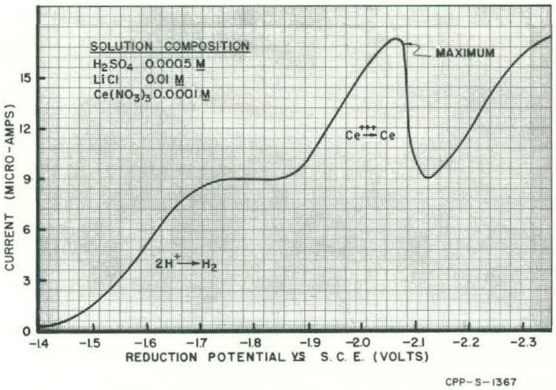

FIGURE 13

Polarographic Reduction of Cerium in Acid Solution

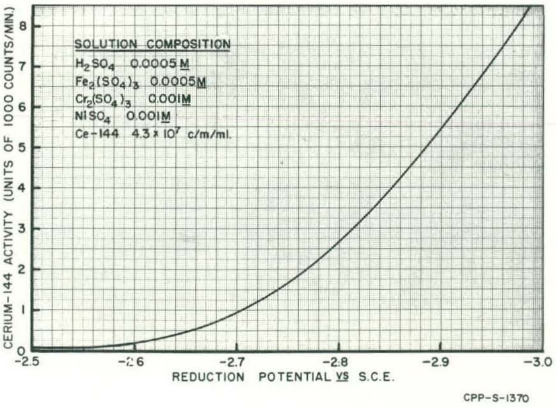

FIGURE 14

Polarographic Reduction of Cerium 144 in Acidic, Alloy Metal Ion Solution

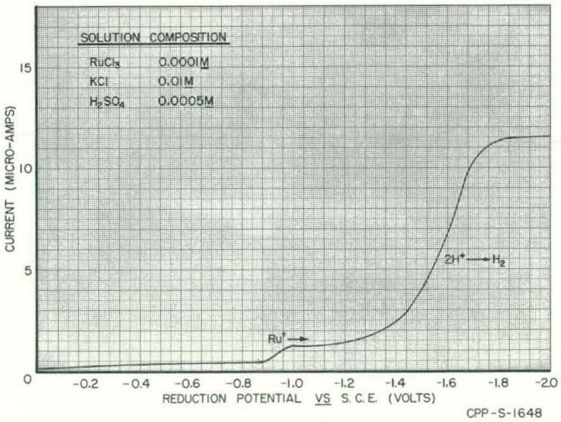

FIGURE 15

Polarographic Reduction of Ruthenium 106 in Potassium Sulfate Solution

Cerium behavior, in summary, was found to be surprisingly anomalous in all studies, in dilute solution. Since no removal was observed below -2.5 volts in dilute solution and at the highest potentials that can be studied in "waste composition" solutions, cerium probably will not be significantly co-removed in a separation process.

## H. Ruthenium

The polarogram of ruthenium trichloride in potassium chloride-sulfuric acid supporting electrolyte showed no wave above -2.0 volts and only a very small one near -1.0 volt. This result may represent a reduction of one ruthenium species to another, although the small size of the wave suggests that it may be due to an impurity present in ruthenium trichloride. The polarogram is shown in Fig. 15.

Ruthenium is strongly complexed by chloride ions, and since chloride would be absent in some waste solutions, the mercury drop-washing cell was converted to an all-sulfate system. A saturated mercurous sulfate-potassium sulfate reference electrode was used, separated from the potassium sulfate supporting electrolyte by a saturated potassium sulfate-agar plug. The potential of this electrode was 0.40 volt positive with respect to the calomel electrode, and all reported voltages have been corrected back to the S.C.E. reference. Polarographic studies of ruthenium in this chloride-free system showed a series of polarographic maxima that were difficult to suppress; but when sufficient gelatin was added to obtain a smooth curve, it was observed that the only well-defined reduction wave was again near -1.0 volt vs S.C.E.

A tracer study of the removal rate of $Ru^{106}$ from a potassium sulfate supporting electrolyte showed a very rapid rate increase above -1.8 volts, with some removal as low as -0.6 volt, as shown in Fig. 16. No wave was produced, and the rate became very rapid above -2.3 volts. Similar behavior was observed in a solution of "polarographic composition" with chloride present. A study of ruthenium removal from a solution of "waste composition" showed no significant removal up to the experimental limit of -1.8 volts vs S.C.E.

The removal of ruthenium tracer from solution is not easily explained. The removal rate curve for ruthenium tracer (Fig. 16) does not correspond to a reduction curve in the ruthenium polarogram (Fig. 15); nor does it seem to be a co-removal phenomenon, since it occurs in a solution of supporting electrolyte alone. No significant removal occurred from "waste composition" solutions, but the fact that some ruthenium is removed from the more dilute solutions at fairly low potentials suggests that it would appear as a contaminant in the steel-alloy material removed by electrolysis if the concentrations of metals in the waste solutions were reduced to low levels.

## I. Zirconium

The results of studies of the polarographic behavior of zirconium in this laboratory are in agreement with the observations of other investigators. A wave was produced in the polarogram of zirconium which has been identified previously as being due to the catalytic reduction of hydrogen ion(10). The $E_{1/2}$ value of the wave varies widely through the range -0.9 to -0.16 volt, depending on acidity and solution composition.

Removal rate curves from "polarographic composition" and from supporting electrolyte solutions were identical. The latter is shown in Fig. 17. All tracer data were obtained using $Zr^{95}$ previously separated from $Nb^{95}$ daughter by thenoyltrifluoroacetone (TTA) solvent extraction(11). Removal started near -1.8 volts and increased through the -3 volt maximum of the experiment. As with ruthenium, there seemed to be no obvious explanation for this curve.

The investigation of zirconium tracer removal from a solution of "waste composition" produced the results shown in Fig. 18. In this case the mechanism may be ascribed to co-removal in the presence of other material. The removal rate was significant even at zero applied potential and continued to be significant to nearly -3 volts, although the rate decreased with increasing potential. The only reaction which

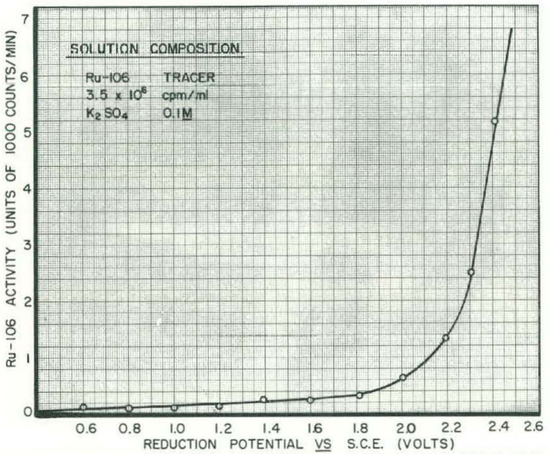

FIGURE 16

Polarographic Reduction of Ruthenium 106 in Potassium Sulfate Solution

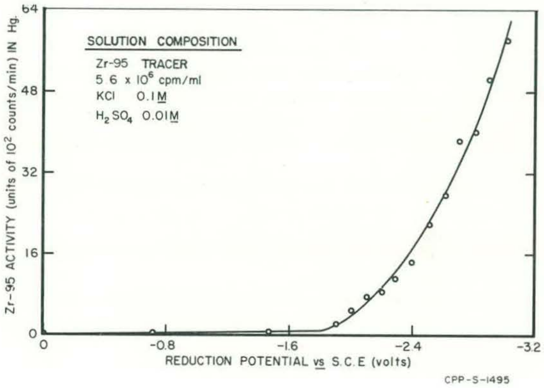

FIGURE 17

Polarographic Reduction of Zirconium 95 in Potassium Chloride Solution

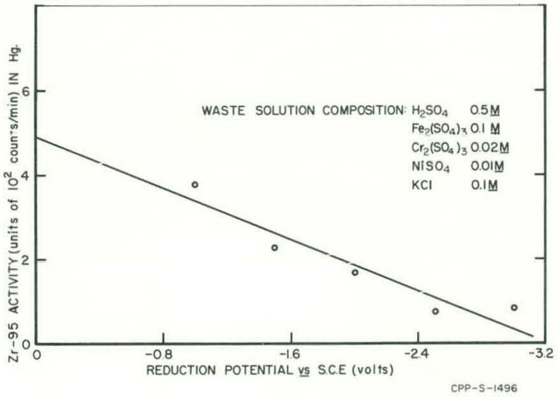

FIGURE 18

Polarographic Reduction of Zirconium 95 in Acidic, Alloy Metal Ion Solution

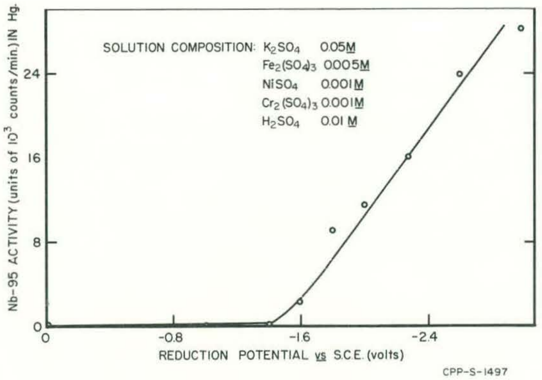

FIGURE 19

Polarographic Reduction of Niobium 95 in Acidic, Alloy Metal Ion Solution occurred at zero potential vs S.C.E. was the reduction of the ferric to ferrous ion, and while it is possible that the removal of zirconium tracer may be associated with the reaction, no specific mechanism seems obvious. A similar curve was obtained in a solution identical to the above except that the acid concentration was reduced to 0.01M. The only difference observed was that the rate did not fall off appreciably with increasing potential.

The addition of carrier zirconium to the $Zr^{95}$ solution did not alter the removal rate up to -2 volts, but thereafter carrier zirconium caused a rapid rate decrease through the next 1-volt range. The data were rather erratic above -2 volts, indicating that macro zirconium was perhaps hydrolyzed to some extent and making the data obtained with carrier zirconium open to question.

Zirconium seems to be the fission product most likely to give difficulty in obtaining a clean separation of steel-alloy metals from fission products. Although its behavior in dilute solution seems reasonable, it will evidently be co-removed from more concentrated solutions of the steel-alloy ions. This might be avoided by adding a zirconium complexing agent to the solution, but results of a preliminary study with oxalic acid were not encouraging.

### J. Niobium

Since $Nb^{95}$ was obtained as a by-product in the separation of $Zr^{95}$, it was cursorily studied, although its 35-day half-life makes it relatively unimportant. Fig. 19 shows the removal of $Nb^{95}$ from a solution of "polarographic composition". It is quite similar in behavior to zirconium under these conditions, except that its removal begins at a lower voltage.

## VII. CONCLUSIONS

A summary of the data obtained in this study is presented in Table 2. The $E_{1/2}$ values are weighted numbers based on all of the curves obtained.

An approximate minimum removal potential is given for each ion, based on a polarogram for that ion, or, as indicated, on the tracer removal rate curve for the fission product elements where the two values differ. The latter is the more signficant to a waste treatment process.

This investigation was conducted under conditions which allowed essentially-complete removal of the adsorbed aqueous phase from the mercury surface. In an actual process, adsorption might contribute significantly to the amount of fission product removal, in which case a mercury washing step might be included in the process.

TABLE 2

SUMMARY OF POLAROGRAPHIC DATA

| Ion | Product | $-E_m^o$ | Observed $-E_{1/2}$ | $-E_{min}$ | Remarks |
|---|---|---|---|---|---|
| $H^+$ | $H_2$ | 0.25 | 1.55 | 1.4 | Irreversible |
| $Ni^{+2}$ | Ni | 0.50 | 1.03 | 0.8 | Irreversible |
| $Cr^{+3}$ | $Cr^{+2}$ | 0.66 | 0.92 | 0.7 | Irreversible |
| $Cr^{+2}$ | Cr | 0.99 | 1.49 | 1.3 | Irreversible |
| $Fe^{+2}$ | Fe | 0.69 | 1.49 | 1.2 | Irreversible |
| $Cs^+$ | Cs | 3.17 | 2.16 | 3.1 | $E_s$ = +1 volt |
| $Ba^{+2}$ | Ba | 3.15 | 1.99 | 1.9 | Large value of $E_s$ |
| $Sr^{+2}$ | Sr | 3.14 | 2.15 | 2.2 | Large value of $E_s$ |
| $Y^{+3}$ | $Y^{+2}$ | | 1.86 | 1.8 | |
| $Y^{+2}$ | Y | | | 2.0 | Anomalous |
| $Ce^{+3}$ | Ce | 2.75 | (1.95) | 2.5* | Anomalous |
| Ru? | ? | | (1.0) | 1.8* | Anomalous |
| Zr? | ? | | | 1.8* | $E_{min}$ = 0 from conc. soln. |

*From tracer removal experiments

The data obtained in this investigation demonstrated how the removal rate of a fission product can be expected to vary with changing mercury cathode potential in an acidic sulfate system. It was not possible to obtain relative removal rates for the fission products, because the maximum rates were limited by the concentration polarization characteristic of a dropping mercury electrode.

The large potentials necessary for the reduction of fission products indicate that a separation of iron, nickel, and chromium from most of the fission products by electrolysis will be possible. The lowest potential at which an important fission product was reduced was -1.8 volts for ruthenium. No co-removal by mechanisms other than reduction was detected, with the single exception of zirconium, which was removed at 0 volts vs S.C.E. The 63-day half-life of $Zr^{95}$ makes this fission product of secondary importance, and thus contamination of the alloy-metal material by zirconium may be relatively unimportant.

In an actual waste disposal process, it will doubtless be impracticable to attempt exceptionally clean separation of alloy metals from fission products, since it is expected that the stainless steel will contain significant amounts of $Co^{60}$ as a nuclear reaction-produced impurity. Cobalt ion will be reduced to the metal along with iron, chromium, and nickel, furnishing a significant amount of radioactive contamination to the separated material. The amount of $Co^{60}$ will depend mainly on the purity of steel used in fabrication and will thus vary significantly for each fuel element design.

The results of this investigation indicated that it is technically feasible to develop a process in which most of the iron, nickel, and chromium can be removed from a solution containing fission products by mercury cathode electrolysis. The major radioactive contamination of the alloy-metal phase will probably be $Co^{60}$ and $Zr^{95}$-$Nb^{95}$. It may be necessary to wash adsorbed aqueous material from the mercury phase and limit the percent removal of alloy metals to a final concentration similar to that of the fission products, but with these precautions it is felt that a satisfactory electrolytic separation can be made.

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