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STAINLESS STEEL WASTES: III. LABORATORY STUDIES
OF THE RATE OF REMOVAL OF STAINLESS STEEL
IONS BY MERCURY CATHODE ELECTROLYSIS

D. R. Anderson
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February 12, 1962

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**NATIONAL REACTOR TESTING STATION
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Printed in USA

IDAHO CHEMICAL PROCESSING PLANT

IDO-14570
AEC Research and Development Report
Waste Disposal and Processing
TID-4500 (17th Ed.)

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Contract AT(10-1)-205

Idaho Operations Office

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A B S T R A C T

The reported experiments studied the removal rates of iron, nickel, and chromium from synthetic stainless steel waste solutions during electrolysis over a mercury cathode. The loading capacity of the mercury for the stainless steel metals is estimated on the basis of laboratory experiments to be about two per cent by weight. The laboratory data indicate that, at an electrode potential of -1.80 volts vs S.C.E., 85 ampere-hours per liter of waste removed essentially all of the stainless steel ions from a sulfuric acid solution containing 0.13M metal ions at 35°C.

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I. SUMMARY

A laboratory study to develop a method for separating iron, nickel, and chromium from the fission products in aqueous stainless steel waste was undertaken at the Idaho Chemical Processing Plant (ICPP) as part of a long-range waste disposal program to separate the bulky alloy metals and process chemicals from the fission products in highly radioactive process wastes. The separated bulky alloy metals presumably could be stored in low-cost pits without cooling, and the small volume of fission products could be stored as a small, heat-conducting, non-leachable solid.

The results of the laboratory study indicate that iron, nickel, and chromium can be removed from a dilute sulfuric acid solution, without appreciable contamination by fission products, by electrolysis over a mercury cathode at -1.80 volts vs S.C.E. Calculated on the basis of laboratory results, the quantity of electricity required to effect this removal is approximately 85 amp-hours per liter of waste, with a current efficiency of about 12 per cent. The loading capacity of the mercury for the alloy metals appeared to be about two per cent by weight, although it may be somewhat higher with a more efficient cell design. Calculations based on the current requirements indicate that 5.3 square meters of mercury are required to remove the stainless steel metal ions from 3740 liters of a "typical" stainless steel waste containing 0.1M stainless steel metal ions in 24 hours. This quantity of waste results from the chemical processing of 10 kg of uranium. Similar calculations based on the estimated mercury-loading capacity indicate that 1200 kg of mercury are required to remove the stainless steel ions in a single pass.

Areas requiring additional chemical research include more precise determination of the mercury-loading capacity under process conditions, development of methods for the regeneration of mercury, fundamental

studies of the electrode kinetics, and development of methods for permanent disposal of the separated components.

II. INTRODUCTION

An electrolytic method for the removal of fuel alloy metal ions from aqueous stainless steel process wastes or dissolver solutions has been studied on a laboratory scale at the ICPP. This method involves separation of the alloy metal ions, iron, nickel, and chromium, from the fission products and other waste constituents by mercury cathode electrolysis. The alloy metal ions are transferred to a pool of mercury, and the fission products remain in the aqueous waste. The slightly contaminated alloy metals are then separated from the mercury and stored in low-cost containers. The remaining acidic solution of fission products can be concentrated for storage as an aqueous solution or converted to a solid for final disposal.

The initial phases of the study of the separation of the alloy metal ions from fission products by mercury cathode electrolysis have been reported earlier^(3,4,5). These reports established the technical feasibility of separating the alloy metal ions from the fission products. This report discusses recent investigations to determine the rate of electrolysis of the alloy metal ions from a synthetic stainless steel waste and to estimate the loading capacity of the stainless steel alloy metals in the mercury.

III. EQUIPMENT AND PROCEDURES

The equipment used in determining metal ions removal rates from synthetic stainless steel waste solutions consisted of a conventional Dyna-Cath electroanalyzer⁽⁴⁾ with associated reference cell, meters, and temperature regulators.

The mercury-loading experiments were performed initially in a Bolger cell assembly (Figure 1). Later experiments used either a conventional Dyna-Cath cell or a special cell designed for use with the Dyna-Cath electroanalyzer (Figure 2). This special cell was designed to permit agitation of the mercury cathode by gas purging or by continuously

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Figure 1

Bolger Electrolysis Cell for
Amalgam Preparation

CPP-S-2099

Figure 2

Electrolysis Vessel with Continuous
Circulation of Aqueous Phase

introducing aqueous feed solution at the bottom of the mercury cathode, but performed best when aqueous solution was passed through the mercury continuously without gas purging.

The temperature of the aqueous solution in the special cell and in the conventional Dyna-Cath cell was controlled by intermittent circulation of a cooling liquid through glass coils immersed in the cell. A small pump and thermoregulator assembly were used to control the circulation. Measured temperatures of the aqueous solution during electrolysis were within $\pm 1^\circ\text{C}$ using this system. Temperature control was not attempted in the Bolger cell, and the temperature of the aqueous phase approached $80\text{--}90^\circ\text{C}$ during electrolysis.

Chemicals used in the experiments were C.P. sulfate salts of the metals. Both the so-called "crystal" and "powder" forms of chromic sulfate were used because of apparently different electrolysis

characteristics of the two types of salt in sulfuric acid solutions. An Electrochemograph "Type E" polarograph was used to compare the purity of the different samples of chromium salts.

Approximately 5- to 10-milliliter samples of the aqueous solutions undergoing electrolysis were removed for analysis. The concentration of iron, nickel, and chromium in these samples was determined by emission spectroscopy, and the amount transferred to the mercury was obtained by difference.

The applied voltage between the mercury cathode and the saturated calomel electrode that was immersed in the solution was maintained constant at -1.80 ± 0.025 volts. The distance between the calomel electrode and the mercury cathode was one-half inch. The initial current on the Dyna-Cath equipment was approximately five amperes but increased as the solution was depleted of metals. The surface area of the mercury in the Dyna-Cath cell was 43 square centimeters, and up to 200 ml of mercury was used in each run.

Fission product distribution data obtained in a previous study⁽⁵⁾ by polarographic techniques were checked in the Dyna-Cath apparatus using a mercury pool cathode. The concentration of fission products in the mercury was determined by measuring the emitted radiation in a well-type scintillation crystal.

IV. EXPERIMENTAL RESULTS

The results of the laboratory work are reported below. The majority of the experiments were intended to determine the rate of removal of the stainless steel alloy ions from solution. However, some data were obtained on the loading capacity of the mercury for the stainless steel metal ions, and preliminary information was obtained on possible methods for regeneration of the mercury.

A. Electrolysis Rate Measurements

The reaction that takes place during electrolysis can be represented by the equation

where M^{+n} is the ionic species of charge n , e^- is the electron, M is the reduced species, and $M(Hg)$ represents the mercury phase containing the reduced species. The reduction potentials for the alloy metals and the important fission products for this reaction have been determined and reported previously⁽⁵⁾.

1. Effect of Acid

Although the half-wave reduction potential for hydrogen ion was exceeded by operating at -1.80 volts vs S.C.E., the acidity in the aqueous system actually increased during electrolysis, as indicated by titration analysis. For example, the electrolysis of a synthetic stainless steel waste in $3N$ H_2SO_4 produced an aqueous solution containing $3.6N$ H_2SO_4 at the completion of the electrolysis. This is slightly more acid than would be expected on the basis of conversion of the metal sulfates to sulfuric acid. Obviously, additional studies to define the mechanisms of the reactions taking place at the electrodes are needed.

To study the rate of removal of the alloy metals, iron, nickel, and chromium, the initial acid concentration in synthetic stainless steel waste solutions was varied from $0.2N$ to $3N$ sulfuric acid, and the temperature of the solutions was maintained at $25 \pm 5^\circ C$ during electrolysis. The results are shown in Figure 3.

Figure 3

Removal of Alloy Metal Ions from a Synthetic Stainless Steel Waste Solution by Mercury Cathode Electrolysis as a Function of Concentration of Sulfuric Acid in the Original Solution at $25^\circ C$

The data in Figure 3 suggest that, at 1.0N sulfuric acid concentration, the ions of one or more of the alloy metals form a hydrated species or a complex species with the sulfate ions, or possibly a surface film on the mercury cathode which inhibits electrolysis of the metals. Preliminary studies indicated that chromium was the most likely suspect in retarding the electrolysis. Two forms of chromic sulfate, the so-called "crystal" and "powder" forms (both of which were amorphous to X-ray diffraction), were used in combination with nickel and ferric sulfates in 1N sulfuric acid solution to determine the effect of different sources of chromium. The results of two experiments using the Dyna-Cath equipment and the two forms of chromic sulfate are shown in Figure 4.

Figure 4

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Removal of Alloy Metal Ions from 1N Sulfuric Acid Solution at $27 \pm 1^\circ\text{C}$

The results in Figure 4 clearly suggest that at room temperature chromium ions from the "powder" chromic sulfate, or a surface film formed by reduction of the chromic ions from the "powder" chromic sulfate, reduce the rate of removal of iron and nickel as well as chromium. Electrolysis of the three metals, individually, indicated that the removal of iron and nickel in the absence of chromium could be represented by the curves for iron and nickel in Figure 4-II. Electrolysis of the "powder"

and "crystal" forms of chromium produced the results shown in Figure 5. These data suggest that the two sources of chromium produced different species in solution or formed a different amalgam with the mercury at room temperature. A detailed study to define the interference mechanism was beyond the scope of this investigation.

2. Effect of Temperature

Experiments were conducted to determine the effect of solution temperature on the rate of removal of the alloy ions from a solution containing $0.1M$ Fe^{+3} , $0.01M$ Ni^{+2} , and $0.02M$ "powder" Cr^{+3} as the sulfate salts in $1N$ sulfuric acid solution and the "powder" chromium sulfate were used because of their apparent inhibiting effect on removal of the metal

Figure 5
Removal of Chromium from $1N$
Sulfuric Acid Solution at $27^\circ C$
as a Function of
"Form" of Chromium

ions (Figures 3 and 4). The effect of temperature at three different electrolysis times is shown in Figures 6, 7, and 8. At $35^\circ C$, nearly complete removal of iron, nickel, and chromium was obtained after 30 ampere-hours of electrolysis, regardless of the "type" of chromium sulfate used as a source of chromium ions. Increasing the temperature above $35^\circ C$, had little or no additional effect up to a temperature of $85^\circ C$. From the practical standpoint, increasing the temperature to at least $35^\circ C$ appeared to be sufficient treatment to remove the inhibiting effect of the electrolysis-resistant chromium species that formed at room temperature.

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Figure 6

Removal of Iron from 1N H_2SO_4 by Mercury Cathode Electrolysis as a Function of Temperature

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Figure 7

Removal of Nickel from 1N H_2SO_4 by Mercury Cathode Electrolysis as a Function of Temperature

CPP-S-2105

Figure 8

Removal of Chromium from 1N H_2SO_4 by Mercury Cathode Electrolysis as a Function of Temperature

CPP-S-2106

Figure 9

Removal of Alloy Metal Ions from Electrolytic Dissolver Solution After Dilution to Waste Concentration and Addition of H_2SO_4

No attempt was made to identify the chromium species that inhibited the electrolysis reaction at room temperature. However, electrolysis at 25°C of a synthetic stainless steel waste, which was obtained by diluting the dissolver solution from the electrolytic dissolution of stainless steel metal rods in nitric acid solution with water, indicated that the chromium was present in the solution in a form amenable to electrolysis. The synthetic waste was made 1N in H_2SO_4 prior to electrolysis. The results of this experiment are shown in Figure 9.

3. Voltage Current Relationships

During the course of the electrolysis reaction, the current increased gradually as the concentration of metal ions in the solution decreased and as the voltage was adjusted to a constant value of -1.80 volts vs S.C.E. The approximate increase in amperage as a function of time for the electrolysis of a synthetic stainless steel waste in the Dyna-Cath electrolysis equipment is given in Figure 10. Since the area of the mercury cathode was about 43 cm², the range of the current density during the experiment varied from approximately 0.16 to 0.35 amp/cm² at -1.80 volts vs S.C.E.

Figure 10

Variation of Current with Time
During Electrolysis of a Synthetic
Stainless Steel Waste Solution

B. Mercury Loading Capacity

Laboratory experiments were conducted using a Bolger electrolysis vessel (Figure 1) with 15-20 ml of mercury as the cathode and a platinum screen as the anode. A battery charger supplied 6.0 volts DC to the system. The temperature was not controlled during the electrolysis and rose to as high as 80-90°C. Solutions of ferric sulfate, nickel sulfate, and chromic sulfate in sulfuric acid were electrolyzed.

Electrolysis of a ferric sulfate solution yielded an amalgam containing 3.05 per cent iron by weight. At this point the amalgam became "lumpy" and

difficult to agitate. Electrolysis of a nickel sulfate solution gave an amalgam containing 2.10 per cent nickel by weight. At this concentration the amalgam became extremely viscous. Only about 0.06 per cent chromium was electrolyzed into the mercury in a similar experiment, and a black precipitate formed (probably chromic oxide) after a few hours. These values for the amount of reduced metals in the mercury are greatly in excess of the reported solubilities for iron, nickel, and chromium in mercury. The measured solubilities for the stainless steel metals in mercury are reported⁽⁶⁾ to be 1.0×10^{-17} , 5.9×10^{-4} , and 3.1×10^{-11} weight per cent for iron, nickel, and chromium, respectively. Apparently the amalgam formed by mercury cathode electrolysis actually consists of finely divided iron, nickel, and chromium metal or metal oxides dispersed throughout the mercury.

An attempt was made to obtain information relative to the rate of removal of the alloy metals, as well as the mercury loading capacity as the mercury became increasingly loaded with reduced alloy metals. Successive batches of synthetic stainless steel waste were electrolyzed over a single batch of mercury in the Dyna-Cath apparatus, and the rate of removal of the alloy metals from each batch was determined. The data from this experiment are shown in Figure 11. A slight general increase

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Figure 11

Removal of Alloy Metal Ions from Successive
Batches of Synthetic Waste Solution Over a
Single Batch of Mercury (Cathode) at 35°C

in the time required to effect complete reduction of the alloy metal ions as the amalgam became more concentrated is evident in Figure 11. This effect was most pronounced for the chromium. Increasing concentration of the alloy metals in the mercury caused a bridging of the amalgam between the cathode and anode at 1.05 per cent total alloy metals, so the experiment was terminated.

By using the cell illustrated in Figure 2 with continuous circulation of the aqueous waste solution at 35°C, -1.8 volts vs S.C.E., and 0.5N initial sulfuric acid concentration, the mercury loading was increased to 1.68 per cent Fe, 0.18 per cent Ni, and 0.10 per cent Cr (1.96 per cent total metal loading) before the amalgam shorted across the electrodes. With better cell design and better agitation of the mercury, the upper limit for loading with iron, nickel, and chromium may be increased. For example, mercury cathode electrolysis to remove nickel from HRT fuel solutions⁽⁷⁾ resulted in short-circuiting by amalgam growth from the cathode to the anode at about two per cent deposited metals. By means of a cell design to provide adequate agitation of the amalgam during electrolysis, a loading of about five per cent deposited metals was achieved.

The loading capacity for stainless steel alloy metals needs to be investigated in more detail. The viscosity of the amalgam as a function of stainless steel metal loading should be determined, since this property would be important in mercury handling. Also, the loading capacity as a function of the iron/nickel/chromium ratio should be investigated. An electrolysis cell design that would eliminate amalgam growth between the electrodes would be helpful in obtaining loading capacities which are limited by high viscosity rather than short-circuiting between the electrodes.

C. Regeneration of Mercury

The amount of mercury required to handle a given load of stainless steel waste will be dependent, among other things, on the rate at which the mercury can be recovered from the amalgam. Preliminary data using nitric acid solutions to remove the alloy metals from mercury were reported by McLain⁽⁴⁾. This method dissolved the iron and nickel and removed the chromium as an oxide.

A separation without dissolution of any of the alloy metals is probably the most desirable approach, because the alloy metals or their oxides would then be in solid form for disposal. Distillation of the mercury is a possible method. The low latent heat of vaporization of the mercury suggests that distillation may be a feasible approach; however, oxidation of the metals prior to distillation might be necessary to eliminate the possible presence of very finely divided and possibly pyrophoric particles of metal. Brief scoping experiments in the laboratory demonstrated that a large fraction of the iron could be removed from the amalgam by a magnetic field, suggesting that partial removal of the metals might be accomplished in this manner. Centrifugation of the amalgam produced two distinct mercury phases of different densities, suggesting that density differences might permit at least a partial recovery of the mercury.

Considerably more experimental work is needed to determine the best method for regeneration of the mercury. The only methods for which sufficient data are available at present to permit the development of even crude flowsheets for a process are distillation or nitric acid scrubbing of the mercury.

D. Fission Product Behavior During Electrolysis

The transfer of fission products into the mercury during reduction of the stainless steel alloy metal ions was investigated previously by polarographic techniques⁽⁵⁾. The applicability of the polarographic results to the Dyna-Cath equipment, where the cathode was a pool of mercury instead of a dropping mercury electrode, was investigated by adding strontium or cesium to synthetic aqueous wastes and measuring the amount of the fission product element that was transferred to the mercury during electrolysis.

At -1.80 volts vs S.C.E. and a concentration of 0.02 g/l of strontium (approximately ICPP waste concentration) traced with 2×10^5 d/(m)(ml) of strontium-85, no detectable strontium within the detection limit (0.1 per cent of the added Sr) was transferred to the mercury during electrolysis of a synthetic stainless steel waste. Similarly, cesium at ICPP waste concentrations (0.06 g/l) traced with cesium-137 indicated

essentially no transfer of cesium to the mercury within the detection limit (0.1 per cent of the added Cs). These data are in agreement with previous data obtained by polarographic techniques⁽⁵⁾, which indicated that cesium and strontium would remain in solution during the electrolysis of stainless steel wastes provided the electrode potential did not exceed -1.80 volts vs S.C.E.

V. DISCUSSION

A. Process Implications

It is of interest to examine the removal of iron, nickel, and chromium from a synthetic stainless steel waste solution in terms of the quantity of electricity required to effect essentially complete removal of all three metals. Assuming a waste composition of 0.1M Fe^{+3} , 0.01M Ni^{++} , 0.02M Cr^{+3} , and 1N H_2SO_4 , the theoretical quantity of electricity required to reduce the metal ions in the solution to the metallic state is as follows:

	<u>Electricity Required</u> <u>amp-hrs/liter</u>
0.1M Fe^{+3}	8.1
0.01M Ni^{+2}	0.5
0.02M Cr^{+3}	<u>1.6</u>
Total	10.2

Based on the removal rate for iron, nickel, and chromium depicted in Figure 4 (II), the current required to effect complete removal of all three metals was 85 amp-hrs/liter for an overall efficiency of $10.2/85 = 0.12$. The overall efficiency probably would be reduced somewhat as the mercury became loaded with alloy metals; however, Figure 10 (V) indicates an efficiency of about 12 per cent for the removal of iron and nickel even with a mercury loading of one per cent total metals.

Assuming a stainless steel fuel which is 30 weight per cent uranium and 70 weight per cent stainless steel, a reprocessing rate of 10 kg of uranium per day would result in the disposal of about 24 kg/day of stainless steel to waste. Using a stainless steel process flowsheet (sulfuric acid dissolution) that has been demonstrated at the ICPP⁽²⁾,

the 24 kg of stainless steel would be dissolved in 3740 liters of aqueous solution having the composition 0.1M stainless steel, 0.54M $\text{SO}_4^{=}$, 2.99M NO_3^- and 3.80M H^+ . The nitric acid concentration must be reduced to below 1.0N before electrolysis⁽³⁾. This could be accomplished readily by treatment with paraformaldehyde⁽¹⁾. Treatment of the resulting waste would require 85 amp-hrs per liter to remove the stainless steel ions, or, for 3740 liters of waste, 317,900 amp-hrs at a rate of 13,240 amperes/day. At a current density of 0.24 amp/cm², the area of mercury required in the electrolytic cells would be about 5.3 square meters of mercury surface.

The amount of mercury required to furnish this surface area would, of course, depend upon the efficiency of the electrolysis cell and the regeneration rate of the mercury. If the regeneration rate of the mercury was rapid, the required surface area (5.3 m²) conceivably could be supplied by a relatively small quantity of mercury. However, another factor, the loading capacity of the mercury, must also be considered in determining the amount of mercury required to process the 3740 liters of waste.

Although data on the mercury-loading capacity are obviously incomplete, they strongly suggest that two per cent by weight of alloy metals is probably the upper limit for stainless steel metals. Assuming a mercury-loading capacity of two per cent by weight, the amount of mercury required to process 24 kg of stainless steel would be $24/0.02 = 1200$ kg. It is likely that the loading capacity of the mercury could not be increased enough to reduce this mercury inventory appreciably.

Assuming that 1200 kg are required to remove all of the reduced metals from 3740 liters of stainless steel waste, this could be supplied by a volume of mercury 5.3 square meters in area and 1.7 cm thick. If the regeneration rate was such that the mercury could be used twice in a 24-hour day, a volume of mercury 5.3 square meters in area and 1 cm thick, or 2.6 square meters in area and 2 cm thick, would be more than adequate to remove the reduced metals from 3740 liters of stainless steel waste.

B. Disposal of the Separated Components

The primary purposes for separating the fission products from the alloy metal ions are two-fold: (1) to permit disposal of the bulky, slightly contaminated alloy metals in low cost containers with no artificial cooling and with control of the storage facilities required for only a few years; and (2) to permit concentration and conversion of the fission product waste into a small high specific activity solid, which also has high heat transfer properties and low leachability with respect to ground waters. The alloy metals recovered from the mercury will be somewhat contaminated by zirconium-95, cobalt-60, possibly some ruthenium-106, and trace amounts of other fission products. It is estimated, however, that this solid could be stored in covered earth pits in areas of low rainfall, depending on the extent of contamination and leachability of the solid. A test using an actual process waste would be required to evaluate this problem adequately.

A calcination process would be necessary to convert the fission product sulfates to solid granular oxides. Assuming that this could be accomplished by known conventional techniques, the solid granules could then be "fixed" in a metal matrix within a stainless steel tube by vacuum aspiration of molten metal into the voids, a process which has been demonstrated on a laboratory scale at the ICPP, and the ends sealed with aluminum. The resulting high heat-conducting, metal-metal oxide solid could then be stored in concrete or other vaults and cooled by water or forced air with zero leachability of fission products.

C. Additional Development

Additional laboratory data are needed before adequate information will be available to prepare an acceptable flowsheet. A more complete study of the reactions which take place, such as the mechanism of the reduction of chromium from its ionic form to the metal or oxide form and the formation of excess hydrogen ion during electrolysis, would be helpful. Although regeneration of the mercury is possible by distillation or liquid scrubbing, the use of magnetic forces or centrifugation should be explored more fully as alternate possibilities. If the amalgam becomes too viscous to handle in process equipment at a concentration considerably below the loading capacity of the mercury, the amount of

mercury required to remove a given amount of metal from a waste solution may be increased appreciably. Thus, viscosity of the amalgam vs concentration of stainless steel metals should be determined. Methods for permanent disposal of the separated components of the waste need to be defined more completely, especially the disposal of the fission product "package". Conversion of the sulfuric acid-fission product solution to a solid is essential if long-term storage in a metal matrix or other solid form is to be realized.

Finally, an evaluation of the possible advantages and disadvantages of this process should be made and the process compared with other possible methods in terms of cost and safety for long-term storage.

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