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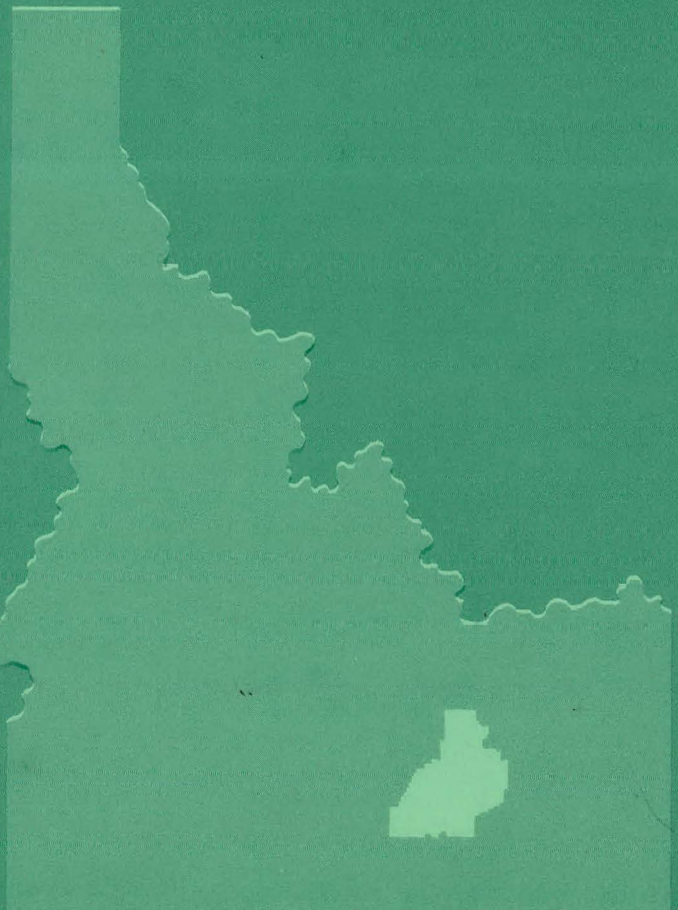
STAINLESS STEEL PROCESS WASTES:
I. REMOVAL OF ALLOY METALS FROM WASTE SOLUTIONS BY MERCURY CATHODE ELECTROLYSIS

M. E. McLain
D. W. Rhodes

September 30, 1960



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M. E. McLain
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STAINLESS STEEL PROCESS WASTES: I. REMOVAL OF ALLOY METALS FROM WASTE SOLUTIONS BY MERCURY CATHODE ELECTROLYSIS

by

M. E. McLain
D. W. Rhodes

I. SUMMARY

A method is proposed for the separation of the metal ions iron, nickel and chromium, from the fission products in wastes resulting from the chemical processing to recovery uranium from reactor fuels clad or alloyed with stainless steel (ss). A separation of the alloy metals and the fission products was accomplished in the laboratory by electrolysis of the alloy metals over a mercury cathode. The standard reduction potentials at the mercury cathode of the major long-lived fission products are such that they are difficult to reduce electrolytically in acid solution.

The removal of alloy metal ions from solution by mercury cathode electrolysis permits the alloy constituents and the fission products to be treated as separate wastes. The alloy constituents may be converted to a solid and stored in low integrity containers without danger of self-heating from fission product decay. The fission product waste can be reduced to a very small volume for storage, recovery of valuable fission products, or converted to a solid for permanent disposal.

II. INTRODUCTION

This report is the first in a series of three reports, which will discuss the results of laboratory research on the electrolysis of highly radioactive stainless steel type wastes as a pre-treatment for permanent disposal. The second report will discuss the effect of the electrolysis process on the individual fission products in the waste solution, and the third report will consider recovery and recycle of the mercury from the mercury-alloy mixture, as well as other properties of the system, which are important in designing a waste treatment process. In addition, a report will be prepared at some future date to describe methods for converting the separated components to a solid form that will be suitable for permanent disposal.

The separation of the bulk alloy metals from trace constituents by mercury cathode electrolysis is a technique that has been used by the analytical chemists for many years. This technique permits removal of the bulk metals so that the trace constituents in a solution can be concentrated before the analyst applies techniques for identification of the trace materials.

An electrolytic method that would transfer the fuel alloy metals iron, nickel and chromium, from an aqueous stainless steel waste to mercury, without carryover of appreciable fission product contamination, would be an improved waste treatment for most stainless steel wastes. Although complete decontamination of the alloy metals may not be achieved by this method, the metals could be recovered from the mercury and converted to a solid of small volume which would minimize the danger of self-heating from fission product decay during storage, reduce the potential for contamination of the water table by tank failure, and reduce storage vessel corrosion. The remaining small volume of concentrated fission products would require cooling if stored as an aqueous solution, or if converted to a solid, could be stored in small units or incorporated into a matrix having a high thermal conductivity, low leachability, and high physical integrity.

III. EQUIPMENT AND PROCEDURES

All experiments were conducted with the Eberback Dyna-Cath mercury cathode apparatus. Figure 1 shows the design of the electrolytic cell used for these experiments. Thirty-five ml of mercury were added to the cell, followed by 100 ml of the metal solution to be electrolyzed. The potential was adjusted until the desired flow of current through the solution was obtained. Electrolysis was continued with intermittent sampling until the solution was colorless. The temperature of the solution was maintained at 30° ± 5°C for all runs. Fresh mercury was used for each run, and a fresh contact surface between the mercury and the solution was maintained by stirring both the aqueous solution and the mercury by means of a magnetic field intersecting the electric field between the cell cathode and anode. Current density was varied in the metal removal studies, but for the decontamination experiments was held constant at about 0.5 ampere per square centimeter.

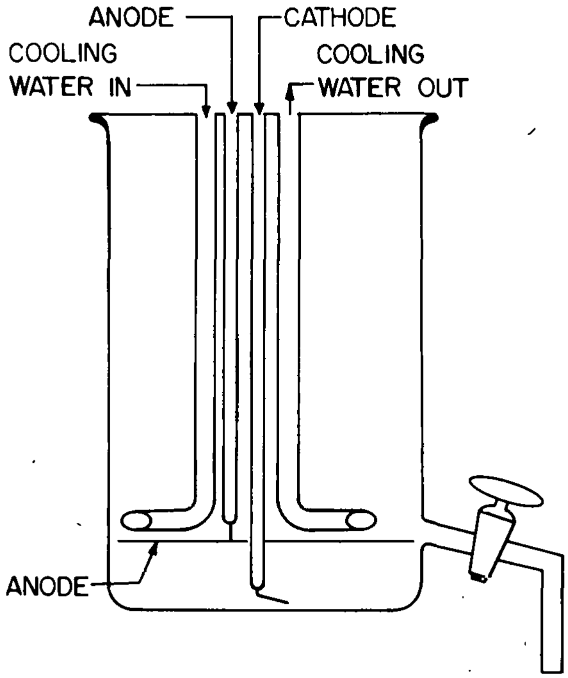

Fig. 1. Cell Used for Mercury Cathode Electrolysis.

IV. METAL REMOVAL STUDIES

Scoping experiments indicated that iron, nickel and chromium could be removed electrolytically from sulfuric acid waste solutions; however, the effect of some variables was unknown. Nitric acid (and possibly nitrate ion) interfered, due to the reduction of the nitrate ion at the mercury cathode. Formaldehyde pre-treatment to remove the nitric acid was a possible method for reducing the nitrate concentrations prior to electrolysis, but the formaldehyde remaining in the denitrated waste might possibly form a redox buffer system and interfere with the removal of the iron, nickel and chromium. In addition, it was known(1) that high concentrations of sulfuric acid interfered with the removal of chromium by mercury cathode electrolysis. The efficiency of the electrolysis is generally a function of current density, but no data were available regarding this factor for the system under investigation.

An experiment was statistically designed,(2) in which the concentrations of nitric acid, nitrate ion, sulfuric acid, formaldehyde, and the current density were varied to determine the effect of these variables on the removal of iron, nickel and chromium. The levels of the five variables are shown in Table I.

TABLE I

Experimental Levels for Five Variables to Study the Removal of Iron, Nickel and Chromium from Solution by Mercury Cathode Electrolysis

Conc. \ Level	HNO_3 N	$NaNO_3$ M	H_2SO_4 N	CH_2O M	Current Density Amperes/Cm^2
I	0	0	0.10	0	0.05
II	0.20	0.12	0.25	0.12	0.10
III	0.40	0.25	0.50	0.25	0.25
IV	0.60	0.38	0.75	0.38	0.38
V	0.75	0.50	1.00	0.50	0.50

The metal concentrations in all of the experiments were 0.10M iron, 0.01M nickel, and 0.02M chromium prepared according to a flowsheet for a stainless steel fuel process using a Darex dissolution.(3) The concentrations of the metals in the samples, which were taken periodically during the electrolysis, were determined by the emission spectrographic method.

The removal of the metals as a function of ampere-hours was fitted to the inverse growth expression:(2)

$$\text{Concentration} = \frac{1}{2\sqrt{\pi\sigma}} \quad e^{-\frac{1}{2}x^2/\sigma^2}$$

where x = ampere-hours and σ = point of inflection of the metal concentration _vs_ ampere-hours curve or the point of maximum rate of removal as shown in Figure 2. Therefore, the smaller the value of σ for a particular metal under a particular set of experimental conditions, the more rapidly it was removed.

An analysis was then made on the variation of σ within the experimental design to determine the influence of the five variables on the removal of iron, nickel and chromium. Table II shows the results of this analysis. The numbers indicate the shift in σ caused by each level of the experimental variables. A negative number means a small and a more rapid removal of metal from solution, and a positive number means a larger value of σ and a corresponding slower rate of electrolysis. The last column gives the significant level of the effect of each variable. Ninety percent indicates a definite effect and 50% indicates a lack of evidence for the variable seriously affecting the metal removal.

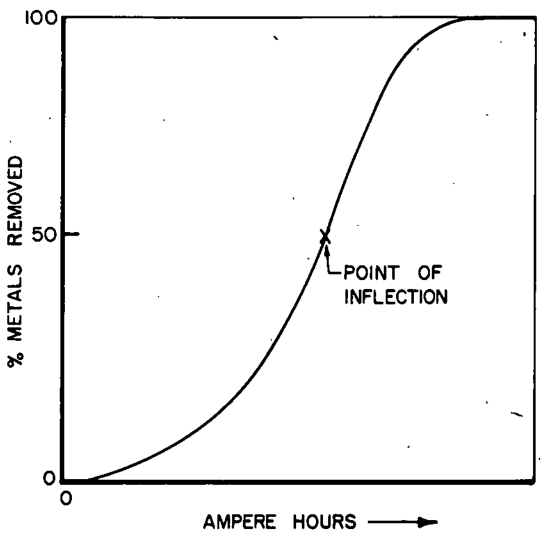

Fig. 2. Removal of Metal Ions From Solution by Mercury Cathode Electrolysis.

TABLE II

Effects of Experimental Variables on σ for the Metals Iron, Nickel and Chromium

Ni

Variable/Level	I	II	III	IV	V	Significant Level
HNO_3	-1.870	-1.616	-2.340	-3.940	+9.764	94%
$NaNO_3$	-2.868	+0.714	+0.922	+0.012	+1.218	<50%
H_2SO_4	-5.706	-5.100	+2.198	+5.374	+3.232	93%
CH_2O	+5.882	-0.488	+0.684	-3.568	-2.512	80%
Current	+12.106	-1.432	-2.820	-6.334	-1.522	97%
			Cr			
HNO_3	-4.264	-1.054	-1.050	-0.214	+6.580	83%
$NaNO_3$	-1.840	-0.616	-0.598	-1.278	+4.330	58%
H_2SO_4	-0.210	+1.312	+0.214	-1.224	-0.094	<50%
CH_2O	-1.134	+0.282	+0.646	+0.134	+0.070	<50%
Current	+2.892	+0.062	+0.012	-1.872	-1.096	<50%
			Fe			
HNO_3	-3.823	-2.657	-2.097	-0.591	+9.167	95%
$NaNO_3$	-1.133	-0.915	-2.831	+0.287	+4.591	70%
H_2SO_4	-0.435	-0.657	+3.457	-2.135	-0.231	<50%
CH_2O	-2.083	-2.049	+3.111	-0.017	+1.037	50%
Current	+5.775	+0.373	-1.481	-0.963	-3.705	80%

The following conclusions can be drawn from the data in Table II. The removal of nickel from solution by mercury cathode electrolysis was essentially unaffected by nitric acid until the concentration of nitric acid in the solution increased to 0.75M. At this concentration, a definite interference was evident. Nitrate ion as sodium nitrate did not show a detrimental effect up to the limit of concentration studied. Sulfuric acid above 0.5N exhibited a retarding effect on the removal of nickel. Formaldehyde possibly aided the electrolysis although the significant level was not high. Increasing current density increased the efficiency for the reduction of nickel ion.

The variation in the rate of chromium removal as a function of the five experimental variables was not as obvious as in the case of nickel. Nitric acid at 0.75M interfered seriously. No definite statements can be made concerning the influence of the remaining variables.

The electrolysis of iron exhibited the same dependence on the nitric acid concentration as nickel and chromium. A reduction in iron removal efficiency with increasing $NaNO_3$ concentration was noted beginning at about 0.38M. Sulfuric acid and formaldehyde in the range of concentration studied showed no retarding effect on chromium electrolysis. As with nickel and iron, higher current density accelerated the reduction of chromium ion.

Optimum conditions for each of the variables in the removal of iron, nickel, and chromium by mercury cathode electrolysis can be summarized as follows: $<0.75M$ HNO_3, $<0.38M$ $NaNO_3$, $\sim 0.5N$ H_2SO_4, no effect CH_2O, current density $\geq$ 0.50 amperes/cm^2. Under these conditions, approximately 20 ampere-hours were required to remove one gram of Type 304 ss from solution.

V. FISSION PRODUCT REMOVAL

An important aspect of a waste treatment process designed around mercury cathode electrolysis is the degree of separation of the alloy metal ions and the fission products. As an indication of the effectiveness of this separation, removal factors were determined for some long-lived fission products by scoping studies. The removal factor is defined as the total amount of fission product in the original solution divided by the total amount of fission product in the mercury after electrolysis. Table III shows the removal factors observed in the experiments performed to date. In all experiments, the solution was 0.1M iron, 0.01M nickel, 0.02M chromium (as the sulfates), and 1.0N sulfuric acid. (These experiments were run before it had been established that a sulfuric acid concentration $>0.5N$ retarded the electrolysis of the metal ions.)

One-hundred ml of the solution containing the metal ions were used in each experiment. Radioactive tracer was added to the solution, a sample taken, and electrolysis carried out using the Eberback Dyna-Cath mercury cathode apparatus. When all the ss metal ions were removed from solution, as evidenced by the disappearance of coloration, electrolysis was stopped and a sample of the mercury removed. The mercury sample was washed gently with dilute HNO_3 and water to remove any fission products adsorbed on the surface, and then placed in a well-type scintillation counter and the fission product concentration measured. The concentration of gamma-emitters in the aqueous solution was measured directly in the well counter, but chemical separation prior to counting was necessary for the determination of strontium-90. The results of the removal studies are shown in Table III.

TABLE III

Fission Product Removal Factors for the Removal by Electrolysis of Iron, Nickel and Chromium

Isotope	Removal Factor
Ce^{144}	5×10^3
Cs^{137}	8×10^3
Sr^{90}	5×10^4

$$\text{Removal factor} = \frac{\text{Total fission product in solution before electrolysis}}{\text{Total fission product in mercury after electrolysis}}$$

An attempt was made to obtain removal factors for ruthenium and zirconium, but the results were very erratic. It was evident that a systematic study of the factors affecting the reduction by mercury cathode electrolysis of ruthenium and zirconium, and also cesium, strontium and cerium, would be necessary to design a waste treatment process having high removal factors for the more important radioisotopes.

VI. MECHANISMS OF METAL REDUCTION

Sandborn(4) established the mechanisms for the reduction of iron(III) and nickel(II) at the mercury cathode in a perchloric acid medium. He concluded that a simple transfer of electrons between the mercury electrode and the metal ion in the electrical double layer was the mechanism for the reduction of these two ions. McLain(5) studied the polarographic reduction of the chromium(III) ion to chromium(II) in nitrate solution, and concluded that a mechanism somewhat more complex than the iron and nickel mechanism was responsible for the reduction of chromium. At potentials more positive than the polarographic half-wave potential, electron transfer occurred. However, on the negative side of the half-wave potential a second reduction reaction became prominent. Chromium(II) ions near the surface of the mercury cathode reduced chromium(III) ions in the solution by electron exchange. The heat of activation for the two reactions was determined to be 34 and 27 kcal mole^{-1}, respectively. The data further indicated that the presence of surface active substances in the waste to be electrolyzed, such as traces of organic solvents, should not affect the reduction of the alloy metal ions at the mercury cathode.

VII. RECOVERY OF MERCURY FROM THE MERCURY-ALLOY METAL MIXTURE

Apparently iron, nickel and chromium do not form an amalgam with the mercury, but exist in a finely divided state dispersed throughout the mercury. One of the very important aspects of a waste treatment process using a mercury cathode for removing the alloy metals from solution is recovery of the mercury from the mercury-alloy metal mixture. This recovery process must be both efficient and economical to minimize the mercury inventory and losses. Possible methods to separate the mercury-alloy metal mixture include dissolution of the alloy metals in an acid or acid-oxidizing solution or a physical separation method such as distillation, filtration, magnetic methods and centrifugation.

A few scoping experiments were conducted to attempt to remove the alloy metals from a mercury-iron, nickel, chromium mixture by dissolution of the alloy metals in acid and oxidizing solutions. Table IV gives the results of these experiments and Figure 3 shows the cell that was used in the laboratory experiments.

TABLE IV

Removal of Metals from Cathode Mercury Using Various Wash Compositions and Sparge Gases

Wash Liquid	Sparge Gas	% of Metals Removed From Mercury			Mercury Dissolved in Wash Solution	
		Fe	Cr	Ni	(g/l)	(% of Total Mercury)
H_2O	Nitrogen	1	5	0	-----	-----
H_2O	Air	8	5	6	.087	0.002
HNO_3 0.6N	Air	51	57	35	2.51	0.053
HNO_3 1.3N	Air	86	77	87	31.8	0.68
HNO_3 1.9N	Air	78	75	74	35.8	0.76
HNO_3 2.5N	Air	88	78	69	82.4	1.75
HNO_3 2.5N	Nitrogen	55	54	43	41.2	0.88
HNO_3 3.1N	Air	82	74	100	46.1	0.98
HCl 3N	Air	20	16	13	-----	-----
HCl 6N	Air	17	16	9	.005	0.0001
HCl 6N	Nitrogen	1	86	1	-----	-----
$Fe_2(SO_4)_3$ 0.1<u>M</u>	Nitrogen	3	40	18	1.72	0.036
$Fe_2(SO_4)_3$ 0.4<u>M</u>	Nitrogen	4	79	29	-----	-----
Saturated $KMnO_4$		78	20	36	0.32*	0.007

* Saturated $KMnO_4$ in 6N H_2SO_4 acted rapidly to oxidize the metals, but also attacked the mercury, leaving 59 grams of solid Hg_2SO_4.

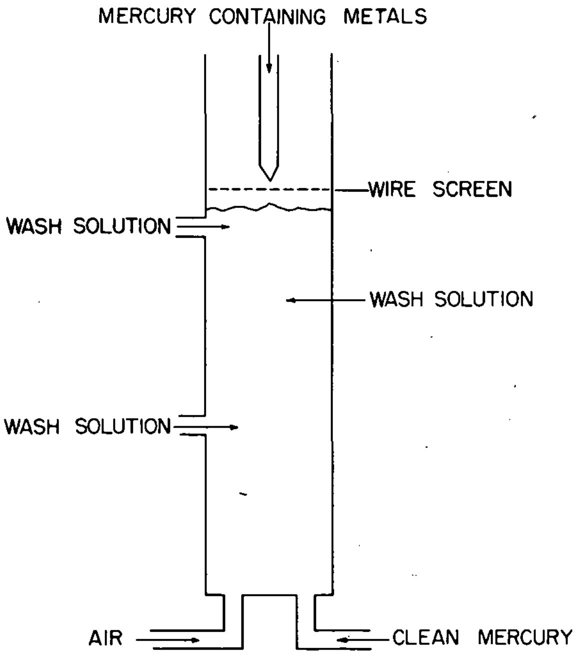

Fig. 3. Cell for the Removal of Iron, Nickel and Chromium From Mercury.

The data indicate that a solution of an oxidizing substance will remove the base alloy metals from the more noble mercury. Nitric acid, ferric sulfate, and acidic potassium permanganate were all effective in removing the alloy metals from the mercury. Dilute nitric acid was preferable because it added no additional solids to the waste. One molar nitric acid with an air sparge in the wash cell (Figure 3) proved effective in removing iron and nickel as soluble salts, but chromium was obtained as an insoluble oxide, probably CrO. This solid was quite dense, although finely divided. No wash was found that removed chromium as a soluble compound.

Although an acid-oxidizing wash can be used to remove the alloy metals from the mercury, a solid state separation might be preferable, because it would not be necessary to convert the dissolved metals to a solid again for permanent disposal. The preliminary data obtained in this investigation indicate that a systematic and thorough investigation of methods for the recovery of mercury will be necessary to design a complete waste treatment process around the principle of separation of the alloy metals and fission products by mercury cathode electrolysis.

VIII. CONCLUSIONS

The use of a mercury cathode to effect an appreciable separation of iron, nickel and chromium from the fission products in ss type aqueous wastes appears to be technically feasible. The preliminary data indicate that the process will require at least partial destruction of the nitric acid prior to removal of the metals, as well as the presence of sulfuric acid to prevent precipitation of the alloy metals and to provide a conducting medium for the electrolysis reaction to proceed to complete removal of the metals.

Decontamination factors good enough to prevent self-heating of the separated alloy metals stored as a dry solid appear possible although more detailed data will be required to define the optimum conditions for obtaining maximum decontamination. In addition, methods for recovery of the mercury from the mercury-alloy metal mixture must be developed, and quantitative measurements to determine deposition rates of the alloy metals and current efficiencies will be required to provide data for the design of a complete waste treatment process.

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