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# THE PREPARATION OF $Ru^{106}$ TRACER FROM WASTE METAL SOLUTION

A.T. Gresky

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# THE PREPARATION OF $Ru^{106}$ TRACER FROM WASTE METAL SOLUTION

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## 1.0 Abstract

A process is presented for the recovery of 290 day $Ru^{106}$ from Oak Ridge National Laboratory waste metal solutions. This process is based on the carrying of ruthenium on $Fe(OH)_2$ and subsequent distillation from $KMnO_4$-$H_2SO_4$.

[redacted]

## 2.0 Introduction

The materials stored in tanks W-7 and W-10 at Oak Ridge National Laboratory are waste solutions from the plutonium bismuth phosphate process. Sometime ago, sodium hydroxide was added to the tanks and the supernatant solution decanted after sodium diuranate had settled, to provide needed storage space. These supernatant solutions contain significant amounts of the long-lived fission products $Cs^{137}$, $Ru^{106}$, $43^{99}$, and $Sr^{90}$. The $Ru^{106}$ has a half-life of 290 days and is a 0.03 Mev beta emitter. It decays to $Rh^{106}$ which has a half-life of 30 seconds and emits 2.8 Mev (20%) and 3.9 Mev (80%) betas as well as 0.3 and 0.8 Mev gammas. These supernatant solutions form the starting solution for the ruthenium recovery process to be described.

A previous report, MonT-223, outlined a process for the preparation of ruthenium tracer by silver oxide carrying, followed by distillation of $RuO_4$ from $H_3PO_4$-$KMnO_4$. Although applicable for use on the original W-10 storage tank solutions, low Ru yields were experienced in the silver carrying step with solutions from W-7. This report outlines a procedure utilizing ferrous iron as a carrier followed by distillation of $RuO_4$ from $KMnO_4$-$H_2SO_4$ as a purification step. It is believed that this method will suffice as a general process for all the complex waste solutions which are encountered.

[redacted]

## 3.0 Summary

A $Ru^{106}$ recovery process, operable for large volumes and by remote control, was developed for the production of sizeable quantities of this isotope from the waste metal solutions in storage at ORNL. Concentration by carrier and final purification by distillation of $RuO_4$ have resulted in yields of about 60%.

The ruthenium was scavenged from the W-7 supernatant solution by a ferrous hydroxide precipitation which was allowed to settle and then separated by decantation. The thick slurry of $Fe(OH)_2$ containing ruthenium activity was subsequently dissolved in $H_2SO_4$ and transferred to a reactor for distillation of the product.

Distillation of $RuO_4$ was accomplished, at 85°C and under vacuum, by the addition of $KMnO_4$ to the $Fe_2(SO_4)_3$ solution. For ease of operation, the product was collected under HCl and subsequently concentrated as ruthenium chloride (probably a mixture of $RuCl_3$ and $RuCl_4$).

The procedure outlined in this report has been used for the preparation of $Ru^{106}$ from W-7 wastes and has been found to be satisfactory on a 500 gallon (100 millicurie) scale by the Operations Division.

## 4.0 Experimental Results

To obtain the desired quantities of $Ru^{106}$ from the waste supernatant solutions, it was required, for considerations of time and efficiency, that rather large equipment (500-1000 gal.) be used in the process. A carrier endowed with the ability to effect sizeable concentrations and yields of the ruthenium activity was needed. Low solubility and rapid settling were also desired so that filtration or centrifugation could be eliminated.

For purification of the tracer by distillation it was desirable that this carrier be easily soluble in $H_2SO_4$ or $H_3PO_4$. A vacuum distillation from $KMnO_4$ solution was found to be the optimum method for speed of operation, high yields, and concentration of the product. The system used should have facilities (a) for introducing air under the solution, (b) for introducing reagents and removing residues, (c) for temperature and vacuum control, and (d) for trapping the liquid spray in the collector side. The product traps should consist of a series arrangement designed to prevent "suck-backs" to the reactor and to allow collection under some reducing agent such as HCl, or $HNO_3$-$H_2O_2$. A safety trap of NaOH should be provided to protect the vacuum system.

### 4.1 Concentration by Carrier

Several carriers were studied to establish those holding some promise for ruthenium recovery. Silver oxide, which had afforded yields as high as 95-100% in studies with the solution from waste tank W-10, carried only about 10-12% ruthenium from the W-7 solution, even with excessively large amounts of the carrier.

Manganese dioxide, both preformed and co-precipitated, failed to carry over 10%. Other carriers studied, which gave low yields, included $Fe(OH)_3$, $Mn(OH)_2$, $Ce(OH)_3$, and $Ce(OH)_4$. It was observed, however, that $Fe(OH)_2$ gave yields of 60-70% and relatively small amounts of the carrier were effective.

Using freshly prepared 1.0 M $FeSO_4$ as reagent, it was found that a ferrous iron concentration of 0.004 M gave yields of about 30% ruthenium and concentrations as high as 0.06 M gave a yield of 76%. Since the ferrous iron reagent oxidized fairly rapidly to ferric iron on standing, $H_2SO_4$ was added to the reagent to stabilize the solution. It was observed that if the 1.0 M $FeSO_4$ reagent were made up in 0.8 M $H_2SO_4$, the yield from a 0.004 M ferrous iron concentration could be increased from 30% to 50%. $H_2SO_4$ concentrations higher than 1.0 M were found to cause a steady decrease in yield (see Table II). The use of $FeSO_4 \cdot (NH_4)_2SO_4$ instead of $FeSO_4$ gave yields 13% lower for 0.004 M $Fe^{++}$ concentrations and as much as 45% lower at a concentration of 0.06 M. The addition of methanol (ca. 0.05 M) to the supernatant solution before $FeSO_4$ addition increased yields about 10%. Thus, with a 0.004 M ferrous iron concentration, yields of about 55% could be obtained (see Table III).

A study of the temperatures of precipitation indicated that yields with 0.004 M ferrous iron concentrations could be increased from 55% at 27°C to 69% at about 65 to 85°C. The maximum ruthenium yield obtained with high concentrations of ferrous iron(0.03 M ) was approximately 88%.

4.2 Settling and Dissolving

The iron precipitate was white when first formed, gradually turning to green, and finally black. Occasionally, a small amount was converted to the reddish-brown $Fe(OH)_3$, depending on the extent of contact with air. The bulk of this precipitate settled in about 30 minutes even from volumes as large as 500 gallons, with complete settling obtained in 4-6 hours. In 4-6 hours the precipitate occupied a volume roughly 2% of the starting volume and with ageing a few days became a thick slurry occupying less than 1% of the original volume. Thus, about 90% of the starting volume may be decanted 4-6 hours after precipitation, and a reduction factor of up to 100 can be obtained after ageing several days.

The thick slurry dissolved slowly in $HNO_3$, $H_3PO_4$, $H_2SO_4$, and very rapidly in HCl. Sulfuric acid was the most desirable for plant use and solution was effected by adding approximately two volumes of concentrated $H_2SO_4$ to five volumes of the thick slurry. Empirically, it was found that a specific gravity of 1.4 to 1.5 indicated a desirable concentration of the $Fe_2(SO_4)_3$ solution for the distillation step.

4.3 Distillation of $RuO_4$ from $H_2SO_4$-$KMnO_4$

The $H_2SO_4$-$KMnO_4$ process, described by D. Hume in CC-2828, when applied to solutions containing large amounts of iron, presented difficulties due to excessive decomposition of the $KMnO_4$. This necessitated the use of large quantities of reagent and yields were lowered considerably by excessive amounts of insoluble $MnO_2$ which formed in the reactor.

It was found that by applying a slight vacuum through the system, the distillation could be accomplished very effectively at about 85°C without boiling the mixture. Also, by introducing $KMnO_4$ into the still during distillation, at intervals and in amounts sufficient to barely sustain the purple color, required quantities of this reagent could be reduced considerably. Working with 500 ml. volumes of the $Fe_2(SO_4)_3$ solution, it was found that 85-90% of the ruthenium could be distilled at 85°C, with only 50-75 ml. of 0.3 M $KMnO_4$.

The use of the vacuum system presented several advantages. Air or oxygen could be drawn through the still pot to afford agitation as well as a sweeping action to remove the $RuO_4$. Temperatures below the boiling point of the mixture made possible the attainment of good yields of product with a minimum of distillate volume and plating of ruthenium. Also, the time required for obtaining high yields was decreased considerably.

For collection of the product it was found that HCl afforded the most rapid and certain reduction of the $RuO_4$, and it appeared more adaptable for product concentration than $HNO_3$-$H_2O_2$. Two sets of double traps in series were used to fore-stall the hazards of back-pressures in the system, and were sufficient to reduce all of the $RuO_4$. A sodium hydroxide trap was used to eliminate the corrosive acid vapors from the vacuum system. All glass equipment was used for the distillation and, from present considerations, it does not appear necessary to use stainless steel.

The specific activity of the product was found to be the order of 1 milicurie $Ru^{106}$ per mg. ruthenium. The brown color of the

product solution in the HCl traps was probably ruthenium chloride ($RuCl_3$ or a mixture of $RuCl_3$ and $RuCl_4$). The product ruthenium was spectrographically pure and contained no iron or manganese which might have contributed the brown color. Absorption curves indicated the product was issentially free of all radioactive contaminants except small amounts of $Ru^{103}$.

## 5.0 Appendix

Table I

Radioactive and Ionic Constituents of Metal Waste Tank Supernatant Solutions

| Constituent | Concentrations (Ions in mg/ml - activities d/min/ml) Tank W-7 | Tank W-10 |
|---|---|---|
| Phosphate | 10.3 | 20.0 |
| Carbonate | 36.0 | 330.0 |
| Sulfate | 14.3 | 27.5 |
| Nitrate | 33.4 | 31.0 |
| Hydroxide | 59.0 | 65.0 |
| Uranium | 0.25 | 1.59 |
| Total | 153.0 | 473.0 |
| Ru $\beta$ | $0.26 \times 10^6$ | $0.95 \times 10^6$ |
| Cs $\beta$ | $0.82 \times 10^6$ | $3.2 \times 10^6$ |
| Other $\beta$ | $0.07 \times 10^6$ | $1.3 \times 10^6$ |
| $\gamma$ | $0.01 \times 10^6$ | $0.06 \times 10^6$ |
| Total $\beta+\gamma$ | $1.16 \times 10^6$ | $5.5 \times 10^6$ |

These data for W-7 were obtained December, 1947, and the data for W-10 on November, 1946.

Table II

EFFECT OF $H_2SO_4$ CONCENTRATION OF 1 M $FeSO_4$ REAGENT ON $RU^{106}$

CARRYING FROM W-7 SUPERNATANT

Conditions: 0.004 M $Fe^{++}$ at Room Temperature

| $H_2SO_4$ Conc.: | 0.0 M | 0.2 M | 0.4 M | 0.6 M | 0.8 M | 1.0 M | 1.2 M | 1.4 M | 1.8 M |
|---|---|---|---|---|---|---|---|---|---|
| % Ru carried: | 30 | 37 | 39 | 54 | 54 | 46 | 45 | 45 | 39 |

Table III

PER CENT RUTHENIUM CARRIED UNDER VARIOUS CONDITIONS IN THE FERROUS

IRON CARRYING STEP

| Final Fe Concentration M | % Ru yield under various precipitation conditions | | | | | |
|---|---|---|---|---|---|---|
| | Ppt'n. with 1 M $FeSO_4$ at 25°C | Ppt'n with 1 M $FeSO_4$ 0.8 M $H_2SO_4$ 25°C | Addition of 0.05 M $CH_3OH$ followed by Ppt'n with 1.0 M $FeSO_4$-0.8 M $H_2SO_4$ | | | |
| | | | 25°C | 45°C | 65°C | 85°C |
| 0.004 | 24 | 30 | 54 | 65 | 69 | 69 |
| 0.008 | 45 | 53 | 62 | 76 | 77 | 79 |
| 0.016 | 55 | 63 | 70 | 86 | 86 | 88 |
| 0.03 | 62 | 72 | 78 | 86 | 88 | 88 |
| 0.06 | 72 | 76 | - | - | - | - |

5.1 Recommended Procedure for Plant Use

For convenience in utilizing the procedures discussed in this report, a detailed outline of the various steps proposed is presented.

To five hundred volumes of the W-7 supernatant at 60-80°C:

1. Add one volume $CH_3OH$ and begin agitation.
2. Add two volumes of 1 M $FeSO_4$-0.8 M $H_2SO_4$ and continue agitation until the precipitate is uniformly dispersed in the solution. Agitation should be gentle and of short duration to minimize conversion of Fe++ to Fe+++ by air oxidation.
3. Allow the precipitate to settle for four to six hours, then decant the supernatant liquid.
4. Wash with four hundred volumes of $H_2O$, allow to settle, and decant. (With ageing, the precipitate occupies from 0.5 to 1.0% of the original volume, and is closely aggregated, and allows good separation by decantation).
5. To five volumes of the settled slurry, add carefully two volumes of concentrated $H_2SO_4$ and allow to stand for several hours. Separate any undissolved material by decantation or filtration and transfer the solution to a reactor for distillation.
6. With the distillation system under vacuum, add the $Fe_2(SO_4)_3$ solution and heat to about 85°C.
7. Add just enough 0.3 M $KMnO_4$, and make additions as required during the distillation to sustain a purple color. The $RuO_4$ begins to distill immediately after the $KMnO_4$ addition and under optimum conditions approaches 85-90% removal in one to two hours.

Experimental data covering the information in this report can be found in Notebooks CL-1863 and CL-1673, the work being completed in March, 1948. Acknowledgement is made to T. C. Runion for editorial assistance in the preparation of this report.

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