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UNITED STATES ATOMIC ENERGY COMMISSION
PROBABILITY OF RUTHENIUM REDUCTION
IN H-4 BY SELF-RADIATION

By
 U. L. Upson

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Hanford Atomic Products Operation
 Richland, Washington

Technical Information Extension, Oak Ridge, Tennessee

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F.J. Leitz
Head - Radiochemistry Sub-Unit
ENGINEERING DEPARTMENT

PROBABILITY OF RUTHENIUM REDUCTION IN H-4 BY SELF-RADIATION

The following calculations have been made at the request of H.R. Schmidt to determine the probability that self-radiation may play a substantial role in the decomposition of the ruthenium tetroxide in the reflux scrubber section of the Redox Ruthenium Oxidizer (H-4). The validity of the derived data necessarily depends upon the correctness of the basic assumptions made with regard to process conditions and to possible radiation-activated mechanisms of disintegration. It is estimated that the extent of solid ruthenium formation in the tower which results from radiation effects should not exceed 100 micrograms per batch. This rate is negligible compared to that now found in the presence of stainless steel packing, or to that which might be expected from thermally-activated disintegrations alone.

For the purpose of these calculations, neither of the more probable modes of disintegration; chemical reduction and thermally-activated disintegration, are considered to exist; all the ruthenium in the process stream is assumed to be available for radiation-activated disintegration. Prior formation of a solid ruthenium compound is assumed, however, thus constituting a radiation source of high intensity. The vapor-phase ruthenium is assumed to be subjected to the resultant high beta flux throughout its entire transit period through the tower. Although in the present packed tower the steel packing and the refluxed water constitute a very substantial shield with respect to irradiation of the ruthenium vapor, no corresponding correction has been applied. In order to simplify the calculations and to assume maximum

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possible energy absorption by the ruthenium tetroxide vapor, the tower has been considered as an unpacked cylindrical column, with all solid ruthenium build-up distributed over the inner surface of the column, and with all the vapor assumed to be in a flux similar to that prevailing at the center of the column. Reflux water is assumed to return to the pot without substantially reducing the average flux in the column. Thus the hypothetical situation assumed corresponds to that which might exist in such an unpacked column if the reflux water were returned externally or in a narrow stream down a small portion of the wall.

The present calculation is based upon an assumed ruthenium content in the Redox feed of 1.4 gram Ru-103 and 2.6 gram Ru-106 per ton of uranium. These values were calculated on the basis of 200 days exposure at an average flux of 3×10^{13} neutrons/cm² followed by a 90-day cool. For a batch size of 1900 gallons of 2.2 molar uranium solution, or 4.15 tons U, this amounts to 5.8 grams Ru-103 and 10.8 grams of Ru-106 per batch or a total of 16.6 grams. The corresponding beta activity is found to be 183,000 curies Ru-103 and 45,000 curies Ru-106 per batch.* The vapor flow rate used here is that which would obtain for an unpacked column. It is assumed that the overall ionization-reduction efficiency is 50%. In all phases, the factors are heavily weighted in favor of the reduction of ruthenium by radiation, hence the resultant estimate of 100 micrograms per batch may be considered a maximum probable value, with an uncertainty factor of at least 100.

CALCULATIONS

This estimation of the amount of ruthenium which might be reduced by radiation is based upon the following premises. It is assumed that 50% of the total ruthenium in the pot is evolved during the first minute of the first permanganate strike, and that the average ruthenium concentration during the first minute represents an effective mean for that period. It is also assumed that there exists a prior build-up of solid ruthenium in the tower, and that the simplifications imposed with regard to the amount of this activity and to its effective flux do not constitute a serious source of error. Each ruthenium tetroxide molecule in the stream is assumed to be exposed to the assumed flux for the average transit time of the stream through the tower, and the fraction of the flux energy absorbed by the ruthenium is assumed to be equal to its mass-fraction of the total vapor phase.

The calculations follow the form:

$$\text{No. of ruthenium atoms ionized} = \frac{\text{Total energy in beta flux} \times \text{Fractional energy absorbed by vapor stream} \times \text{Mass fraction of ruthenium in vapor stream}}{\text{Assumed energy expended per ionization of one ruthenium atom}}$$

and

$$\text{No. of ruthenium atoms reduced} = \text{No. of ruthenium atoms ionized} \times \text{Ru atoms reduced per atom ionized}$$

* These data are in marked contrast to the reported values of 8 g Ru and 24,000 "countable beta curies" per batch. An earlier calculation, based on the reported values, and assuming all ruthenium to be Ru-103, yielded an estimated ruthenium reduction of 0.2 microgram per batch.

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For which it is assumed that:

Total energy in beta flux = Average energy per beta particle
 X no. of beta particles per second
 X seconds exposure
 X geometry of source

Fractional energy absorbed by vapor streams = Value estimated from:
 .density of vapor
 .estimated beta range
 .average path length in vapor
 .scattering probability

A. Flow Conditions in Tower**

Air input = 20 cfm = 0.33 ft³/sec.
 Steam input = 100 lb/hr = 0.28 lb/sec = ~ 7.3 ft³/sec.
 RuO₄ input*** = $\frac{4.15 (1.4 + 2.6) 0.5 (22.4)}{105 (28.3) 60}$ = ~ 0.001 ft³/sec. (negligible)
 Total vapor flow = ~7.6 ft³/sec. or ~ 450 ft³/min.

Cross-section of tower (Diameter = 2 ft.; free volume of packing = ~70%)

Cross-section area (unpacked) = 3.14 ft²
 Cross-section area (packed) = 2.20 ft²
 Linear velocity (packed) = 7.6/2.2 = 3.4 ft/sec.
 Linear velocity (unpacked) = 7.6/3.14 = 2.4 ft/sec.

Time in transit, average for 10.5 ft. tower

Transit time (packed) = 10.5/3.4 = 3.1 sec.
 Transit time (unpacked) = 10.5/2.4 = 4.4 sec.

The average transit time for the unpacked column will be taken as the "average exposure period" in the following calculations.

B. Radiation Flux Intensity

1. Ruthenium Build-Up in Tower

For a uniform accumulation rate, the total accumulation activity is represented by

$$R \int_0^{\theta} e^{-\lambda t} dt \text{ or } R' \int_0^{\theta} (1/2)^t dt$$

where θ is the time in numbers of half-lives, and R and R' are the corresponding rates of accumulation. If we assume that 10% of the total throughput has accumulated over a preceding one-year period, and if we assume an average of two batches per day, the amounts of accumulation Ru-103 and Ru-106 are estimated as follows:

** Process data supplied by R.J. Sloat and K.J. Schneider.

*** First-min. of first strike, assuming 50% of evolution in that period. Volume not corrected for temperature and pressure. A mean mass of 105 is assumed for the Ru-103, Ru-106 mixture.

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Ru-103: $R' = (0.1)(183,000) 2 (40) = 1.46 \times 10^6$ curies/half-life

At one year, $\theta = 365/40 = 9.1$
 Accumulated Ru-103 = $R' \int_0^{9.1} (1/2)^\theta d\theta = R' \left[\frac{(1/2)^\theta}{\ln 2} \right]_0^{9.1}$

$$= \frac{1.46 \times 10^6}{0.693} \left[1 - (1/2)^{9.1} \right] = \frac{1.46 \times 10^6 \times 0.998}{0.693}$$

$$= 2.1 \times 10^6 \text{ curies Ru-103}$$

Ru-106: $R' = 0.1 (45,000) 2 (290) = 2.6 \times 10^6$ curies/half-life

At one year, $\theta = 365/290 = 1.26$
 Accumulated Ru-106 = $\frac{2.6 \times 10^6}{0.693} \left[1 - (1/2)^{1.26} \right] = \frac{2.6 \times 10^6 \times 0.583}{0.693}$

$$= 2.2 \times 10^6 \text{ curies Ru-106}$$

Note: If, instead of a one-year accumulation, we had assumed accumulation over an infinite period, the amount to Ru-103 would be the same, but the amount of Ru-106 would be $2.6 \times 10^6 / 0.693 = 3.8 \times 10^6$ curies.

2. Current Ruthenium in Transit

The ruthenium in transit as the vapor phase is a negligible beta source compared to that of the assumed build-up: e.g., Ru-103 = $\frac{0.5 (183,000) 10.5}{450} = 6700$ curies; and Ru-106 = $\frac{0.5 (45,000) 10.5}{450} = 1650$ curies (during the first minute of the first strike).

C. Radiation Flux Energy

Only beta radiation is calculated, since gamma interactions can be expected to be less than 5% efficient in the vapor path, and since all the build-up has been assumed to be ruthenium.

Ru-103: Max. energy of predominant beta = 0.22 MeV
 Ave. beta energy = $\sim 0.4 (0.22) \times 10^6 = 9 \times 10^4$ eV

Ru-106: Max. energy of predominant beta = 3.5 MeV
 Ave. beta energy = $\sim 0.35 (3.5) \times 10^6 = 1.2 \times 10^6$ eV

D. Energy Absorption by Ruthenium

1. If we consider all the accumulated ruthenium to be uniformly distributed on the inner surface of the cylindrical tower, and to have an effective geometry approaching that of a flat source, i.e., 50%, the total beta exposure of the vapor stream can be estimated as follows. The total exposure from Ru-103 betas is given by

$$0.5 (2.1 \times 10^6) 3.7 \times 10^{10} (4.4) = 1.7 \times 10^{17} \text{ electrons}$$
 at an average energy of 9×10^4 eV, possessing a total energy of 1.5×10^{22} eV. Similarly, the total exposure from Ru-106 betas is calculated at 1.8×10^{17} electrons at 1.2×10^6 eV average energy, or a total energy of 2.2×10^{23} eV.

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2. Energy Absorption by Vapor Stream

The average path** across the void space of a 2-foot diameter by 10 1/2 foot high cylinder is estimated at 1.68 feet, or 51 cm. Beta particles striking the tower wall may have an extended path due to scattering. Assuming a probability of two scatterings per beta particle, the effective path length is ~ 150 cm. The density of the vapor stream is essentially that of the water vapor alone, or about 4.3×10^{-5} g/cm³. Thus, for a 150 cm path, this amounts to ~ 6.5 mg/cm² average absorption. Since the maximum range of the Ru-103 betas is about 45 mg/cm², and that of the average Ru-103 beta is about 12 mg/cm², we can assume these betas to be no more than 30% absorbed by the vapor stream. In the case of Ru-106, for which the maximum range is over 1 gram/cm², and the average range is about 500 mg/cm², we can expect less than 5% effective absorption by the vapor stream.

3. Energy Absorbed by Ruthenium

It is reasonable to assume that ruthenium absorbs only that fraction of the total beta absorption equal to its mass fraction of the vapor stream. This fraction is found to be (as a first-minute average):

$$\frac{0.5 (5.8 + 10.8)}{20 (0.09) + \frac{1000 \times 454}{60} + 0.5 (5.8 + 10.8)} = 1.1 \times 10^{-3}$$

(air) (water vapor) (ruthenium)

On this basis, the energy absorbed by the ruthenium in the stream can be estimated.

$$\begin{array}{llll} \text{From Ru-103:} & 0.3 (1.5 \times 10^2) & 1.1 \times 10^{-3} & = 5 \times 10^{18} \text{ eV} \\ \text{From Ru-106:} & 0.05 (2.2 \times 10^{23}) & 1.1 \times 10^{-3} & = 12 \times 10^{18} \text{ eV} \\ \text{Total energy absorbed by ruthenium} & & & = 17 \times 10^{18} \text{ eV.} \end{array}$$

E. Reduction of Ruthenium by Self-Radiation

The ionization of ruthenium by beta irradiation might occur only by primary interactions. In such case the total number of such interactions, from both Ru-103 and Ru-106, would then be 2×10^{16} interactions** (See D, 2 above), and, hence 2×10^{16} ionized ruthenium atoms would be formed during the first minute of the first strike of each bath. This would amount to only $\frac{2 \times 10^{16}}{6 \times 10^{23}} (106) = \sim 3 \times 10^{-6}$ microgram. If, on the other hand, the energy absorbed by the ruthenium is totally utilized in ionization, and if we assume an ionization energy of 30 eV, the amount ionized is $17 \times 10^{18} / 30 = \sim 6 \times 10^{17}$ atoms, or approximately 100 micrograms, during the first minute.

The effectiveness of ionization in accomplishing a reduction of the ruthenium tetroxide is not known, but might be expected to be high. If we assume an overall ionization-reduction efficiency of 50%, then a yield of 50 micrograms of reduced ruthenium can be estimated for the first minute of the first strike. The efficiency for any subsequent period must be quite low, as the ruthenium composes a progressively smaller fraction of the total absorption path with time. On the other hand, it may well have a greater absorption efficiency

** Calculated by P.M. Anselone, Applied Mathematics

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during the first half-minute, so an overall yield of 100 micrograms per batch is a reasonable estimate. It is felt that the true value probably is much lower than this, and it is believed highly unlikely that the amount of radiation-reduced ruthenium could exceed 1 milligram per batch.

J. L. Upson

Chemistry Unit
Technical Section
ENGINEERING DEPARTMENT

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