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PRODUCTION OF THALLIUM-204 FROM THALLIUM OXIDE

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PRODUCTION OF THALLIUM-204
FROM THALLIUM OXIDE

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ABSTRACT

A sample of natural Tl_2O_3 was irradiated. The
specific activity and power density of the irradiation
product were in good agreement with the predicted
values. A specific power value of 0.00164 watt/curie
of ^{204}Tl was obtained from radiometric and calorimetric
measurements.

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INTRODUCTION

Thallium-204 is one of a small number of essentially pure beta emitters with half-lives sufficiently long to be attractive as heat sources for the generation of electrical power (others are ^{3}H, ^{147}Pm, and ^{171}Tm). Pure beta emitters require little shielding and thus are ideal sources for those applications where minimum weight is required.

^{204}Tl is produced by neutron irradiation of ^{203}Tl. If natural thallium is irradiated, the combination of a low thermal absorption cross section (11 barns) of ^{203}Tl and a low abundance of ^{203}Tl (29.5 atom %) theoretically restricts the maximum specific activity of ^{204}Tl that can be obtained under practical irradiation conditions to about 35 curies/gram of natural thallium. This specific activity corresponds to a power density of ~0.06 watt/gram, which is much lower than the 0.75 watt/gram of pure ^{204}Tl (Arnold[1] gives a value of 0.73 watt/gram). Higher specific activities could be achieved only by isotopically separating ^{203}Tl from ^{205}Tl prior to irradiation. Power densities of ~0.15 watt/gram could be obtained with isotopically pure ^{203}Tl.

A disadvantage of thallium metal as a source material is its low melting point (~300°C), which restricts the maximum temperature at which a ^{204}Tl-fueled heat source could operate. The use of thallium oxide (Tl_2O_3) with a melting point of ~750°C would increase the range of operating temperatures with little sacrifice in power density.

The Savannah River reactors are capable of producing large quantities, >100 kw(t) per year, of ^{204}Tl either in charges specifically designed for ^{204}Tl production or in charges in which ^{204}Tl is one of a number of product isotopes.

As part of a program to determine the feasibility of large-scale production of ^{204}Tl at Savannah River, a test sample of Tl_2O_3 was irradiated and analyzed after irradiation. The results of the test irradiation are described in this report.

SUMMARY

A measured specific power value for ^{204}Tl of 0.00164 watt/curie was obtained from radiometric and calorimetric measurements on irradiated Tl_2O_3. The measured value agrees well with a calculated value of 0.00162 watt/curie reported by Arnold.[1]

Specific activities of irradiated Tl_2O_3 closely approximate those calculated on the basis of known fluxes and exposures. Thus, a specific activity of about 35 curies/gram can be produced by the irradiation of natural thallium metal for one year at a thermal neutron flux of 10^{15} $n/(cm^2)(sec)$. The irradiation of natural Tl_2O_3 under the same conditions would produce a specific activity of 31 curies/gram.

DISCUSSION

BACKGROUND

^{204}Tl is produced by the absorption of neutrons in ^{203}Tl. The irradiation sequence is as follows:

$$^{203}\text{Tl} \xrightarrow[\sigma \ = \ 11 \ \text{barns}]{n, \gamma} \ ^{204}\text{Tl} \xrightarrow[t_{\frac{1}{2}} \ = \ 3.8 \ \text{yr}]{\beta^-} \ ^{204}\text{Pb}$$
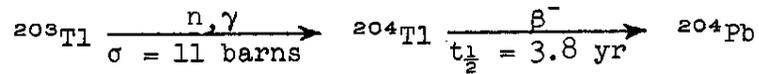
where σ is the absorption cross section of ^{203}Tl for thermal neutrons.

If natural thallium is irradiated, ^{206}Tl is also formed according to the following sequence:

$$^{205}\text{Tl} \xrightarrow[\sigma \ = \ 0.11 \ \text{barn}]{n, \gamma} \ ^{206}\text{Tl} \xrightarrow[t_{\frac{1}{2}} \ = \ 4.3 \ \text{min}]{\beta^-} \ ^{206}\text{Pb}$$
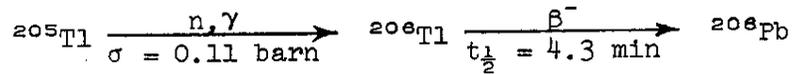
The production of ^{206}Tl is of no practical concern due to the very low cross section of ^{205}Tl and the rapid decay of ^{206}Tl.

An integrated rate equation for the production of ^{204}Tl can be written as follows:

$$N^{204} = \frac{\alpha}{\beta} N_o^{203} e^{-\alpha t} [e^{\beta t} - 1]$$

where $\alpha = \Phi\sigma_{203}$

$\beta = \Phi\sigma_{203} - \lambda_{204}$

and Φ = flux in neutrons/(cm^2)(sec)

σ_{203} = thermal neutron absorption cross section of ^{203}Tl, 10^{-24} cm^2

λ_{204} = radioactive decay constant of ^{204}Tl, sec^{-1}

N_o^{203} = number of atoms of ^{203}Tl per gram of starting material

N^{204} = number of atoms of ^{204}Tl at time t

The specific activity (curies/gram) can be written as follows:

$$A = K \frac{\alpha}{\beta} e^{-\alpha t} [e^{\beta t} - 1]$$

where A = the specific activity, Ci/g

K = 135.7 for natural thallium metal

121.3 for natural thallium oxide

463.3 for isotopically pure ^{203}Tl metal

414.3 for isotopically pure ^{203}Tl oxide

Assuming irradiation at a flux of 10^{15} n/(cm^2)(sec) for one year as an upper practical limit for the production of large quantities of ^{204}Tl, a maximum specific activity of ~35 Ci/g can be calculated for the irradiation of natural thallium metal. This activity corresponds to ~0.06 watt per gram of thallium metal or about 0.7 watt per cubic centimeter. Corresponding values for the natural oxide would be 31 Ci/g, ~0.05 w/g, and ~0.5 w/cc (assuming theoretical density of Tl_2O_3). Higher specific activities (by a factor of 2.5) could be produced if ^{203}Tl were isotopically separated before irradiation. Isotopic separation, however, would add to the cost of ^{204}Tl, and technology for the separation of large-scale quantities is not available.

RADIATION AND POWER CHARACTERISTICS OF ^{204}Tl

^{204}Tl decays in 98% of its disintegrations by beta emission (maximum energy = 0.764 Mev) to stable ^{204}Pb with a half-life of 3.8 years. In about 2% of its disintegrations, decay is by electron capture to ^{204}Hg with the emission of a Hg X-ray (0.071 Mev). Most of the shielding required for ^{204}Tl is necessitated by the presence of bremsstrahlung accompanying beta decay rather than by X-ray emission. Arnold[1] estimated the bremsstrahlung energy from ^{204}Tl as 8.0 x 10^{-3} Mev/disintegration, and the X-ray energy can be estimated ~1.4 x 10^{-3} Mev/disintegration.

Arnold[1] calculated the average beta energy of ^{204}Tl as 0.27 Mev and the specific power as 0.00162 w/Ci. Because pure ^{204}Tl has a specific activity of 461 Ci/g, the calculated power density of pure ^{204}Tl is 0.73 w/g.

STARTING MATERIAL AND SLUG PREPARATION

Tl_2O_3 of the highest available purity was obtained from Semi-
Elements Inc., Saxonburg, Pa., and was irradiated without further
treatment. The material as received was a brown-black powder.
For irradiation, the Tl_2O_3 powder was compacted by tamping into
an aluminum can (~0.94-inch diameter x 10 inches long) to a
density 30% of the Tl_2O_3 theoretical density (9.65 g/cc). Attempts
to melt the Tl_2O_3 and cast it into the aluminum can (to prepare a
high-density compact) failed because of excessive fuming of the
Tl_2O_3 near its melting point. Likewise, attempts at vibratory
compaction did not yield a compact of significantly higher density
than that obtained by tamping. However, no detailed study of
the compaction of Tl_2O_3 was made.

IRRADIATION OF Tl_2O_3

The Tl_2O_3 (251.2 g total) was irradiated to a total exposure
of 1.88 x 10^{21} nvt.

POSTIRRADIATION RECOVERY OF Tl_2O_3

The irradiated Tl_2O_3 was recovered by cutting off one end
of the slug and pouring out the powdered oxide. No change in
the color or consistency from the unirradiated oxide was observed.
About one half of the powder flowed out freely, while the remainder
stayed as a crust around the sides of the can. This crust was
removed by scraping with a special tool. About 95% of the total
Tl_2O_3 (251.2 g) was recovered. Since the Tl_2O_3 was compacted only
to about 30% of its theoretical density, it is difficult to
estimate the ease of recovery of an oxide compacted to a density
nearer theoretical. However, an alternative method of recovery
would be to dissolve the aluminum can in caustic, a process that
would minimize losses of Tl_2O_3 and allow essentially complete
recovery, since Tl_2O_3 is not appreciably soluble in caustic.

The ease of recovery of irradiated Tl_2O_3 powder suggests
the irradiation of Tl_2O_3 in large quantities in the form of powder
or low-density compacts. Preparation of targets would thus be
simplified. If circumstances demanded the irradiation of high-
density Tl_2O_3, studies of the compaction, or perhaps pelletization,
of Tl_2O_3 would have to be made. Pelletization should provide
reasonably high-density Tl_2O_3, but the end form might be restricted
to green (unsintered) pellets because of limitations on possible
sintering temperatures (because of the 750°C melting point of Tl_2O_3).

RADIOMETRIC ANALYSIS OF IRRADIATED Tl_2O_3

The specific activity of the irradiated Tl_2O_3 was measured radiometrically by counting the beta emission of two weighed samples in a 4π beta counter. The samples were dissolved in HNO_3 and mounted on foils for counting. Corrections for transmission of the beta particles through the foil were made according to the method of Pate and Yaffe.[2] Calibration of the counter was confirmed by counting the beta emission from a known ^{137}Cs source. The results, corrected to time of discharge, were 2.60 and 2.74 Ci/g or an average of 2.67 Ci/g. Uncertainties in counting were estimated at ±3% relative.

CALORIMETRIC ANALYSIS OF IRRADIATED Tl_2O_3

About three months after discharge, three calorimetric measurements were made on the total slug (251.2 g of Tl_2O_3) over a period of several days. An isothermal calorimeter, designed and built for the measurement of heat outputs of ^{238}Pu samples, was used for these measurements.[3]

Combining the counting and calorimetric data, a measured specific power of 0.00164 w/Ci (or its reciprocal, 610 Ci/watt) can be deduced. This measured value is in good agreement with a calculated value of 0.00162 w/Ci (616 Ci/w) reported by Arnold[1] and is believed to be the first measured value reported for Tl_2O_3. The corresponding power density is 0.75 w/g of thallium metal.

COMPARISON OF OBSERVED AND EXPECTED ACTIVITIES

The observed activity (2.67 Ci/g) was about 10% higher than the 2.46 Ci/g calculated from the exposure received. This is satisfactory correlation in light of possible uncertainties in the cross section and the use of an average flux value.

As expected from the small production cross section for ^{204}Tl, no serious flux depression problems exist in the irradiation of ^{203}Tl. From the observed results, it can be inferred that ^{204}Tl can be produced with activities closely approximating those calculated from known fluxes and irradiation times.

CONCLUSIONS

Large-scale quantities of ^{204}Tl at an activity level of ~35 Ci/g of natural thallium metal (0.06 w/g) could be produced at Savannah River at a flux of approximately 10^{15} n/(cm^2)(sec). Higher power densities can be achieved only if isotopically enriched ^{203}Tl becomes available.

The use of irradiated Tl_2O_3 instead of thallium metal as a heat source would raise the operating temperature but would require somewhat lower power densities due to stoichiometric and density differences between Tl_2O_3 and thallium metal.

BIBLIOGRAPHY

1. E. D. Arnold. <u>Handbook of Shielding Requirements and</u>
   <u>Radiation Characteristics of Isotopic Power Sources for</u>
   <u>Terrestrial, Marine, and Space Applications.</u> USAEC Report
   ORNL-3576, Oak Ridge National Lab., Tenn. (1964).

2. B. D. Pate and L. Yaffe. "Disintegration - Rate Determination
   by 4π-Counting. Part II. Source-Mount Absorption Correction."
   <u>Can. J. Chem</u>. <u>33</u>, 929-937 (1955).

3. J. H. Birden. <u>Operating Procedures for Calorimeters 93 and</u>
   <u>94</u>. Report MD-20092, Monsanto Research Corporation, Mound
   Laboratory, Miamisburg, Ohio (1964).