REFERENCE

OBSERVATIONS OF GAMMA EMISSIONS ASSOCIATED
WITH THORIUM REMOVAL FROM A U^{233} SAMPLE

by

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THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
U.S. ATOMIC ENERGY COMMISSION
CONTRACT AT (29-1) -1106

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CONTENTS

	Page
INTRODUCTION	1
CHEMISTRY PROCEDURES	2
INSTRUMENTATION.	3
RESULTS.	3
Uranium Oxide	3
Filter Cake Residue	4
Green Salt.	4
Sand and Slag	6
Metal Button.	7
CONCLUSIONS.	8
APPENDIX A -- Gamma Energy Spectra	A-11
APPENDIX B -- Theoretical Treatment of Age and Efficiency Effects.	B-13
APPENDIX C -- References	C-19

INTRODUCTION

When U^{233} is produced by neutron activation of natural thorium, a small amount of U^{232} is produced and is carried through the separation processes. The concentration of U^{232} varies from a few parts per million to about 100 ppm depending on reactor parameters. The samples used in this study contained 42 ppm of U^{232} .

U^{233} and daughters cause few radiation problems other than by their alpha emissions. U^{232} does, however, cause a significant gamma hazard due to the emissions of its daughters. Figure 1 shows the theoretical gamma dose rates from U^{233} containing 47 ppm $U^{232}(*).$

Figure 1. GAMMA DOSE RATE FOR 1 KG. U^{233} CONTAINING 47 PPM U^{232} VS. THICKNESS OF EMITTER (d) AND AGE OF U^{232}

These graphs are the result of previous theoretical calculations on an assumed 47 ppm U^{232} content. Content of material actually studied was 42 ppm U^{232} .

Figure 2 shows the decay scheme of U^{232} with the types of emissions, half lives, and most abundant gamma energies. From the decay scheme it is apparent that a significant reduction in gamma levels can be attained by removal of Th^{228} . This study was conducted to determine the optimum times, after the "thorium strike" and subsequent chemistry, for handling the materials.

Figure 2. DECAY SCHEME OF U^{232}

CHEMISTRY PROCEDURES

The chemistry consisted of making a metal button from 47 grams of U^{233} oxide. The oxide was approximately $2\frac{1}{2}$ years old, and contained 42 ppm of U^{232} . The oxide was dissolved in 400 ml of 30% nitric acid, and $1\frac{1}{2}$ grams of natural thorium nitrate and 20 ml of 48% HF solution were added. This solution was kept at boiling for a short period of time and then allowed to cool. After cooling the solution was filtered to remove as much thorium as possible. The filtrate was heated to boiling and the U^{233} was precipitated as a hydrated green salt ($UF_4 \cdot \frac{3}{2} H_2O$) by adding ascorbic acid to the hot fluoride solution. The green salt was collected on a filter and washed with water. It was then dried at $600^\circ C$ for 7 hours, producing UF_4 . The green salt was reduced to a U^{233} metal button (18.6 grams) by calcium-iodine bomb reduction. A temperature of approximately $1250^\circ C$ was reached in the reactor during the reduction.

INSTRUMENTATION

A Nuclear-Chicago Model 2586 was used to obtain direct gamma readings in mr/hr. A 512-channel isotopic analyzer with a 3- by 3-inch NaI detector was used for pulse-height analysis. All results from the analyzer were corrected for crystal and photopeak efficiency. The above instrumentation was used to count samples of U^{233} oxide, green salt and filter cake residue obtained during chemistry operations. The samples listed, plus the metal button and sand and slag residue were counted showing existing gamma radiation abundance by energy, and changes in activity during separation and production processes of U^{233} .

RESULTS

URANIUM OXIDE

Figure 3 shows the activity of the uranium oxide sample with time. There was no noticeable change in activity. The constant activity level was expected since the material was approximately $2\frac{1}{2}$ years old.

Figure 3. URANIUM OXIDE SAMPLE

FILTER CAKE RESIDUE

Figure 4 shows an initial rapid increase in the activity of the thorium precipitate sample. This curve follows closely a theoretical buildup from a pure thorium sample. It appears, therefore, that few of the thorium daughters are removed and they can therefore be expected to contribute significantly to the initial activity levels of the UF_4 .

Figure 4. FILTER CAKE SAMPLE
(THORIUM STRIKE RESIDUE)

GREEN SALT

Figures 5 and 6 show the effect of the thorium strike on the green salt sample. The initial decrease is due to the decay of the radium²²⁴ and its daughters which were carried along with the green salt. The minimum reading was reached at about 25 days, at which time buildup of thorium from U^{232} caused an increase in radiation levels. The rate of increase conforms closely to those predicted by Figure 1.

Figure 5. GREEN SALT SAMPLE (UF_4)

Figure 6. GREEN SALT SAMPLE

SAND AND SLAG

Figure 7 indicates that Ra^{224} is driven off during reduction to the uranium button and is trapped in the slag and sand. (Radium volatilizes at 1140°C .) The initial buildup is due to the establishment of equilibrium of the Ra^{224} with its daughters. The buildup of gamma activity is primarily controlled by the 10.6-hour half life of Pb^{212} . After equilibrium is attained, the decrease in activity is due to the decay of Ra^{224} (half life of 3.6 days). If a subsequent increase in activity occurs, as is noted at about the 35th day, it is due to any Th^{228} which is carried into the sand and slag.

Figure 7. SAND AND SLAG RESIDUE FROM BUTTON FIRING

METAL BUTTON

Figure 8 again indicates that Ra^{224} is being driven off during reduction to the button. The initial large decrease in activity is due to the rapid decrease (controlled by Pb^{212}) in activity from Tl^{208} . The eventual slow increase is due to Ra^{224} "growing in" from any Th^{228} still in the metal and from the production of Th^{228} from the U^{232} . The rate of increase is dependent on both of the above factors and consequently is related to the efficiency of the thorium strike.

Figure 8. METAL BUTTON

CONCLUSIONS

The curves give an insight into the effectiveness of thorium removal on gamma dose rates from U^{233} containing U^{232} impurities. They also demonstrate the advantage of working with the materials during particular time intervals after the thorium strike.

When using the curves it is important to keep in mind that the original uranium oxide sample was $2\frac{1}{2}$ years old when the thorium strike was performed. If the material of concern is considerably different from this in age, the curves will have a somewhat different shape. This difference is because of the great effect of age on the gamma dose rates.

The effect of the age of the initial uranium on the green salt and the metal button can be predicted from Figure 1 and the decay constants involved. The efficiency of the thorium strike also affects the shape of the curves. For the green salt, the time for minimum dose rate decreases, and the rate of rise (after the minimum) of the curve increases as the age of the initial material becomes less. As efficiency of the thorium strike decreases, the time for minimum dose rates also decreases. The rate of rise of the curve for the metal button (Figure 8) will also increase as age of the initial uranium decreases. This means that the importance of working the material quickly and at the optimum times becomes more important as age of the material decreases.

If the green salt is allowed to stand, it does not reach its minimum for about 25 days. If it is reduced to a button this minimum is reached in about 2 days due to the volatilization of the radium. If, however, the green salt can be loaded for firing without excessive exposure and provided that the volatilization temperature of radium is exceeded, there is no overall advantage (as far as metal fabrication is concerned) in waiting for the green salt minimum to be reached. The most favorable time for starting work with the metal button is between 36 and 48 hours after firing.

Since only thorium is removed in the filter cake, the gamma dose rates from it will rise rapidly during the first few days. There is, therefore, considerable advantage to packaging this for disposal immediately after the filtration is completed. It is important to remember that the dose rates will rise approximately 2 orders of magnitude during the first 2 weeks and the shipping container should be chosen accordingly. See Figure 4.

Since the sand and slag (from the button production) traps some of the radium driven off during button firing, it appears to be advantageous to wait 3 or 4 weeks before any extensive work is done on this material. If this delay is impractical, the work should be completed during the first 2 days after button firing. See Figure 7.

APPENDIX A

GAMMA ENERGY SPECTRA

Figures 9 through 12 contained in Appendix A illustrate the gamma radiation abundance by energy obtained from counting the various samples in the isotopic analyzer. The days shown on the figures are a selected few from many taken over a period of 2 months.

Figure 9. URANIUM OXIDE SAMPLE

Figure 10. FILTER CAKE SAMPLE (THORIUM STRIKE RESIDUE)

Figure 11. GREEN SALT SAMPLE

Figure 12. METAL BUTTON

APPENDIX B

THEORETICAL TREATMENT OF AGE AND EFFICIENCY EFFECTS

Since all of the uranium used for the experiment was approximately $2\frac{1}{2}$ years old, it is necessary to use theoretical considerations to determine the effect of materials of other ages. The effect of the efficiency of the thorium strike is also important and is interrelated with the age effect. To illustrate the effects of age and efficiency the curve for the green salt (Figure 5) will be used for comparison.

The curve of dose rate versus time can be considered a summation of three individual curves. These curves will be designated X, Y, and Z. See Figure 13.

Figure 13. DEVELOPMENT OF DOSE RATE VS TIME CURVES

Curve X represents the decay of the Ra^{224} and daughters which are not removed by the thorium strike. The rate of decay is initially governed by the Pb^{212} half life (10.6 hrs.) and eventually by the Ra^{224} half life (3.6 days).

Curve Y represents the increase in activity due to the Th^{228} which was not removed by the thorium strike. If 95% of the material is removed, the remaining 5% is assumed to continue to grow at the rate dictated by its initial age. The effect of this curve is closely related to both efficiency and the initial age of the material.

Curve Z represents the growth of Th^{228} and daughters from U^{232} . This curve assumes no Th^{228} is present after the thorium strike. This assumption is valid because curve Y accounts for thorium not removed by the strike.

The following symbols will be used:

- λ_1 = decay constant of Th^{228}
- λ_2 = decay constant of Ra^{224}
- A_1 = activity of Th^{228}
- A_2 = activity of Ra^{224}
- N = number of atoms of the isotope present
- t = time after thorium strike
- t_a = age of uranium sample
- t_s = age of uranium at time of thorium strike
- E = efficiency of thorium strike
- F = fraction of equilibrium attained

For a decaying sample the rate of decay can be expressed as

$$\frac{dN}{dt} = -\lambda N \quad (1)$$

If there is only one isotope of concern, the expression can be solved for N_1 :

$$N_1 = N_{01} e^{-\lambda_1 t} \quad (2)$$

where N_{01} is the number of atoms at $t = 0$. For a second daughter the

expression is:

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \quad (3)$$

or substituting equation 2

$$\frac{dN_2}{dt} = \lambda_1 N_{01} e^{-\lambda_1 t} - \lambda_2 N_2 \quad (4)$$

by integrating and letting $N_{02} = N_2$ at $t = 0$ gives

$$N_2 = \frac{\lambda_1 N_{01}}{\lambda_2 - \lambda_1} \left[e^{-\lambda_1 t} - e^{-\lambda_2 t} \right] + N_{02} e^{-\lambda_2 t} \quad (5)$$

These equations can be expressed in terms of activity by using $A = \lambda N$. The total activity (A) of the two daughters is:

$$A = A_1 + A_2 = A_{01} e^{-\lambda_1 t} + A_{01} \frac{\lambda_2}{\lambda_2 - \lambda_1} \left[e^{-\lambda_1 t} - e^{-\lambda_2 t} \right] + A_{02} e^{-\lambda_2 t} \quad (6)$$

If it is assumed that there are no daughters present initially (i.e. $N_{02} = 0$ at $t = 0$) the final term drops out.

Each of the individual curves can be expressed in terms of the fraction of Th^{228} equilibrium reached. The efficiency of the thorium strike and the initial equilibrium conditions are used to normalize the curves to each other. By considering only times greater than 2 days after the thorium strike, curve X can be simplified and expressed as:

$$F_x = E(1 - e^{-\lambda_1 t_s}) e^{-\lambda_2 t} \quad (7)$$

If the initial uranium is assumed to be at least 15 days old, curve Y reduced to

$$F_y = (1 - E) (1 - e^{-\lambda_1 t_a}) \quad (8)$$

For curve Z it is assumed that the initial material contains no Th^{228} or Ra^{224} at $t = 0$. It can therefore be expressed as

$$F_z = E(1 - e^{-\lambda_1 t}) \left[\frac{\lambda_2}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \right] \quad (9)$$

The total curve is expressed as

$$F = F_x + F_y + F_z \quad (10)$$

The above expression (Equation 10) can be used for the metal button by substituting the decay constant (λ) for Pb^{212} as λ_a in curve X (Equation 7). Using this substitution removes the restriction of considering only times greater than 2 days. It is also necessary to have E in Equation 7 represent the efficiency of the radium removal.

Figure 14 shows the effect of the age of the initial material on dose rate. The most noteworthy effect is the change in the time at which the minimum dose rate occurs. For material $2\frac{1}{2}$ years old the minimum occurs at about the 25th day after the thorium strike, while for 30 day old material the minimum is at 8 days. The material used for the experiment was somewhat over $2\frac{1}{2}$ years old.

Figure 14. EFFECT OF AGE ON DOSE RATES

Figure 15 shows the effect of the efficiency of the thorium removal. There is some slight decrease in the time at which the minimum occurs as efficiency decreases. The most prominent effect of efficiency is on the magnitude of the dose reduction.

Figure 15. EFFECT OF THORIUM STRIKE EFFICIENCY ON DOSE REDUCTION

APPENDIX C

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