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ORNL/TM-10394

EXTRACTION OF GADOLINIUM  
FROM HIGH FLUX ISOTOPE REACTOR  
CONTROL PLATES

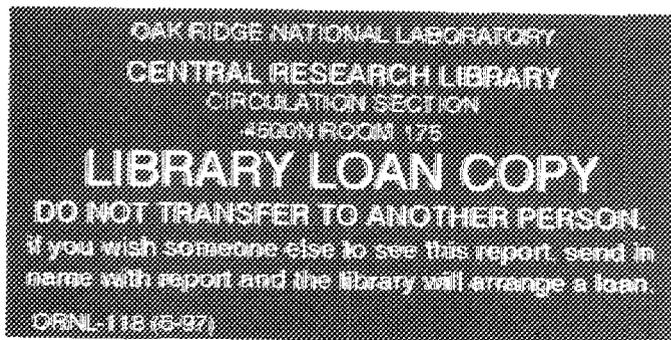
Operations Division

M. W. Kohring

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## ABSTRACT

Gadolinium-153 is an important radioisotope used in the diagnosis of various bone disorders. Recent medical and technological developments in the detection and cure of osteoporosis, a bone disease affecting an estimated 50 million people, have greatly increased the demand for this isotope.

The Oak Ridge National Laboratory (ORNL) has produced  $^{153}\text{Gd}$  since 1980 primarily through the irradiation of a natural europium-oxide powder followed by the chemical separation of the gadolinium fraction from the europium material. Due to the higher demand for  $^{153}\text{Gd}$ , an alternative production method to supplement this process has been investigated. This process involves the extraction of gadolinium from the europium-bearing region of highly radioactive, spent control plates used at the High Flux Isotope Reactor (HFIR) with a subsequent re-irradiation of the extracted material for the production of the  $^{153}\text{Gd}$ .

The ORIGEN2 computer code was used to predict the gadolinium and europium isotopic concentrations and compositions at various axial positions along one spent HFIR control plate. The calculational results, although based on rough estimates of the perturbed neutron flux intensities present at each local site, supported the decision to proceed with the experimental determination of the viability of the proposed supplemental  $^{153}\text{Gd}$  production scheme.

## INTRODUCTION

The High Flux Isotope Reactor (HFIR) is a 100-MW (thermal), light-water-cooled and -moderated, beryllium-reflected, flux-trap type research reactor operated by Martin Marietta Energy Systems, Inc., at the Oak Ridge National Laboratory (ORNL). The HFIR was designed and built in the 1960s primarily for the production of transuranic isotopes in a high thermal-neutron flux field on the order of  $3$  to  $5 \times 10^{15}$  neutrons/cm<sup>2</sup>-s, one of the highest in the world.

Thirty-eight vertical irradiation facilities are located in the 30-cm concentric ring of beryllium which surrounds the fuel region (Fig. 1). This arrangement was designed to accommodate various materials irradiation damage studies and lighter radioisotope production. Since the HFIR first achieved criticality in 1965, these facilities have been the site of over 5000 irradiations to produce isotopes for a variety of applications ranging from the preservation of food through gamma irradiation (cobalt-60) to the nondestructive testing of structural welds in submarines (iridium-192).

One of the most important radioisotopes produced in the HFIR is gadolinium-153 (<sup>153</sup>Gd), an extremely useful radionuclide for the diagnosis and monitoring of osteoporosis, a disease which affects the mineral content and structural integrity of the bones of an estimated 50 million people. The low energy decay characteristics (gamma doublet at 100 keV and x-ray doublet at 44 keV) and the 242-day half-life combine to make this isotope an ideal source for a medical imaging technique known as dual-photon absorptiometry or

commonly referred to as DPA. This bone-scanning method measures the difference between the emitted intensity of the source and the detected intensity after passing through the soft tissue and bone of the scan medium. The bone mineral content can be calculated from this difference and compared to normal values to determine the severity of the disease or to monitor the progress of the prescribed treatment. By using a radioisotope such as  $^{153}\text{Gd}$  with photon emissions at two different energy levels, the need for a constant soft tissue thickness (required for single-photon absorptiometry) across the scan path can be eliminated. This allows for the use of DPA in previously inaccessible areas such as the spine where bone loss first becomes apparent due to a greater rate of mineral turnover.<sup>1-5</sup>

ORNL first began producing  $^{153}\text{Gd}$  in HFIR in 1980, and until recently has been the world's sole supplier. The demand for  $^{153}\text{Gd}$  sources in 1985 necessitated a rapid step-up in its production at ORNL (Fig. 2).<sup>6</sup> Experts in the field of radiation medicine practices estimated that due to technological developments like DPA and improvements in the treatment of bone diseases, the demand for imaging services would increase to the point where the use of absorptiometry to diagnose and monitor osteoporosis could possibly exceed all other medical procedures combined.<sup>7</sup>

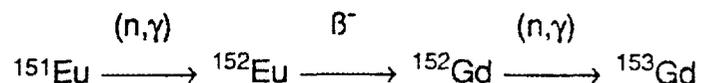
For eleven consecutive HFIR cycles from the summer of 1985 to the spring of 1986, every available vertical experiment facility (VXF) position was used for the irradiation of target capsules to produce  $^{153}\text{Gd}$ . To supplement this

## GADOLINIUM-153 PRODUCTION AT ORNL

Irradiation of Europium Targets

Gadolinium-153 is produced primarily by a neutron capture reaction in the stable isotope,  $^{152}\text{Gd}$ . Various methods of producing  $^{153}\text{Gd}$  have been investigated. One involves the neutron activation of natural gadolinium. However, due to the scarcity of  $^{152}\text{Gd}$  occurring in nature (0.2%) and the large absorption cross sections and higher abundance of the heavier gadolinium isotopes ( $^{154}\text{Gd}$  through  $^{158}\text{Gd}$  and  $^{160}\text{Gd}$ ), the resulting specific activity of  $^{153}\text{Gd}$  (curies of radionuclide per combined unit mass of all gadolinium isotopes) is too low to be useful for medical radiography. A higher specific activity is attainable if the gadolinium is enriched in the stable isotope  $^{152}\text{Gd}$ ; however, the cost of such enrichment raises the price per curie of  $^{153}\text{Gd}$  considerably. A third method, also very expensive, consists of the accelerator activation of europium-153 ( $^{153}\text{Eu}$ ) by a (p,n) reaction.<sup>8</sup>

The most successful production method for  $^{153}\text{Gd}$  at ORNL has been through the irradiation of  $^{151}\text{Eu}$  and the resultant reaction chain:



This process is accomplished through the irradiation of a natural-europium (0.48  $^{151}\text{Eu}$  and 0.52  $^{153}\text{Eu}$ ) oxide powder ( $\text{Eu}_2\text{O}_3$ ) in the HFIR VXF's followed by the chemical separation of the resultant gadolinium fraction from the

Europium-oxide powder is routinely loaded into a standard target rod designed specifically for isotope production in one of the HFIR VXF's. While the reactor is operating, the target materials are exposed to a neutron flux on the order of  $2 \times 10^{14}$  neutrons/cm<sup>2</sup>-s. Europium-151 undergoes a neutron capture to one of three isomers of <sup>152</sup>Eu -- <sup>152g</sup>Eu, <sup>152m1</sup>Eu, and <sup>152m2</sup>Eu. The relatively large capture cross section for the production of the ground state and first isomeric state (5900 barns and 3300 barns respectively) result in a rapid burnup of <sup>151</sup>Eu. The second isomeric state is characterized by a small production cross section (3.8 barns) and decays to the other metastable isomer, <sup>152m1</sup>Eu with a 96-min half-life. Its contribution can be neglected and both metastable isomers can be expressed together as <sup>152m</sup>Eu.

Both <sup>152g</sup>Eu and <sup>152m</sup>Eu are removed from the chain by (1)  $\beta^+$  decay to <sup>152</sup>Sm, (2)  $\beta^-$  decay to <sup>152</sup>Gd, and (3) an (n, $\gamma$ ) reaction to <sup>153</sup>Eu. Despite its extremely large absorption cross section (70000 barns), the contribution of <sup>152m</sup>Eu to the production of <sup>152</sup>Gd far exceeds that of <sup>152g</sup>Eu because of its much shorter decay half-life (9.3 h compared to 13.6 years) and the branching ratio which favors <sup>152</sup>Gd over <sup>152</sup>Sm.

As the activation time is lengthened, the specific activity of <sup>153</sup>Gd begins to decrease as the heavy gadolinium isotopes, primarily <sup>154</sup>Gd and <sup>156</sup>Gd, are produced. These stable isotopes are formed both through the decay of the heavy europium radionuclides resulting from neutron capture reactions on europium isotopes and the activation of <sup>153</sup>Gd (36000 barns) and <sup>155</sup>Gd

of the perturbed flux levels within the target capsules is hampered by the self-shielding and flux depression present within the targets. Without the knowledge of an accurate local neutron flux and the dependency on the HFIR cycle length for target exposures, the optimum irradiation length can only be determined through trial and error. Several configurations have been attempted and thus far, a one-cycle irradiation in one of the inner VXF positions has been concluded as the closest to optimum arrangement. Since  $^{153}\text{Gd}$  is sold by the curie, an attempt to maximize the quantity without adversely affecting the quality of the product has been achieved by loading the target capsules to capacity with  $\text{Eu}_2\text{O}_3$  powder. This tends to perturb the local flux within the capsules additionally, but does not significantly affect the product specific activity.

Two additional factors that contribute to the reduction of the specific activity are the ingrowth of the heavy gadoliniums and the decay of  $^{153}\text{Gd}$  during processing. The first of these factors is minimized by the relatively short (21-day) irradiation periods. Mass spectrographic analyses have shown that about 84% of the product gadolinium is  $^{152}\text{Gd}$  and only 14% is  $^{154}\text{Gd}$  and  $^{156}\text{Gd}$ . The second factor, however, can not always be avoided. Quite often the processing time (time from reactor shutdown or "push" time until product shipment) exceeds three to four weeks resulting in a 6 to 8% reduction in the specific activity of  $^{153}\text{Gd}$  due to decay.

### Alternate Production Scheme

Since the HFIR control plates have as a constituent the same  $\text{Eu}_2\text{O}_3$  powder as is irradiated for the europium target production process, an identical neutron activation and isotope decay scheme will effect the conversion of a large portion of the europium to gadolinium. The intention of the 1970's research was to locate and extract the portions of the control plates which contained a high concentration of  $^{152}\text{Gd}$ , separate out the gadolinium fraction, and re-irradiate the product gadolinium oxide powder using the HFIR hydraulic tube as an irradiation vehicle for the production of  $^{153}\text{Gd}$ . This process is attractive in that the chemical separation of the europium fraction occurs before the  $^{153}\text{Gd}$  production irradiation, thus reducing process and decay losses and, most significantly, a higher specific activity of  $^{153}\text{Gd}$  can be obtained since the concentration of heavy gadoliniums can be significantly reduced by selecting a portion of the plate with a low total exposure and thus, a high  $^{152}\text{Gd}$  isotopic assay.

The control plate research of the 1970s was abandoned at that time due primarily to the inability to chemically separate the gadolinium and europium fractions to a radiochemical purity level sufficient to obtain  $^{153}\text{Gd}$  specific activities above 30 Ci/g. In addition, reliable yields and specific activities could not be predetermined since the flux and cross section parameters vary greatly depending upon the region and total exposure of the plate analyzed.<sup>13</sup> A review of the data obtained in the 1970's analyses raised some doubt as to the

## HFIR CONTROL PLATES

### Description

The neutron-generation chain reaction of the HFIR is controlled by altering the effectiveness of the beryllium reflector. This is accomplished by moving the control elements in such a manner as to regulate the flow of thermal and epithermal neutrons from the fuel region to the reflector and back into the core. Figure 4 is a schematic view of the HFIR core region showing the relative positions of the fuel, the control components, and the beryllium reflector.

The control components are located in the annular region between the fuel assembly and the beryllium reflector. They consist of two 6.4-mm-thick concentric cylinders separated by a 3.3-mm coolant channel. The outer cylinder is divided into four shim-safety quadrants each having its own drive rod and scram mechanism. The inner cylinder, which is a single unit, serves as both a shim and regulating element. Since the inner cylinder is the equivalent of four outer control plates welded together, references to the term "control plates" will generally include the inner cylinders as well. To control the reactor reactivity, the absorber section of the control elements is driven out of the core. The outer control plates are driven upward to increase reactivity while the inner cylinder is driven downward for the same effect.

The control cylinders are divided into three longitudinal sections, each having different neutron absorption characteristics (Fig. 5).<sup>14</sup> The lower section

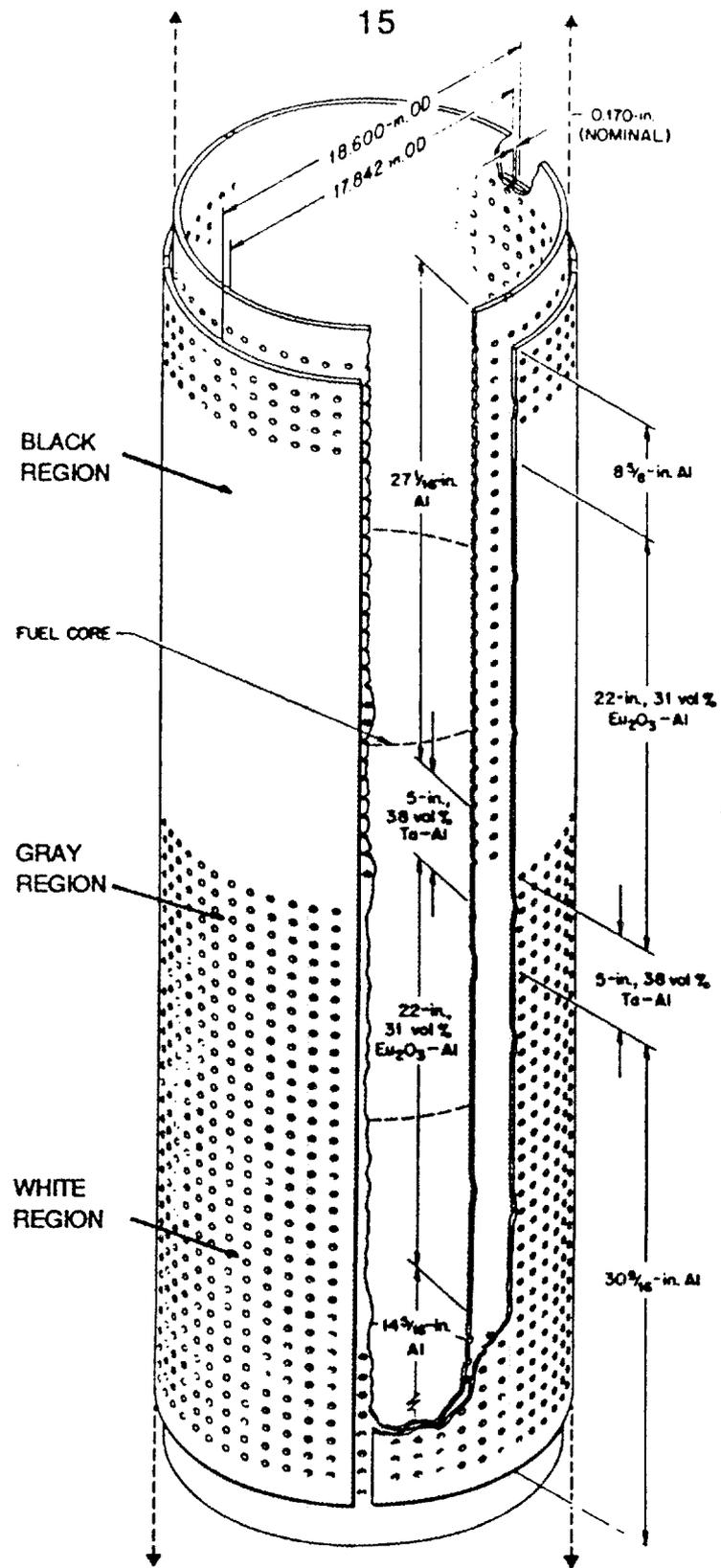


Fig. 5. Cutaway view of HFIR control components.

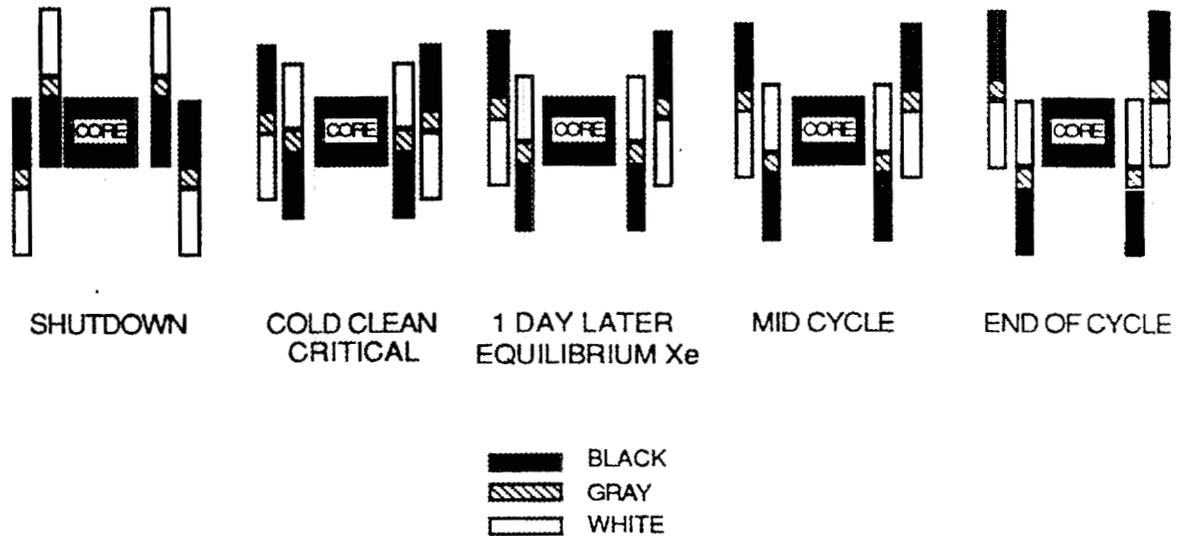


Fig. 6. HFIR control plate positions during a cycle.

66 cm. This wide range of motion has a considerable effect on the neutron exposure of the control plate. The axial thermal neutron flux distribution in the HFIR at the beginning of a fuel cycle is demonstrated in Fig.7. Similar plots have been made for fluxes of other spectral groups for both the beginning and end of cycle. These two-dimensional representations, based on computational analysis performed during the design of the HFIR<sup>15</sup> and validated with measurements made subsequent to initial reactor startup, convincingly display the effect of the strong absorbent, <sup>151</sup>Eu, on the neutron flux intensity at the control plate location. This variation in local neutron fluence in the control plate contributes to a large diversity in the concentration and composition of the gadolinium isotopes along the length of the europium-bearing region. It was initially conjectured in the early research that the highest concentrations could

be extracted from that portion of the control plate near the europium-tantalum ("black-gray") interface. However, due to the relatively higher fluxes near this interface, burnup of the lighter gadolinium isotopes and subsequent production of the heavier ones, resulting in a low  $^{152}\text{Gd}$  isotopic composition, would appear to argue against this supposition. The actual flux intensities within the control plates had not been determined at this time and without some knowledge of the europium exposure and burnup, the residency of the optimum gadolinium fraction could not be resolved.

## COMPUTATIONAL ANALYSIS

### Description of ORIGEN2

The ORIGEN2 (Oak Ridge Isotope Generation and Depletion)<sup>16</sup> computer code was used to calculate the optimum location of <sup>152</sup>Gd in a selected HFIR control plate whose usable lifetime had expired. This code, an updated version of the ORIGEN code written by the Chemical Technology Division at ORNL in the late 1960s and early 1970s, is used primarily to calculate the buildup and depletion of isotopes in nuclear materials. It accomplishes this through a matrix exponential method which solves a large system of coupled, linear, first-order ordinary differential equations of the form

$$\frac{dX_i}{dt} = \sum_{j=1}^N f_{ij}\lambda_j X_j + \phi \sum_{k=1}^N g_{ik}\sigma_k X_k - (\lambda_i + \phi\sigma_i) X_i, \quad i = 1, \dots, N \quad (1)$$

where

- $X_i$  = atom density of nuclide  $i$ ,
- $N$  = number of nuclides,
- $f_{ij}$  = fraction of radioactive disintegrations by other nuclides ( $j$ ) which lead to the formation of nuclide  $i$ ,
- $\lambda_j$  = radioactive decay constant of nuclide  $j$ ,
- $\phi$  = position- and energy-averaged neutron flux,
- $g_{ik}$  = fraction of neutron absorptions by other nuclides ( $k$ ) which lead to the formation of nuclide  $i$ ,
- $\sigma_k$  = spectrum-averaged neutron absorption cross section of nuclide  $k$ .

Table 1. Estimated neutron flux intensities at selected control plate locations

Control plate location	Thermal flux <sup>a</sup>		Epithermal flux <sup>a,b</sup>	
	BOC	EOC	BOC	EOC
Eu-Ta interface	7.5	1.0	25.0	1.5
100 mm from Eu-Ta interface	1.0	0.5	15.0	0.9
250 mm from Eu-Ta interface	0.5	0.3	10.0	0.6

<sup>a</sup>In units of  $10^{13}$  neutrons/cm<sup>2</sup>-s.

<sup>b</sup>Flux from 0.414 to 101 eV.

BOC - beginning of cycle.

EOC - end of cycle.

epithermal fluxes at three control plate locations at the beginning and end of the operating cycle. The europium-tantalum (Eu-Ta) interface is the line of demarcation between the "black" and "gray" regions of the control plate.

The large time-dependent variations and uncertainty in determining the local neutron flux intensities from these flux maps make it extremely difficult to model the control plates to obtain a time-dependent or cycle-integrated neutron flux at each location of the control plate with flux intensity as a variable. However, the accuracy necessary to determine the region of useful gadolinium does not require that the flux be "pinpointed" at each location. Thus, a range of values were used as input parameters to ORIGEN2. For each value chosen, ORIGEN2 results were obtained for the isotopic compositions and concentrations that would be present if the control plate had been exposed to the input "effective" neutron flux over its entire lifetime. This analysis requires

```

TIT   IRRADIATION OF CONTROL PLATE 7-1 FOR 92178 MW IN HFIR
CUT  -1
RDA   SPECIFY DATA BASES TO BE PRINTED
LIP   0 0 0
RDA   SPECIFY DECAY AND CROSS SECTION DATA TO BE SUBSTITUTED
LPU 641530 631540 -1
LPU 631521 641530 -1
RDA   READ DECAY AND CROSS SECTION DATA BASES
LIB 0 1 2 -3 204 205 -206 9 3 0 1 1
RDA   INPUT CASE BASIS FOR CALCULATION
BAS   1 GRAM NATURAL EUROPIUM OXIDE POWDER
INP  -1 1 -1 -1 1 1
MOV  -1 1 0 1.0
SUP
RDA   INPUT IRRAD/DECAY SCHEME AND EFFECTIVE FLUX - TIME IN DAYS
IRF  93.04 1.500E13 1 2 4 2
DEC  105.96          2 3 4 2
IRF  92.10 1.500E13 3 4 4 2
DEC  111.90          4 5 4 2
IRF  93.15 1.500E13 5 6 4 2
DEC  121.85          6 7 4 2
IRF  94.42 1.500E13 7 8 4 2
DEC  1454.58         8 9 4 2
IRF  91.69 1.500E13 9 10 4 2
DEC  177.31          10 11 4 2
IRF  67.01 1.500E13 11 12 4 2
DEC  787.99          12 1 4 2
IRF  91.19 1.500E13 1 2 4 2
DEC  1802.81         2 3 4 2
IRF  153.59 1.500E13 3 4 4 2
DEC  447.41          4 5 4 2
IRF  145.59 1.500E13 5 6 4 2  IRRAD TO END OF LIFE 10/2/84
DEC  378.0           6 7 4 2  DECAY TO GAMMA SCAN DATE 10/15/85
DEC  549.0           7 8 4 0  DECAY TO 1ST MASS SPEC ANALYSIS DATE 4/4/86
DEC  724.0           8 9 4 0  DECAY TO LAST MASS SPEC ANALYSIS DATE 9/26/86

SUP
RDA   PRINT CALCULATED RESULTS
OPTL 24*8
OPTA 24*8
OPTF.3.3*8 3 8 3 17*8
RDA   INPUT OUTPUT COLUMN HEADINGS
HED 6 10/2/84
HED 7 10/15/85
HED 8 4/4/86
HED 9 9/26/86
OUT 9 1 -1 0
END
3 631510 0.479 631530 0.521 0.0 0.0 1 GM NATURAL EU203 POWDER
0
/*
//GO.FT03F001 00 *
/** SUBSTITUTION DATA FOR DECAY CONSTANTS AND CROSS SECTIONS
3 641530 4 241.6 0 1.0 3*0.0
3 2*0.0 0.1524 0.0 3.000E-09 2.0E-04
3 631540 5 8.8 5*0.0
3 2*0.0 1.509 0.0 1.0E-10 2.0E-05
206 631521 12000 5*0.0 -1.0
206 641530 6000 5*0.0 -1.0
/*
//
ENDINPUT

```

Fig. 8. Typical input program to ORIGEN2 for control plate calculations.

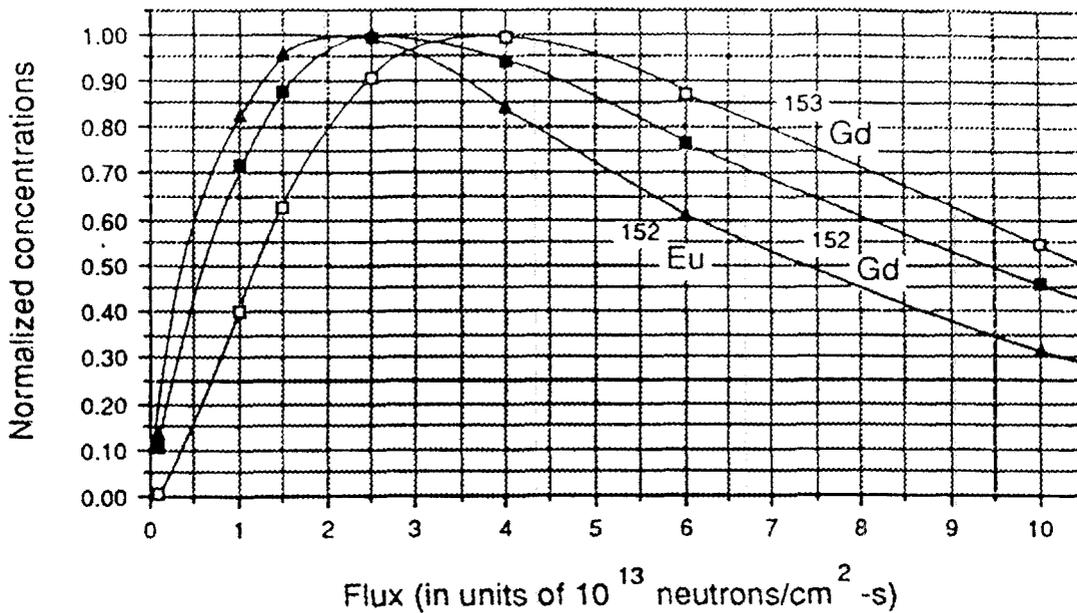


Fig. 9. Normalized concentrations vs effective neutron flux intensity.

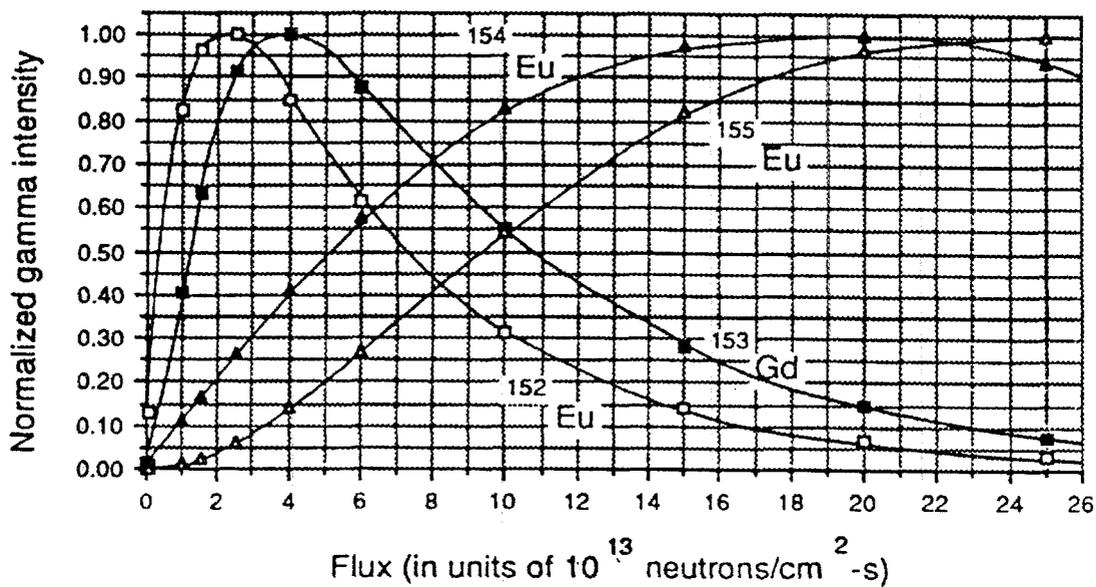


Fig. 10. Radioactivity vs effective neutron flux intensity.

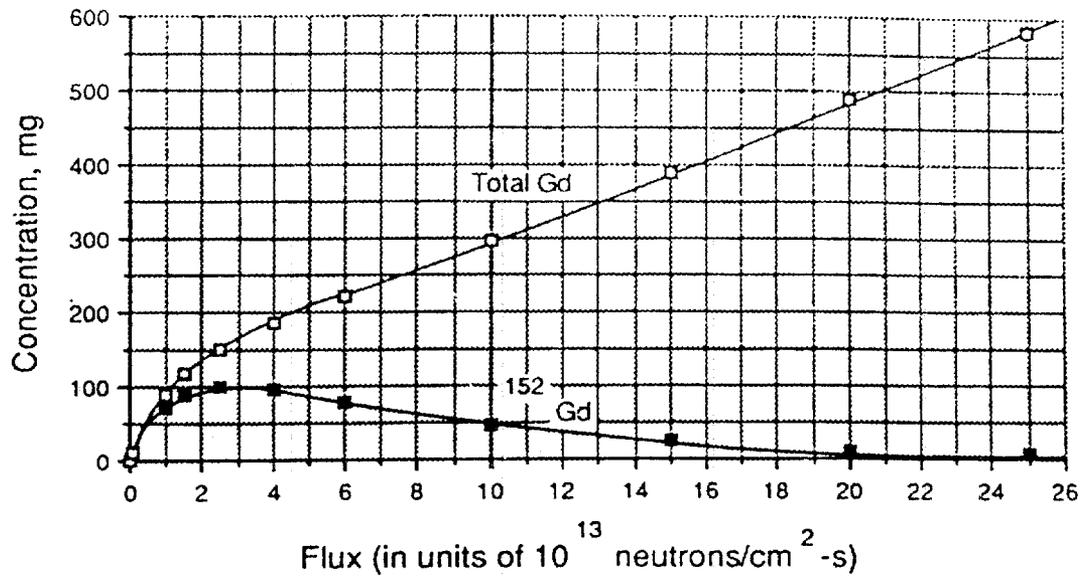


Fig. 12. Gadolinium concentration vs effective neutron flux intensity.

$2.7 \times 10^{13}$ , the point of maximum <sup>152</sup>Gd concentration. The "upper" bound would depend on the actual quantity of gadolinium found in those locations during the experimental analysis phase.

## EXPERIMENTAL ANALYSIS

### Overview

The experimental phase of this research was conducted using the same outer control plate chosen for the computational analysis. To facilitate management and transfer between the HFIR and the High Radiation Level Experiment Laboratory (HRLEL) where the initial assays were to be performed, one of the spent outer control plates was chosen for this investigative program over the more cumbersome inner cylinders. The control plate chosen had been retired from service on October 2, 1984, after accumulating 92,178 MWd. The black region was separated from the white region by an underwater tool that cuts through the material with a "nibbling" type action. The europium-bearing portion was then transferred to the HRLEL in a shipping cask where it was moved into one of the hot cells for further study.

The overall plan for the control plate research included five separate operations and assays:

1. an axial scan at the HRLEL to locate the regions of highest gamma activity for each of the four major contributing radioisotopes;
2. the dissection of the control plate into thin strips and small pieces for localized analysis;
3. the separation of the gadolinium and europium fractions;
4. the mass spectrographic analysis at various axial locations to establish the local isotopic compositions; and

Table 2. Measured gamma intensity in photons/s at selected control plate locations

Axial location (mm)	$^{153}\text{Gd}$ (97.4 keV)	$^{152}\text{Eu}$ (344.3 keV)	$^{154}\text{Eu}$ (1274.5 keV)	$^{155}\text{Eu}$ (86.6 keV)
-25	$0.70 \pm 0.12$	•	$31.4 \pm 0.11$	$1.0 \pm 0.12$
-12.5	$0.60 \pm 0.13$	$1.3 \pm 0.18$	$154.1 \pm 0.26$	$12.3 \pm 0.21$
25	•	$18.4 \pm 0.25$	$173.2 \pm 0.31$	$11.5 \pm 0.34$
50	$2.80 \pm 0.19$	$38.9 \pm 0.30$	$155.0 \pm 0.31$	$10.3 \pm 0.27$
75	$2.75 \pm 0.19$	$51.0 \pm 0.29$	$131.5 \pm 0.33$	$6.2 \pm 0.40$
100	$2.31 \pm 0.19$	$58.0 \pm 0.28$	$89.3 \pm 0.23$	$4.7 \pm 0.23$
125	$1.00 \pm 0.12$	$52.9 \pm 0.31$	$54.9 \pm 0.17$	$2.3 \pm 0.18$
150	$0.69 \pm 0.12$	$46.2 \pm 0.18$	$34.2 \pm 0.14$	$1.5 \pm 0.18$
250	*	$19.8 \pm 0.04$	$6.4 \pm 0.02$	$0.3 \pm 0.02$
325	•	$5.0 \pm 0.03$	$1.6 \pm 0.02$	$0.3 \pm 0.03$
ARE <sup>a</sup>	13.0	2.13	0.35	6.46

\*No data obtained.

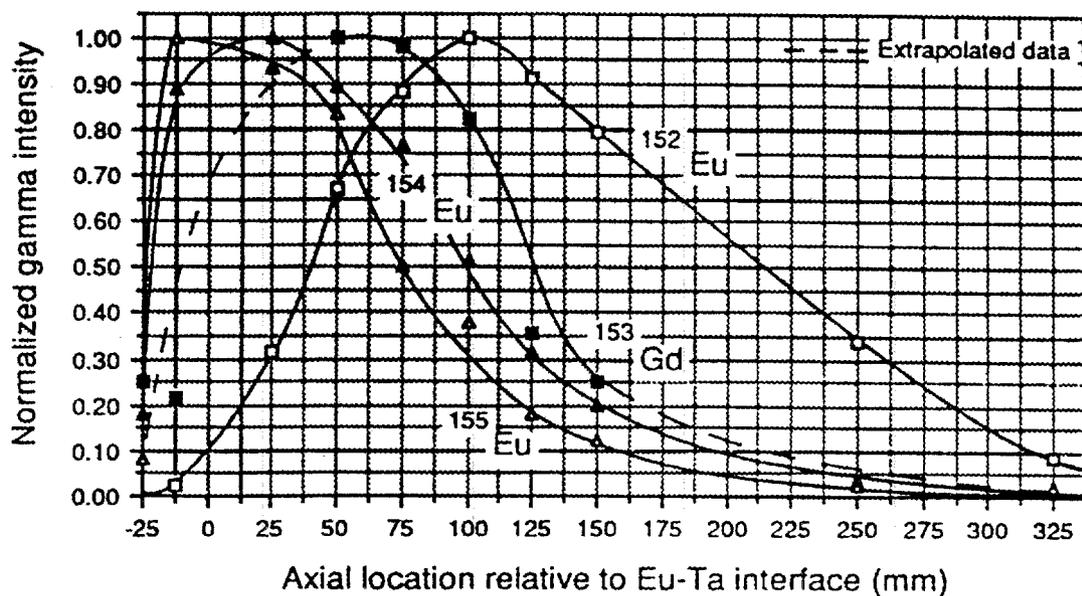
<sup>a</sup>Average relative error in percent.

Fig. 13. Measured radioactivity vs axial location.

increases. The gamma scan measurements mark the peak concentration of  $^{152}\text{Gd}$  between the 75- and 100-mm locations where the peak activities of its parent and activation product isotopes occur. However, the lower boundary for the purpose of the experimental assays was set at the 25-mm location to ensure that all possible residencies of gadolinium concentrations were investigated. The next step in the procedure was to dissect the control plate into smaller pieces so that localized analyses could be performed.

#### Dissection of Control Plate and Separation of Gadolinium Fraction

At the HRLEL, a tool similar to the underwater nibbling tool at the HFIR was used to divide the control plate into smaller segments. Ten "cuts" were made radially through the control plate. By the action of the "nibbler," each cut resulted in several small, approximately 6-mm cube, pieces, or "nibbles" of control plate. The first cut was made 25 mm from the inferred Eu-Ta interface based on the gamma intensities observed in the gamma scans. Additional cuts were made every 25 mm out to the 250-mm position. The nibbles from each cut were segregated into a small canister and labelled for further study. The resultant strips of control plate between each cut (approximately 19-mm wide) were marked and stored for possible future gadolinium extraction after the experimental analysis phase was completed.

Following the preparation of the localized samples, the plan called for the chemical separation of five nibbles from selected axial locations. The first set to be analyzed was taken from the 50-mm lot which corresponded to the

Table 3. Mass spectrographic analysis results for europium isotopes

Axial location (mm)	Percent of total europium				
	$^{151}\text{Eu}$	$^{152}\text{Eu}$	$^{153}\text{Eu}$	$^{154}\text{Eu}$	$^{155}\text{Eu}$
100	13.00±0.01	8.00±0.01	70.78±0.11	6.58±0.01	1.64±0.01
125	18.10±0.27	8.00±0.12	67.40±1.00	5.40±0.08	1.20±0.02
150	29.89±0.06	6.40±0.02	60.75±0.06	2.62±0.01	0.34±0.003
200	37.11±0.04	4.91±0.02	56.70±0.06	1.19±0.006	0.09±0.001
250	45.75±0.05	1.25±0.01	52.76±0.05	0.25±0.003	0.004±0.0002

Table 4. Mass spectrographic analysis results for gadolinium isotopes

Axial location (mm)	Percent of total gadolinium				
	$^{152}\text{Gd}$	$^{153}\text{Gd}$	$^{154}\text{Gd}$	$^{155}\text{Gd}$	$^{156}\text{Gd}$
50	7.44±0.04	0.044±0.01	25.85±0.08	1.34±0.01	63.18±0.13
100	37.20±0.07	0.151±0.01	33.62±0.07	2.00±0.01	26.68±0.05
125	43.80±0.44	0.147±0.01	33.40±0.33	2.00±0.02	20.40±0.20
150	60.79±0.12	0.150±0.01	29.76±0.06	1.55±0.005	7.68±0.02
200	71.60±0.36	0.130±0.01	24.40±0.12	0.98±0.005	2.81±0.01
250	74.50±1.49	0.060±0.03	24.60±0.49	0.49±0.02	0.26±0.01

In performing the mass spectrographic analyses, extreme care was taken to discriminate between the isobars of europium and gadolinium. The errors associated with each analysis are variable depending on the quantity of each isotope present in the sample analyzed and the corrections applied to each measurement.<sup>22</sup> At the 250-mm location, the expected concentration of europium relative to gadolinium is expected to be very high due to the low neutron exposure. Thus, the error associated with the europium analysis is on

## DETERMINATION OF OPTIMUM LOCATION

Quantitative Analysis

The remaining variable to be determined at this point in the analysis was the quantity of gadolinium available for use. To obtain this information, three sets of nibbles from the 150-, 200-, and 250-mm locations were transferred from the HRLEL for chemical separation. The intent of this phase of the program was to separate the gadolinium fraction, prepare an aliquot for a mass spectrographic analysis for comparative purposes, and load a portion of the extracted gadolinium oxide ( $Gd_2O_3$ ) powder into a small quartz capsule for irradiation in the HFIR hydraulic tube. The amount of  $Gd_2O_3$  recovered from each set of nibbles would determine the number of production capsules prepared. The optimum time period in the hydraulic tube could then be bracketed for the maximum specific activity yield of  $^{153}Gd$ .

Prior to the separation of the gadolinium fraction, a rough "material balance" was attempted on one gram of nibble from the three selected locations. A set of gamma scans was performed on an aliquot of dissolved, pre-weighed nibble. The data obtained included the measured activity per unit volume of solution which was converted to grams of nuclide per gram of control plate. The isotopic percents from the mass spectrographic analyses were applied to the quantities of radionuclide obtained from the gamma scans. This produced an estimate of the quantity of each gadolinium and europium

Table 5. Quantitative analysis at selected control plate locations

Axial location (mm)	Quantity of rare earths (g/g <sub>nibble</sub> )	Quantity of gadolinium (g/g <sub>nibble</sub> )	Percent of initial rare earth <sup>a</sup>	Quantity of Gd per cm strip (g/cm)
100	.357	.077	.849	5.43
150	.439	.041	1.043	2.89
200	.333	.033	.791	2.33

<sup>a</sup>Initial rare earth quantity - 0.421 g/g<sub>nibble</sub>

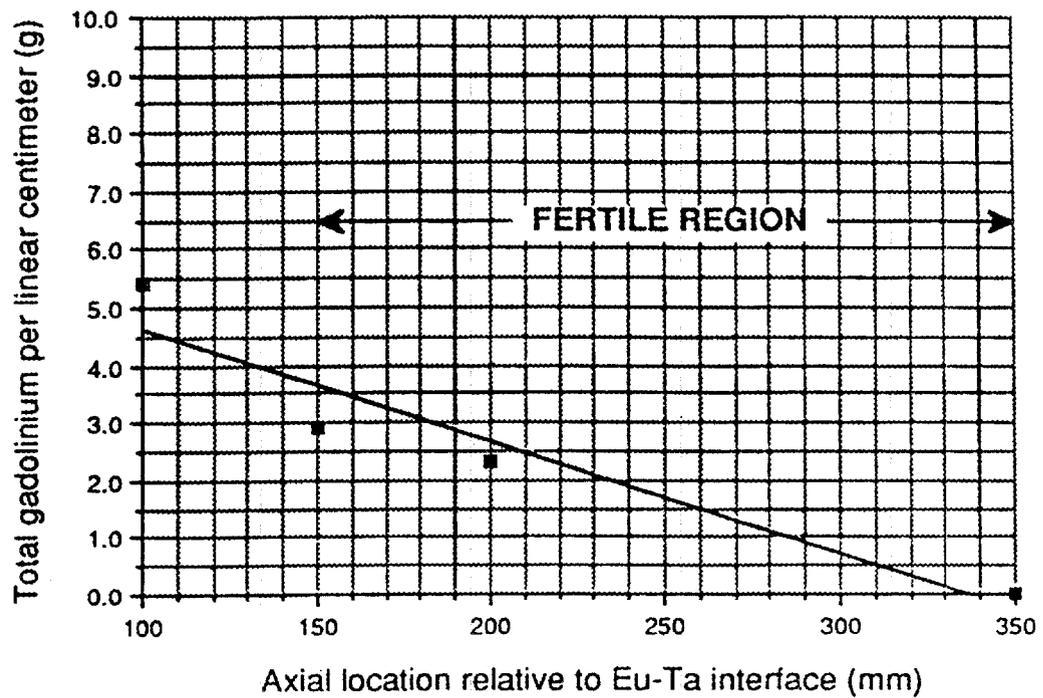


Fig. 15. Total gadolinium per linear centimeter of control plate.

for an extensive ventilation system overhaul in the fall of 1986 which forced the storage of the control plate nibbles and strips into an inaccessible shipping cask while the lengthy shutdown was in progress. Since no other facility existed to store and handle all of the highly radioactive nibbles, three sets which would provide the best information were selected for chemical separation and re-irradiation of the gadolinium fraction. The three data points obtained with regard to the total gadolinium extracted, the isotopic compositions, and the achievable specific activities for each enrichment would be extrapolated to supply information concerning the remainder of the control plate beyond the 250-mm location.

Due to an unanticipated overloading of the ion exchange column and some dissolution chemistry problems, the chemical separation process was only carried out to completion on one set (150-mm location) of nibbles. This was attributable to a miscalculation in the total quantity of rare earths contained in the nibbles which resulted in unknowingly loading the electroreduction cell and the HPIE column to more than their maximum allowable capacity. Normal chemical separation procedures require only a single pass through the electroreduction cell and HPIE column with a recovery efficiency >70%.<sup>26</sup> However, for this batch of material, four complete passes through the chemical separation process were required to achieve the required radiochemical purity. In addition, it was discovered that the rare earth fraction was contaminated with cesium-137 (<sup>137</sup>Cs) which had originated in the HRLEL hot cells. By the time this problem was detected, four gadolinium product runs had been cross

of time to investigate the nature of a possible brittle fracture of the reactor pressure vessel. No further analytical data could be obtained until the HRLEL overhaul was completed and the HFIR restarted. Thus, the gadolinium extraction research experimental phase was terminated.

#### Comparison of Experimental and Computational Results

The computational estimates that preceded the experimental phase of the gadolinium extraction program were compared to the analytical data by a "best fit" method of associating an effective neutron flux intensity with an axial location along the control plate. The ORIGEN2 outputs used for this comparison were the normalized activities of the four major contributing radioisotopes (Fig. 10), the gadolinium isotopic compositions (Fig. 11), and the europium isotopic compositions. These data were compared to the normalized activities from the axial gamma scans and the measured compositions of the mass spectrographic analyses respectively. The method used to find a correlation between estimated effective flux intensity and axial location was to assume that each set of analytical compositions for an individual isotope was correct and then to associate the control plate location for that percentage to an effective flux from the ORIGEN2 data that would yield the same percentage composition. This procedure was used for each radionuclide in the axial gamma scans and for the major gadolinium and europium isotopes that were present in the mass spectrographic analyses. The results are tabulated in Table 6.

The magnitudes of the peak isotopic compositions for  $^{153}\text{Gd}$  and  $^{154}\text{Gd}$  as calculated by ORIGEN2 (0.28% and 60% respectively) were nearly twice that assayed in the mass spectrographic analyses (see Table 4). Therefore, no correlation data could be obtained for these isotopes. Since these percentages as determined by ORIGEN2 were considered to be erroneous, the isotopic compositions of  $^{152}\text{Gd}$  and  $^{156}\text{Gd}$  were also questionable. Thus, the values listed in Table 6 for  $^{152}\text{Gd}$  and  $^{156}\text{Gd}$  were not used in deriving the "best fit" correlation curve of control plate location vs effective neutron flux intensity shown in Fig. 16.

This relationship was obtained as an approximation to the best average flux that exists at each axial location over the lifetime of the control plate. Total flux intensities (thermal and resonance) as listed in Table 1 for the beginning and ending of the HFIR cycle are plotted for comparison. The derived effective flux curve appears to underestimate the actual flux intensity beyond the 150-mm location; however, the flux information for this region of the control plate is highly uncertain.

Since each control plate has its own irradiation history, the total neutron exposure or fluence will vary from plate to plate. By inputting this irradiation history and the effective flux into the ORIGEN2 code, an estimate of the concentrations by flux, and thus, by axial location, can be acquired. To compare the results of the experimental data and the ORIGEN2 data for plate 7-1, computational analyses were conducted for three other spent HFIR control plates.

Table 7. Comparison of calculated gadolinium concentration in selected control plates

Control plate	Accumulated MWd	Lower boundary (mm)	Upper boundary (mm)	Gd concentration in fertile region (g)
7-1 <sup>a</sup>	92178	150	350	33.3
7-1 <sup>b</sup>				18.4
8-4	96533	155	355	16.5
6-3	69952	135	335	17.9
4-2	41622	105	305	14.8

<sup>a</sup>Mass balance calculations

<sup>b</sup>ORIGEN2 calculations

The derived relationships between the axial control plate locations and the effective neutron fluxes and exposures (fluence) are recognized as incomplete and open for significant improvement. However, for the purpose of estimating the location of usable gadolinium concentrations within a spent HFIR control component, this correlation can be used to supply adequate information. Comparison of the computational efforts thus far to the experimental results indicates that the current ORIGEN2 model for the HFIR control plates conservatively estimates the total gadolinium concentrations and overestimates the <sup>152</sup>Gd assays. It is hoped that future experimentation using the recovered material will assist in determining better gadolinium cross section information and allow some tailoring of the ORIGEN2 inputs to better simulate actual flux conditions.

## CONCLUSION

In summary, the research which investigated the feasibility of extracting enriched gadolinium from spent HFIR control plates was considered successful even though it could not be carried out to its desired completion. The confidence in the data obtained through the mass spectrographic analyses has inspired an investigation into the isotopic composition of the gadolinium powder that had been shelved as surplus from the europium target irradiation process. It was determined that over 85% of the gadolinium in the processed material awaiting shipment was  $^{152}\text{Gd}$ , considerably higher than that of the small amounts of control plate analyzed. Plans are currently being studied for the re-irradiation of these targets as well as the material recovered from the 150-mm location of control plate 7-1 in the HFIR hydraulic tube. It has been calculated that a short irradiation will not adversely increase the radiochemical composition of the europium radionuclides and that marketable specific activities of  $^{153}\text{Gd}$  can be produced from other depleted gadolinium sources without further chemical separation.

The confidence placed in the calculated quantities of gadolinium recoverable from the irradiated control plates and the lessons learned in the chemical separation process have encouraged researchers to continue with this program as soon as operations at ORNL permit. By applying the expected 70% recoverability of the gadolinium fraction in the "fertile" (>60% enriched) region of the control plate and a 40 Ci/g specific activity, a yield of up to 700

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## REFERENCES

1. H. W. Wahner, W. L. Dunn, and B. L. Riggs, "Noninvasive Bone Mineral Measurements," *Seminars in Nuclear Medicine*, Vol. XIII, No. 3, 282-9, (July, 1983).
2. P. L. Kimmel, "Radiologic Methods to Evaluate Bone Mineral Content," *Annals of Internal Medicine*, 1984, **100**, 908-11.
3. R. B. Mazess, "Absorptiometric Measurements in Bone Disease," proceedings of the Workshop on Noninvasive Techniques for Assessing Bone Mass, Am. Soc. Bone and Mineral Research held at Washington D.C. on June 15, 1985.
4. L. Nilas et al., "Comparison of Single- and Dual-photon Absorptiometry in Postmenopausal Bone Mineral Loss," *J Nucl Med.*, **26**, 1257-62, (November, 1985).
5. P. Tothill, M. A. Smith, and D. Sutton, "Dual photon absorptiometry of the spine with a low activity source of gadolinium 153," *The British Journal of Radiology*, **56**, 829-35, (November, 1983).
6. T. L. Dahl, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., personal communications to M. W. Kohring, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., August 8, 1986 and December 18, 1986.
7. E. F. Kuntz, "Demand for absorptiometry to expand dramatically -- experts," *Modern Healthcare*, 94-5, (October 11, 1985).
8. A. Jurewicz, "Application of nuclear reactions in activation of europium to preparation of gadolinium-153," *Nucleonika*, Vol. 19, **11**, 1016-25, (1974).
9. S. F. Mughabghab, M. Divadeenam, and N. E. Holden, *Neutron Cross Sections*, Academic Press, New York, 1981.
10. D. C. Kocher, *Radioactive Decay Data Tables*, DOE/TIC-11026, U. S. DOE, Technical Information Center, 1981.
11. T. C. Quinby, D. W. Ramey, and M. Petek, *The Application of Electroreduction of Europium in the Production of Gadolinium-153*, ORNL/TM-10284, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., January 1987.

23. G. A. Bowden, G. R. Hicks, and R. W. Knight, *Fabrication Procedures for HFIR Control Plates*, ORNL/TM-9365, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., October 1984.

24. Ref. 7.

25. W. R. McKissick, Abercrombie Radiological Consultants, Inc., Knoxville, Tenn., personal communication to M. W. Kohring, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., Oak Ridge, Tenn., October, 1986.

26. Ref. 11.

27. D. W. Ramey et al., "Gadolinium Production and Development," pp. 29-31 in *Isotopes Section Progress Report, July - September 1986*, ORNL/CF-86/357, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., December 1, 1987.

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