A Preliminary Experiment on Radial Distribution of Cs-137, Sr-89-90 and Zr-95 in Sintered Uranium Dioxide Pellet

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This paper reports on the determination of the radial distribution of fission products (Cs, Sr and Zr) in neutron irradiated UO$_2$ pellets. The first part gives the results obtained by gradual dissolution of a pellet. In the second part the fission products distribution has been determined by micro-sampling along the cross-sectional surface of a UO$_2$ pellet.

I. INTRODUCTION

The migration of fission products in UO$_2$ during irradiation has significant practical implications in connection with burn-up determination, fuel swelling and reactivity in a reactor. The extent and the nature of fission product migration has been studied in recent years by several groups at Hanford, Bettis, Vallecitos and Chalk River. The Hanford workers$^{(1)}$ have developed special equipment for micro-sampling highly irradiated fuel and have carried out many experiments on UO$_2$, UO$_2$-PuO$_2$ and U alloys. They have reported that the concentration of $^{95}$Zr, $^{103}$Ru, $^{137}$Cs, $^{144}$Ce and Pu relative to U is a function of radius in a cylindrical UO$_2$ pellet$^{(2)}$. The experiments at Vallecitos$^{(3)}$ have also indicated a large concentration of $^{137}$Cs in the region near the surface of UO$_2$ pellets irradiated under severe conditions. Similar results for $^{137}$Cs migration have been obtained at Chalk River$^{(4)}$. The Bettis$^{(5)}$ laboratory, where differential dissolution of grains taken from irradiated sintered UO$_2$ plates have been undertaken, has reported the accumulation of $^{137}$Cs, $^{89-90}$Sr, $^{95}$Zr and $^{155}$Eu near the grain boundaries.

The present report describes the results of preliminary measurements of the radial distribution of $^{137}$Cs, $^{89-90}$Sr and $^{95}$Zr in irradiated UO$_2$ pellets.

A slightly irradiated pellet (ca. 10$^{17}$ fiss./cm$^3$) was dissolved with nitric acid successively in six fractions. $^{137}$Cs, $^{89-90}$Sr and $^{95}$Zr were separated from the resulting solutions, and the specific activities of these isotopes and of the gross $\beta$-emitters and $\gamma$-emitters were determined in terms of counts per minute per milligram of dissolved U.

Two UO$_2$ pellets having a burn-up of 1,400 MWD/T and 4,300 MWD/T respectively were used in a drilling experiment. Several UO$_2$ samples were taken from fixed positions along one cross-sectional surface of these pellets by a simple equipment of our own design. After dissolving these samples in nitric acid, $^{117}$Cs, $^{89-90}$Sr and $^{95}$Zr in each solution were determined by radiochemical analysis. Determination of U was carried out partly by gravimetric method and partly by polarography.

II. DISSOLUTION EXPERIMENT

1. Experimental

In the dissolution experiment, natural UO$_2$ pellets of 10 mm diameter and 10 mm length were slightly irradiated. Five pellets were sealed in an Al capsule filled with He gas and the capsule further was contained in a Scalay type capsule. The capsule was irradiated for 24 hr in the pool side facility of the HFR, where the thermal neutron flux is about 10$^{13}$ n/cm$^2$-sec. The average $\int T_d K_d T$ is estimated to be about 4.0 W/cm and the maximum temperature at the center of a pellet was well below 50°C. After 2 months cooling, the capsule was opened for the experiments.

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described below. No significant change in the external appearance of the pellets was observed.

A pellet placed in a Pt cage was dipped in a 50 ml beaker filled with 20 ml of 3 - 6 M nitric acid containing 1 ppm each of Cs, Sr and Zr as carriers. The cage was kept at the center of the nitric acid solution in order to avoid heterogeneous dissolution of the pellet. After leaching the pellet for several minutes, the cage was removed from the solution. This procedure was repeated with new nitric acid solution until the pellet was entirely dissolved. The volumes of the resulting six batches were measured and the solutions were analyzed for $^{137}$Cs, $^{89-90}$Sr and $^{95}$Zr as described below.

For the $^{137}$Cs and $^{89-90}$Sr analysis, interfering activities were eliminated with an anion exchange resin (Amberlite IRA-400)\(^6\). Cs and Sr were eluted with water from the resin column, while the other active elements were absorbed on the resin. These two elements were finally separated as cesium perchlorate and strontium oxalate respectively. $^{95}$Zr was purified first by coprecipitating most other activities with lanthanum fluoride, followed by the precipitate as barium fluozirconate\(^7\). After redissolution of the precipitate and an intermediate zirconium hydroxide precipitate, the Zr was finally collected as mandelate. The concentration of U was determined by the usual method of oxinate precipitation.

2. Discussion of Results

The compositions of the six fractions are given in Table 1. For $^{137}$Cs the specific activity is expressed in $\mu$C/mg U; for $^{89-90}$Sr and for $^{95}$Zr the concentration is expressed in counts/min/mg U. If one assumes the pellet to be of a single and uniform phase causing no preferential dissolution, the diameter at the end of each dissolution step can be estimated from calculation. From Fig. 1 it can be seen that in the peripheral zone the fission products (including gross-$\beta$ and $\gamma$) would appear to be prominently concentrated in the layers near the surface. In the inner part of the pellet, however, they are quite uniformly distributed. This apparent fission product concentration toward pellet center might be attributed to three possible factors. One is the non-uniform flux distribution across the fuel pellet. An estimation of the flux ratio between surface and center of the pellet can be made by the formula\(^8\)

$$\phi_0 = AI_0(Kr),$$

Table 1 Specific Activities of Isotopes from Successive Layers in the Dissolution Experiment

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$^{137}$Cs (A/mg U)</th>
<th>$^{89-90}$Sr (A/mg U)</th>
<th>$^{95}$Zr (A/mg U)</th>
<th>Gross $\beta$ (A/mg U)</th>
<th>Gross $\gamma$ (A/mg U)</th>
<th>U (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.20</td>
<td>3.99</td>
<td>7.98</td>
<td>2.23</td>
<td>4.85</td>
<td>50.5</td>
</tr>
<tr>
<td>2</td>
<td>1.87</td>
<td>3.68</td>
<td>7.57</td>
<td>2.28</td>
<td>4.00</td>
<td>284.0</td>
</tr>
<tr>
<td>3</td>
<td>1.55</td>
<td>3.20</td>
<td>6.27</td>
<td>2.29</td>
<td>4.10</td>
<td>1,470.0</td>
</tr>
<tr>
<td>4</td>
<td>1.65</td>
<td>2.65</td>
<td>6.20</td>
<td>2.22</td>
<td>3.88</td>
<td>1,123.0</td>
</tr>
<tr>
<td>5</td>
<td>1.65</td>
<td>2.58</td>
<td>6.10</td>
<td>2.29</td>
<td>4.05</td>
<td>1,482.0</td>
</tr>
<tr>
<td>6</td>
<td>1.68</td>
<td>2.48</td>
<td>6.70</td>
<td>2.22</td>
<td>4.10</td>
<td>1,572.0</td>
</tr>
</tbody>
</table>

Remark: A expressed in counts per minute.

Fig. 1 Distribution of Fission Products in the Dissolution Experiment

* Referred to a $^{137}$Cs standard by the IAEA, Vienna.
where $K$ is obtained from

$$\frac{K}{(\Sigma_a + \Sigma_s)} = \tan h(K/S_d).$$

Here $K$ is the solution of a transcendental equation.

$\phi_0$: Thermal neutron flux

$A$: Arbitrary constant

$I_0$: Modified Bessel function of the first kind

$\Sigma_a$: Total absorption cross-section

$\Sigma_s$: Total scattering cross-section

$r$: Radius of the pellet

This estimation leads to a ratio of 1.02 in our case. Since this is not sufficient to account for the actual deviations, the reason must be attributed to either fission product migration or to selective dissolution of fission products. Since even a small amount of leaching from the outer layer would introduce a relatively large increase in the specific concentration of fission products in the first dissolved fraction, it is most likely that this observed pattern can be attributed to the dissolution procedure. The rise of specific activity towards the sample periphery is higher for $^{137}$Cs, than for the other elements; this might be caused by difference in leachability. The relatively constant level of the specific activity over the rest of the pellet suggests the absence of fission product migration under these irradiation conditions, and supports the above argument.

### III. Drilling Experiment

1. Experimental

The specimens used for this experiment were provided by the metallurgical group of the "Reactor Centrum Nederland". The specifications are presented in Table 2. After cutting the fuel capsules, a specimen of a few millimeters thickness was mounted in a perspex tube with a cold setting epoxy resin, as shown in Photo. 1. The specimen was ground with wet SiC paper and was polished with 2% chromic acid solution containing $\gamma$-almina. Finally, it was cleaned in ultrasonically water and in ethyl alcohol.

Etching was performed by dipping the specimen in a mixture of sulfuric acid and then in 30% hydrogen peroxide solution (1:4) for 1.5 min.

A drilling technique was applied for remote micro-sampling. For taking a large number of micro-samples from the surface of a small pellet, a precise $x$-$y$-$z$ positioner, as developed at Hanford, would be required. As it is however rather expensive and needs a long delivery time, a simple apparatus, as shown in Photo. 1, was designed. This equipment consists of three parts: a holder for the mounted specimen, a drill with weight and a positioner for the drill.

The specimen is placed into the holder; the positioner then fixed over the specimen by a pin; then the drill with weight is inserted into the positioner. All of the operations, including drilling is done by tong manipulators in a $7''$ Pb cell.

The drilling location is measured from a photograph taken after sampling. A large
enough sample for analysis is obtained by
this procedure under suitable operating con-
tions (a weight of 500~700 g and a drilling speed
of 100~200 r.p.m. for 10 min). Photo.2 is a photo-
graph of a specimen after drilling.

Photo.2 Micro-drilled Holes (pellet diameter
12.5 mm) 4,300 MWD/T

Difficulties in collecting the drilled powder
from the surface were encountered. An
attempt to gather the powdered sample on
Scotch cellulose tape or on the top of a wet
sintered glass rod was unsuccessful; and a
sampler method of sampling was found more
practical: After drilling, the positioner, drill
and weight were removed from the equip-
ment and a small bottle was placed over the
specimen; the equipment was then turned
upside down to let the powder drop into the
bottle; it was further transferred to another
bottle for dissolution in the glove box. The
sample obtained was dissolved in 1ml of 6N
nitric acid containing 1 ppm of nonactive Cs,
Sr and Zr as carriers. After evaporation of
the solution on a sand bath, the sample was
redissolved in 0.8 ml of 6N nitric acid to
bring the acid concentration to a well estab-
lished value for the subsequent polarographic
determination of U. Finally, the solution was
diluted with water to 10 ml.

U was determined by cathode-ray polaro-
graphy. Half a milliliter of the sample solu-
tion was put in a micro polarographic cell
and 50 mg of potassium chloride were added.
After deaerating with pure N₂ gas for 10 min,
the applied potential was swept from 0 to
-0.5 V with respect to the Hg pool electrode.
In this electrolyte solution, (0.5 molar in nitric
acid and 0.5 molar in potassium chloride), the
reduction peak of U appears at a potential of
0.30 V with respect to the Hg pool. The U
content of the solution was determined by
comparing the peak height with a calibration
line prepared by using a standardized U
solution. Provided that the concentration of
nitric acid in the electrolyte solution is con-
stant, the method of adding a standardized U
solution is applicable. In this analysis, the
mean probable error is less than 10% and the
limiting lower concentration is 5×10⁻⁵ molar.

The other fission products were determin-
ed in the same manner.

2. Discussion of Results

The data obtained from chemical analysis
of specimens Nos. 1 and 2 are shown in
Tables 3(a),(b). From these data and the
location of the samples, as measured after
sampling, the relation between the distance
from the center and the specific activities of
the fission products is obtained as shown in
Fig. 2(a),(b). It should be noted, however,
that the seven sample positions in drilling
No.1 are not situated on a diametric line as
in the case of the second drilling. In both ex-
periments, considerable differences from one
sample position to an other are observed in
the concentrations relative to U for ¹³⁷Cs,
⁸⁹⁻⁹⁰Sr and ⁹²Zr; yet these isotopes have
nearly the same distribution pattern. At the
center of the pellet, the concentration is low
and it seems to reach a maximum at a
distance of several millimeters from the center.
The data reveal a symmetric distri-
bution of the fission products in the pellet.
The areas of maximum and minimum con-
centration appear to be associated with the
characteristics of the UO₂ micro-structure,
which can however change during irradiation.
Photographs of the pellets used for these
experiments do not reveal any central void,
nor grain growth, even at the center of
specimen No. 2. This would indicate that no
change of UO₂ structure had occurred. Thus
Table 3 Specific Activities of Isotopes from Specimens

(a) Pellet No. 1

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mm from center (A/mg U.10^6)</th>
<th>^137Cs (A/mg U.10^6)</th>
<th>^89-90Sr (A/mg U.10^6)</th>
<th>^90Zr (A/mg U.10^6)</th>
<th>Gross (A/mg U.10^6)</th>
<th>Gross (A/mg U.10^6)</th>
<th>U (mg)</th>
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<td>5.95</td>
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<td>0.393</td>
</tr>
<tr>
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(b) Pellet No. 2

<table>
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<th>Sample No.</th>
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<th>^89-90Sr (A/mg U.10^6)</th>
<th>^90Zr (A/mg U.10^6)</th>
<th>Gross (A/mg U.10^6)</th>
<th>Gross (A/mg U.10^6)</th>
<th>U (mg)</th>
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<td>0.463</td>
<td></td>
</tr>
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</table>

Remark: A expressed in counts per minute.

Fig. 2 Distribution of Fission Products in the Drilling Experiment

the concentration of fission products observed in specimens Nos. 1 and 2 must be due to diffusion of the isotopes.

IV. CONCLUSIONS

The radial distribution of ^137Cs, ^89-90Sr and
$^{95}$Zr in the slightly irradiated UO₂ pellet seem to be determined solely by thermal neutron flux. In the moderately irradiated pellet (with a high operating central temperature and a burn-up of 4,300 MWD/T), these isotopes are concentrated in a region 1~2 mm from the center. All these isotopes have about the same distribution pattern. From these results one can conclude that it is difficult to use any of these isotopes as a burn-up indicator for fuels irradiated at high temperatures.

**Acknowledgement**

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--- References ---

(7) **USAEC**: NAS-NS 3011, (1960).