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POST-IRRADIATION EXAMINATION OF THORIA-URANIA FUEL RODS

— Quarterly Progress Report No. 3 —

December 1967 - February 1968

RESEARCH & DEVELOPMENT
DIVISION

NUCLEAR DEVELOPMENT
CENTER

Lynchburg, Virginia

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Springfield, Virginia 22151
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THORIA-URANIA FUEL RODS**

— Quarterly Progress Report No. 3 —

December 1967 - February 1968

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AEC Contract No. AT(30-1)-3809

B&W Contract No. 59-3103

Prepared for
THE UNITED STATES ATOMIC ENERGY COMMISSION

by
THE BABCOCK & WILCOX COMPANY
Nuclear Development Center

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CONTENTS

	Page
1. INTRODUCTION	1
2. SUMMARY	2
3. ISOTOPIC ANALYSIS OF THORIA-URANIA FUEL	3
3.1. Dissolution Studies	3
4. METALLURGICAL ANALYSIS	6
4.1. Visual Examination	6
4.2. Gamma Scanning	6
4.3. Fission Gas Release	7

List of Tables

Table

1. Status of Hot Cell Examination of $\text{ThO}_2\text{-UO}_2$ Fuel Rods . . .	8
2. Results of Fission Gas Puncture	9

1. INTRODUCTION

The objectives of this program are to perform isotopic and metallogical analyses on thorium-uranium fuel, stainless steel cladding, and a Zircaloy fuel can taken from Core A of the Consolidated Edison Indian Point Reactor Number 1. The isotopic content of the several actinide and fission product elements in the fuel will be determined. Metallographic examinations will be made on the fuel and cladding. Specimens of the stainless steel cladding and Zircaloy can will be tensile tested under several conditions.

This report, the third in a series of quarterly progress reports on this program, covers the period from December 1, 1967 through February 28, 1968. The previous reports issued are as follows:

BAW-3809-1 Progress Report No. 1, March - August 1967

BAW-3809-2 Progress Report No. 2, September - November 1967

2. SUMMARY

The dissolution of thorium-uranium fuel was studied, and it was shown that 13 M nitric acid-0.05 M fluoride under reflux was effective for both irradiated and unirradiated material.

Nondestructive examination of the fuel rods showed that they were in excellent condition, and in some cases pellets were intact and free to move within the rods. Eight of the 13 rods have been sectioned, and chemical and metallurgical examinations are in progress.

3. ISOTOPIC ANALYSIS OF THORIA-URANIA FUEL

3.1. Dissolution Studies

Complete dissolution of the selected thoria and thoria-urania fuel specimens is essential to the success of this investigation. Because refractory oxides of this type frequently resist the usual acid dissolution techniques, it was first necessary to determine whether satisfactory dissolution could be obtained.

In two recent studies, the effects of many variables on the rate of thoria dissolution were surveyed.^{1, 2} The results of both indicate that 13 M nitric - 0.05 M hydrofluoric acid approaches the optimum dissolution rate. However, these reports and others on the same subject disagree on how the dissolution rate is affected by (1) the burnup level of irradiated thoria fuel and (2) the presence of other cations which form strong fluoride complexes. Since there were not enough data to allow the behavior of unirradiated thoria to be extrapolated to that of irradiated thoria at varying burnup levels, a two-part approach to the dissolution problem was taken. First, the adequacy of the selected solvent was demonstrated with unirradiated thoria and thoria-urania fuels. Next, a more drastic alternate technique was devised to dissolve any irradiated fuel specimens that might prove to be much less reactive.

3.1.1. Dissolution of Unirradiated Thoria-Urania Fuels

The dissolution of unirradiated thoria-3% urania pellets was evaluated with 13 M HNO₃-0.05 M HF under reflux conditions. Complete dissolution of 1.5-gram specimens was obtained in 6 to 8 hours using 50 ml of acid. Pure thoria pellet specimens required more time but were usually completely dissolved within 12 hours. A small amount of flocculent white residue was observed after these dissolutions. Because this precipitate seemed to increase rather than diminish when boric acid was added (to complex the residual fluoride), it was tentatively

identified as silica etched from the glass flask. The residue from one thorium-uranium solution was filtered, weighed, and counted. The 25 mg of residue contained less than $10^{-3}\%$ of the total solution activity; this result tends to verify that it was silica rather than undissolved fuel. (In later work, where dissolution times were about one hour, little or no residue was observed.)

The second dissolution technique involves a variation of the sealed-tube technique of Metz and Waterbury.³ Refractory oxides are dissolved at an increased temperature made possible by a completely sealed system. Our modification of this technique replaces the one-piece sealed tube with a two-piece Pyrex dissolving vessel sealed with a Teflon O-ring. The glass parts are commercially available O-ring joints that have been sealed to the appropriate size; an outer stainless steel vessel contains water to provide a compensating external pressure. The water vapor pressure, registered on a pressure gage, may be converted to the internal temperature. In practice, a pressure of 50 to 60 psi, corresponding to about 150 C, is maintained.

When the high-temperature dissolver was evaluated with unirradiated thorium and thorium-uranium fuels, it was found that it required two or three times as long as the reflux system required for complete dissolution. The poor performance was attributed to the lack of mixing in this non-boiling system. The addition of a magnetic stirring bar, which was operated during heating by an external magnetic stirrer, remedied the problem, and complete dissolution was then obtained within one hour.

Subsequent to the dissolution of irradiated fuel specimens reported in section 3.1.2, studies were initiated using a lower fluoride concentration. Reduction of the fluoride concentration to 0.025 M did not appreciably increase the dissolution times, but it did prevent any formation of silica.

3.1.2. Dissolution of Irradiated Thorium-Uranium Fuel

The results of the studies described in section 3.1.1 indicated that successful dissolution might be obtained in a reasonable time by using 13 M HNO_3 -0.05 M HF under reflux. The first sample, weighing approximately 3 grams, was still in the cladding; it was completely

dissolved in 8 to 12 hours. The exact time of dissolution could not be determined because of the deep coloration that resulted from dissolution of the cladding. Subsequent samples, each weighing approximately 0.8 gram, were declad. Considerable fragmentation of the fuel occurred in the decladding operation. Four of the declad samples have been dissolved in 13 M HNO_3 -0.05 M HF , and in all four cases complete dissolution was obtained in less than one hour.

4. METALLURGICAL ANALYSIS

During this report period the visual examination, gamma scanning, and puncturing for fission gases were completed, and 8 of the 13 fuel rods were sectioned. The current status of the overall examination of the fuel rods is summarized in Table 1.

The design was completed for the equipment for elevated-temperature testing of the irradiated cladding, and procurement and assembly of the equipment was initiated.

4.1. Visual Examination

The visual examination indicated that all 13 fuel rods were in excellent condition. The rods were coated with a dark gray oxide film, and there were no signs of deterioration of the cladding or the ferrules. However, this examination did reveal that the cladding on 9 of the fuel rods had been penetrated when the rods were removed from the elements; thus, only 4 of the 13 fuel rods were available for fission gas analyses.

4.2. Gamma Scanning

After the rods were examined visually, they were gamma scanned through a collimating slit. The radiation passed through a section 17 inches long with a cross section of 0.017×0.5 inch, then through a section 25 inches long with a cross section of 0.25×0.5 inch, before impinging on a 2×2 -inch sodium iodide detector. Figure 1 shows a typical gross gamma profile. The positions of end caps, ferrules, and spacers are easily located, and in many cases the pellet interfaces are obvious.

It was noticed during gamma scanning that fuel pellets had moved into the void volume provided for the accumulation of fission gases. This shifting resulted in some separation of pellets. Inverting the rods after this first gamma scan and repeating the scanning showed that the

pellets had moved again. This vertical movement of the fuel pellets seems to indicate that there was little swelling and/or cracking of the pellets during irradiation. We will attempt to confirm this hypothesis during the destructive examination. The gamma scanning also showed that a pellet of higher enrichment than specified had been inadvertently inserted into two of the rods.

Gamma energy spectra were recorded at points of interest selected from the gross gamma profiles. Cobalt-60, ^{137}Cs , ^{134}Cs , and ^{144}Ce - ^{144}Pr were clearly identified, but other shorter-lived nuclides, such as ^{95}Zr , ^{233}Pa , ^{106}Ru , and ^{58}Co , had decayed below detectable limits during the 27 months since core discharge. The presence of ^{54}Mn could not be definitely established because of interference by ^{134}Cs .

The relative amounts of the nuclides at different positions is completely consistent with the expected behavior. The ratio of ^{60}Co to ^{137}Cs increases where end caps, ferrules, spacers, and fuel voids are located, but this ratio is relatively constant elsewhere. The ratio of ^{134}Cs to ^{137}Cs is highest where the neutron flux is greatest.

4.3. Fission Gas Release

Fuel rods 105 D, 105 D₁, 105 E, and 105 F were punctured, and the fission gases were collected and submitted for analyses. The amount of gas collected from each rod is shown in Table 2. Interpretation of the gas-release data will be completed after the compositions of the gases are determined and the fuel burnup analyses are accomplished.

Table 1. Status of Hot Cell Examination of ThO₂-UO₂ Fuel Rods

Pin No.	Th/U ratio	Peak bundle burnup, GWD/T	Visual	Gamma scan	Diameter	Profilometer	Gas puncture	Gas analyses	Sectioning	Metallography	Micro-hardness	Tensile test	Burnup	Isotopic analyses	Specimens for OSU - BMI
20 A	33	38	x	x					*			*	*		
61 A	33	42	x	x	*	*			*	*	*	*	*	*	
62 A	33	31	x	x					x			*	*		
66 A	33	36	x	x					*			*	*		
105 A	33	33	x	x					x	*	*	*	*	*	
105 B	23	33	x	x					x	*	*	*	*		*
105 C	17	33	x	x	*	*			x	*	*	*	*		*
105 D	12	33	x	x	*	*	x	x	*	*	*	*	*	*	
105 D ₁	12	33	x	x			x	x	x	*	*	*	*		*
105 E	10	33	x	x			x	x	*	*	*	*	*		*
105 F ^(a)	∞ & 33	33	x	x			x	x	x	*	*	*	*		*
106 A	33	18	x	x	*	*			x	*	*			*	*
106 B	23	18	x	x					x	*	*				*

^(a)One third of rod contains pure ThO₂, and the remainder contains ThO₂-UO₂ with a Th/U ratio of 33.

Code

x Completed.
 * In progress or planned.
 Blank Not planned.

Table 2. Results of Fission Gas Puncture

<u>Fuel pin No.</u>	<u>Volume of gases collected at STP, cc</u>	<u>Calculated pressure, ^(a) mm Hg</u>
105 D	7.75	1987
105 D ₁	9.45	2357
105 E	9.24	2336
105 F	5.46	1385

(a) Based on calculated void volume of 3.0 cc per rod.

Chart
Inches

Chart
Inches

Figure 1. Gross Gamma Profile
of Rod 62 A

Figure 1. (Continued)

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