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BURNABLE POISON DEPOSITION
ON
ZIRCONIUM HYDRIDE FUEL —
PROCESS DEVELOPMENT AND EVALUATION

AEC Research and Development Report

Atomics International Division
Rockwell International

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R. VAN HOUTEN

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ABSTRACT

This report reviews the development and evaluation of a process for depositing thin rare earth oxide burnable poison films on fuel rods. The burnable poison films are formed by controlled-rate, electron-beam-heated, high-vacuum evaporation of the oxides from water-cooled crucibles. Coating uniformity (mg poison/cm²) and reproducibility are good (to $\pm 5\%$), and rapid, accurate nondestructive x-ray fluorescence analytical procedures permit up to 100% inspection (all surface areas of all coated fuel rods). The report reviews poison placement screening criteria, recommended coating and measuring equipment performance, and swelling and aging test results. All test results for Gd₂O₃, Er₂O₃, and Y₂O₃ coatings are promising. Vapor-deposited coatings containing Eu₂O₃ and/or Sm₂O₃ are not recommended, because of rapid transfer of Eu and Sm to the SCB hydrogen barrier; but preliminary tests on the incorporation of up to 9 wt % Eu in an SCB-type sleeve showed good Eu retention through 1510 hr at 1430°F, and good SCB stability. Tests extended to 18,584 hr at 1300°F, to 10,000 hr at 1400°F, and to 5000 hr at 1500°F.

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I. INTRODUCTION

The use of a burnable poison in the reactor core permits a significant increase in allowable fuel life of a reflector-controlled reactor. Gadolinium oxide is a preferred burnable poison for SNAP-type reflector-controlled reactors, and the use of nominal 1μ Gd_2O_3 films on the fuel rod surfaces is a preferred placement.

This report will review the selection, development, fabrication, and evaluation factors for the current rod-coating process for these gadolinium-base burnable poison films, and for similar erbium- and yttrium-base films. Europium and samarium oxide coatings will also be discussed.

The basic characteristics of SNAP-type reactor fuel elements (1972-1973) fall within the following envelope (nominal):

- 1) Diameter — 0.5 to 1 in.
- 2) Length — 16 to 20 in.
- 3) Cladding — finned 25-mil Hastelloy X
- 4) Fuel Loading — 10.5 wt % U^{235} , in zirconium hydride
- 5) Fuel Rod Segment Lengths — 3 to 4 in.
- 6) Fuel Operating Temperature — 1300°F , max.

The distribution of the poison within the core is determined, in part, by the required rates for initial neutron absorption and subsequent burnout of the poison. Table 1 shows the reasons why the poison should be placed either on the surface of the fuel rod or in (on) a foil surrounding the fuel rod, and why other poison locations are unacceptable.

The poison of choice is natural gadolinium or one of the gadolinium isotopes, because they burn out at about the right rate to compensate for loss of reactivity by fuel burnup, fission fragment production, hydrogen loss, cross-section changes due to transmutation, etc.

Where large amounts of gadolinium are required, another poison must be added to compensate for the positive temperature coefficient or reactivity contribution of the gadolinium. The two poisons which have appropriate resonance

TABLE 1
POISON LOCATION COMPARISON*

	Location							
	Vapor Deposition	In Foil	On Foil	In Fins	Between Segments	In Fuel [†]	In SCB	Combi- nations
	Evaluation Parameter							
	A	B	C	D	E	F	G	H
Poison Inventory in Core	2	2	2	5	5	1	2	2
Process Complexity	2	2	2	4	3	2	2	5
Quality Assurance and Inspection	1	2	1	4	2	5	5	5
Scrap and Losses	2	1	2	3	2	5	4	3
Development	1	1	1	4	2	4	4	3
Nuclear Penalty	1	3	2	3	4	1	1	1
Thermal-hydraulic Penalty	1	1	1	2	3	1	1	1
Potential for Poison Motion	2	1	2	2	1	1	1	2
Flexibility	1	2	1	3	4	4	2	3
Total	13	15	14	30	26	24	22	25

*Qualitative ranking, with 1 = good, 5 = bad

[†]Eu₂O₃ is incompatible with the fuel

absorption characteristics to compensate for the gadolinium cross-section behavior are erbium and europium, as shown in Figure 1. Erbium has a better resonance absorption curve, and better physical properties for this application, than europium or its compounds. Europium and samarium neutron absorption characteristics were of sufficient interest that they were included in several of the early test matrices, but physical properties of these two elements and their compounds were markedly less satisfactory than those of gadolinium and erbium.

Gadolinium and erbium are characterized by Gschneider⁽¹⁾ as typical heavy rare earths. Their sesquioxides are very refractory, with very high melting points (see Table 2), and are among the most thermodynamically stable known, with free energies of formation of -434 kcal/g-mole and -453.6 kcal/g-mole, respectively. These are used, sometimes together with yttrium sesquioxide diluent, as the burnable additives of choice. Yttrium and its sesquioxide are structural homologs of erbium and gadolinium and of their sesquioxides, respectively. The free energy of formation of yttrium sesquioxide is -455.4 kcal/g-mole. Crystal structures of these sesquioxides are summarized in Table 3.

Based on the current reactor designs, fuel rod surface concentrations of gadolinium of 5 to 10×10^{-4} gm Gd/cm² are required (e. g., for \$4 to \$8 control worth). These concentrations correspond roughly to 0.5- to 1 μ -thick films of gadolinium oxide, or volume concentrations of 2 to 4% in a 1 mil foil.

Films of nominal 1 μ thickness are easily deposited in controlled quantities by electron-beam-heated, high-vacuum, thin-film coaters. Coating thickness and composition are predictably uniform; accurate methods of controlling deposition rates and measuring surface concentrations are either readily available or can be developed easily.

Mechanical problems associated with the use of foil-wrapped fuel rods are assuring uniformity of foil thickness, insertion of the foil-wrapped fuel rod segments into the element, assurance of foil nonwrinkling during operation, etc. These mechanical problems are amenable to solution, but the use of vapor-deposited coatings on the fuel simplifies the heat transfer analyses and general

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Figure 1. Burnable Poison Neutron Capture Cross Section

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TABLE 2
PHYSICAL PROPERTIES OF Er_2O_3 , Gd_2O_3 , AND Y_2O_3

	Melting Point (°C)	Boiling Point (°C)	Coefficient of Expansion
Er_2O_3	2400	3000	-
Gd_2O_3	2340 ± 10	-	$10 \times 10^{-6} / ^\circ\text{C} (30-840^\circ\text{C})$
Y_2O_3	2415	4300	$9.3 \times 10^{-6} / ^\circ\text{C} (20-1000^\circ\text{C})$

TABLE 3
CRYSTAL STRUCTURES OF Er_2O_3 , Gd_2O_3 AND $\text{Y}_2\text{O}_3^{(1)}$

<u>'C' Form - Cubic</u>			<u>Transformation Temperatures</u>		
	<u>$\rho(\text{gm/cm}^3)$</u>	<u>$a(\text{\AA})$</u>			
Er_2O_3	8.65	10.548 ± 2	-		
Gd_2O_3	7.608	10.817 ± 4	Stable (Landelli) Stable to 1350°C (Curtis & Tharp) $\longrightarrow \beta$ Stable to 1025°C (Shafer & Roy) $\longrightarrow \beta$		
Y_2O_3	5.03	10.603 ± 2	Stable to 1800°C		
<u>'B' Form - Monoclinic</u>					
	<u>ρ</u>	<u>$a(\text{\AA})$</u>	<u>$b(\text{\AA})$</u>	<u>$c(\text{\AA})$</u>	<u>$\beta(^{\circ})$</u>
Gd_2O_3	8.33	14.061 ± 13	3.566 ± 6	8.760 ± 7	100.10 ± 8

fuel element fabrication and evaluation as well. Also, the loss of fuel fraction, and the additional parasitic neutron absorption, are major items against the use of foil.

This report will stress the current process, but will review the evaluation of the process for applying burnable poison coatings, from the preliminary screening of coating equipment and burnable poison compositions, through the development of coating and analytical techniques. Included will be the background on fabrication of a total of 27 test fuel elements, test data through 18,584 hr, post-test evaluation, and the summary conclusions that the recommended materials and process should be suitable for at least 40,000 hr at scheduled operating conditions.

II. THE COATING PROCESS

The rare earth oxide thin-film coating process, as detailed in the February 1973 process specification, incorporates the evaporation of rare earth oxides, and their condensation onto rotating clean reactor fuel substrates (nominal 200°C) at rates of 10 to 30 Å/sec. The fuel rod specimens are rotated during coating, to keep coating thickness and composition and morphology as uniform as possible.

Evaporation (deposition) rates and chamber vacuum (no higher than 10⁻⁴ torr) are carefully controlled within the prescribed ranges.

The immediately preceding process description is broad enough to apply to all test fuel rod specimens coated with burnable poisons since early 1968. The numerous specific differences between the earlier and present processes are of course related to changes in equipment, but largely reflect the present significantly better understanding of the coating process.

The current process places special emphasis on the following facets: (1) the use of only the most thermodynamically stable and refractory heavy rare earth type oxides, (2) rigid fuel surface preparation procedures, (3) careful control of specimen surface temperature during coating deposition, (4) careful control of coating deposition rates, and (5) use of planetary-type specimen holder fixtures, to assure maximum coating uniformity for all specimens in a given coating run.

Items 2, 3, and 4 are directed toward assuring maximum adherence of the coating both during and after processing, and throughout the operating lifetime of the reactor. Items 3 and 4 are directed toward reducing deposit stress, particularly during the fuel rod coating and the fuel element fabrication and acceptance testing steps. All tests to date indicate that any coating recrystallization and/or stress relaxation of these thermodynamically stable oxides is substantially complete by the end of the 1300°F acceptance test, and that subsequent high-temperature aging further improves the adhesion of these coatings. The selected substrate temperature is necessarily a compromise. Higher substrate temperatures during coating would normally eliminate the coating

recrystallization which now occurs during the leak checking cycle, but would mean significantly greater hydrogen loss to the vacuum, which is undesirable.

Collectively, the current process yields a good, adherent, satisfactorily abrasion resistant, qualitatively and quantitatively measurable, burnable poison coating, the properties of which either improve, or at least have not been found to deteriorate, with age and elevated temperature. Further, the coating is quantitatively strippable in minutes (with 6 N HNO₃) without a measurable damage to the substrate, so that short lead-time changes in poison loadings for different missions can be accommodated readily, and at comparatively low cost.

III. DEPOSITION EQUIPMENT

The basic coater is built up primarily from modules originally developed for the thin-film integrated-circuit industry. These consist of:

- 1) A rectangular stainless steel vacuum chamber, 24 by 24 by 36 in. high, with large front access door
- 2) A high-capacity (2400 l/sec) vacuum system (10^{-4} to 10^{-7} torr normal working range), with liquid nitrogen cold trap
- 3) Four large-hearth capacity (30 cm^3), single or multi-hearth, 180 or 270° bent beam, electron beam guns for evaporating the rare earth oxides (or other materials, as required), with full ability to vary electron beam sweep across the hearth in both X and Y directions
- 4) Sufficient 10,000-v power supplies to operate all four of the electron beam gun evaporators simultaneously (total power, 12 kw min.), with complete overload and short circuit (operator safety) protection.
- 5) Four quartz crystal (5 MHz) deposition rate sensor - controllers, one for each electron beam gun, capable of monitoring and controlling deposition rates of 1 to 10,000 Å/sec.
- 6) Four remotely indexed optical flat holders, one for each electron beam gun, to permit rapid verification of coating thickness prior to removing any fixtured specimens.
- 7) A revolving fixture, custom designed to provide uniform coating of all fuel rod cylindrical surfaces with each of up to four different evaporants, which may be applied either consecutively or simultaneously.
- 8) Full safety interlocks for operator and equipment protection.

All system modules were manufactured, and system integrated, by a single manufacturer. This manufacturer's electron beam guns were favored, because they combined the largest available hearth size in a smaller gun. At the time

the equipment was purchased, the deposition rate monitors and controllers had been described as the industry reference by both Autonetics Division, Rockwell International, personnel and by several independent vacuum system suppliers. Performance of the equipment to date has been excellent.

IV. COATING EVALUATION EQUIPMENT AND PROCEDURES

Coating evaluation is divided into three parts. First, the amount of evaporant from each gun condensing on an optical flat in its penumbra is measured, using a mechanical-stylus surface-profile-measuring device. This device is capable of recognizing a step change of 10 to 25 Å in thickness. Instrument calibration is checked, using another optical flat with step heights calibrated by the U. S. National Bureau of Standards. The quantity of material deposited on each optical flat is then checked against the amount of material reported deposited on the adjacent quartz crystal by the deposition rate controller. Second, the integrated deposit thickness on the work pieces is checked by measuring the step height at masked areas on dummy fuel rods. Third, the local rare earth concentration of each coating constituent on the fuel rod surface is monitored by x-ray fluorescence measurements. The areas fluoresced are typically at the fuel rod segment center and/or 3/4-in. from the segment ends. From one to four points are fluoresced at each of the three positions along the rod, the points being taken around the circumference in 90° increments. The area fluoresced at each point is nominally 1/8 in.²

The fluorescence measurements are standardized by a three-step process:

- 1) X-ray fluorescence measurements are made on a set of standard gadolinium solutions, each containing a known amount of 99.9% Gd₂O₃ in 6 N nitric acid (0, 0.1, 0.2, 0.4, 0.7, 1.0, and 1.4 mg Gd₂O₃/ml). The seven sets of XRF measurements are then plotted. The x-ray fluorescence readings vary linearly with Gd concentration, over the 0 to 1.4 mg Gd₂O₃/ml range. The seven points of the first calibration run yielded the following curve of best-fit:

$$\text{mg Gd}_2\text{O}_3/\text{ml} = 0.02422 + 8.23176 \times 10^{-5} \times (\text{XRF reading} - \text{background}) \quad \dots (1)$$

- 2) Gd₂O coated fuel rods and/or dummy rods are masked with Teflon tape, so that a nominal 10 cm² surface area is exposed, about a 0.9 in. length on the 0.528-in. diameter rods. Nominal film

thicknesses on the reference set were 0.5, 0.6, 0.7, 0.8, and 0.9μ , to yield ~ 0.37 , 0.45, 0.52, 0.59, and $0.66 \text{ mg Gd}_2\text{O}_3/\text{cm}^2$, respectively. XRF readings are taken of the exposed area at four azimuthal positions, each 90° apart. XRF data are tabulated for use after the next step.

- 3) The coating in the 10 cm^2 unmasked area is leached with 10 ml of $6 \pm 0.15 \text{ N}$ nitric acid. Aliquots of the leach liquor are sealed in EP 16 cap plugs with 0.25 mil Mylar film held by a Kirsch 1405 curtain ring, just as the $\text{Gd}_2\text{O}_3/\text{HNO}_3$ standard solutions are, and x-ray fluorescence measurements are made on the leach liquor aliquots. The XRF measurements on the leach liquor are then checked against those for the standard solutions. The XRF readings on the liquors used to leach the reference set of coated specimens corresponded to Gd_2O_3 concentrations falling between 0.349 and 0.643 mg/ml , well within the linear 0 to 1.4 mg/ml range covered by the standard solutions. The leached area is checked by caliper. The effective Gd surface concentration on the five masked surfaces was found to vary from 0.357 to $0.65/\text{mg Gd}_2\text{O}_3/\text{cm}^2$.

The surface concentrations, as determined by XRF analysis of the leach liquor, are plotted against the averaged surface readings on each masked area, as measured in the previous step. On the reference set of coated rods, two of the three intermediate points lay exactly on the line connecting the extreme points, with the third intermediate point falling near the line, a total disparity of 25 units in 1330 (i. e., 1.9 to 2.4% apparent disagreement in the one set of surface readings). This yielded the following curve of best fit:

$$\text{mg Gd}_2\text{O}_3/\text{cm}^2 = 0.13726 + 5.3834 \times 10^{-4} \dots (2)$$

$$\times (\text{XRF reading} - \text{background})$$

The three parts of the coating evaluation operation serve the following purposes:

- 1) The optical flat mechanical stylus measurements provide a quick check on the total deposit measured by each evaporation rate

controller, so that any discrepancy can be caught and the unit repaired or replaced before another coating run is started.

- 2) The dummy rod mechanical stylus measurements provide a quick check on the fixture performance (e. g., uniform rod rotation) before another coating run is started.
- 3) The x-ray fluorescence measurements on the fuel rods permit nondestructive determination of local burnable poison concentrations on up to 100% of the surface of all rods. X-ray fluorescence measurements on the dummy element glass rods, and then on the nitric acid leach liquor after stripping these rods, permit regular recalibration of the x-ray fluorescence unit surface readings against the standard solution readings.

The excellent agreement between the individual standard solution readings, and between the rod surface and leach liquor readings, would indicate that calibration of the x-ray fluorescence unit is needed only before each data run (using several of the standard Gd_2O_3 solutions), to compensate for any detector drift.

V. SPECIAL TOPICS

A. ALLOWABLE COATING THICKNESS

Early work in the program, done by W. A. Young, showed that the adherence of nominal 6μ Gd_2O_3 coatings applied to a heavily oxidized substrate was marginal, but that somewhat thinner, 3 to 4μ , coatings of the same composition applied to clean substrates adhered well. Total gadolinium-erbium-yttrium oxide coating thicknesses in the current test series varied from ~ 0.35 to 3.5μ . However, most current burnable poison requirements could be satisfied with coatings of 2.5μ or less, and all but the second series of 8 tests employed these thinner coatings. If the fuel rod surface was grit blasted prior to coating, no adherence problems were seen, at least through 18,584 hr at temperatures of 1300°F . Use of a heated substrate also served to improve adherence and reduce deposit stress.

The equipment has been used to deposit adherent metallic coatings as thick as 500μ , and adherent multiple-layer metal and ceramic composite coatings as thick as 100μ . If rare earth oxide coatings thicker than $\sim 3\mu$ are needed, the application of multiple, thinner, rare earth oxide layers, with intermediate metallic layers (e.g., molybdenum), should be considered. Preliminary tests on rare earth oxide - molybdenum laminates were promising, but no long-time thermal aging tests were run.

Based on the foregoing, any program incorporating long-time use of rare earth oxide coatings thicker than $\sim 3\mu$ should be preceded by extensive testing (e.g., of multi-layer, metal oxide - metal type coatings).

B. PROCESS LOSSES

The fixture holding the fuel rods to be coated is designed for maximum uniformity of coating on the fuel rods, rather than maximum collection of the vapor species on the rods. Accordingly, as much as 85 to 90% of the evaporant does not condense on the fuel rods. Gadolinium, erbium, and yttrium sesquioxides are all readily dissolved in cold-to-warm 6 N HNO_3 , so that cleaning of the coater fixture, walls, and shields is relatively simple. Recovery cost for the dissolved unmixed oxides has been estimated at \$125 to \$250/kg of oxide in multi-kilogram-quantities, and this approaches the cost of the natural

isotopic abundance gadolinium oxide raw material. Scrap value of the nitrate has not yet been determined. Since typical core loadings require <30 gm of gadolinium oxide total, there is little economic concern about the recovery of the scrap oxide, unless it is isotopically enriched gadolinium-155. The cost of this isotope is currently \$1100/gm, and makes inventory control and scrap recovery almost a necessity.

Efforts were made to examine the problem of recoating fuel rods which had had the original burnable poison coatings stripped off with nitric acid. The zirconium and uranium contents of the nitric acid leach liquor were below the detection thresholds, so acid attack on the substrate is apparently insignificant. The stripped fuel rod surface looked slightly darker, but otherwise unchanged, even at 20X. The tentative fuel rod coating recycle approach is to abrade an average of 2.5 mg/cm^2 from the stripped surface with a grit blaster, removing an average 4μ from the radius, prior to recoating the specimen. This amounts to ~0.17 gm for a 1-in. diameter, 3-in. long segment, or an average loss of 0.07% of the fuel rod weight per recoating. It should be repeated that the coating process yield to date has been effectively 100% of all rods coated, but the ability to strip one coating and apply another provides program flexibility and ready compliance with any burnable poison change orders.

C. COATING UNIFORMITY

As a first approximation, the local coating deposition rate per unit surface area may be considered to vary: (1) inversely as the square of the distance between the work and the crucible (i. e., the length of the evaporant ray connecting the crucible to that point on the work surface), and (2) directly as the cosine of the plane angle between the work surface and the planes normal to the evaporated ray.

Good coating uniformity on a large batch of fuel rod segments can be achieved by placing them like spokes in a wheel which is mounted parallel to the plane containing the evaporant sources, and then having the fuel rod segments rotate about their own longitudinal axes as the wheel rotates at some uniform speed. Most simply, the wheel should rotate about an axis passing through the point of symmetry in the plane containing the evaporant sources. The crucible

centers should be located slightly outboard of the radius that would place them directly under the midpoint of the rod above them.

A variety of alternate coating fixture designs are possible, but the selected fixture and gun placement design offer immediate interchangeability of module lengths between 1 and 6 in. for fuel rod diameters of 0.52 to 0.78 in., and short lead time interchange of holders for larger or smaller diameter fuel rods. Gun placement was chosen to permit coating of significantly longer modules (20 to 24 in.). Coating uniformity would be good, but not as good as the $\pm 5\%$ attainable on a 4 in. fuel rod segment in the carrousel fixture at 10 in. plane spacing.

D. PREDICTED IRRADIATION EFFECTS

As an indication of the irradiation stability of the heavy rare earth oxide type structure, massive Y_2O_3 and Dy_2O_3 have been irradiated [e. g., by the author (Dy_2O_3) and by his co-workers (Y_2O_3)], and showed no visible microstructural changes at 1000X after any of the reactor tests. (Ref., e. g. GEMP 400B and 475B.)

With respect to the expected radiation stability of the oxides of gadolinium, erbium, and yttrium, examination of BNL 325, Second Edition, Supplement No. 2 (1966) indicates that most of the high-neutron capture cross section isotopes of gadolinium will be transmitted to low neutron capture cross section isotopes of the same element. Small quantities (est., $<0.1\%$) of terbium may be formed, as well as even smaller quantities of europium. The high neutron capture cross section isotope of erbium will behave in a similar fashion, producing a low capture cross section isotope of erbium. Similarly also, very small quantities of holmium and thulium may also be formed. In contrast, the single stable isotope of yttrium (89) has a very low thermal neutron capture cross section, which would lead to production of small amounts of zirconium (est., $<0.1\%$), and possible trace strontium formation (e. g., by n , $2n$, e).

None of the transmutation products or their oxides should present any chemical stability problem. The possibility of knock-on by fission fragment recoil exists, but this should merely drive the affected atoms into the hydrogen barrier. The contiguous atoms should withstand the thermal spike well, because each of the oxides shows excellent stability at elevated temperature (e. g., high melting point and low vapor pressure).

The foregoing comments on projected radiation stability are offered to indicate promise of adequate performance, and do not provide quantitative radiation stability data on thin heavy rare earth oxide films. Only a reactor test of these films would do that, but should be planned primarily as a demonstration, because these films should perform well.

VI. CURRENT COATING TESTS

Initial tests were run in 1967-1968 on Gd_2O_3 deposited on the fuel rod surface with a work-accelerated electron beam gun. ⁽²⁾ Coating performance was good after thermal exposures of 500 hr at 1400°F, or 2000 hr at 1500°F, and after a simulated "Saturn V" launch vibration test.

Critical experiments showed an unwanted overall positive temperature coefficient of reactivity response for cores with higher Gd loadings. For several years, Eu- and Sm-base burnable poison coatings, which exhibit compensating negative temperature coefficients, were investigated.

For the initial tests on Eu_2O_3 and Sm_2O_3 , fuel rods were coated, fabricated into fuel elements, and placed on 2000-hr test at 1400°F, to determine how Eu_2O_3 and Sm_2O_3 coatings compared with the Gd_2O_3 coatings. The new oxides were fairly easy to evaporate, compared with Gd_2O_3 . However, Eu_2O_3 - Sm_2O_3 coatings on fuel rods exhibited loss of integrity after 2000 hr at 1400°F. Before testing, the Eu_2O_3 - Sm_2O_3 coatings were iridescent, strongly adherent to the substrate, and similar in appearance to the pre-test and post-test Gd_2O_3 films. After testing, the Eu_2O_3 - Sm_2O_3 films were gray to dull black, and less adherent, as evidenced by the large quantities of film which could be removed by rubbing the coated fuel rod surface with cleansing tissue.

Efforts were made to stabilize Eu_2O_3 - Sm_2O_3 films by diluting them with Y_2O_3 , Gd_2O_3 , and/or ZrO_2 , and by isolating them with over-layers of Y_2O_3 and/or Gd_2O_3 . The demonstrated stability of Gd_2O_3 films, the successful use of Y_2O_3 - Eu_2O_3 in the high-vacuum, electron-bombarded environment of a color television picture tube, the certain presence of ZrO_2 and the known existence of several europium-zirconium-oxygen compounds, and the known thermodynamic stabilities of the oxides of Gd, Y, and Zr led to their selection as stabilizers.

During the program, preliminary tests had been made on the compatibility of ZrO_2 -, TiO_2 -, and Y_2O_3 -diluted and undiluted Eu_2O_3 - Sm_2O_3 discs with ZrH_x -U fuel and with the hydrogen barrier material. The Y_2O_3 -diluted Eu_2O_3 - Sm_2O_3 discs showed little or no change in appearance and microstructure and/or interaction with either the fuel or the hydrogen barrier at the 1000- and 2000-hr 1430 and 1500°F test conditions. Eu_2O_3 - Sm_2O_3 discs had reacted

significantly with the hydrogen barrier, and adhered tightly to it. The TiO_2 -diluted Eu_2O_3 - Sm_2O_3 discs showed more reaction with the hydrogen barrier material than had the undiluted Eu_2O_3 - Sm_2O_3 discs.

The problems associated with maintaining, or even predicting, the fuel rod-hydrogen barrier interface environment, particularly the problems related to maintaining the anticipated and unanticipated variations of impurity content with time at temperature, made testing of proposed burnable poison films in an actual fuel element almost mandatory.

In October 1970, a series of multiple-layer coatings were vapor deposited on the fuel rods for assembly into fuel elements (see Table 4). One to four simultaneously operating bent-beam heated crucibles, mounted 10 to 13 in. under and normal to four horizontal rotating fixtures, were used. Each fixture was capable of holding an 8.5 in. long fuel rod or segmented rod assembly.

The coated rod segments were cut into short lengths (generally, 1 in.) and loaded into fuel elements [i. e., one segment from each of 14 test coatings in each of 6 test elements (see Figure 2)]. Table 5 shows the position of each coated fuel rod segment (14), each uncoated reference fuel rod segment (3), and the spacer member in Fuel Elements E, F, G, H, I, and J. Table 5 also gives the measured thickness of each sublayer, starting at the left with the sublayer first deposited on the substrate. The measured total film thickness and the burnable poison atom ratios are also indicated. A typical coating profile is shown in Figure 3.

A total of 15 elements were placed on test for times of 1,000 to 17,000 hr at temperatures of 1300, 1400, or 1500°F. Fuel elements A, B, C, and D each contained a spacer, an uncoated reference fuel rod, and a fuel rod coated at Autonetics with a Y_2O_3 -base layer, a Y_2O_3 -diluted, graded Sm_2O_3 - Eu_2O_3 layer, and a Y_2O_3 cover layer. Burnable poison fuel rod coatings in these four elements were evaporated, using work-accelerated electron guns rather than bent beam guns, but the tests provided needed data on long-time barrier stability, fuel-barrier reaction, and Eu and Sm transport. Fuel elements E, F, G, H, I, and J (17 fuel rod segments each) were described previously, and in Table 5. Fuel elements K, L, M, N, and O each contained a spacer, an uncoated reference fuel rod, a Y_2O_3 -coated fuel rod (Sloan Run No. 15),

TABLE 4
SLOAN COATING RUNS
(Sheet 1 of 2)

Sloan Coating Run No.	Poison Loading Equivalent	Objective ("To Study the Stabilizing Effect of. . . .")	Compare the Data for This Run With (Run No. 's)
A	\$3 Eu	Co-deposited Y_2O_3 stabilizer	1, 3, 4, 5
1	\$5 Eu/\$3.50 Gd	Co-deposited Gd_2O_3 stabilizer	A, 2, 3, 4, 7, 8
2	\$5 Eu/\$3.50 Gd	Co-deposited ZrO and Gd_2O_3 stabilizers, plus sandwiching between thin Y_2O_3 (0.4μ) layers	1, 3, 5, 6, 13
3	\$5 Eu/\$3.50 Gd	Co-deposited Gd_2O_3 and Y_2O_3 stabilizers	A, 1, 2, 6
4	\$2 Eu/\$5 Gd	Co-deposited Gd_2O_3 stabilizer (higher Gd/Eu ratio)	A, 1, 5, 7
5	\$2 Eu/\$5 Gd	Co-deposited Gd_2O_3 stabilizer (higher Gd/Eu ratio), plus sandwiching between thin Y_2O_3 (0.4μ) layers	A, 2, 4, 10
6	\$5 Eu/\$3.50 Gd	Co-deposited Gd_2O_3 and Y_2O_3 stabilizers, plus sandwiching between thin Y_2O_3 (0.25μ) layers	2, 3, 13
7	\$5 Eu/\$10 Gd	Co-deposited Gd_2O_3 stabilizer (higher Gd/Eu ratio, thicker layer)	4, 8, 10
8	\$9 Eu/\$6 Gd	Co-deposited Gd_2O_3 stabilizer (lower Gd/Eu ratio, thicker layer)	1, 7, 11
9	\$12 Gd	Stability of Gd_2O_3 (1.1μ thick) films	
10	\$4.50 Eu/\$9 Gd	Co-deposited Gd_2O_3 stabilizer (high Gd/Eu ratio, thicker layer), plus sandwiching between Y_2O_3 (0.5μ) layers	5, 7, 11, 12, 13
11	\$9 Eu/\$6 Gd	Co-deposited Gd_2O_3 stabilizer (lower Gd/Eu ratio, thicker layer), plus sandwiching between Y_2O_3 (0.3μ , 0.5μ) layers	8, 10, 12
12	\$12 Eu/\$4 Gd	Co-deposited Gd_2O_3 stabilizer (low Gd/Eu ratio, thicker layer), plus sandwiching between Y_2O_3 (0.45μ) layers	10, 11
13	\$3.50 Eu/\$9 Gd	Co-deposited Gd_2O_3 and ZrO_2 stabilizers (high Gd/Eu ratio, thicker layer), plus sandwiching between Y_2O_2 (0.4μ) layers	2, 6, 10
14	\$5 Eu/\$1 Sm	Sandwiching co-deposited Eu_2O_3/Sm_2O_3 between Y_2O_3 (0.3μ) layers	20
15	—	Stability of Y_2O_3 (0.76μ thick) films	9
16	\$6 Eu/\$6 Gd	Co-deposited Y_2O_3 stabilizer, plus (double) sandwiching between $0.25 Y_2O_3$ layers	17, 18, 20

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TABLE 4
SLOAN COATING RUNS
(Sheet 2 of 2)

Sloan Coating Run No.	Poison Loading Equivalent	Objective ("To Study the Stabilizing Effect of. . . .")	Compare the Data for This Run With (Run No. 's)
17	\$6 Eu/\$6 Gd	Co-deposited Y_2O_3 stabilizer, plus (double) sandwiching between $0.1 \mu - 0.2 \mu$ Y_2O_3 layers, sandwiched between $0.3 \mu - 0.4 \mu$ Gd_2O_3 layers	16, 18, 20
18	\$3 Eu/\$6 Gd	Double sandwiching a thinner (0.35μ) Eu_2O_3 layer; (base to top, 0.3μ Gd/ 0.25μ Y/ 0.35μ Eu/ 0.3μ Gd/ 0.2μ Y), reversal in sequence with respect to Eu, to study diffusion kinetics differences	16, 17, 20
20	\$12 Eu/\$5 Gd	Sandwiching a thick (1.7μ) Eu_2O_3 layer between a 0.4μ Gd_2O_3 base layer and a 0.7μ Y_2O_3 covering layer	14, 16, 17, 18, 22
21	\$6 Eu/\$5 Gd	Co-deposited Y_2O_3 stabilizer, plus sandwiching between a 0.4μ Gd_2O_3 base layer and a 0.25μ Y_2O_3 covering layer	20, 22
22	\$6 Eu/\$5 Gd	Sandwiching a 0.8μ Eu_2O_3 between a 0.4μ Y_2O_3 base layer and a 0.5μ Gd_2O_3 covering layer	20, 21

Figure 2. Pre-Test View of Coated Fuel Rod Segments, Ready for Loading Into Test Fuel Elements E, F, and G

TABLE 5
BURNABLE POISON COATINGS ON FUEL ROD SEGMENTS IN
FUEL ELEMENTS E, F, G, H, I, AND J

Position	Sloan Run No.	Sub-Sub	Sub	Center	Super	Super-Super	Total Film Thickness (μ)	Atom Ratio Gd/Eu
Spacer								
1	20		$0.42 \mu \text{Gd}_2\text{O}_3$	$1.71 \mu \text{Eu}_2\text{O}_3$	$0.73 \mu \text{Y}_2\text{O}_3$		2.86	4/17
2	22		$0.43 \mu \text{Y}_2\text{O}_3$	$0.77 \mu \text{Eu}_2\text{O}_3$	$0.48 \mu \text{Gd}_2\text{O}_3$		1.68	4.4/8
3	15			$0.76 \mu \text{Y}_2\text{O}_3$			0.76	
4	Uncoated							
5	16	$0.28 \mu \text{Y}_2\text{O}_3$	$0.23 \mu \text{Gd}_2\text{O}_3$	$0.46 \mu \text{Eu}_2\text{O}_3 + 0.15 \mu \text{Y}_2\text{O}_3$	$0.23 \mu \text{Gd}_2\text{O}_3$	$0.23 \mu \text{Y}_2\text{O}_3$	1.58	5/5
6	17	$0.37 \mu \text{Gd}_2\text{O}_3$	$0.18 \mu \text{Y}_2\text{O}_3$	$0.23 \mu \text{Y}_2\text{O}_3 + 0.67 \mu \text{Eu}_2\text{O}_3$	$0.1 \mu \text{Y}_2\text{O}_3$	$0.29 \mu \text{Gd}_2\text{O}_3$	1.84	7/7
7	18	$0.31 \mu \text{Gd}_2\text{O}_3$	$0.26 \mu \text{Y}_2\text{O}_3$	$0.36 \mu \text{Eu}_2\text{O}_3$	$0.27 \mu \text{Gd}_2\text{O}_3$	$0.19 \mu \text{Y}_2\text{O}_3$	1.39	6/4
8	21		$0.43 \mu \text{Gd}_2\text{O}_3$	$0.48 \mu (\text{Y}_2\text{O}_3 + \text{Eu}_2\text{O}_3)$	$0.24 \mu \text{Y}_2\text{O}_3^*$			
9	Uncoated							
10	14		$0.31 \mu \text{Y}_2\text{O}_3$	$0.85 \mu (\text{Eu}_2\text{O}_3 + \text{Sm}_2\text{O}_3)$	$0.33 \mu \text{Y}_2\text{O}_3$		1.49	
11	13		$0.41 \mu \text{Y}_2\text{O}_3$	$1.20 \mu (\text{ZrO}_2 + \text{Gd}_2\text{O}_3 + \text{Eu}_2\text{O}_3)$	$0.36 \mu \text{Y}_2\text{O}_3$			8/4
12	15			$0.76 \mu \text{Y}_2\text{O}_3$			0.76	
13	Uncoated							
14	5		$0.29 \mu \text{Y}_2\text{O}_3$	$0.75 \mu (\text{Gd}_2\text{O}_3 + \text{Eu}_2\text{O}_3)$	$0.23 \mu \text{Y}_2\text{O}_3$		1.27	5/2.5
15	6		$0.23 \mu \text{Y}_2\text{O}_3$	$1.47 \mu (\text{Y}_2\text{O}_3 + \text{Gd}_2\text{O}_3 + \text{Eu}_2\text{O}_3)$	$0.24 \mu \text{Y}_2\text{O}_3$		1.94	2.5/5
16	2		$0.38 \mu \text{Y}_2\text{O}_3$	$1.14 \mu (\text{ZrO}_2 + \text{Gd}_2\text{O}_3 + \text{Eu}_2\text{O}_3)$	$0.30 \mu \text{Y}_2\text{O}_3$		1.82	2.5/5
17	Archival Gd†			$0.6 \mu \text{Gd}_2\text{O}_3$			0.6	
Closure End								

*Was Gd_2O_3 in plan

†Pre-tested at 1400°F for 2000 hr with no change in appearance

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Figure 3. Optical Flat – Dektak Surface Profile, Sloan Run 6

and a Gd_2O_3 -coated fuel rod (Sloan Run No. 9). Table 6, part 1, shows the test times and temperatures for each of the 15 fuel elements.

Visual inspection of the first ten fuel elements removed from test showed the following:

- 1) General retention of the initial coating colors and sheens on the coated fuel rods
- 2) Varying loss of barrier lustre—generally much greater on barrier regions opposite uncoated fuel rod segments and opposite No. 20 (very high Eu, equivalent to $1.7 \mu \text{Eu}_2\text{O}_3$)
- 3) Appreciable loss of barrier sheen adjacent to all specimens after 3000 hr at 1500°F .

The lack of change in fuel element coating appearance, and the slight changes in the shininess of the adjoining barrier regions, were in marked contrast with the previously observed major changes in the appearances of straight Eu_2O_3 - Sm_2O_3 films and adjacent barriers.

Several of the fuel elements (E, L, and K) had shown excessive hydrogen loss rates during acceptance testing. The cladding envelope was removed from these elements, and the fuel rod assemblies inserted into replacement cladding envelopes. It was necessary to re-clad Fuel Element E twice. The recladding gave the opportunity to check for any short-time (150 to 200 hr) visible changes in barrier and fuel rod surfaces. The adjacent barrier, after the first decanning, the second decanning, and after the completed test, showed few differences in appearance. There was virtually no change in appearance of the coated fuel rod segments.

Pre- and post-test x-ray fluorescence (XRF) measurements were made of barriers, fuels, and replicas pulled from barriers and from fuel surfaces. The replicas and the barriers were flattened, and then fluoresced. The convex surfaces of fuel rod segments were fluoresced directly. It is estimated that convex-surface fluorescence intensities are lower than equivalent flat-surface fluorescence intensities, perhaps by a factor of two or more; and data from fuel surfaces require correction, to allow direct comparison with data from barriers. The following general observations do appear to be valid, based on evaluation of XRF data.

TABLE 6
BURNABLE POISON FUEL ELEMENT TESTS

Fuel Element Identification	Coating Thickness (μ)	Temperature ($^{\circ}$ F)	Time (hr)	Comments
Part 1. - Y_2O_3 - Stabilized Vapor-Deposited Films				
I	1-4	1500	1,500	Each element contained 14 vapor-coated segments (see Table 5). Gd/Eu atom ratios were 6/3, 4/6, or 2/9. Selected specimens had no Y_2O_3 stabilizer
E	1-4	1500	3,000	
H	1-4	1400	3,000	
J	1-4	1400	10,000	
F	1-4	1300	10,000	
G	1-4	1300	16,584	Each element contained a Y_2O_3 - vapor-coated fuel rod, a Gd_2O_3 - vapor-coated fuel rod, and an uncoated reference fuel rod
K	1	1500	3,000	
M	1	1500	1,500	
N	1	1400	3,000	
O	1	1400	10,000	
L	1	1300	10,000	Each element contained an uncoated fuel rod, and a fuel rod with a coating of Eu_2O_3 - Sm_2O_3 - Y_2O_3 between coatings of Y_2O_3
A	1	1500	752	
B	1	1500	1,354	
C	1	1400	1,880	
D	1	1400	10,000	
Part 2 - Recent Fuel Element Tests				
P	0.8-1.5	1500	72	Er $_2O_3$ and Er $_2O_3$ -Gd $_2O_3$ coating screening test, Gd $_2O_3$ coatings as standards Swelling tests—specimens swelled 5 to 11 vol % after aging, with no loss of Gd, Y, Er adherence. Eu in SCB (4 and 9 wt %)
Q	0.8-1.5	1500	1101	
R	0.8-1.5	1400	6846	
S	0.8-1.5	1400	6846	
T	0.5-2	1400	2079	
U	0.5-2	1400	2079	
V	0.5-2	1300	2079	
W	0.5-2	1300	2079	
X-22	-	1430	112	
X-25	-	1430	1510	
				<u>Semi prototype elements</u>
AA	0.7	1300 gradient	4228	Gd $_2O_3$ coating
AB	0.7	1000-1300	4228	Gd $_2O_3$ coating
AC	1.5	1400 gradient	4228	Gd $_2O_3$ -Er $_2O_3$ coating
AD	1.5	1000-1300	4228	Gd $_2O_3$ -Er $_2O_3$ coating
AE	1.5	1300	4228	Gd $_2O_3$ -Er $_2O_3$ coating

A. GADOLINIUM AND YTTRIUM

- 1) Coated fuel surfaces showed no measureable changes in Gd and Y intensities.
- 2) Barriers adjacent to fuel rods coated with Gd_2O_3 - and/or Y_2O_3 - rich coating showed no measurable transfer of Gd or Y.

B. EUROPIUM AND SAMARIUM

- 1) Coated fuel surfaces showed a significant loss of Eu and of Sm, in as short a time as 150 hr at 1300°F.
- 2) Uncoated fuel surfaces showed virtually no Eu or Sm content.
- 3) Barrier surfaces adjoining coated fuel surfaces showed very high Eu and Sm contents. XRF of replicas pulled from those barrier surfaces showed virtually no Eu or Sm.
- 4) Barrier surfaces adjoining uncoated fuel rods, and of replicas pulled from those barrier surfaces, showed virtually no Eu or Sm.

The foregoing implies early Eu transport, possibly vapor transport and subsequent early reaction with the barrier, since no Eu was pulled off on the replicas. Based on the increased reaction between the barrier and Eu_2O_3 and Sm_2O_3 when the rare-earth was doped with TiO_2 (see description of preliminary tests, in first part of Section VI), perhaps the Ti in the barrier is the coupling agent.

Reduction of Eu_2O_3 by Zr and U is expected, based on free energies of formation (see Table 7). The vapor pressures of Sm and SmO (see Table 8) are sufficiently high that reduction of Sm_2O_3 and vapor transport of these species also occurs despite the relatively high free energy of formation of Sm_2O_3 . The latter was verified independently by distilling off massive quantities of Sm/SmO from a mixture of $\text{Sm}_2\text{O}_3/\text{ZrH}_{1.8}$ heated to 824°C at 10^{-6} torr.

C. SILICON

There is a very high silicon content on the 1500°F post-test surface of uncoated fuel rods. There is an appreciably lower silicon content on the 1400°F post-test surface of uncoated fuel rods. The measured XRF intensity indicates a concentration at least 1.2X as high as that on the pre-test barrier surface, and thickness equivalences as high as 1.2 μ of SiO (e. g., an uncoated fuel rod

TABLE 7
FREE ENERGY OF FORMATION

Element	Normal Oxide	Free Energy of Formation at 1340° F (kcal/gm atom O ₂)
H	H ₂ O	45.6
Si	SiO ₂	83.3
Ti	TiO ₂	91.
Eu	Eu ₂ O ₃	106.5
Zr	ZrO ₂	108.0
Al	Al ₂ O ₃	109.
U	UO ₂	109.1
Ba	BaO	111.
Sm	Sm ₂ O ₃	121.5
Gd	Gd ₂ O ₃	122.1
Y	Y ₂ O ₃	126.4

TABLE 8
CANDIDATES FOR VAPOR TRANSPORT,
AND THE TEMPERATURE AT WHICH
EACH SPECIES ATTAINS A VAPOR
PRESSURE OF 10⁻⁴ torr

Element	Temperature (°C)
Eu	480
Sm	573
SiO	~600 ← SmO*
Ba	735
SiO ₂	~850
TiO ₂	~1000 ← EuO*
Al	1010
Y	1157 ← ThO* ⁽⁴⁾
Gd	1175
BaO	~1200
TiO	~1300
Al ₂ O ₃	1325
Si	1337
Ti	1453
U	1582
Zr	1987
ZrO ₂	~2200

*Estimated values

tested at 1500°F for 752 hr— 1.4×10^{-4} gm Si/cm², or $\sim 1.2 \mu$). The Si-rich film on the fuel surface is thin and the crystallite size may be very small; in any case, no x-ray diffraction pattern of Si or of any silicon-rich material (e. g., SiO, Zr Si, or U₃ Si, etc.) could be seen.

The 1500° F tests show an appreciably lower, but still significant, silicon content on the post-test surface of the burnable poison coatings, as compared with the surfaces of the uncoated fuel rods. The equivalent Si thickness is generally 30% (or less) of that on the companion uncoated fuel rod segments. There is a significant difference between fuel elements, in the amount of silicon transported to the fuel rod surface at the given combination of time at temperature, but the relative silicon transfer ratios between uncoated and various coated fuel rod segments remain relatively constant.

There is generally much less transport at 1400°F than at 1500°F (only 15 to 20% as much). These two observations possibly imply that transport is affected only by very dry hydrogen, and that, after a sufficient fraction of Zr and/or U is coated with an adherent film, it can no longer getter the water vapor produced when the hydrogen reduces the barrier oxides, i. e., the rates of the forward and reverse reactions.

$H_2 + SiO_2(s) \rightleftharpoons SiO(g) + H_2O(g)$ are equal, and there is no further net evaporation of SiO from the barrier.

The post-test surface layers of barriers adjacent to uncoated specimens are depleted by 30 to 60% at 1500°F, and 15 to 30% at 1400°F. The 1500°F barriers next to coated specimens generally show less than half as much Si depletion as those next to uncoated fuel. Since the post-test (Si) content of the 1500°F test barrier surfaces is so low, there is the inference that, in at least these cases, any SiO deposited on the fuel rod may be further reduced to the less volatile Si, so there is little reverse transfer.

D. TITANIUM, BARIUM, AND ALUMINUM

Almost no Ba or Al are transported from the barrier to the fuel rod surface. The Si/Ba and Si/Al ratios on the fuel surface are at least 100X the corresponding initial ratios in the pre-test barrier. This is probably also true of the Si/Ti ratios.

The Ti content of debris on replicas pulled from the post-test barrier surfaces is very much higher than the Ti content of the virgin pre-test barrier, and much more than the Ti content of the post-test barriers. X-ray diffraction (XRD) patterns of this debris show only α - Al_2O_3 and BaAl_2O_4 , implying a very fine crystallite size for the Ti species.

Replicas were taken of the fuel and barrier surfaces for examination with an electron microscope. The results of these examinations were:

- 1) Replicas of the barrier in regions not contacted by the fuel show definite progressive changes with increased time at temperature and with increased temperature. There is a significant difference between elements, in the changes produced by a given combination of time and temperature. This, coupled with similar observations reported on differences in Si transport at a given time at temperature, may reinforce the dry hydrogen-active fuel rod surface area hypothesis discussed previously. Figure 4 shows a shadowed replica* of a typical pre-test barrier. Figure 5 shows the appearance of a barrier region not contacted by fuel, after 1354 hr at 1500°F.
- 2) Replicas of post-test uncoated fuel surfaces are very different from those of pre-test surfaces (see Figures 6 and 7). Differences are accentuated by increases in time at temperature and by temperature. Significant differences between elements tested at the same time and temperature are observed, following the pattern of the observations on Si transport and nonfuel-region-barrier changes discussed earlier.
- 3) Pre-test and post-test replicas of all coatings with high Gd_2O_3 and Y_2O_3 content showed virtually no changes in appearance, despite Si pickup (see Figures 8 and 9).
- 4) A post-test replica of barrier next to an uncoated fuel rod is shown in Figure 10. Normally, these barriers showed significantly greater debris and evidence of surface damage than the post-test replicas from barriers not adjoining fuel rods. Post-test replicas of barriers next to coated fuel rods were much better in appearance

*Note: Figures 4 through 12 are chromium-shadowed carbon-coated replicas

49711

Figure 4. Pre-Test Appearance of Barrier (Note crystallites extending above surface)

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Figure 5. Appearance of Barrier in Shielded Region After 1354 hr at 1500°F (Fuel Element B) (Note advanced clustering of pores, and erosion of spongy region around crystallites)

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Figure 6. Pre-Test Appearance of Fuel Surface

4971H10

Figure 7. Post-Test Appearance of Uncoated Reference Fuel Rod in Test B (1354 hr at 1300°F) (Surface reaction product in suspected fuel-barrier reaction region)

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120715

Figure 8. Appearance of Y_2O_3 -Coated Fuel Surface After 136 hr at 1200°F Plus 48 hr at 1300°F

4871B9

Figure 9. Post-Test Appearance of Y_2O_3 -Coated Fuel Surface (Test I) After 1496 hr at 1500°F (Note similarity to pre-test appearance, Figure 8)

4971A3
Figure 10. Appearance of Barrier Next to Uncoated Fuel
After 1354 hr at 1500°F (Fuel Element B)(Note depressed
islands of continuously arrayed pores)

(Figures 11 and 12) than those of barriers next to uncoated fuel rods, but did show (contact related) barrier contour and texture changes at 1500°F.

Test results, prior to November 1971, may be summarized as follows:

- 1) Gd_2O_3 - and/or Y_2O_3 -rich coatings on fuel rods show excellent adherence and stability, and appear to reduce markedly the observed reaction between the hydrogen barrier and the fuel rod.
- 2) Stabilizing Eu_2O_3 and Sm_2O_3 films with Y_2O_3 greatly improves the post-test appearance of the films. However, x-ray fluorescence measurements show that these films are subject to early, massive transport of Eu or Sm from the fuel rod to the adjacent barrier, possibly in a vapor species. To date, little lateral transport of Eu or Sm along the barrier has been seen, possibly implying minimum Eu or Sm revolatization after reaction with the barrier.
- 3) Massive transport of Si from the barrier to the fuel rod surface was observed at 1500°F. Lesser transport was observed at 1400°F. Transport of Si is apparently the result of (hydrogen) reduction of SiO_2 to SiO.
- 4) At 1500°F, the barrier adjoining Y_2O_3 - and/or Gd_2O_3 -coated fuel rod surfaces showed appreciably less loss of Si than the barrier next to uncoated fuel. This observation is theoretically consistent with the previous observation.
- 5) Almost no Ba or Al, and probably no Ti, are transported from the barrier to the fuel rod surface, but the debris which can be pulled from the post-test barrier regions adjacent to uncoated fuel rods is very high in Ti. X-ray patterns of this debris show only $BaAl_2O_4$ and $\alpha-Al_2O_3$, implying a very fine crystallite size for the Ti species.
- 6) Post-test replicas of the barrier, in regions not contacted by the fuel, show definite progressive changes with increased time at temperature and with increased temperature.
- 7) Post-test replicas of the barriers next to uncoated fuel rods generally showed greater evidence of surface damage, and greater amounts of debris, than did replicas from barriers not adjoining fuel rods.

4871A15

Figure 11. Appearance of Barrier Next to Composite (Y_2O_3 - Y_2O_3 - Eu_2O_3 - Sm_2O_3 - Y_2O_3)-Coated Fuel After 1354 hr at 1500°F (Fuel Element B) [Note spongy porous surface, like that in Figure 5, but with more numerous small crystal regions visible (may actually be much larger "icebergs")]

48719

Figure 12. Appearance of Barrier Next to Composite (Y_2O_3 - Y_2O_3 - Eu_2O_3 - Sm_2O_3 - Y_2O_3)-Coated Fuel After 1880 hr at 1400°F (Fuel Element C) (Note regions of individual pores and pore clusters)

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- 8) Post-test replicas of barriers next to coated fuel rods were much better in appearance than post-test replicas of barriers next to uncoated fuel rods, but did show (contact-pressure related) contour and texture changes, as compared with replicas from barrier areas not contacted by fuel.
- 9) Post-test replicas of Gd_2O_3 - and Y_2O_3 -rich coatings were substantially identical with pre-test replicas of the same coatings.

These results supported the decision to concentrate further work on Gd_2O_3 evaluation, with less attention to Er_2O_3 (and Y_2O_3) evaluation, and very limited attention to Eu_2O_3 and Sm_2O_3 evaluation.

TABLE 9

STABILITY OF Er_2O_3 , $\text{Er}_2\text{O}_3\text{-Gd}_2\text{O}_3$, AND Gd_2O_3 COATINGS
IN FUEL ELEMENT S (No. 6-4) (6846 hr at 1400°F)

Position	Description	XRF Readings*							
		Archive (As-Fabricated) Fuel Rod		Fuel Rod Post-Test		Barrier Post-Test			
		Er	Gd	Er	Gd	Er	Gd	U	Zr
S-0	Collarbutton (Blind End Region)	-	-	-	-	1	ND	ND	ND
S-1	Er(0.8 μ)	1600	ND	1520	ND	1	ND	ND	1
S-2	Er(0.45 μ) + Gd(0.45 μ)	980	410	1000	400	ND	ND	ND	1
S-3	Er(0.8 μ) + Gd (0.7 μ)	1600	470	1600	560	1	ND	ND	1
S-4	Uncoated Fuel (Control)	ND	ND	ND	ND	1	ND	12	50
S-5	Gd(0.8 μ)	ND	860	ND	860	ND	ND	ND	1
S-6	Er(0.8 μ)	1660	ND	1440	ND	ND	ND	ND	1
S-7	Er(0.45 μ) + Gd(0.45 μ)	980	250	780	300	ND	ND	ND	2
S-8	Er(0.8 μ) + Gd(0.7 μ)	1600	470	1340	460	2	1	ND	1

*Intensity 500 at full scale

ND = not detected

For Gd, Er, Zr, and U on barrier, and Gd on Fuel, ND < 1 at 500

For Er on Fuel, ND < 1 (S-4) or 2 (S-5) at 500

VII. CURRENT COATING TESTS

Early in 1972, mixed erbium-gadolinium burnable poison was identified as yielding acceptable reactor thermal coefficients of reactivity, with the promise of greater physical stability than burnable poisons containing europium or samarium. In 1972 and early 1973, test efforts were concentrated on:

- 1) Development of deposition methods for Er_2O_3
- 2) Determination of 10,000-hr properties of Er_2O_3 at 1300 and 1400° F
- 3) Determination of 10,000-hr properties of Er_2O_3 and Gd_2O_3 coatings at 1300 and 1400° F, plus gradients (semi-prototypic fuel elements)
- 4) Determination of the Y_2O_3 and Gd_2O_3 coating condition in the longest running test (16,584 consecutive hours at cutoff, 18,584 hr for the contained Gd_2O_3 -coated fuel rod)
- 5) Logging sufficient equipment operating time to establish long-term equipment and process performance, and the need, if any, for future equipment changes
- 6) Incorporation of Eu_2O_3 in barrier-type glasses, and determination of the resultant glass stability.

The test elements are listed in Table 6, Part 2.

Each of these efforts proved to be demonstrations, because:

- 1) The Gd_2O_3 vapor deposition procedure worked very well for Er_2O_3 , and the Er_2O_3 coatings exhibited excellent stability and adherence in all tests (the longest test, 6846 hr at 1400° F). Table 9 summarizes the x-ray fluorescence test results. It shows that there was effectively no Er or Gd loss from, or transfer to, any fuel rod surface, and a barely detectable transfer (<0.05%) of Er to the barrier, the latter primarily as a result of the forcing of the fuel elements out of the out-of-round cladding cylinder after test. Figure 13 shows the excellent post-test appearance of the coated fuel rods and the hydrogen barrier. The basic elements of the recommended coating procedure are presented in Sections II and III.

Figure 13. Post-Test Appearance of Gd_2O_3 , Er_2O_3 , and Gd_2O_3 - Er_2O_3 Coatings and Adjacent Barrier Regions in Fuel Element S (No. 6-4) After 6846 hr at 1400° F (Fuel rod ends uncoated)

- 2) The Gd_2O_3 and $\text{Gd}_2\text{O}_3\text{-Er}_2\text{O}_3$ coatings on the fuel rods in the semi-prototypic elements showed excellent stability and adherence (the longest test, 4228 hours at 1400°F). Tables 10 and 11 summarize the x-ray fluorescence data for the semi-prototypic elements. There was no detectable transfer of Gd to the hydrogen barrier in either the 1300°F or the 1400°F tests. There was only one point on the 1400°F test barrier at which Er could be detected ($\sim 0.05\%$ of the amount on the adjacent fuel rod). The excellent post test appearance of the fuel rods and the hydrogen barriers is shown in Figures 14 and 15.
- 3) The longest test (16,584 hr at 1300°F) showed excellent Gd_2O_3 and Y_2O_3 film stability. Table 12 shows the very small amounts of Gd and Y found transferred to the barrier or to uncoated fuel rod specimens. This small transfer ($\sim 0.1\%$) is caused by the poorer abrasion resistance of the Y_2O_3 - and Gd_2O_3 -stabilized $\text{Eu}_2\text{O}_3\text{-Sm}_2\text{O}_3$ coatings, which permitted the limited Gd and Y transfer when the fuel segments were removed from the cladding tube. Figure 16 shows the good post-test appearance of the specimens and the hydrogen barrier after the 16,584 hr test. Figure 17 shows the similarly good post-test appearance of companion specimens and cladding aged at 1300°F for 10,000 hr.
- 4) The 20 coated fuel rod segments swelled to 5 to 11 vol % after aging for 2074 hr at 1300°F (10) or 1400°F (10) all showed excellent coating adherence, with no spalling, powdering, or flaking. Table 13 shows the excellent agreement between as-aged pre-swelling x-ray fluorescence measurements and post-swelling x-ray fluorescence measurements of local Y, Er, and Gd surface concentrations. Figure 18 shows the coating freedom from flaking or other loss. This amount of swelling (5 to 11 vol %) is at least as great as is expected during any operating mode of the fuel. The as-deposited adherence of all these heavy rare earth type oxide coatings is excellent, particularly if the surface is grit blasted shortly prior to coating, and if the substrate is held under high vacuum at $\sim 400^\circ\text{F}$ during coating.

TABLE 10
STABILITY OF Gd₂O₃ COATINGS
IN SEMI-PROTOTYPE FUEL ELEMENT AA (X-24)
(4228 hrs at 1300°F)

Position	Description	XRF Readings*					
		Fuel Rod As Fabricated	Fuel Rod Post-Test	Barrier Post-Test			
		Gd	Gd	Gd	Y	U	Zr
1	Collarbutton (Blind end region)	-	-	ND	ND	ND	6
2a	358B31 Numbered End (Bottom surface)	620	450				
2b	358B31 Middle (Top surface)	690	570	ND	ND	ND	9
2c	358B31 Opposite End (Bottom surface)	760	680				
3	Central Inconel 800 Spacer	-	-	ND	ND	ND	9

*Segment 358B31
Intensity 500 at full scale
ND — not detected
For Gd, Y, U on barrier, ND < 1 at 500

TABLE 11
STABILITY OF Er_2O_3 - Gd_2O_3 COATINGS
IN SEMI-PROTOTYPE FUEL ELEMENT AC (X-31)
(4228 hr at 1400°F)

Position	Description	XRF Readings*								
		Fuel Rod As Fabricated		Fuel Rod Post-Test		Barrier Post-Test				
		Er	Gd	Er	Gd	Er	Gd	Y	U	Zr
1	Collarbutton (Blind end region)	-	-	-	-	ND	ND	ND	ND	6
2a	373D24 Numbered End (Bottom surface)	1700	540	1550	490					
2b	373D24 Middle (Top surface)	1840	595	1640	550	1	ND	ND	ND	10
2c	373D24 Opposite End (Bottom surface)	1950	640	1790	600					
3	Central Inconel 800 Spacer	-	-	-	-	ND	ND	ND	ND	9

*Segment 373D24
Intensity 500 at full scale
ND — not detected
For Gd, Er, Y, U, $\text{ND} < 1$ at 500

Figure 14. Post-Test Appearance of Gd_2O_3 Coatings and Adjacent Barrier Regions in Fuel Element AA (X-24) After 4228 hr at $1300^\circ F$ (Fuel rod ends coated with Y_2O_3)

Figure 15. Post-Test Appearance of Gd_2O_3 - Er_2O_3 Coatings and Adjacent Barrier Regions in Fuel Element AC (X-31) After 4228 hr at $1400^\circ F$ (Fuel rod ends coated with Y_2O_3)

TABLE 12
STABILITY OF Gd_2O_3 AND Y_2O_3 COATINGS
IN SCREENING TEST ELEMENT G (No. 9194)
(16,584 hr at 1300°F)

Position (from blind end)	Description	XRF Readings*							
		Archive (As-Fabricated) Fuel Rod		Fuel Rod Post-Test		Barrier Post-Test			
		Gd	Y	Gd	Y	Gd	Y	U	Zr
0	Collarbutton	-	-	-	-	ND	ND	ND	1
3	First No. 15 (Y_2O_3)	ND	940	3	860	ND	ND	ND	1
4	Uncoated Fuel (Control)	ND	ND	5	10	ND	1	ND	2
12	Second No. 15 (Y_2O_3)	ND	940	2	1000	1	4	ND	2
13	Uncoated Fuel (Control)	ND	ND	4	2.5	1	4	ND	3
17	Gd_2O_3 (previously tested at 1400°F for 200 hr)	900 1060 [†] 1120 [§]	ND	1060	ND	ND	ND	ND	1

*Intensity 500 at full scale
ND = not detected
For Gd, Y, U, and Zr on barrier, ND < 1 at 500
For Y on fuel, ND < 5 at 500

[†]Fuel Element J post-test (10,027 hr at 1400°F) reading

[§]Fuel Element F post-test (10,029 hrs at 1300°F) reading

Figure 16. Post-Test Appearance of Burnable Poison Coatings and Adjacent Barrier Regions in Screening Test Fuel Element G (No. 9194) After 16,584 hr at 1300°F
(Note specimens in positions listed in Table 12)

Figure 17. Appearance of $Gd_2O_3-Y_2O_3-Eu_2O_3$ Coatings After 10,029 hr at 1300°F

TABLE 13

TEST ELEMENT T (0-4) (2079 hr at 1400°F),

AS THERMALLY AGED (PRE-SWELLING) AND POST-SWELLING

Position (From blind end)	Fuel Segment Coating Run	XRF Readings					
		As-Aged (Pre-Swelling)			Post Swelling		
		Y	Er	Gd	Y	Er	Gd
1	Run 31 at Factory (Y)	-			-		
2	Run 32 at Factory (Y, Sm)	-			-		
3	Run 33 at Factory (Y, Eu, Sm, Gd)	430		200	390		126
4	Run 34 at Factory (Y)	310			300		
5	Run 35 at Factory (Y, Sm)	330			390		
6	A001 $1 \mu \text{Y}_2\text{O}_3$	470			440		
7	A018 $0.8 \mu \text{Er}_2\text{O}_3$		1060			970	
8	A019 $0.8 \mu \text{Gd}_2\text{O}_3$			500			480
9	A020 $\begin{cases} 0.45 \mu \text{Er}_2\text{O}_3 \\ 0.45 \mu \text{Gd}_2\text{O}_3 \end{cases}$		850	400		780	350
10	A021 $\begin{cases} 0.8 \mu \text{Er}_2\text{O}_3 \\ 0.7 \mu \text{Gd}_2\text{O}_3 \end{cases}$		1260	640		1300	610

Figure 18. Appearance of Coated Fuel Rods From Test T (0-4), Aged 2079 hr at 1400° F, and Then Swelled to 5 to 11 vol % by Increasing Hydrogen Content From 1 to 2.15 wt % (nominal)

The previous section, on earlier work, included electron micrographs showing the initial glass-like coating of yttrium sesquioxide, and its conversion, after short-time (nominal 100 hr) aging at 1200 to 1300°F, to a block-like coating which remained effectively unchanged after 1500 hr at 1500°F. The behavior of Gd_2O_3 films is analogous. Figures 19 through 23* show, respectively: (1) the as-deposited Gd_2O_3 coating, (2) the recrystallized Gd_2O_3 coating appearance after aging for 136 hr at 1200°F, then 48 hr at 1300°F, (3) the Gd_2O_3 coating appearance after 2000 hr at 1400°F (unchanged from Item 2), (4) the Gd_2O_3 coating appearance after an additional 1496 hr at 1500°F (unchanged from Item 3), and (5) the appearance of the Gd_2O_3 coating after aging 2000 hr at 1400°F and then hydriding to produce a 0.3% linear dimensional increase in the fuel rod.

The as-deposited appearance of the Gd_2O_3 coating shown in Figure 19 is identical with that of the uncoated fuel surface and the as-deposited Y_2O_3 coating on the same type surface. Figures 20, 21, and 22 show that there is very little change in the appearance of the recrystallized Gd_2O_3 coating with long-time thermal aging. The three figures of the uncrystallized, thermally aged Gd_2O_3 films look very much like Figures 8 and 9, which show the as-recrystallized Y_2O_3 film and the aged (1496 hr at 1500°F) Y_2O_3 film. The good adherence of the Gd_2O_3 film under moderate swelling is apparent.

No electron micrographs of the Er_2O_3 coatings were made, but they are expected to be similar to those of Y_2O_3 and Gd_2O_3 .

*Note: Figures 19 through 23 are chromium-shadowed carbon coated replicas

11871A-13
Figure 19. As-Deposited Appearance of Gd_2O_3 -Coated Fuel
(Note similarity to uncoated fuel, Figure 6)

1207112
Figure 20. Appearance of Gd_2O_3 -Coated Surface After
136 hr at 1200° F Plus 48 hr at 1300° F

247115

Figure 21. Appearance of Gd_2O_3 -Coated Fuel Surface After 2000 hr at 1400° F

4871B5

Figure 22. Appearance of Gd_2O_3 -Coated Fuel Surface Shown in Figure 21, After an Additional 1496 hr at 1500° F

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4871B19

Figure 23. Appearance of Gd_2O_3 -Coated Fuel Surface Shown in Figure 21, After Swelling Substrate 0.3 Linear Percent by Rehydriding (After 2000 hr at 1400° F)

VIII. CONCLUSIONS

All test elements showed good adherence of vapor-deposited Y_2O_3 , Gd_2O_3 , and Er_2O_3 films. The longest tests of each were:

Film	Longest Test Time at Temperature (hr)		
	1300° F	1400° F	1500° F
Gd_2O_3	18,584	10,027	5,000
Y_2O_3	16,584	10,027	3,000
Er_2O_3	4,228	6,846	1,104

Gd_2O_3 -, Y_2O_3 -, and Er_2O_3 -coated fuel rod specimens showed good adherence after thermal aging for 2079 hr at 1300 or 1400° F, followed by swelling the fuel substitute by as much as 4 linear percent. This exceeds the maximum swelling projected for any SNAP fuels during their operating lifetime. The x-ray fluorescence readings and visual examination at 20X showed the coatings to be substantially unchanged in appearance or rare earth content, despite the 4% stretching of the substrate. There was no evidence of spalling, so coating adherence was obviously good.

Five semi-prototype fuel elements, fabricated to demonstrate the behavior of coated fuel rods fabricated in full accordance with all specifications covering the fabrication of SNAP-type reactor fuel elements, showed the excellent appearance of the fuel rod segments and the hydrogen barriers at the end of the 4228 hr 1400° F test, and indicated that the fabrication equipment, materials, and procedures are satisfactory, with good process control of coating thickness and uniformity.

The multiple-gun, multiple-hearth, electron beam evaporation equipment proved its capability to deposit well-controlled, high-quality coatings of both mixed oxide deposits and layered deposits, with coating uniformity and reproducibility to $\pm 5\%$.

The mechanical stylus, vibrating quartz crystal, and x-ray fluorescence nondestructive tests collectively provided rapid, accurate, relatively inexpensive process control and coating quality evaluation, with good test data reproducibility and 100% inspection capability (all surface areas of all fuel rods).

Eu and Sm showed rapid transfer from the coating to the hydrogen barrier in all test coatings (substantially 100% transfer in <150 hr at 1300° F), but preliminary tests on the incorporation of up to 9 wt % Eu in an SCB-type sleeve showed good Eu retention through 1510 hr at 1430° F, and good SCB stability. Despite the loss of Eu and Sm, vapor-deposited films containing significant amounts of Y_2O_3 and/or Gd_2O_3 stabilizer (≤ 60 vol % stabilizer) retained mechanical integrity, while unstabilized Eu_2O_3 and/or Sm_2O_3 films did not maintain mechanical integrity.

Gd_2O_3 , Er_2O_3 , and Y_2O_3 electron beam deposited coatings of trace thickness, to 2.5μ thickness (at least), deposited in conformance with current specifications, performed well under all tests, and should perform satisfactorily under all currently projected mission conditions, as should films of all the heavy rare earth type sesquioxides.

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