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FOREWORD

With the publication of this issue, the BETTIS TECHNICAL REVIEW continues to report developments at the Bettis Laboratory under the general heading of Reactor Technology.

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Three constitutionally different ceramic fuels sealed in Zircaloy-2 were exposed to reactor irradiation in a hot water loop to burnups of about 10^{21} fissions/cc. It was found that dispersion fuels of 28 w/o UO_2 in a BeO matrix were dimensionally unstable due to the formation and subsequent agglomeration of large fission gas bubbles and also because of the destruction of the BeO crystal lattice by fission fragments. Two-phase ceramic fuels consisting of cubic stabilized ZrO_2 and CaZrO_3 were only slightly affected by irradiation but exhibited gross dimensional instability when exposed to simultaneous irradiation and corrosion; solid solutions of 14 w/o UO_2 in ThO_2 were found to be essentially unaffected by the irradiation exposure.

THE EFFECTS OF IRRADIATION ON $\text{BeO} + \text{UO}_2$, $\text{ThO}_2 + \text{UO}_2$, AND $\text{ZrO}_2 + \text{CaO} + \text{UO}_2$

W. Yeniscavich and M. L. Bleiberg

A continuing research effort at Bettis Atomic Power Laboratory has been applied to the determination of the burnup limitations of oxide fuel materials. A previous article (Ref 1) described the mechanism of failure of UO_2 at high fission depletions. It is the purpose of this paper to compare the behavior of UO_2 with that of other ceramic fuels. Several combinations of metal oxides with UO_2 are possible: those selected for this study were based upon the following criteria: tolerable dimensional stability up to fission depletions of $30\text{--}35 \times 10^{20}$ fissions/cc, adequate corrosion stability, reasonably high thermal conductivity, and a low neutron absorption cross-section.

Three constitutionally different ceramic fuels were thus selected for this experiment. These were (1) dispersions of approximately 28 w/o UO_2 in BeO, (2) a mixture of 17 w/o UO_2 + 13 w/o CaO in ZrO_2 , and (3) a solid solution of 14 w/o UO_2 in ThO_2 . The BeO dispersion represents a ceramic composed of two insoluble constituents in which UO_2 is present as discrete particles, and hence the fissioning and fission fragment damage are confined to discrete regions. The mixture of 17 w/o UO_2 + 13 w/o CaO in ZrO_2 is a two-phase

ceramic consisting of cubic stabilized $\text{ZrO}_2\text{--UO}_2$ solid solution and CaZrO_3 . In this ceramic, the additions of UO_2 and CaO to ZrO_2 cause the normally monoclinic ZrO_2 to become cubic. The 14 w/o UO_2 in ThO_2 is a solid solution and has the same calcium fluoride crystal structure as UO_2 . This material was included in the irradiation test to gain further insight into the irradiation stability of this crystal structure.

These fuels were sealed in plate-type fuel elements and exposed to irradiation in a pressurized hot water loop.

FUEL AND FUEL ELEMENT FABRICATION

The ceramic fuel materials tested in this experiment were in form of platelets 1.500 in. long x 0.250 in. wide x 0.040 in. thick and had full radius edges on the width (0.125 in. radius). Fabrication of a fuel element consisted of placing four identical fuel cores (platelets) in a single compartment of a copper plated Zircaloy-2 picture-frame receptacle and diffusion bonding Zircaloy-2 clad sheets (approx 0.016 in. thick) to each face of the receptacle (see Fig. 1). The cladding was not bonded to the fuel; in fact, a graphite barrier was placed on the fuel to prevent fuel/clad reaction.

Fuel core fabrication varied for each particular composition but, in general, consisted of mixing the desired constituents, pressing in steel dies to form the platelets, and sintering in hydrogen at 3180°F. The platelets were then ground to final size by lapping with silicon carbide grit. The chemical compositions, densities, and remarks on the phases present are given in Table I.

Fig. 1 Zircaloy-2 Fuel Element Used for Containing the Ceramic Fuel Cores in this Experiment; All Dimensions in Inches.

The BeO + UO₂ fuels are dispersions of insoluble UO₂ particles in a continuous BeO matrix. To illustrate the effects of irradiation as a function of particle size, both a fine and coarse dispersion were selected for testing. Metallographic examination of the fine dispersion (Fig. 2) reveals UO₂ particles of up to 50 microns diam. A typical coarse dispersion (Fig. 3) shows most of the UO₂ particles were about 150 microns diam; however, metallography at 1000X on this same fuel also shows fine particles less than 3 microns diam.

Also included in this test was a BeO + 35.0 w/o UO₂ coarse dispersion in which the nominal UO₂ content was reduced to an average 30.1 w/o by leaching the UO₂ particles from the surface of the fuel core. This sample will be referred to in the remainder of the text as 30.1 w/o UO₂. It was anticipated that this leached fuel could be compared with the BeO + 28.7 w/o UO₂ coarse dispersion to illustrate possible detrimental effects caused by

A

B

C

Fig. 2 As-Fabricated BeO + 25.3 w/o UO₂; Fine UO₂ Particles Dispersed in BeO; UO₂ Etched. White Particles are UO₂; Dark Matrix Is BeO. A, 100X; B, 400X; C, 1000X.

TABLE I
FABRICATION DATA ON CERAMIC FUEL CORES

<u>Fuel Element Number*</u>	<u>Composition (w/o)</u>	<u>Density (g/cc)</u>	<u>Theoretical Density (%)</u>	<u>Remarks</u>
1	BeO + 25.3 UO ₂ (fine)	3.56 - 3.59	96	Dispersion of 0 to 50 micron diam UO ₂ particles in BeO. No open porosity.
2	BeO + 28.7 UO ₂ (coarse)	3.43 - 3.48	90	Dispersion of approx 150 micron diam UO ₂ particles in BeO. 2-1/2 to 3% open porosity.
3	BeO + 30.1 UO ₂ (coarse leached)	3.56 - 3.58	91	Dispersion of approx 150 micron diam UO ₂ particles in BeO. UO ₂ particles leached from surfaces of platelets.
4 and 5	ZrO ₂ + 13 CaO + 17 UO ₂	5.52 - 5.61	98	Two phases with partial mutual solid solubility. No open porosity.
6	ThO ₂ + 14 UO ₂	9.59 - 9.71	94	Solid solution. No open porosity.

*Four fuel cores in each fuel element.

A

B

C

Fig. 3 As-Fabricated $\text{BeO} + 30.1 \text{ w/o } \text{UO}_2$; Coarse UO_2 Particles Dispersed in BeO ; UO_2 Particles Leached from Surface; UO_2 Etched. White Particles Are UO_2 ; Dark Matrix Is BeO . A, 100X; B, 400X; C, 1000X.

direct recoil of fission fragments out of the fuel core. Even though the fuel element containing the leached fuel cracked through the Zircaloy cladding during irradiation and exposed the fuel to simultaneous irradiation and corrosion for the last few days of testing, no significant difference was observed between the coarse dispersion fuels after irradiation. As-fabricated metallography of the coarse and coarse leached fuels was identical; hence, only the metallography of the coarse leached fuel is shown (Fig. 3).

The second fuel material tested in this experiment was $\text{ZrO}_2 + 13 \text{ w/o } \text{CaO} + 17 \text{ w/o } \text{UO}_2$ (fuel element Nos. 4 and 5, Table I). The as-fabricated microstructure, as shown in Fig. 4, consists of two distinct phases and also some unidentified grain boundary impurities suspected to be Al_2O_3 . Identification of these phases is based on ternary phase diagram studies by Zuromsky (Ref 2) which show that the white phase is stabilized face-centered cubic ZrO_2 and the twinned phase is CaZrO_3 . In this ternary system all the UO_2 and approximately 10 w/o CaO are in solid solution in the cubic stabilized ZrO_2 phase. The CaZrO_3 phase, which is present because the stabilized cubic phase is already at its CaO solubility limit, is believed to contain no UO_2 in solid solution.

The third fuel material irradiated in the test was a solid solution of 14 w/o UO_2 in ThO_2 . As-fabricated metallography (Fig. 5) shows a single phase containing some voids and also some small particles of impurities. These impurities were identified as being mostly Al_2O_3 (chemical analyses revealed approx 1100 ppm Al_2O_3 in this fuel).

One fuel element containing each type of fuel, making a total of five, was included in this experiment. In addition a sixth, defected fuel element containing the $\text{ZrO}_2 + 13 \text{ w/o } \text{CaO} + 17 \text{ w/o } \text{UO}_2$ fuel was also included. The defect consisted of a 0.005-in. diam hole in one face of the cladding which exposed the fuel to hot water corrosion during irradiation.

A.

B.

C.

Fig. 4 As-Fabricated $ZrO_2 + 13 \text{ w/o } CaO + 17 \text{ w/o } UO$. A, As-Polished, 400X; B, Etched, 400X; C, Etched, 1000X.

A

B

C

Fig. 5 As-Fabricated $ThO_2 + 14 \text{ w/o } UO_2$; Etched. A, 100X; B, 400X; C, 1000X.

IRRADIATION

The experiment, consisting of six fuel elements, was irradiated in the VH-3 loop of the Materials Testing Reactor (MTR), at Arco, Idaho. During irradiation the loop water flowed past the specimens at a velocity of about 16 fps and was maintained at about 480°F under a pressure of 2200 psi. The pertinent irradiation data as calculated from the loop calorimetry are given in Table II. Also included are radiochemical burnup analyses which verify within 15% the calculated calorimetric burnups.

The experiment was inserted into the irradiation facility on December 23, 1958 and operated without incident until August 31, 1959. At that time the activity of the loop water increased, and the experiment was temporarily discontinued. Examination at the reactor site disclosed cladding cracks in fuel element No. 4—the fuel element that had been intentionally defected with a 0.005-in. diam hole prior to testing. The experiment was reinserted without the failed fuel element and continued to operate satisfactorily until November 21, 1959, when increased activity of the loop water again necessitated removal of the experiment from the reactor. This time the experiment was terminated and returned to Bettis for post-irradiation evaluation.

RESULTS AND DISCUSSION

Post-irradiation evaluation of these fuel elements consisted of dimensional measurements, determination of fission gas release, metallography, and X-ray diffraction analyses. Dimensional measurements were made on the thicknesses of the fuel elements over fuel cores using a remotely operated Selsyn micrometer. A minimum of 12 measurements were made on each fuel element, three over each fuel core location. Fission gas release determinations were performed on each undefected fuel element by puncturing the cladding while the element was contained in an evacuated chamber. Gases entrapped in the fuel compartment void volume

expanded into the chamber and from there were pumped into sampling flasks. The collected gases were counted for Kr^{85} and also analyzed by mass spectrometric techniques for the total quantity of gases present. These results were compared with the total theoretical amount of stable fission gases produced, based on loop calorimetry burnup, and the percentage of gas release calculated. Metallography was performed by remote hot laboratory techniques on samples cut from the fuel elements by a water-submerged abrasive cutoff wheel. The X-ray diffraction analyses were performed on pieces of fuel cores using a double-crystal spectrometer. The X-ray apparatus is described in Ref 3.

For clarity in presentation, the results obtained from the above operations are presented and discussed in three separate groups corresponding to the three different ceramic fuels tested in this experiment. For brevity all data are tabulated in Table III.

BeO + UO₂

Results

Average thickness increases of 2.3, 4.2, and 11.3 mils were measured on the fuel elements containing, respectively, coarse, coarse leached, and fine BeO + UO₂ fuels after exposures of about 11×10^{20} fissions/cc (Tables II and III). These measurements were made at the points of maximum deflection, i.e., at the fuel element centerline. Fuel element cross-sections showing intimate contact between core and cladding (Fig. 6) show the fuel element swelling was caused by swelling of the fuel cores. Thus the increases in fuel element thickness were actually increases in fuel core thickness. Using the measured thickness increases, the percentage increases in fuel core thickness were calculated and are shown in Table III. The results showed that for essentially the same exposure, the fine UO₂ dispersion sample exhibited the greatest amount of swelling, while the coarse UO₂ dispersion (28.7 w/o UO₂) exhibited the least swelling. Furthermore, the extent of fuel swelling

TABLE II
IRRADIATION DATA

Fuel Element Number	Fuel Composition (w/o)	From Loop Calorimetry*				Radiochemical Burnup Analyses (fiss/cc x 10 ⁻²⁰)	
		Ave Heat Flux (Btu/hr-ft ²)	Ave Temp (°F)		Ave Burnup (fiss/cc x 10 ⁻²⁰)	Mass Spec Isotopic Analyses	Cs ¹³⁷ Analyses
			Clad	Fuel**			
1	BeO + 25.3 UO ₂ (fine)	360,000	530	890	11.1	10.4	9.5
2	BeO + 28.7 UO ₂ (coarse)	390,000	535	930	12.1	11.6	10.7
3	BeO + 30.1 UO ₂ (coarse leached)	300,000	530	830	10.7	9.9	9.3
4 [†]	ZrO ₂ + 13 CaO + 17 UO ₂	370,000	530	900	9.9	--	--
5	ZrO ₂ + 13 CaO + 17 UO ₂	370,000	530	900	11.8	--	10.5
6	ThO ₂ + 14 UO ₂	360,000	540	880	12.5	11.4	11.1

*Using the thermal neutron flux distribution in the irradiation facility calculations indicates that peak values of heat flux and burnup of 12% to 25 % higher than those given above were obtained on the high flux end of each fuel element. However, no variation in behavior was observed over the length of any fuel element.

**Fuel thermal conductivities are assumed to be 1 Btu/hr-ft-°F.

[†] Fuel element No. 4 contained an intentional 0.005-in. diam defect hole in the cladding.

TABLE III
DIMENSIONAL DATA AND FISSION GAS RELEASES

Fuel Element Number	Fuel Composition (w/o)	Measured Thickness Increase over Individual Fuel Cores (mils)				Ave Fuel Element Thickness Increase (mils)	Percent Increase in Fuel Core Thickness	Percent Fission Gases in Fuel Compartment Void Volume	Clad Integrity
		A	B	C	D				
1	BeO + 25.3 UO ₂ (fine)	<u>10.8</u>	12.0	11.5	11.0	11.3	27.3	19.9	No defects
2	BeO + 28.7 UO ₂ (coarse)	1.2	3.2	1.8	<u>2.9</u>	2.3	5.8	6.9	No defects
3	BeO + 30.1 UO ₂ (coarse leached)	4.3	5.1	11.0*	<u>3.3</u>	4.2	10.5	N. O.	Cladding cracked over fuel compartment
4	ZrO ₂ + 13 CaO + 17 UO ₂	13.9	15.1	<u>15.8</u>	17.6	15.6	39.0	N. O.	Fabricated with 5 mils diam inten- tional defect. Clad cracked on both faces of fuel element.
5	ZrO ₂ + 13 CaO + 17 UO ₂	<u>1.6</u>	1.2	0.9	0.2	1.0	2.5	3.3	No defects
6	ThO + 14 UO ₂	0.1	0.4	<u>1.0</u>	0.7	N. S.	N. S.	0.7	No defects

*The cladding over this fuel core was cracked and bulged away from the fuel platelet; therefore this value is not used in calculating the average increase in fuel element thickness or the percentage increase in fuel thickness.

Notes:

- 1) Underlined thickness increases indicate those fuel cores which were used for metallography from each fuel element.
- 2) N. O. = Not obtainable. N. S. = Not significant.

appeared to be very sensitive to cladding restraint as shown in Fig. 6, where it may be seen that the maximum swelling occurred at the center of the fuel compartment where the cladding restraint was at a minimum.

Fig. 6 Cross-Sections of Two BeO + UO₂ Fuel Elements; A, Element No. 2; B, Element No. 1.

Also noted was intimate contact between the edges of fuel core and fuel element cladding edges in the fine dispersion fuel element cross-section shown in Fig. 6B. In the as-fabricated condition this fuel element had a gap of 0.021 in. between the edges of the fuel core and the receptacle. The post-irradiation cross-section in Fig. 6B shows that this gap has been closed by swelling and flow of the fuel. On the other hand, the coarse dispersions, fabricated with approximately 0.010-in. end gaps, showed only partial closing of their end gaps, as seen in Fig. 6A, and hence experienced less flow. The difference in the amount of swelling between the fine and coarse dispersions was also illustrated by the

larger thickness increases measured on the fine dispersion fuel element.

Photomicrographs of the irradiated BeO + UO₂ fuels are shown in Figs. 7 and 8. By comparing these figures with the unirradiated microstructures shown in Figs. 2 and 3 it can be seen that a shell of fission-fragment-damaged matrix exists around each UO₂ particle. This shell is similar to that observed by Barney and Wemple in stainless steel-UO₂ dispersions (Ref 4). Calculations based on Suzor's (Ref 5) value of the range of fission fragments in aluminum indicate the fission fragment range in BeO to be about 10 microns, which is in agreement with the microstructural observations. Also, the UO₂ particles exhibit a high degree of porosity indicative of the agglomeration of fission gases which is similar to that observed in stainless steel-UO₂ dispersions (Ref 4) and bulk UO₂ (Ref 1) at these exposures. These features are indicated in Figs. 7C and 8C. Another feature of this material is cracking which occurred between particles in the undamaged matrix and which is shown most clearly in Fig. 8C. Similar observations of cracking have been made in stainless steel-UO₂ dispersions and were attributed to stresses imposed upon the matrix by swelling of the fissile regions. The unique feature differentiating these BeO-UO₂ microstructures from the microstructures of other irradiated metallic dispersions is the formation of large black voids in the fission-fragment-damaged zone of the BeO (see Figs. 7 and 8), tentatively attributed to agglomeration of fission gases recoiled into the BeO matrix. This identification of the voids is based upon the high fission gas concentration in the recoil zone, a low solubility of the fission gases in the damaged BeO matrix, and a suspected plastic behavior in BeO when exposed to fission fragments. A similar plastic behavior observed in irradiation of UO₂ has been reported by Barney (Ref 6).

Quantitative results were obtained on the percentage of the total amount of fission gases released

Fig. 7 Irradiated BeO 25.3 w/o UO_2 ; 11.1×10^{20} fissions/cc. Fine UO_2 Particles Dispersed in BeO (from Fuel Element No. 1). A, As-Polished, 400X; B, UO_2 Etched, 400X; C, UO_2 Etched, 400X.

from the fuel core into the fuel compartment void volume. The fine dispersion released 19.9% of the total theoretical fission gases into the fuel compartment, while the coarse dispersion released 6.9%. Small quantities of helium mixed with the fission gases were also detected and were estimated as being about 10 v/o of the fission gases collected. During irradiation the coarse leached fuel developed a cladding defect which permitted escape of the gases; hence, gas release measurements on this fuel were not possible. It may be noticed that a rough correlation exists between the fuel element thickness increases and the fission gas release, i.e., the greatest swelling occurred in the fine UO_2

dispersion, and this element also evidenced the greatest fission gas release. However, Fig. 6 clearly shows that the fuel element thickness increases were caused by fuel core swelling and not by fission gas pressure in the compartment void volume. This higher gas release most probably reflects a higher diffusion rate in the amorphous BeO lattice of the fine dispersion, and this is discussed in greater detail below.

X-ray diffraction patterns of the irradiated BeO + UO_2 fuels are shown in Fig. 9. The sample of BeO + 30.1 w/o UO_2 (coarse leached) shows an X-ray diffraction pattern consisting solely of BeO

Fig. 8 Irradiated BeO 28.7 w/o UO_2 ; 12.1×10^{20} fissions/cc; Coarse UO_2 Particles Dispersed in BeO (from Fuel Element No. 2). A, As-Polished, 400X; B, UO_2 Etched, 400X; C, UO_2 Etched, 400X.

peaks, while the sample of BeO + 25.3 w/o UO_2 (fine) shows no X-ray diffraction pattern at all, either from the BeO or from the UO_2 . The loss of the X-ray diffraction pattern of the UO_2 is consistent with data obtained on this material showing that the crystal lattice is destroyed at exposures greater than about 9% uranium atoms fissioned (Ref 1). Although the average burnups were about 11×10^{20} fissions/cc in these fuel cores, the discrete UO_2 particles attained burnups of 54%, 54%, and 44% of the uranium atoms fissioned for the fine, the 28.7 w/o UO_2 coarse, and the 30.1 w/o UO_2 coarse dispersions, respectively. The destruction of the BeO lattice in the fine UO_2 dispersion and not in the coarse dispersion can be attributed to the relative fractions of the BeO

matrices subjected to fission fragment damage as discussed in detail below. It is estimated, based on the X-ray results, that greater than 90% of the crystalline BeO was destroyed in the fine dispersion.

Discussion

Destruction of BeO Crystal Structure—It has been suggested by Berman, et al. (Ref 3) that displacements caused by the fission fragments distort the structure of certain ceramic materials anisotropically until the entire structure becomes unstable and transforms to an amorphous body. Previous work by Gilbreath and Simpson (Ref 7) on BeO + 10 w/o UO_2 , in which the entire BeO matrix was subjected to fission fragments, showed

Fig. 9 Typical X-ray Diffraction Patterns Obtained on Unirradiated and Irradiated BeO - UO₂ Fuels.

that the BeO retained its crystallinity to exposures as high as 12.5×10^{18} fissions/cc. The number of fission events per unit volume required to cause one displacement per atom by knock-on collisions was calculated by the method described by Kinchin and Pease (Refs 8 and 9) and was found to be 8.8×10^{18} fissions/cc. Hence, even though all the matrix

atoms in these samples were displaced by knock-on collisions, the BeO still retained its crystallinity. From this it may be inferred that, in the experiment described herein, the BeO matrix of the fine dispersion of BeO + 25.3 w/o UO₂, which showed no diffraction pattern after having been exposed to 11.1×10^{20} fissions/cc, was destroyed by an

impurity effect of the fission fragments rather than through displacement effects.

It was observed by X-ray diffraction that crystalline BeO was still present in the coarse dispersions after irradiation even though, as discussed above, BeO subjected to fission fragment bombardment of this magnitude becomes amorphous. This undamaged BeO is present because the UO_2 particles are larger and more distant from one another; hence, an appreciable fraction of the BeO was untouched by the fission fragments which recoiled out of the UO_2 particles. To illustrate this, calculations were made using the dispersion model and methods described by White, Beard, and Willis (Ref 10). This model assumes that the dispersed fuel is a cubical array of spherical particles of constant diameter and is not rigorously applicable to the fuels of this experiment since the dispersed fuel, UO_2 in this case, consisted of irregularly shaped particles in a range of particle sizes and a random array. Nevertheless, a rough approximation was obtained by assuming the fine dispersion, which contained particles up to 50 microns diam, was equivalent to an ideal dispersion of 25-micron diam particles. It was also assumed that the coarse dispersions were equivalent to an ideal dispersion of 150-micron diam particles. These calculations showed that about 44% of the BeO is damaged in the fine dispersion and only about 5% of the BeO is damaged in the coarse dispersions, as shown in Table IV, column 4. Although only an approximation, these calculations illustrate the much larger fraction of BeO damaged in the fine dispersion. Repeating these calculations using 15- and 130-micron diam particle sizes gave 100% and 7% of the BeO damaged in the fine and coarse dispersions, respectively. Hence, the X-ray diffraction data which showed no BeO crystal structure in the fine dispersion could easily be explained by assuming the fine dispersion was equivalent to an ideal dispersion of approximately 15-micron diam particles.

Swelling of BeO + UO_2 Dispersions—Maximum thickness increases occurred along the center axis of the fuel elements, and these are measured and converted to percentage increases in fuel core thicknesses as shown in Table III. However, these increases in fuel core thickness are not a direct measure of the volume swelling of the fuel because of the observed flow and growth of the fuel in the width direction and because the increase in thickness was not uniform across the width of the platelet, as mentioned above. For these samples the volume swelling was estimated from pre-irradiation measurements of the fuel core and from the post-irradiation metallographic fuel core cross-sections. The results of these calculations are listed in Table IV, column 6.

The swelling noted in this material can be attributed to the effects of accommodation of fission fragments and the agglomeration of the fission gases in both the UO_2 and BeO. In addition, on the basis of Berman's work (Ref 3), it may be anticipated that the complete destruction of the BeO lattice in the fine dispersion also contributed significantly to swelling. The effects of fission fragment accommodation and agglomeration of fission gases in fissile materials have been discussed in other investigations (Refs 10 and 11); however, no quantitative calculation can be made for the volume increase concurrent with the destruction of the BeO crystal lattice. It is the purpose of the discussion below to determine, semi-quantitatively, whether this latter effect was a significant factor in the behavior of the fuel in-pile. This is done by assuming the maximum conditions for total fuel swelling due to both fission fragment accommodation and fission gas agglomeration. These values are compared with the experimental swelling, and the difference is attributed to swelling concurrent with destruction of the crystal lattice. In this manner it is shown below that this latter effect is a significant factor in the ultimate performance of this fuel material in-pile.

TABLE IV
TABULATED CALCULATIONS OF DISPERSION PARAMETERS AND SWELLING CALCULATIONS

Fuel Sample	Assumed Spherical Particle Size (microns)	Wei. Perce. UO ₂	Volume Percent of BeO Damaged by Fission Fragments	Fraction of Fission Products Escaped from UO ₂ Particles	Experimental Swelling (% ΔV)	Contribution to Swelling by Accommodation of Fission Products		Total Contribution to Swelling by Accommo- dation of Fission Products (% ΔV)	Swelling from Fission Gas Bubbles (% ΔV)	Total Swelling by Accommo- dation of Fission Fragments Plus Gas Bubbles (% ΔV)
						In UO ₂ (% ΔV)	In BeO (% ΔV)			
Fine	25	25.3	43.6	0.537	27.5	-1.6	2.9	1.3	12.1	13.4
Coarse	150	28.7	4.6	0.094	5.9	1.8	0.5	2.3	15.3	17.6
Coarse* Leached	150	30.1	5.0	0.094	7.9	1.5	0.5	2.0	13.3	15.3

*Although the coarse leached fuel contained a gradient in UO₂ content, which was zero on the surface and 35.0 w/o in the center of the fuel core, it was treated as an ideal dispersion with the nominal UO₂ content of 30.1 w/o obtained by chemical analysis.

The total fuel core swelling which occurs as a result of accommodation of fission fragments was calculated by adding together the swelling due to fission fragment accommodation in UO_2 and BeO . In this calculation the idealized dispersion model of White, et al. was invoked, with the same assumptions used above in discussing the destruction of the BeO crystal lattice, to obtain the fraction of fission fragments which escape from the UO_2 particles (see Table IV, column 5). The experimental swelling rate of bulk UO_2 made by fission fragment accommodation is not more than about 1/2% per atom percent burnup, or 2.25×10^{-23} cc/fission (Ref 1). Using this value and the total number of fission fragments remaining within the UO_2 particles, the UO_2 particle swellings were calculated and are shown in Table IV, column 7.

It may be seen that the amount of fuel core swelling attributed to accommodation of fission fragments in the UO_2 particles amounts to almost 2% in the coarse dispersions, while in the fine dispersion the UO_2 particles actually shrank and gave a decrease of 1.6% in fuel core volume. This is a consequence of the large fraction of fission fragments which escape by recoil from the UO_2 particles in the fine dispersion.

An experimental swelling rate in the BeO caused by accommodation of fission fragments which recoil from the UO_2 particles can be calculated from the data of Gilbreath and Simpson (Ref 7). These data indicate a swelling rate of 4.4×10^{-23} cc/fission. However, their samples were 92% of theoretical density and attained only small burnups; hence, accommodation of fission fragments in pores (voids) within the fuel core may have made their swelling rate low.

The calculations made using these experimentally determined swelling rates inherently include swelling due to the gaseous fraction of the fission fragments. Gases are considered separately below and should not have been included here, but since no clear method of modifying these experimental

values is available, they were not changed and thus give more conservative answers (i.e., greater swelling). However, the experimental swelling rate for BeO still appears extremely small, and a more realistic rate is obtained from the data of Howe and Weber, reported by Brinkman (Ref 11), on fission fragment yields and volumes. The maximum theoretical swelling rate is calculated by using the difference in nongaseous fission fragment volume and U^{235} volume. This assumes no accommodation of fission fragments within interstitial spaces or in internal pores, and the swelling rate is 4.8×10^{-23} cc/fission. With this swelling rate and the fraction of fission fragments recoiled into the BeO matrix, the contribution to fuel core swelling caused by nongaseous fission fragments in BeO were calculated to be 2.9% for the fine and 0.5% for the coarse dispersions and are shown in Table IV, column 8.

Adding the contributions to swelling by accommodation of fission fragments in both UO_2 and BeO , it can be seen that only a fraction of the experimental swelling can be accounted for by accommodation of fission fragments even under the assumed maximized swelling conditions (see Table IV, columns 6 and 9).

The volume swelling which results from the agglomerated fission gases is dependent on many unknown parameters such as surface tension, creep strength of BeO in-pile and at operating temperatures, and effects of cladding restraint. In order to obtain an approximation of the maximum possible contribution of fission gas agglomeration to total fuel core swelling, it was assumed that all fission gases remaining in the fuel core collected into randomly dispersed bubbles, that in these bubbles they behaved as an ideal gas at 760°F (the average of the maximum temperature distribution in the fuel cores) and 2200 psi, and that no restraining forces acted upon the fuel body. These calculated values are given in Table IV, column 10 and show that the gas swelling in the coarse dispersions is about twice the experimental values, as would be

expected from the maximizing assumptions made. However, even under these maximized conditions of gas bubble swelling and after adding the swelling due to fission fragment accommodation, the calculated value of 13.4% increase in volume for the fine dispersion is still far less than the experimental value of 27.5%.

The above discrepancy, which is a minimum of 14% difference in experimental and calculated volume swelling, appears to be explainable by a volume increase accompanying the destruction of the BeO crystal structure. Published data on the density of amorphous BeO are not available; however, data on the swelling of $\text{Al}_2\text{O}_3 + \text{UO}_2$ dispersions during irradiation have been reported (Ref 3) and indicate about a 30% increase in Al_2O_3 volume concurrent with the destruction of its crystal lattice. A more common example of volume swelling accompanying destruction of an oxide crystal structure is found in quartz, where a density or specific volume difference of 20% exists between crystalline and amorphous SiO_2 (Ref 12). Thus, it appears that a volume change of 14% occurring simultaneously with the destruction of the BeO crystal lattice is not unreasonable.

Considering the coarse dispersions, the maximized gas bubble swelling and fission fragment accommodation can account for more than the observed experimental swelling. The experimental swelling is considerably less in these coarse dispersions because the volume increase accompanying the destruction of the BeO crystal lattice is not a significant contribution to total fuel core swelling. This is evident from the calculations made above which show only about 5% of the BeO lattice was damaged by fission fragments in the coarse dispersions. Hence, the volume increase concurrent with destruction of the BeO crystal structure in the coarse dispersions is only about 1/20th as effective in causing fuel core swelling as it is with the fine dispersion.

Fission Gas Releases from BeO + UO_2 Dispersions—It has been shown above that 19.9% and 6.9% of the stable fission gases produced escaped from the fuel cores of the fine and coarse dispersions, respectively. A mechanism which accounts for the higher release rate of gases from the fine dispersion can be postulated if it is assumed that only negligible quantities of gas escaped through cracks in the fuel core; the escape of gases by recoil from surface UO_2 particles can be shown to be about 0.5% of the total gas produced and is also neglected. Under these conditions the gas is required to diffuse through the BeO lattice to escape from the fuel core. The higher diffusion rate of fission gas atoms in the fine dispersion can be attributed to the amorphous structure of the BeO. Since the crystalline structure of BeO is more dense than the amorphous structure, the more open arrangement of atoms in the amorphous structure would give a high diffusion rate and result in a greater release of stable fission gas atoms. This effect is similar to that noted in glasses where the diffusion coefficients are shown to be 2 to 4 orders of magnitude greater than in crystalline structures (Ref 13). Therefore, the relative quantities of stable fission gas atoms released by the fine and coarse dispersions support the above conclusion that the crystal structure of the BeO in the fine dispersion was destroyed during irradiation and that this amorphous structure allows greater diffusion of these gases.

$\text{ZrO}_2 + 13 \text{ w/o CaO} + 17 \text{ w/o UO}_2$

Results

Irradiation exposure of $\text{ZrO}_2 + 13 \text{ w/o CaO} + 17 \text{ w/o UO}_2$ to 11.8×10^{20} fissions/cc results in an average thickness increase of 2.5% at the center of the fuel compartment. However, when this same fuel was exposed to simultaneous irradiation and corrosion to 9.9×10^{20} fissions/cc, an average thickness increase of 39% was observed (see Tables II and III). These thickness measurements were made on fuel elements rather than fuel cores,

but verification that the fuel cores did swell was obtained from metallographic cross-sections of the fuel elements. Figure 10, which is a cross-section of one of the fuel cores exposed to simultaneous irradiation and corrosion in the defected element, shows that the fuel core swelled and followed the contour of the cladding.

Also visible in Fig. 10 is a surface reaction on the fuel core apparently caused by the presence of steam in the fuel compartment interior. Entrance of water into this fuel element occurred through the intentional 0.005-in. defect hole in the cladding, and the much hotter interior of the fuel element ($> 650^{\circ}\text{F}$) kept the water in the steam phase. This surface reaction apparently occurred most rapidly at the edges of the fuel because the edges became perceptibly rounded. This is illustrated in the line drawing in Fig. 11 where pre- and post-irradiation fuel core cross-sections are drawn, one on top of the other, to depict the changes which occurred during the exposure. In this drawing it can also be seen that a decrease occurred in the width of the fuel core. The decrease in width and the rounding of edges is interpreted to indicate a chemical reaction of the steam environment with the fuel core during irradiation, accompanied by fuel swelling which caused the thickness increase at the center.

Higher magnification photomicrographs of the center of the fuel core are shown in Fig. 12. In these photomicrographs it can be seen that the reaction also occurred both intergranularly and transgranularly. However, the intergranular spaces also contain black voids located within the CaZrO_3 phase described earlier and shown as the twinned phase in Fig. 4B.

Metallography of the $\text{ZrO}_2 + 13 \text{ w/o CaO} + 17 \text{ w/o UO}_2$ fuel from the nondefected fuel element is shown in Fig. 13. This fuel was fabricated in the same manner as that shown in Fig. 12, but was exposed to a slightly greater burnup (11.8×10^{20} fission/cc) and was in a nondefected fuel element; therefore, it was not exposed to the corrosion environment. In these photomicrographs it can be seen that irradiation has caused considerable damage in the CaZrO_3 phase, while the stabilized ZrO_2 phase is essentially unaffected. This observation is somewhat unusual since the CaZrO_3 phase contains essentially no UO_2 and hence did not undergo any appreciable amount of fissioning. However, the recoil range of fission fragments in CaZrO_3 is about 10 microns; since the CaZrO_3 particles are approximately 25 microns in diameter, essentially all the CaZrO_3 is subjected to fission fragment recoils from the

Fig. 10 Cross-Section of Fuel Element No. 4 Which Shows the Swelled Fuel Core, $\text{ZrO}_2 + 13 \text{ w/o CaO} + 17 \text{ w/o UO}_2$, after Exposure to Simultaneous Irradiation and Corrosion. (The Sharp Notches in the Clad Are a Consequence of Fitting Together Circular Photographs to Make the Composite Cross-Section.) 35X; Reduced $\sim 1/3$ in Printing.

Fig. 11 Relative Change in Fuel Core Cross-Section of $\text{ZrO}_2 + 13 \text{ w/o CaO} + 17 \text{ w/o UO}_2$ during Exposure to Simultaneous Irradiation and Corrosion.

stabilized ZrO_2 fissile phase. Another important feature is the change in shape of the CaZrO_3 particles. These were nearly spherical in the as-fabricated condition; however, after exposure to irradiation these particles formed an almost completely continuous phase in the grain boundaries.

Measurements on photomicrographs of the as-fabricated $\text{ZrO}_2 + 13 \text{ w/o CaO} + 17 \text{ w/o UO}_2$ revealed that the two-phase structure consisted of approximately 20 v/o (volume percent) CaZrO_3 and 80 v/o stabilized ZrO_2 . If all the UO_2 is presumed to be contained in the stabilized ZrO_2 phase, the specific burnup attained by this phase was 14.8×10^{20} fissions/cc, whereas the burnup for the total fuel core was 11.8×10^{20} fissions/cc. Irradiation of the stabilized ZrO_2 phase to an exposure of 14.8×10^{20} fissions/cc produced no distinguishable microstructural changes.

Fission gas analyses showed that 3.3% of the stable fission gas atoms escaped from the fuel exposed only to irradiation.

X-ray diffraction analyses on this fuel before irradiation revealed only the lines of the stabilized face centered cubic ZrO_2 phase. After irradiation, X-ray diffraction analyses of both the irradiated samples and the defected sample simultaneously exposed to irradiation and corrosion again revealed only lines of the stabilized face centered cubic ZrO_2 phase with no change in lattice parameter.

Discussion

Exposure of the stabilized cubic ZrO_2 phase to 14.8×10^{20} fission/cc had no apparent effect. This

A

B

C

Fig. 12 $\text{ZrO}_2 + 13 \text{ w/o CaO} + 17 \text{ w/o UO}_2$ Exposed to Simultaneous Irradiation and Corrosion; 9.9×10^{20} fissions/cc (from Fuel Element No. 4); Etched. A, 250X; B, 400X; C, 1000X.

was also verified by the X-ray diffraction patterns which showed no change in the cubic lines between the samples as-fabricated and after irradiation.

Irradiation exposure of the CaZrO_3 phase caused flow and probably destroyed the crystal structure of this phase. However, conclusive proof of destruction of this crystal structure was not obtained and can only be strongly inferred from the metallographic observations, the high fission gas release, and the observed swelling. The viscous behavior of this phase during irradiation, as shown in the post-irradiation metallography in Fig. 13, is indicative of amorphous or glassy material. The swelling of the fuel core in the nondefected fuel element, which was indicated by a 2-1/2% increase in thickness, can be attributed to swelling which would occur simultaneously with destruction of the crystal structure of the CaZrO_3 phase. Finally, the fission gas release of 3.3%, which is high compared with the release of 0.7% from the $\text{ThO}_2\text{-UO}_2$ fuel irradiated to the same exposure (see the following section), can be explained if the CaZrO_3 phase is assumed to be amorphous. Using this assumption, a high gas release occurs because the diffusion coefficient is 2 to 4 orders of magnitude higher for the amorphous phase than for the crystalline phase (Ref 15) and also because this phase is almost a continuous grain boundary phase and provides passageways for rapid diffusion of gases to the surface of the fuel core.

The effects of steam corrosion occurring simultaneously with irradiation can be considered in light of the assumption that irradiation destroys the crystal structure of the CaZrO_3 phase. The structure in Fig. 12 can then be attributed to reaction of steam, diffusing through the amorphous CaZrO_3 phase, with fission product cations. However, lacking further identification of the reaction product, additional speculation is unwarranted.

From these results and the assumed mechanism of behavior of this material in-pile, it may be

Fig. 13 Irradiated $\text{ZrO}_2 + 13 \text{ w/o CaO} + 17 \text{ w/o UO}_2$; 11.8×10^{20} fissions/cc (from Fuel Element No. 5); Etched; 400X.

speculated that CaO additions which are sufficiently high to form the CaZrO_3 phase are detrimental to the in-pile behavior of these fuels. This tentative conclusion is being checked by irradiation of $\text{ZrO}_2\text{-UO}_2$ fuel samples containing no CaO additions.

$\text{ThO}_2 + 14 \text{ w/o UO}_2$

Results

Irradiation of $\text{ThO}_2 + 14 \text{ w/o UO}_2$ to an exposure of 12.5×10^{20} fissions/cc resulted in no significant dimensional changes (i.e., less than 0.001 in. increase in thickness).

Metallography of the irradiated fuel is shown in Fig. 14. Essentially no discernable effects of irradiation are observed on this fuel, except for possibly a change in the shape and distribution of the as-fabricated voids (see Fig. 5 for as-fabricated structure). The grain boundaries are not seen in the irradiated structure because a light etch was used.

Fission gases collected from the fuel compartment void volume showed 0.7% of the stable fission gas atoms escaped from the bulk fuel.

X-ray diffraction patterns obtained on this fuel before and after irradiation showed no crystal

Fig. 14 Irradiated $\text{ThO}_2 + 14 \text{ w/o } \text{UO}_2$; 12.5×10^{20} fissions/cc (from Fuel Element No. 6); Lightly Etched; 400X.

structure changes and no perceptible changes in unit cell dimensions.

Discussion

Thoria (ThO_2), like UO_2 , has a calcium fluoride type crystal structure, and hence these oxides are mutually soluble. It has been proposed by other authors that the remarkable irradiation stability of UO_2 is attributed to its open structure (Refs 14 and 15). Recent results have shown an upper limit of burnup exists for bulk UO_2 (Ref 1), i.e., swelling was observed in bulk UO_2 after exposures of 21.5×10^{20} fissions/cc. However, at the exposure of 12.5×10^{20} fissions/cc obtained by the $\text{ThO}_2 + 14 \text{ w/o } \text{UO}_2$ in this experiment, excellent dimensional stability would be predictable on the basis of its similarity to UO_2 .

CONCLUSIONS

Reactor irradiation of both fine and coarse dispersions of approximately 28 w/o UO_2 in BeO to exposures of about 11×10^{20} fissions/cc showed that these materials had very poor dimensional stability, that they released large percentages of the stable fission gas atoms produced during irradiation, and that the concentration of fission fragments in the damaged BeO matrix was sufficient to destroy the BeO crystal lattice. The experimental

swelling in the coarse dispersions was accounted for solely on the basis of fission product accommodation and gas agglomeration. However, to account for the swelling of the fine dispersions, a volume expansion accompanying the destruction of the BeO crystal lattice also had to be included. Confirmation of this interpretation was obtained by (1) X-ray diffraction data which showed complete destruction of the BeO crystal lattice in the fine dispersion, (2) the larger release of fission gases from the fine dispersions which can be attributed to a higher diffusion rate in an amorphous phase, and (3) the more plastic- or amorphous-like behavior of the fine dispersion fuel core demonstrated by its ability to expand and fill the entire fuel element void volume.

Reactor irradiation of $\text{ZrO}_2 + 13 \text{ w/o } \text{CaO} + 17 \text{ w/o } \text{UO}_2$ to an exposure of 11.8×10^{20} fissions/cc resulted in a slight thickness increase of the fuel core, plastic flow of the CaZrO_3 phase, and moderately high release of fission gases from the fuel core. These results were interpreted as indicating that irradiation destroyed the crystal structure of the CaZrO_3 and transformed it to an amorphous, semi-continuous, grain boundary phase. The high gas release is explainable by the high diffusion rate of gases through this amorphous phase, and the volume increase concurrent with destruction of the crystallinity of the CaZrO_3 phase accounts for the slight thickness increase.

Exposure of this same material to simultaneous irradiation and corrosion resulted in a reaction with the steam environment which caused loss of fuel core material and an increase in thickness of 39% at the center of the fuel core. Complete grain boundary penetration of the reaction was also observed and was postulated to occur by rapid diffusion through the amorphous CaZrO_3 phase and by oxidation of the fission fragment cations contained therein.

Reactor irradiation of $\text{ThO}_2 + 14 \text{ w/o } \text{UO}_2$ to an exposure of 12.5×10^{20} fissions/cc produced no

appreciable irradiation effects. This material showed behavior analogous to that which would be expected for bulk UO_2 irradiated to the same exposure.

Although the fuels of this experiment did not obtain their initial goal of $30\text{--}35 \times 10^{20}$ fissions/cc, the results on the $\text{BeO} + \text{UO}_2$ and $\text{ZrO}_2 + \text{CaO} + \text{UO}_2$ fuels were quite conclusive and exclude their use as fuels for pressurized water type reactors. The excellent irradiation behavior of the cubic stabilized ZrO_2 phase in the two-phase $\text{ZrO}_2 + \text{CaO} + \text{UO}_2$ fuel of this experiment indicates that cubic stabilized ZrO_2 fuels with reduced amounts of CaO and possibly with no CaO additions will exhibit irradiation stability at least to exposures of 15×10^{20} fissions/cc. The solid solution of $\text{ThO}_2 + \text{UO}_2$ exposed to 12.5×10^{20} fissions/cc exhibited excellent stability and will certainly require higher irradiation exposures to determine its operational burnup limits.

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REFERENCES

1. M. L. Bleiberg, G. Maskarinec, D. Clark, and W. Yeniscavich, "Burnup Limitations of Bulk UO_2 Prototype Fuel Elements—An Interim Examination of the CR-IV-X-3-1 Test and an Interim Examination of the CR-V-m Experiment," BETTIS TECHNICAL REVIEW, WAPD-BT-18 (April 1960), p 107.
2. G. Zuromsky, "The Development and Testing of Homogeneous Ceramic Fuels," Cend 84, NYO-2990 (May 1960).
3. R. M. Berman, M. L. Bleiberg, and W. Yeniscavich, "Fission Fragment Damage to Crystal Structures," Journal of Nuclear Materials, Vol 2, (1960). pp 129-140.
4. W. K. Barney and B. D. Wemple, "Metallography of Irradiated UO_2 —Containing Fuel Elements," KAPL-1836 (January 1958).
5. F. Suzor, "Fluctuations De Parcours Dan L'aluminium et dans L; or d'un Fragment de Fission donne' de L'uranium," Compt. rend., Vol 226 (1948), pp 1081-1083.
6. W.K. Barney, "The Swelling of UO_2 at High Burnup," Symposium on Effects of Irradiation on Fuel and Fuel Elements, IMD Special Report Series Number Nine, American Institute of Mining Engineers, New York (1959), p 71.
7. J. R. Gilbreath and O. C. Simpson, "The Effect of Reactor Irradiation on the Physical Properties of Beryllium Oxide," Second Geneva Conference on Peaceful Uses of Atomic Energy, Vol 5 (1958), p 367.
8. G. H. Kinchin and R. S. Pease, "The Displacement of Atoms in Solids by Radiation," Repts. Progr. in Phys., Vol 18 (1955), p 1.

9. G. N. Walton, "Fission Recoil and Its Effects," Progress in Nuclear Physics, Vol 6, O. R. Frisch, Ed. (New York: Pergamon Press, 1957), p 192.
10. D. W. White, A. P. Beard, and A. H. Willis, "Irradiation Behavior of Dispersion Fuels," Fuel Elements Conference, Paris, TID-7546, Book 2 (1957), p 717.
11. J. A. Brinkman, "Fundamentals of Fission Damage," Symposium on Effects of Irradiation on Fuel and Fuel Elements, IMD Special Report Series Number Nine, American Institute of Mining Engineers, New York (1959), p 1.
12. International Critical Tables of Numerical Data, Physics, Chemistry, and Technology (New York: McGraw Hill Book Co., Inc., 1928), p 20.
13. R. M. Barrer, Diffusion in and through Solids (Cambridge, England: The University Press, 1951), p 141.
14. B. Lustman, "Engineering Effects of Radiation on Nuclear Fuels," Symposium on Radiation Effects on Materials, Vol 2, ASTM Special Technical Publication, No. 220, American Society for Testing Materials, Philadelphia, Pa. (1958), p 84.
15. J. D. Eichenberg, P. W. Frank, T. J. Kisiel B. Lustman, and K. H. Vogel, "Effects of Irradiation on Bulk UO_2 ," WAPD-183 (October 1957).

The sintering behavior of some 35 well characterized UO_2 powders was studied. Pressing pressures and sintering time, temperature, and atmosphere were varied. Definite relationships were found between the sinterability of the powders and their preparation method, surface texture, particle size and shape, and aggregate size and distribution.

A STUDY OF THE SINTERING BEHAVIOR OF SOME URANIUM DIOXIDE POWDERS

J. C. Clayton and L. Berrin

When UO_2 particles are fabricated into sintered compacts, the densities attained are affected to a marked degree by the physical characteristics of the original UO_2 powder as well as by the pressing procedures and sintering time, temperature, and atmosphere (Refs 1-27). In addition, the chemical properties of UO_2 powders are also important since chemical contamination or deliberate additions seriously influence pressing and sintering (Refs 6, 9, 17, 18, and 29-31). The sintering of UO_2 has been the subject of many studies (Refs 1-27), but there is conflict among the results obtained. In addition the data encompass only a few types of powders limited in characterization. In the present investigation a large number of completely characterized UO_2 powders was studied in order to make any conclusions more generally applicable.

EXPERIMENTAL

The preparation and characterization of the UO_2 powders have been the subject of a previous report (Ref 32). The UO_2 was made by several oxidation and reduction methods including hydrogen reduction of the higher uranium oxides (UO_3 , $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ and U_3O_8) at temperatures ranging from 500° to 1000°C

and steam and air oxidation of uranium hydride and uranium metal. Some UO_2 was also prepared from precipitated U(VI) salts—ammonium diuranate, uranyl oxalate and uranium peroxide. The UO_2 powders were characterized by fluid and bulk densities, total (B.E.T.) and external (permeability) surface areas, and microstructure and agglomerate size distribution analyses. The O/U ratios were determined by wet chemical methods. Spectrographic analyses indicated that metallic impurities were less than 0.1%.

The UO_2 powders were blended with 1 w/o Carbowax 20 M, and the granulated powders were cold pressed at 15, 35, and 50 tsi into tablets approximately 0.5 in. in diam and 0.25 in. high. These green compacts were placed on molybdenum trays and sintered in both hydrogen and argon atmospheres. Densities of the green and sintered tablets were calculated from weight and dimension measurements. The increase in density during sintering for a fixed period (15 hr) was used as a measure of sinterability.

RESULTS AND DISCUSSION

Definite relationships were found between the sintering behavior of the UO_2 powders and their

preparation method, surface texture, particle size and shape, and aggregate size and distribution. In Table I the hydrogen sintered densities of the tablets at three different temperatures are compared with the physical characteristics of the UO_2 powders.

The total surface areas were measured by gas adsorption and include surface roughness and internal porosity. The external surface values were obtained by permeability methods. Since this latter technique measures only surface available to flow, it can be used to estimate the UO_2 powder particle sizes (Ref 32). A comparison of the surface areas determined by the gas adsorption and permeability methods gives some indication of the degree of porosity, irregularity, and roughness of the powder particles.

In tabulating the results, the powders have been arranged in groups according to their method of preparation. At the lower sintering temperatures (1550° and 1675°C) the sintered density attained is a function of particle size, total surface, and shape for a particular powder preparation. The smaller particle size powders sinter best, and if powder particles are equivalent in size, the ones with rougher surfaces are superior. As was found by other workers (Refs 6, 7, 21, and 27), uranium dioxide powders prepared by precipitation processes were found to sinter to higher compact densities than those made by steam oxidation and thermal decomposition methods. As shown in Fig. 1A and 1C, steam oxidation of uranium metal foil produced a powder composed of coarse dense particles. Steam oxidation of finely divided uranium powder (Fig. 1B) resulted in finer particle structure and higher sintered density. The same effect was also found for UO_2 powders obtained by hydrogen reduction of U_3O_8 prepared from uranium powder and foil (Fig. 2).

Again, in agreement with previous investigators (Refs 1, 2, 7, 9, 11, 12, 21, and 27), both dry and wet

comminution processes of the parent UO_3 or the UO_2 itself markedly increased the tablet sintered densities. The data in Table I show that this is the

A

B

C

Fig. 1 Comparison of the Two Types of Steam Manufactured UO_2 . A, High Pressure Steam Oxidation, 250X; B, Hydrided Steam Oxidation, 250X; C, High Pressure Steam Oxidation, 6300X.

A

B

Fig. 2 Effect of Form of Uranium Metal on Microstructure of UO_2 Powders Prepared by Reduction of U_3O_8 , 250X. A, Uranium Foil Source; B, Uranium Powder Source.

result of an increase in total surface and a decrease in particle size. The electron micrographs in Fig. 3 confirm this conclusion. The powder particles in Mallinckrodt UO_2 are large in size with relatively smooth surfaces (Fig. 3A) and sinter poorly; the comminuted oxides (Fig. 3B and 3C) are smaller and rougher and sinter well. The influence of particle shape is illustrated in Figs. 4 and 5. The UO_2 particles made from uranyl oxalate are acicular (Fig. 4A) and possess fair sintering properties, possibly because the particles are easily fractured (Fig. 4B and 4C). The higher total surface areas are due to the hair-like projections covering the external particle surface (Fig. 4B and 4C). The excellent sinterability of the UO_2 powder prepared

A

B

C

Fig. 3 The Effect of Milling on the Microstructure of UO_2 , 9000X. A, Mallinckrodt UO_2 ; B, Hydrogen Reduced, Dry Milled UO_3 ; C, Wet Ball-Milled MCW UO_2 .

TABLE I
EFFECT OF SINTERING TEMPERATURE

Method of Preparation	O/U	Density (g/cc)			Surface Area (m ² /cc)		Sintered Density (% T.D.)*		
		Helium	CCl ₄	Bulk	Total	External	1550° C	1675° C	1750° C
<u>Steam Oxidation</u>									
High pressure steam oxidation of uranium	2.01	10.92	10.75	2.76	12.9	3.1	75.9	78.8	81.0
Hydrided-steam oxidation of uranium	2.03	10.98	10.67	1.75	22.6	5.6	80.6	85.4	88.0
<u>Reduction of the Higher Uranium oxides</u>									
Air pyrolysis of U metal to U ₃ O ₈ ; H ₂ reduction	2.01	10.02	10.07	1.93	5.8	3.0	75.9	82.1	84.0
Air pyrolysis of UO ₂ (NO ₃) ₂ · 6H ₂ O to U ₃ O ₈ ; H ₂ reduction	2.02	10.03	9.96	1.98	5.7	3.3	75.7	83.1	90.1
Air pyrolysis of MCW UO ₂ to U ₃ O ₈ ; H ₂ reduction	2.01	10.35	10.32	2.21	5.4	3.3	78.0	86.2	87.6
Air pyrolysis of U powder to U ₃ O ₈ ; H ₂ reduction	2.02	10.32	10.46	1.10	9.4	5.4	80.6	91.4	93.0
Cracked ammonia reduction of UO ₃ (MCW)	2.02	10.16	10.13	2.77	6.4	3.1	72.7	80.6	82.5
Hydrogen reduction of UO ₃ · 2H ₂ O	2.01	10.25	10.25	2.12	8.8	4.1	74.9	85.2	--
Fluidized bed denitration & UO ₃ reduction	2.07	10.54	10.28	4.19	30.6	6.3	80.9	--	82.9
<u>Comminuted Oxides</u>									
Hydrogen reduction of milled UO ₃ at 920° C	2.02	--	10.39	2.00	13.2	3.5	83.7	90.6	92.5
Hydrogen reduction of milled UO ₃ at 800° C	2.02	10.32	10.36	2.03	13.8	4.0	85.0	91.9	93.7
Hydrogen reduction of milled UO ₃ at 480° C	2.04	--	10.44	2.25	24.7	3.4	89.1	92.9	94.3

* 35 tsi, then H₂ for 15 hr

TABLE I (Continued)
EFFECT OF SINTERING TEMPERATURE

Method of Preparation	O/U	Density (g/cc)			Surface Area (m ² /cc)		Sintered Density (% T.D.)*		
		Helium	CCl ₄	Bulk	Total	External	1550°C	1675°C	1750°C
Hydrogen reduction of milled UO ₃ at 700°C	2.03	--	10.42	1.94	18.1	4.7	89.5	92.8	94.4
Hydrogen reduction of milled UO ₃ at 580°C	2.03	--	10.44	1.93	17.8	4.8	91.0	92.4	93.4
Cracked ammonia reduction of UO ₃ (MCW)	2.02	10.16	10.13	2.77	6.4	3.1	72.7	80.6	82.5
Hydrogen reduction of dry milled UO ₃	2.02	10.32	10.36	2.03	13.8	4.0	85.0	91.9	93.7
Microatomized MCW UO ₂	2.04	--	10.19	--	14.2	9.2	86.0	95.1	96.0
Micronized MCW UO ₂	2.04	--	10.22	1.66	19.7	6.8	87.4	94.7	95.6
Micronized MCW UO ₂	2.06	--	10.20	--	14.3	--	88.4	95.9	96.6
Hydrogen reduction of H ₂ SO ₄ milled UO ₃	2.04	10.68	10.32	1.22	17.5	7.7	88.7	91.1	95.8
Wet ball-milled MCW UO ₂	2.05	--	10.22	1.64	17.5	6.6	90.5	94.4	96.6
Hydrogen reduction of micronized UO ₃	2.03	--	10.30	--	16.5	--	92.4	95.0	--
Micronized MCW UO ₂	2.08	--	10.21	--	23.8	--	94.4	97.1	98.1
<u>Reduction of uranyl oxalate</u>									
Direct hydrogen reduction of uranyl oxalate	2.01	10.61	10.61	1.07	7.3	5.0	81.0	87.1	89.5
Air pyrolysis of uranyl oxalate to U ₃ O ₈ ; H ₂ reduction	2.03	--	10.68	0.98	30.4	6.6	84.3	88.1	--
<u>Reduction of uranium peroxide</u>									
Air pyrolysis of uranium peroxide to U ₃ O ₈ ; H ₂ reduction	2.02	--	10.44	1.91	11.9	3.2	80.1	86.0	88.6

* 35 tsi, then H₂ for 15 hr

TABLE I (Continued)
EFFECT OF SINTERING TEMPERATURE

<u>Method of Preparation</u>	<u>O/U</u>	<u>Density (g/cc)</u>			<u>Surface Area (m²/cc)</u>		<u>Sintered Density (% T.D.)*</u>		
		<u>Helium</u>	<u>CCl₄</u>	<u>Bulk</u>	<u>Total</u>	<u>External</u>	<u>1550° C</u>	<u>1675° C</u>	<u>1750° C</u>
Direct hydrogen reduction of uranium peroxide	2.02	---	10.38	2.52	12.0	3.5	80.5	89.1	89.8
Direct hydrogen reduction of uranium peroxide	2.08	11.00	10.78	1.34	28.4	9.8	85.5	90.0	---
<u>Reduction of ammonium diuranate</u>									
Air pyrolysis of urea precipitated diuranate to U ₃ O ₈ ; H ₂ reduction	2.01	10.55	10.43	1.41	6.1	3.7	78.5	86.4	90.2
Direct hydrogen reduction of ammonia precipitated diuranate	2.05	---	10.85	1.79	40.8	3.5	82.6	85.6	86.5
Direct hydrogen reduction of urea precipitated diuranate	2.08	10.74	10.19	0.83	42.1	12.6	84.8	85.2	86.0
Pyrolysis of ammonium hydroxide precipitated diuranate to U ₃ O ₈ ; H ₂ reduction	2.04	---	10.67	---	23.0	---	87.9	92.0	93.7
Pyrolysis of ammonium hydroxide precipitated diuranate to U ₃ O ₈ ; H ₂ reduction	2.14	11.09	10.77	1.38	59.9	12.9	87.8	95.6	---
Direct hydrogen reduction of ammonium hydroxide precipitated diuranate	2.07	11.11	10.81	1.07	37.4	13.9	90.3	90.3	90.6

* 35 tsi, then H₂ for 15 hr

TABLE I (Continued)
EFFECT OF SINTERING TEMPERATURE

<u>Method of Preparation</u>	<u>O/U</u>	<u>Density (g/cc)</u>		<u>Bulk</u>	<u>Surface Area (m²/cc)</u>		<u>Sintered Density (% T. D.)*</u>		
		<u>Helium</u>	<u>CCl₄</u>		<u>Total</u>	<u>External</u>	<u>1550° C</u>	<u>1675° C</u>	<u>1750° C</u>
Pyrolysis of carbonate precipitated diuranate to U ₃ O ₈ ; H ₂ reduction	2.02	--	10.46	1.77	14.1	3.1	90.0	92.3	93.9
Pyrolysis of urea precipitated diuranate to U ₃ O ₈ ; H ₂ reduction	2.11	11.34	10.47	1.00	60.4	10.3	91.4	93.5	94.7
Pyrolysis of ammonia precipitated diuranate to U ₃ O ₈ ; H ₂ reduction	2.13	10.75	10.82	1.50	58.0	16.8	92.0	91.6	--

* 35 tsi, then H₂ for 15 hr

A

B

C

Fig. 4 UO_2 Prepared from Uranyl Oxalate. A, 250X; B, 9000X; C, 6300X.

from ammonium-carbonate-precipitated diuranate (in spite of its relatively low surface area for its class) can be explained by its particle shape. This powder preparation is composed of very rough spheres (Fig. 5). It is claimed (Refs 30 and 31) that compacts made from spherical powder particles have a low, yet uniform porosity and superior sinterability.

As has been stated before, in agreement with the findings of other investigators (Refs 1, 2, 4, 5, 8-13, 17, 21, 23-26, 30, and 31), the compact sintered density is related to the UO_2 powder particle size and morphology. However, even milled UO_2 particles are composed of clusters or aggregates of particles (Refs 27 and 32). These agglomerates influence the formation and type of pores. Both pores between the particles composing the agglomerates and voids between the agglomerates themselves exist (Ref 18). The sintered density of the tablets is, therefore, strongly dependent on aggregate size and distribution. The relation between hydrogen sintered density at 1750°C and powder aggregate size distribution is indicated in Figs. 6 and 7. The agglomerate size distributions were determined by an air sedimentation technique (Ref 32).

The data in Table I further show that sinterability is not a function of powder fluid density—that is, a low density powder can sinter well and a high density powder can sinter poorly. Since the bulk density is a function of particle size distribution, porosity, and particle shape (Refs 30 and 31), it is unwise to base generalizations on this characteristic. The data in Table I, however, indicate that in many cases, for a given type of UO_2 preparation, the powders with the lower bulk densities sintered best. This finding is in agreement with that of other workers (Refs 10, 19, and 28) and is reasonable since for nonmetallic materials bulk density decreases with a decrease in particle size (Ref 31). The comminuted oxides and those prepared by precipitation procedures had low bulk densities and excellent sinterability.

A

B

C

Fig. 5 UO_2 Prepared from $(\text{NH}_4)_2\text{CO}_3$ Precipitated Diuranate. A, 250X; B, 9000X; C, 9000X.

Finally, from the data in Table I, it is seen that those powders with high O/U ratios generally sintered to high densities; however, this may be the influence of their surface areas rather than the excess oxygen (Refs 21, 23, and 26). Studies on the storage stability of UO_2 powders (Ref 32) have shown that the tendency to pick up excess oxygen is directly related to particle size and total surface area.

The relationships between the UO_2 powder source, the pressing pressures, and the green and sintered densities of the tablets are shown in Table II. Again the powders are arranged in order of decreasing particle size and increasing total surface for each type of preparation. For a particular

Fig. 6 UO_2 Agglomerate Size Distribution Analyses. A, MCW UO_2 , 82.5% TD; B, Reduced Dry Milled UO_3 , 93.7% TD; C, Reduced Wet Milled UO_3 , 95.8% TD; Microatomized UO_2 , 98.0% TD; E, Wet Milled UO_2 , 96.6% TD; F, Micronized UO_2 , 98.0% TD.

Fig. 7 UO_2 Agglomerate Size Distribution: Diuranate Preparations. A, Ammonium Carbonate, 93.9% TD; B Urea 94.7% TD; C, Ammonium Hydroxide, 90.6% TD; D, Gaseous Ammonia, 86.5% TD.

TABLE II
EFFECT OF COLD-PRESSING PRESSURE

Method of Preparation	As-Pressed Density (% T. D.)			Sintered Density (% T. D.)*		
	19.5 tsi	35 tsi	50 tsi	19.5 tsi	35 tsi	50 tsi
High pressure steam oxidation of uranium	66.1	69.1	71.0	73.1	75.8	79.0
Hydrided-steam oxidation of uranium	60.4	64.6	67.4	76.7	80.6	84.3
Air pyrolysis of U metal to U_3O_8 ; H_2 reduction	60.1	63.3	65.4	72.8	75.7	79.1
Air pyrolysis of UNH to U_3O_8 ; H_2 reduction	61.2	64.5	66.3	72.0	75.9	79.3
Air pyrolysis of MCW UO_2 to U_3O_8 ; H_2 reduction	60.6	62.5	65.1	76.6	78.0	82.6
Air pyrolysis of U powder to U_3O_8 ; H_2 reduction	57.7	60.6	62.7	79.7	80.6	85.4
Cracked ammonia reduction of UO_3 (MCW)	59.5	63.8	--	72.0	72.7	--
Hydrogen reduction of $UO_3 \cdot 2H_2O$	56.6	59.7	62.2	70.4	74.9	78.0
Fluidized bed denitration & UCl_4 reduction	53.6	59.3	59.6	77.1	80.9	80.2
Hydrogen reduction of milled UO_3 at 920°C	58.1	61.2	63.2	82.6	83.7	87.0
Hydrogen reduction of milled UO_3 at 800°C	58.0	60.8	62.4	83.5	85.0	87.4
Hydrogen reduction of milled UO_3 at 480°C	61.4	63.7	65.6	87.0	89.1	90.4
Hydrogen reduction of milled UO_3 at 700°C	60.5	62.9	64.1	88.6	89.5	91.6
Hydrogen reduction of milled UO_3 at 580°C	62.0	64.0	65.6	89.9	91.0	92.0
Cracked ammonia reduction of UO_3 (MCW)	59.5	63.8	--	72.0	72.7	--
Hydrogen reduction of dry milled UO_3	58.0	60.8	62.4	83.5	85.0	87.4
Microatomized MCW UO_2	63.1	65.8	66.4	85.2	86.0	86.5
Micronized MCW UO_2	61.7	63.4	65.0	88.1	87.4	89.2
Micronized MCW UO_2	62.4	65.4	67.2	87.8	88.4	90.7
Hydrogen reduction of H_2SO_4 milled UO_3	52.5	55.9	--	--	88.7	90.8
Wet ball-milled MCW UO_2	62.1	64.6	65.5	86.7	90.5	89.7
Hydrogen reduction of micronized UO_3	54.7	56.6	--	91.9	92.4	--
Micronized MCW UO_2	63.1	65.3	65.5	94.8	94.4	95.1

* 15 hr at 1550°C in H_2

TABLE II (Continued)
EFFECT OF COLD-PRESSING PRESSURE

Method of Preparation	As-Pressed Density (% T. D.)			Sintered Density (% T. D.)*		
	19.5 tsi	35 tsi	50 tsi	19.5 tsi	35 tsi	50 tsi
Direct hydrogen reduction of uranyl oxalate	65.6	68.6	--	80.6	81.0	--
Air pyrolysis of uranyl oxalate to U_3O_8 ; H_2 reduction	56.2	60.1	--	80.1	84.3	92.1
Air pyrolysis of uranium peroxide to U_3O_8 ; H_2 reduction	57.2	60.2	62.2	75.9	80.1	81.8
Direct hydrogen reduction of uranium peroxide	57.9	60.5	62.4	76.5	80.5	82.0
Direct hydrogen reduction of uranium peroxide	52.3	55.1	57.9	80.3	85.5	85.7
Air pyrolysis of urea precipitated diuranate to U_3O_8 ; H_2 reduction	59.4	62.3	64.4	74.0	78.5	79.4
Direct hydrogen reduction of ammonia precipitated diuranate	51.4	52.7	55.7	--	82.6	84.8
Direct hydrogen reduction of urea precipitated diuranate	49.3	51.5	--	--	84.8	87.9
Pyrolysis of ammonium hydroxide precipitated diuranate to U_3O_8 ; H_2 reduction	54.0	57.1	60.3	87.3	87.9	92.4
Pyrolysis of ammonium hydroxide precipitated diuranate to U_3O_8 ; H_2 reduction	51.3	55.5	68.5	--	86.0	--
Direct hydrogen reduction of ammonium hydroxide precipitated diuranate	50.9	54.4	57.6	--	90.3	91.5
Pyrolysis of carbonate precipitated diuranate to U_3O_8 ; H_2 reduction	53.2	56.9	60.0	88.8	90.0	91.8
Pyrolysis of urea precipitated diuranate to U_3O_8 ; H_2 reduction	51.6	55.2	57.8	89.1	91.4	92.4
Pyrolysis of ammonia precipitated diuranate to U_3O_8 ; H_2 reduction	51.5	53.5	55.6	92.0	92.0	93.3

* 15 hr at 1550° C in H_2

powder the higher the pressing pressure, the higher were the green and sintered densities (Refs 21, 22, and 27). While a small average particle size is necessary for good sintering characteristics, this relation is reversed for the pressing characteristics of UO_2 powders. The experimental evidence in Table II in most cases indicates a decrease of green density with decreasing particle size (Ref 21). This lower green density is due to a higher porosity—that is, a greater number of cavities or voids in the compact. However, the average size of these pores will be smaller in tablets made from small powder particles and will therefore be easier to eliminate by sintering (Refs 7, 22, and 30).

The effect of sintering time and atmosphere at constant temperature is shown in Table III. As would be expected, the density and, consequently, the shrinkage increase with sintering time (Table III) and temperature (Table I) (Refs 19–22 and 26). At a constant pressing pressure (35 tsi), the higher the green density of the tablets, the slower was the rate of densification and shrinkage and the smaller was the actual shrinkage and final density on sintering (Refs 21, 22, and 28). Again the higher rate of shrinkage and sintering with decreasing particle size is the result of pore size and distribution. Since cohesion and shrinkage forces during sintering effect the closing of only the smaller pores, the maximum pore size is usually more important than the total amount of porosity in determining the final density of a compact on sintering (Refs 30 and 31).

Additional information on the pore size and distribution of pressed and sintered UO_2 compacts was obtained from high pressure mercury porosimetry (Ref 7). The volume of mercury absorbed by the UO_2 under a known pressure is measured and pore size distribution curves constructed from the volume measurements. Pore size distribution curves for compacts obtained from three different UO_2 powders are shown in Fig. 8. The

wide variation in compact pore size distribution is due to differences in the parent powder particle size. Ball-milled Mallinckrodt UO_2 with a very small particle size has smaller pores distributed much more uniformly than the coarse Mallinckrodt oxide. Measurements on hydrogen sintered UO_2 compacts indicate a direct correlation between sintering rate and pore size. The UO_2 powder having the highest sintering rate (milled Mallinckrodt oxide) contained the largest volume of small pores. The other two powders contained pores of larger diameter, and their sintering rates were correspondingly lower.

Fig. 8 Effect of Powder Preparation on the Pore Size Distribution of UO_2 Compacted to 65% of TD.

Returning to the data in Table III, it is seen that in many cases higher sintered densities were attained in an argon atmosphere (these densities have not been corrected for any excess oxygen). Other workers have reported greater densification of UO_2 compacts in inert gas than in reducing atmospheres (Refs 14–17 and 26). It has been postulated (Refs 14–17) that the superior sintering of UO_2 bodies in inert gas and steam atmospheres is mainly due to the presence of excess oxygen in the UO_2 lattice. The beneficial effect of the additional oxygen is also believed to result from the increased plasticity of UO_{2+x} compared with $\text{UO}_{2.0}$ (Ref 26).

SUMMARY

The sintering behavior of some 35 well-characterized UO_2 powders is related to their

TABLE III
EFFECT OF SINTERING TIME AND ATMOSPHERE

Method of Preparation	As-Pressed Density (% T. D.) 35 Tsi	Sintered Density (% T. D.)*			
		Hydrogen			Argon
		5m	1 hr	15 hr	15 hr
High pressure steam oxidation of uranium	69.1	70.0	74.3	75.8	76.5
Hydrided-steam oxidation of uranium	64.6	68.9	78.3	80.6	79.1
Air pyrolysis of U metal to U_3O_8 ; H_2 reduction	64.5	69.7	74.0	75.9	81.3
Air pyrolysis of UNH to U_3O_8 ; H_2 reduction	63.3	67.8	71.9	75.7	82.4
Cracked ammonia reduction of UO_3 (MCW)	63.8	66.4	70.9	72.7	81.1
Hydrogen reduction of $UO_3 \cdot 2H_2O$	59.7	63.4	71.6	74.9	84.4
Fluidized bed denitration & UO_3 reduction	59.3	72.2	79.6	80.9	72.4
Hydrogen reduction of milled UO_3 at 920°C	61.2	70.7	77.2	83.7	90.0
Hydrogen reduction of milled UO_3 at 800°C	60.8	70.3	82.7	85.0	87.8
Hydrogen reduction of milled UO_3 at 480°C	62.7	78.2	87.8	89.5	92.5
Hydrogen reduction of milled UO_3 at 700°C	63.7	80.6	86.8	89.1	81.4
Hydrogen reduction of milled UO_3 at 580°C	64.0	81.6	89.4	91.0	92.6
Cracked ammonia reduction of UO_3 (MCW)	63.8	66.4	70.9	72.7	81.1
Hydrogen reduction of dry milled UO_3	60.8	70.3	82.7	85.0	87.8
Microatomized MCW UO_2	65.8	73.2	84.5	86.0	93.4
Micronized MCW UO_2	63.4	75.4	85.1	87.4	87.5
Micronized MCW UO_2	65.4	74.5	82.0	88.4	93.9
Hydrogen reduction of H_2SO_4 milled UO_3	55.9	68.6	83.7	88.7	85.9
Wet ball-milled MCW UO_2	64.6	75.0	85.5	90.5	94.3
Hydrogen reduction of micronized UO_3	56.6	76.8	91.2	92.4	--
Micronized MCW UO_2	65.3	81.1	92.7	94.4	91.3

* 35 tsi; 1550°C

TABLE III (Continued)
EFFECT OF SINTERING TIME AND ATMOSPHERE

Method of Preparation	As-Pressed Density (% T. D.) 35 Tsi	Sintered Density (% T. D.)*			
		Hydrogen			Argon
		5m	1 hr	15 hr	15 hr
Direct hydrogen reduction of uranyl oxalate	68.6	74.7	81.1	81.0	84.2
Air pyrolysis of uranyl oxalate to U_3O_8 ; H_2 reduction	60.1	78.5	82.9	84.3	--
Air pyrolysis of uranium peroxide to U_3O_8 ; H_2 reduction	60.2	68.4	76.9	80.1	85.7
Direct hydrogen reduction of uranium peroxide	60.5	70.0	75.2	80.5	85.2
Direct hydrogen reduction of uranium peroxide	55.1	69.5	80.0	85.5	88.3
Air pyrolysis of urea precipitated diuranate to U_3O_8 ; H_2 reduction	62.3	66.2	73.5	78.5	80.2
Direct hydrogen reduction of ammonia precipitated diuranate	52.7	69.7	79.8	82.6	77.5
Direct hydrogen reduction of urea precipitated diuranate	51.5	59.6	83.6	84.8	--
Pyrolysis of ammonium hydroxide precipitated diuranate to U_3O_8 ; H_2 reduction	57.1	69.9	80.2	87.9	90.8
Pyrolysis of ammonium hydroxide precipitated diuranate to U_3O_8 ; H_2 reduction	55.4	83.8	86.0	87.8	83.0
Direct hydrogen reduction of ammonium hydroxide precipitated diuranate	54.4	76.2	89.7	90.3	81.5
Pyrolysis of carbonate precipitated diuranate to U_3O_8 ; H_2 reduction	56.9	69.1	89.2	90.0	91.1
Pyrolysis of urea precipitated diuranate to U_3O_8 ; H_2 reduction	55.2	81.6	90.1	91.4	93.2
Pyrolysis of ammonia precipitated diuranate to U_3O_8 ; H_2 reduction	53.5	87.4	91.1	92.0	78.4

* 35 tsi; 1550°C

NOTE: The furnaces were idled at 1200°C. The UO_2 tablets were pushed into the hot zone at a slow constant rate, heated to 1550°C, and held at that temperature for the desired period of time.

preparation method, surface texture, particle size, and shape. Although they had lower initial green densities, tablets made from smaller rougher powder particles sintered best. The small particles packed together tightly and yielded a compact with small uniform pores which were more easily eliminated on sintering. The sintered density is also strongly dependent on aggregate size and distribution.

Both density and shrinkage increase with increasing sintering temperature and time. A higher rate of shrinkage and sintering was found for the finer powders. Pore size in the compact is more important than the total amount of porosity in determining the final sintered density of a UO_2 body.

Sinterability is not a function of powder fluid density—that is, a low density powder can sinter well, and a high density powder can sinter poorly. For a given type of UO_2 preparation, the powders with the lower bulk densities generally sintered best, probably because of their smaller particle size. In many cases higher sintered densities were attained in an argon atmosphere than in hydrogen.

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REFERENCES

1. F. H. Gunzel, Jr. and W. A. Lambertson, "Urania Bodies: Fired Density vs Particle Size," ANL-5094 (August 1954).
2. A. G. Allison and W. H. Duckworth, "Ceramic Investigation of Uranium Dioxide," BMI-1009 (June 16, 1955).
3. J. Glatter, H. R. Hoge, and B. E. Schaner, "The Fabrication of Dense UO_2 Cylindrical Compacts by Cold Pressing and Sintering," WAPD-126 (October 14, 1955).
4. M. D. Burdick and H. S. Parker, "Effect of Particle Size on Bulk Density and Strength Properties of Uranium Dioxide Specimens," J. Am. Ceram. Soc., Vol 39 (1956), pp 181-187.
5. W. A. Lambertson and J. H. Handwerk, "The Fabrication and Physical Properties of Urania Bodies," ANL-5053 (February 1956).
6. H. G. Soman and G. L. Ploetz, "An Investigation of the Sintering of Uranium Dioxide," KAPL-1556 (August 17, 1956).
7. J. Belle and B. Lustman, "Properties of UO_2 ," WAPD-184 (September 1957).
8. D. R. Stenquist, B. Mastel, and R. J. Anicetti, "Correlation of Surface Characteristics with the Sintering Behavior of Uranium Dioxide Powders," HW-51712 (July 25, 1957).
9. E. A. Evans, et al., "Fabrication and Enclosure of Uranium Dioxide," TID-7546, Book 2 (March 1958), pp 414-431.
10. L. C. Watson, "The Production of UO_2 for Ceramic Fuels," TID-7546, Book 2 (March 1958), pp 384-401.
11. D. R. Stenquist and R. J. Anicetti, "Fabrication Behavior of Some Uranium Dioxide Powders," HW-51748 (December 1, 1957).
12. D. A. Vaughan, J. R. Bridge, A. G. Allison, and C. M. Schwartz, "Processing Variables, Reactivity, and Sinterability of Uranium Oxides," Ind. Eng. Chem., Vol 49 (1957), pp 1699-1700.
13. D. R. Stenquist, B. Mastel, and R. J. Ancetti, "Note on Correlation of Surface Characteristics of Uranium Dioxide Powders with Their Sintering Behavior," J. Am. Ceram. Soc., Vol 41 (1958), pp 273-274.
14. J. Williams, E. Barnes, R. W. Thackray, and P. Murray, "The Nonstoichiometric Oxides of

- Uranium," Trans. Brit. Ceram. Soc., Vol 56 (1957), pp 608-623.
15. A. H. Webster and N. F. H. Bright, "The Effects of Furnace Atmospheres of the Sintering Behavior of Uranium Dioxide," NP-6667 (February 5, 1958).
 16. P. Murray, S. F. Pugh, and J. Williams, "Uranium Dioxide as a Reactor Fuel," TID-7546, Book 2 (March 1958), pp 432-441.
 17. C. A. Arenberg and P. Jahn, "Steam Sintering of Uranium Dioxide," J. Am. Ceram. Soc., Vol 41 (1958), pp 179-183.
 18. R. Kiessling and U. Runfors, "Sintering of Uranium Dioxide," TID-7546, Book 2 (March 1958), pp 402-413.
 19. U. Runfors, N. Schonberg, and R. Kiessling, "The Sintering of Uranium Dioxide," Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, Vol 6 (1958), pp 605-611.
 20. J. Terraza, J. Cerrolaza, and E. A. Aparicio, "Sintering UO_2 at Medium Temperatures," Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, Vol 6 (1958), pp 620-623.
 21. G. H. Chalder, N. F. H. Bright, D. L. Paterson, and L. C. Watson, "The Fabrication and Properties of UO_2 Fuel," Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, Vol 6 (1958), pp 590-604.
 22. G. H. Chalder, "Fuel Fabrication Studies Related to the N.P.D. Reactor," CRFD-758 (June 1959).
 23. A. Bel and Y. Carteret, "Contribution to the Study of the Sintering of Uranium Oxide," Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, Vol 6 (1958), pp 612-619.
 24. A. Bel, B. Francois, R. Delmas, and R. Caillat, "Frittage d'oxyde d'uranium de Surface Specifique Elevee," Compt. rend., Vol 249 (1959), pp 1045-1047.
 25. A. Bel, R. Delmas, and B. Francois, "Frittage de l'oxyde d'uranium dans l'hydrogene a $1350^\circ C$," J. Nuclear Materials, Vol 1 (1959), pp 259-270.
 26. J. Williams, E. Barnes, R. Scott, and A. Hall, "Sintering of Uranium Oxides of Composition UO_2 to U_3O_8 in Various Atmospheres," J. Nuclear Materials, Vol 1 (1959), pp 28-38.
 27. W. G. Carlson, H. D. Root, and R. S. Shane, "Pressure-Temperature-Density Relationships in Several Samples of UO_2 ," Bull. Am. Ceram. Soc., Vol 39 (1960), pp 69-73.
 28. W. T. Bourns, L. C. Watson, E. Yatabe, and A. R. Bancroft, "Preparation of Uranium Dioxide for Use in Ceramic Fuels," CRCE-716 (1958), Parts I-III.
 29. B. E. Schaner, "The Fabrication of High Density UO_2 Fuel Platelets," Bull. Am. Ceram. Soc., Vol 38 (1959), pp 494-498.
 30. P. Schwarzkopf, Powder Metallurgy, Its Physics and Production (New York: MacMillan Co., 1947).
 31. C. G. Goetzel, Treatise on Powder Metallurgy, Vol I (New York: Interscience Publishers, Inc., 1949).
 32. J. C. Clayton and S. Aronson, "Some Preparation Methods and Physical Characteristics of UO_2 Powders," WAPD-178 (December 1958).

This work was performed to determine changes which occur in the tensile properties of Zircaloy-2 at various stages of fabrication from ingot to cold rolled strip. Material size, test direction, and the effect of round and flat specimens on the tensile properties were studied at both room temperature and 600°F. It was found that the type of specimen had little effect on the strength properties but did influence ductility; both size of material and test direction influenced the results of strength measurements.

A STUDY OF THE TENSILE PROPERTIES OF ZIRCALOY-2 AT VARIOUS STAGES OF FABRICATION

J. G. Goodwin

Zircaloy-2 is used for structural components as well as for cladding components in many nuclear reactors. The quantity of Zircaloy-2 used for structurals is small in comparison with that used for cladding; as a result tensile property data for sizes greater than about 0.2 in. are sparse in comparison with data available for sizes less than 0.2 in. in thickness. Knowledge of the tensile properties expected of larger sections of Zircaloy-2 is quite important to ensure the proper dimensional design of structural components.

Tensile property data for Zircaloy-2 of various sizes obtained at Bettis and from core contractors during the latter part of 1959 and early 1960 indicated differences in the tensile properties which were related to the amount of fabrication which had been performed on the ingot. There were insufficient data available to reliably determine the relationship of tensile properties to the amount of reduction from the ingot stage. A large number of material deviation notices for low elongation and low yield strength had been received from the core contractors with their general comment that the tensile properties of large-sized fabricated sections were lower than those of strip products. The question

arose as to whether or not the tensile property values specified for wrought products in MIL-Z-19859A were realistic for sections with a thickness greater than 0.2 in. since the specification values were determined from data obtained from strip products.

To answer this question, an experimental study was performed in which tensile properties were determined for a Zircaloy-2 ingot at various stages of fabrication. The resulting data were statistically analyzed to determine if differences existed in the tensile properties of Zircaloy-2 at various sizes from cast ingot through cold rolled strip.

PROCEDURE

A 16-in. diam, production-size, vacuum melted ingot was utilized for this study. The fabrication procedure shown in Table I was followed. Samples for longitudinal and transverse testing were removed at each stage of fabrication shown, and sufficient material was removed to permit the machining of both round and flat tensile specimens wherever possible. With the exception of the cold rolled specimens which were annealed for 1 hr at 1450°F in vacuo, all specimens were annealed in air for 15 min at 1550°F prior to machining. This

TABLE I
GENERAL FABRICATION OUTLINE FOR ZIRCALOY-2

Item	Fabrication
1. 16-in diam ingot	Heated at 1750°F for 3-1/2 hr; press forged to 6 x 8 in. x length; conditioned by grit blasting and grinding
2. 6 x 8-in. forged bar	Heated at 1700°F for 2-1/2 hr; hammer forged to 2 x 8 in. x length; conditioned
3. 2 x 8-in. forged bar	Heated at 1550°F for 1 hr; hot rolled to 1 x 8 in. x length; conditioned
4. 1-in. thick hot rolled strip	Heated at 1550°F for 20 min; hot rolled to 1/2 x 8 in. x length; conditioned
5. 1/2-in. thick hot rolled strip	Heated at 1550°F for 15 min; hot rolled to 1/4 x 8 in. x length; conditioned
6. 1/4-in. thick hot rolled strip	Heated at 1550°F for 10 min; hot rolled to 1/8 x 8 in. x length; conditioned
7. 1/8-in. thick hot rolled strip	Cold rolled to 0.100 x 8 in. x length
8. 0.100-in. thick cold rolled strip	Cold rolled to 0.050 x 8 in. x length
9. 0.050-in. thick cold rolled strip	Cold rolled to 0.025 x 8 in. x length
10. 0.025-in. thick cold rolled strip	

NOTE: Samples from Items 1 through 7 were annealed in air at 1550°F for 15 min and samples from Items 8 through 10 were annealed in vacuo at 1450°F for 1 hr.

practice was intended to duplicate as closely as possible current mill practice.

The forging operations were performed using commercial facilities, and the hot and cold rolling operations were performed using laboratory facilities. Tensile tests were performed at both room temperature and 600°F. Three specimens were tested for each combination of size, temperature, and specimen type. Figure 1 illustrates the type of specimens employed.

All H-type specimens were 0.050 in. thick with the exception of those from the 0.025-in. thick material; all F-type specimens were 0.150 in. thick except for material less than 1/4 in. thick. The F-type specimens from the 1/8-in. thick material were 0.100 in. thick and those from cold rolled strip were the same size as the strip.

RESULTS

Tables II and III present the results of the tensile tests. The standard deviation associated with each

Fig. 1 (A) Standard Round Tensile Specimen; (B) Standard Elevated Temperature Flat Tensile Specimen; (C) Standard Flat Tensile Specimen. All Dimensions in Inches.

of the properties measured is presented in Table IV. Figures 2 through 17* illustrate various methods for comparing the data. Analysis of the data was done by both statistical and engineering methods. The statistical evaluation is not reported herein because in many instances differences which were statistically significant but not physically significant were obtained. Interpretation of the results from an engineering viewpoint is presented in the following paragraphs.

Round vs Flat Specimens

A comparison of round vs flat specimens was made for the sizes from ingot through 1/4-in.

thick material. A comparison below this point was not made because of the difficulty in obtaining suitable round specimens.

Yield Strength

Between the 2 x 8-in. bar and the 1/4-in. thick plate there was no significant difference between round and flat specimens when tested in the longitudinal direction at room temperature. The ingot and 6 x 8-in. forged bar, room temperature tests gave yield strengths about 5000 psi higher for flat specimens when compared with round specimens (Fig. 2).

For transverse specimens tested at room temperature there was no significant difference between the yield strength of round and flat specimens at any size (see Fig. 4). The same statement is true for the tests conducted at 600°F (Fig. 5).

*Figures 2 through 17 can be found at the end of this article. The points on the graphs (Figs. 2-17) are connected to indicate trends; however it is not intended that properties for sizes intermediate between those reported should be obtained by interpolation.

TABLE II

AVERAGE TENSILE PROPERTIES FOR ZIRCALOY-2 TESTED AT ROOM TEMPERATURE
(SPECIMENS OBTAINED AT DIFFERENT STAGES OF FABRICATION)

Item		Type of Sample*	Transverse				Longitudinal			
			0.2% Y.S. (1000 psi)	U. T. S. (1000 psi)	Elong (%)	Red. of Area (%)	0.2% Y.S. (1000 psi)	U. T. S. (1000 psi)	Elong (%)	Red. of Area (%)
Round Specimens										
1.	Ingot	R-1	53.4	67.6	19.3	26.0	52.9	67.9	17.8	22.0
2.	6 x 8 in. forged bar	R-1	60.1	71.1	26.3	37.9	49.9	70.3	23.7	32.3
3.	2 x 8 in. forged bar	R-1	56.3	66.7	26.0	55.9	45.7	67.4	22.2	53.6
4.	1 in. thick hot rolled strip	R-1	53.1	66.0	25.8	46.4	49.7	66.8	25.7	51.6
5.	1/2 in. thick hot rolled strip	R-3	52.9	69.0	27.7	44.3	48.7	71.1	26.7	38.6
6.	1/4 in. thick hot rolled strip	R-5	55.3	69.7	24.0	37.3	48.5	74.1	26.0	34.5
Flat Specimens										
1.	Ingot	F-1	49.1	68.8	19.5	23.9	56.9	68.3	20.3	22.0
2.	6 x 8 in. forged bar	F-2	62.1	70.5	28.6	39.5	55.4	71.6	25.0	35.4
3.	2 x 8 in. forged bar	F-1	57.1	67.4	32.0	40.0	45.1	71.0	22.3	35.3
4.	1 in. thick hot rolled strip	F-1	52.8	66.3	27.8	42.0	48.4	67.0	26.8	38.8
5.	1/2 in. thick hot rolled strip	F-1	55.1	66.8	27.7	43.4	46.9	69.0	24.5	39.4
6.	1/4 in. thick hot rolled strip	F-1	53.8	69.0	28.3	46.8	46.1	70.2	25.2	42.2
7.	1/8 in. thick hot rolled strip	F-1	54.8	68.6	27.0	50.6	50.0	73.5	26.8	42.6
8.	0.100 in. thick cold rolled strip	F-1	52.3	66.7	27.0	55.5	47.9	69.7	27.8	47.4
9.	0.050 in. thick cold rolled strip	F-1	47.8	65.8	27.0	51.8	44.8	69.5	28.0	45.6
10.	0.025 in. thick cold rolled strip	F-1	46.3	65.4	27.2	53.7	43.9	69.5	28.7	46.5

*Type of sample refers to tensile test specimen shown in the referenced figure.

Specimen	Figure No.
R-1	1A
R-3	1A
R-5	1A
H-1	1B
H-2	1B
F-1	1C
F-2	1C

TABLE III

AVERAGE TENSILE PROPERTIES FOR ZIRCALOY-2 TESTED AT 600°F
(SPECIMENS OBTAINED AT DIFFERENT STAGES OF FABRICATION)

Item	Type of Sample*	Transverse				Longitudinal			
		0.2% Y.S. (1000 psi)	U. T. S. (1000 psi)	Elong (%)	Red. of Area (%)	0.2% Y.S. (1000 psi)	U. T. S. (1000 psi)	Elong (%)	Red. of Area (%)
Round Specimens									
1. Ingot	R-1	18.8	28.8	30.8	61.8	18.8	30.0	30.7	59.8
2. 6 x 8 in. forged bar	R-1	24.6	33.7	31.0	65.7	15.8	32.6	39.8	66.6
3. 2 x 8 in. forged bar	R-1	20.2	30.1	33.8	66.1	15.7	30.6	33.5	70.0
4. 1 in. thick hot rolled strip	R-1	18.1	28.9	35.5	70.8	16.8	29.5	35.8	64.6
5. 1/2 in. thick hot rolled strip	R-3	19.6	30.8	42.3	66.8	16.9	31.4	39.0	69.5
6. 1/4 in. thick hot rolled strip	R-5	21.2	30.5	34.0	67.1	23.8	33.6	36.0	72.2
Flat Specimens									
1. Ingot	H-1	20.2	30.5	26.8	46.3	19.8	29.8	32.0	42.5
2. 6 x 8 in. forged bar	H-2	23.4	32.9	33.0	49.8	22.7	32.9	40.3	52.1
3. 2 x 8 in. forged bar	H-1	19.5	29.4	40.3	53.7	17.0	28.3	33.5	67.6
4. 1 in. thick hot rolled strip	H-1	19.5	29.4	42.0	67.2	17.6	29.6	38.7	63.4
5. 1/2 in. thick hot rolled strip	H-1	19.9	30.6	40.3	67.0	18.0	31.3	38.0	61.0
6. 1/4 in. thick hot rolled strip	H-1	19.8	30.4	41.8	69.5	17.2	31.9	39.0	64.0
7. 1/8 in. thick hot rolled strip	H-1	22.0	32.8	37.5	67.3	20.4	33.6	36.7	62.4
8. 0.100 in. thick cold rolled strip	H-1	19.7	28.5	50.3	79.4	18.1	31.2	49.2	75.7
9. 0.050 in. thick cold rolled strip	H-1	20.6	28.0	49.3	81.7	21.0	31.9	49.3	76.6
10. 0.025 in. thick cold rolled strip	H-1	20.8	27.4	48.8	80.8	21.0	31.3	46.7	74.9

*Type of sample refers to tensile test specimen shown in the referenced figure.

Specimen	Figure No.
R-1	1A
R-3	1A
R-5	1A
H-1	1B
H-2	1B
F-1	1C
F-2	1C

TABLE IV
ESTIMATED STANDARD DEVIATIONS FOR THE VARIOUS TENSILE PROPERTIES MEASURED

	Longitudinal		Transverse	
	Room Temp	600°F	Room Temp	600°F
Yield strength (psi)	950	1410	960	600
UTS (psi)	900	740	660	570
Elongation (%)	0.9	2.7	1.9	1.9
Red. of Area (%)	3.3	3.2	2.4	5.8

Longitudinal specimens tested at 600°F gave significantly different results for round and flat specimens at the 6 x 8-in. size and at the 1/4-in. size (Fig. 3). Round and flat specimens for the other sizes did not produce significantly different yield strength values.

Ultimate Strength

There was no significant difference between the ultimate strengths attributable to the use of round or flat specimens. Specifically, there was no significant difference between the longitudinal ultimate strength of round and flat specimens tested at room temperature (see Fig. 2). There was no significant difference between the transverse ultimate strength of round and flat specimens tested at room temperature (see Fig. 4). Similar statements are true for tests conducted at 600°F (see Figs. 3 and 5).

Elongation

There was no significant difference between the elongation of longitudinal round and flat specimens tested at room temperature (see Fig. 6). The same is true for longitudinal specimens tested at 600°F (see Fig. 7).

With the exception of the elongation of the 2 x 8-in. forged bar, there was no significant difference between the elongation of transverse round and flat specimens tested at room temperature. The elongation of the flat specimen from the 2 x 8-in. forged bar was about 6% higher than the average value for

the round specimens (see Fig. 8). At 600°F there was a significant difference between the transverse elongation of round and flat specimens. In general, the elongation of the flat specimens was equal to or higher than the values obtained from the round specimens (see Fig. 9).

Reduction of Area

There was a significant difference in the reduction of area of longitudinal round and flat specimens tested at room temperature (see Fig. 6). The same was true for transverse room temperature tests (see Fig. 8) and for longitudinal and transverse 600°F tests (see Figs. 7 and 9). The room temperature tests showed the reduction of area to be the same for round and flat specimens at the ingot, 6 x 8-in., and 1/2-in. stages; between the 6 x 8-in. and 1/2-in. size the round specimens gave considerably higher values, whereas below 1/2 in. it appears that the flat specimens gave the higher values. For the 600°F tests the round specimens gave reduction of area values either equal to or, in most cases, higher than those obtained from flat specimens.

Longitudinal vs Transverse Specimens

Yield Strength

There was a significant difference between the yield strength of flat longitudinal and transverse specimens tested at room temperature (see Fig. 10). With the exception of specimens taken from the

ingot, the transverse specimens gave the higher values. The same was true for tests conducted with flat specimens at 600°F, although the difference between directions was not so great as at room temperature (see Fig. 11). The room temperature and 600°F tests of round specimens showed a significant difference between longitudinal and transverse yield strength values with the transverse values being the higher (see Figs. 12 and 13). There was a very marked difference at the 6 x 8-in. and 2 x 8-in. sizes. This difference diminished at the lesser sizes and was nonexistent at the ingot stage.

Ultimate Strength

There was little difference between the ultimate strength of flat longitudinal and transverse specimens tested at room temperature, although Fig. 10 indicates that the longitudinal specimens were generally the higher of the two. At 600°F this was true for sizes through 1/8 in., but below that size there was a significant difference between the ultimate strengths of longitudinal and transverse specimens, with the longitudinal values being considerably higher than the transverse ones (see Fig. 11).

The ultimate strengths of round specimens tested at room temperature (see Fig. 12) or 600°F (see Fig. 13) showed no differences which were attributable to the direction from which the sample was obtained for sizes from ingot through 1/2 in. in thickness. At the 1/4-in. size the longitudinal values for both the room temperature and 600°F tests were higher than the corresponding transverse values.

Elongation

With the exception of the 2 x 8-in. size, there was no significant difference between the longitudinal and transverse elongation values of flat specimens tested at room temperature (see Fig. 14). The transverse value at the 2 x 8-in. size was approximately 10% higher than the longitudinal value. The curve in Fig. 15 shows that at 600°F and

sizes of 1 in. and lower there was no significant difference between the elongation of flat longitudinal and transverse specimens, whereas above 1 in. there were significant differences.

The elongation values of round specimens tested at room temperature showed no differences which could be attributed to the direction from which the test specimen was obtained (see Fig. 16). The same was true for round specimens tested at 600°F with the exception of the 6 x 8-in. size where the longitudinal value was about 9% higher than the transverse value (see Fig. 17).

Reduction of Area

With the exception of specimens from the ingot, there was a significant difference in the reduction of area of flat longitudinal and transverse specimens when tested at room temperature (see Fig. 14). The reduction of area for the transverse specimens was the higher in all cases with the noted exception. At 600°F there was a significant difference between the reduction of area of flat longitudinal and transverse specimens (see Fig. 15). At sizes of 1/2 in. or less the transverse values were greater than the longitudinal values; at sizes greater than 1/2 in. the transverse values were approximately equal to or less than (note the 2 x 8-in. size in Fig. 15) the longitudinal values.

There was no significant difference between the longitudinal and transverse reduction of area for round specimens tested at room temperature (see Fig. 16); the same was true for round specimens tested at 600°F (see Fig. 17).

Effect of Material Thickness (Fabrication Stage)

Yield Strength

The yield strength of longitudinal flat specimens was not influenced by material thickness at sizes of 2 x 8 in. or less when tested at room temperature (see Fig. 2). Samples from the 6 x 8-in. and ingot material had significantly higher yield strengths. The yield strength of longitudinal round specimens

tested at room temperature was not affected by material size; however, the ingot gave higher than average values (see Fig. 2). When tested at 600°F, similar specimens showed an effect of material size (see Fig. 3). With the exception of the material at the 1/4-in. thick size, there was no effect of material thickness for round specimens. Flat tensile specimens from material from 2 x 8 in. through 1/2-in. thickness exhibited average yield strengths which were about 2000 psi less than those of the other sizes.

Flat transverse specimens indicated significantly lower yield strengths for material less than 0.1 in. when tested at room temperature; flat specimens from the 6 x 8-in. thick material had significantly higher yield strength values than did specimens from the other sizes (see Fig. 4). Round transverse specimens showed an influence of material thickness only at the 6 x 8-in. size (see Fig. 4). At 600°F, both round and flat transverse 6 x 8-in. size specimens showed a significant difference from the other sizes (see Fig. 5).

Ultimate Strength

There did not appear to be a significant difference in the room temperature ultimate strength of the flat or round longitudinal specimens which was attributable to material size (see Fig. 2); however, the round specimens from the 1/4-in. thick material averaged slightly high. At 600°F material size did not appear to influence the ultimate strength, although the point scatter was somewhat high (see Fig. 3).

Material size showed no apparent effect on the ultimate strength of flat or round transverse specimens tested at room temperature (see Fig. 4). Testing at 600°F indicated a physically significant rise in the ultimate strength for both round and flat transverse specimens from the 6 x 8-in. size material; it also indicated a significant lowering of the ultimate strength in sizes of 0.1 in. and less (see Fig. 5).

Elongation

Material size did not cause a significant difference in elongation for longitudinal round or flat specimens taken from fabricated shapes and tested at room temperature (see Fig. 6). The nonfabricated ingot specimens exhibited lower elongation values than did the fabricated shapes (see Fig. 6). There was a trend showing increasing elongation with decreasing thickness (see Fig. 6). At 600°F, the flat specimens showed significantly higher elongation at sizes of 0.1 in. or less and significantly lower elongation in the ingot state than in the other fabricated forms (see Fig. 7).

With the exception of the ingot stage which exhibited low elongation, the transverse round or flat specimens tested at room temperature showed no effect of material size on elongation (see Fig. 8). When tested at 600°F, flat transverse specimens from the ingot and 6 x 8-in. forged bar gave low elongation values, and flat transverse specimens from the strip 0.1 in. thick and less produced significantly higher elongation values than the samples from the other sized material (see Fig. 9). Round transverse specimens indicated an increasing elongation with decreasing size when tested at 600°F (see Fig. 9).

Reduction of Area

Flat longitudinal or transverse specimens tested at room temperature showed a significant increase in reduction of area with decreasing thickness (see Figs. 6 and 8); round longitudinal or transverse specimens showed the reduction of area increasing with decreasing material thickness, reaching a maximum at the 2 x 8-in. size and then decreasing with decreasing material thickness. When tested at 600°F, flat longitudinal specimens had significantly lower reduction of area at the ingot and 6 x 8-in. sizes and significantly higher values at sizes of 0.1 in. or less (see Fig. 7). The round specimens tested at 600°F showed no significant effect of size on reduction of area except at the ingot stage where

the value appeared to be significantly lower than the values for the other sizes (see Fig. 7).

Flat transverse specimens tested at 600°F showed generally increasing reduction of area with decreasing thickness (although it may be noted in Fig. 9 that for sizes of 1 through 1/8-in. thick material the reduction of area was essentially the same). Round transverse specimens tested at 600°F exhibited no significant difference in reduction of area attributable to material size (see Fig. 9).

CONCLUSIONS

The ultimate strength of Zircaloy-2 tested at room temperature was not generally influenced by the type of specimen employed (flat or round) or by the stage of fabrication of the material. The longitudinal tests, for the most part, gave slightly higher average values than the corresponding transverse tests. This agrees with work reported by Weinberg (Ref 1) on strip samples from seven different ingots. When testing was performed at 600°F, the same was true for test direction and for type of specimen; however, there did appear to be some influence of stage of fabrication on the ultimate strength. The influence appears to be random in nature, did not occur for any specific sizes, and was not always higher or lower.

The yield strength of Zircaloy-2 tested at room temperature was not influenced by specimen type. It was significantly influenced by the direction from which the specimens were taken and by the stage of fabrication. In general, the larger material sizes (least reduction) exhibited the higher yield strength values as did the transverse specimens. When tested at 600°F, there was a significant influence of type of sample for longitudinal specimens. There was a difference in yield strength at 600°F influenced by specimen direction and by stage of fabrication. The transverse specimens generally produced the higher values; the influence of material size tended to be of a random nature.

The elongation of Zircaloy-2 tested at room temperature was not, in general, influenced by type of specimen or direction of test; however, it was influenced by stage of reduction. The elongation of material from the ingot was significantly lower than for the fabricated shapes. Testing at 600°F showed no influence of specimen type or direction of test but did show a pronounced influence of fabrication stage. There was a trend of higher elongation with decreasing thickness (increased fabrication).

Room temperature tests showed the reduction of area to be influenced by type of specimen, test direction, and fabrication stage. Round specimens generally exhibited higher values than flat ones, and transverse values were generally higher than longitudinal values. The flat specimens showed increasing reduction of area with increasing fabrication; the round specimens reached a maximum at the 2 x 8-in. size and then decreased with increasing fabrication (to 1/4 in. thick). When tested at 600°F the type of specimen employed showed a marked influence on the reduction of area values. The round specimens exhibited the higher values. With the exception of the round specimens tested at 600°F, the reduction of area generally increased with increasing fabrication. The noted exception showed no influence of fabrication stage. Transverse values for reduction of area of flat specimens were higher than the longitudinal values. Round specimens showed no effect of test direction.

SIGNIFICANCE OF RESULTS

The results and conclusions of the experimental work described in the preceding paragraphs demonstrate the effects of different variables on the tensile properties obtained for Zircaloy-2. It was anticipated from previous work that yield strength would be affected by test direction, and this anisotropy was substantiated by the results. Scattered preliminary information obtained from Bettis and from core contractors, which led to initiation of the experiment, indicated that yield strength

and elongation were influenced by the amount of reduction from the ingot stage. This was found to be the extant situation. Although elongation was affected by the stage of fabrication, it was not by type of specimen or by test direction. Reduction of area was affected by test direction, type of specimen, and fabrication stage. The directional effect from preferred orientation was not unexpected; the effect of type of specimen can be explained by the different stresses developed in specimens of different geometries. The effect of fabricated size on the various tensile properties is probably related to the degree of preferred orientation developed during processing. Although specimens were designed as transverse or longitudinal with respect to their direction in the fabricated shape, transverse specimens (or longitudinal specimens) from one size had a different degree of preferred orientation than similar specimens from another size. This degree of preferred orientation and its relationship to tensile properties cannot be established without extensive X-ray work to determine the actual degree of orientation present at each size.* It will suffice to recognize the reason for the differences obtained, to indicate their magnitudes, and to illustrate the trend of the differences as fabrication progresses. The degree of preferred orientation present at any particular size is related to many factors such as rolling temperature, annealing temperature, alloy content, amount of reduction, etc. and therefore can vary a great deal from ingot to ingot and size to size during fabrication.

This experiment was used to estimate the "within-ingot" tensile property variability that occurs in Zircaloy-2 during various stages of reduction when processed as in Table I. It is not proposed that all Zircaloy-2 will behave this way,

*Work of this nature is being conducted at Oak Ridge National Laboratory to determine the effect of fabrication on the preferred orientation of Zircaloy-2 and the effects of the texturing on the mechanical properties of Zircaloy-2.

but it is suggested that most material fabricated according to the general outline of Table I will produce similar results. The tensile property values from another ingot may differ considerably from the numbers presented here, but on a relative basis the changes experienced during fabrication should be similar. Of course, different fabrication procedures are expected to produce different results. The fabrication procedure used for this work was selected because it was representative of one used for Zircaloy-2 at the time the work was performed.

Because of the pronounced effects that test direction, type of specimen, and stage of fabrication have on the various measures of tensile properties for Zircaloy-2, each must be considered when defining specification or design values. In other words, strip tensile properties should not be expected of forged bar and vice versa; the type of specimen employed must be considered as must the direction from which the samples were taken. If each of these items is not considered when evaluating tensile properties, one runs the risk of rejecting good material or, conversely, accepting bad material.

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REFERENCES

1. J. G. Weinberg, "Summary of Mechanical Property Data on Vacuum-Melted Zircaloy-2," Zirconium Highlights, WAPD-ZH-12 (November 1958), p 12.
2. "Metallurgy Division Annual Progress Report for Period Ending September 1, 1959," ORNL-2839 (December 1959).

Fig. 2 Comparison of Yield and Ultimate Strength of Round and Flat-Type Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests Were Conducted at Room Temperature on Longitudinal Specimens. Each Point Is the Average of Three Specimens.

Fig. 3 Comparison of Yield and Ultimate Strength of Round and Flat-Type Tensile Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests Were Conducted at 600°F on Longitudinal Specimens. Each Point Is the Average of Three Specimens.

Fig. 4 Comparison of Yield and Ultimate Strength of Round and Flat-Type Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests were conducted at Room Temperature on Transverse Specimens. Each Point Is the Average of Three Specimens.

Fig. 5 Comparison of Yield and Ultimate Strength of Round and Flat-Type Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests Were Conducted at 600°F on Transverse Specimens.

Fig. 6 Comparison of the Ductility of Round and Flat-Type Tensile Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests Were Conducted at Room Temperature on Longitudinal Specimens. Each Point Is the Average of Three Specimens.

Fig. 7 Comparison of the Ductility of Round and Flat-Type Tensile Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests Were Conducted at 600°F on Longitudinal Specimens. Each Point Is the Average of Three Specimens.

Fig. 8 Comparison of the Ductility of Round and Flat-Type Tensile Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests Were Conducted at Room Temperature on Transverse Specimens. Each Point Is the Average of Three Specimens.

Fig. 9 Comparison of the Ductility of Round vs Flat-Type Tensile Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests Were Conducted at 600°F on Transverse Specimens. Each Point Is the Average of Three Specimens.

Fig. 10 Comparison of Yield and Ultimate Strength of Longitudinal and Transverse Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests Were Conducted at Room Temperature Using Flat Specimens. Each Point Is the Average of Three Specimens.

Fig. 11 Comparison of Yield and Ultimate Strength of Longitudinal and Transverse Specimens at Various Stages of Reduction from Ingot to Cold Rolled Strip. Tests Were Conducted at 600°F Using Flat Specimens. Each Point Is the Average of Three Specimens.

Fig. 12 Comparison of Yield and Ultimate Strength of Longitudinal and Transverse Specimens at Various Stages of Fabrication from Ingot to Cold Rolled Strip. Tests Were Conducted at Room Temperature Using Round Specimens. Each Point Is the Average of Three Specimens.

Fig. 13 Comparison of Yield and Ultimate Strength of Longitudinal and Transverse Specimens at Various Stages of Fabrication from Ingot to Cold Rolled Strip. Tests Were Conducted at 600°F Using Round Specimens. Each Point Is the Average of Three Specimens.

Fig. 14 Comparison of Elongation and Reduction of Area of Longitudinal and Transverse Specimens at Various Stages of Fabrication from Ingot to Cold Rolled Strip. Tests Were Conducted at Room Temperature Using Flat Specimens. Each Point Is the Average of Three Specimens.

Fig. 16 Comparison of Elongation and Reduction of Area of Longitudinal and Transverse Specimens at Various Stages of Fabrication from Ingot to Cold Rolled Strip. Tests Were Conducted at Room Temperature Using Round Specimens. Each Point Is the Average of Three Specimens.

Fig. 15 Comparison of Elongation and Reduction of Area of Longitudinal and Transverse Specimens at Various Stages of Fabrication from Ingot to Cold Rolled Strip. Tests Were Conducted at 600°F Using Flat Specimens. Each Point Is the Average of Three Specimens.

Fig. 17 Comparison of Elongation and Reduction of Area of Longitudinal and Transverse Specimens at Various Stages of Fabrication from Ingot to Cold Rolled Strip. Tests Were Conducted at 600°F Using Round Specimens. Each Point Is the Average of Three Specimens.

In view of the potential savings that can be realized by direct melting hafnium sponge to ingot, thereby eliminating the crystal bar operation, a continuing effort is being expended on evaluating hafnium plate. Preliminary tests were conducted on ten sponge plates to determine whether this material would meet the specifications required for reactor use. Although results showed the test material to be below specification, much was learned, and the tests reported here served to indicate promising areas for product improvement.

MECHANICAL AND PHYSICAL PROPERTIES OF DIRECT MELTED SPONGE HAFNIUM PLATE

E. H. Sayell and W. B. Haynes

Because of increasing demands for hafnium metal, efforts have been made to increase production and reduce processing costs so that present core production schedules can be met at minimum expense and delay.

One of the most promising methods of increasing production and reducing cost has been initiated by the U.S. Bureau of Mines, Albany, Oregon—that of direct melting hafnium sponge to ingot, thereby eliminating the crystal bar operation. The sponge used for this direct melting is made by converting hafnium oxide to the tetrachloride then reducing the fused salt with magnesium and sodium.

The Bureau produced ingots from this sponge by a double consumable oxide melting process. It is necessary to melt the sponge in vacuum to remove the volatile impurities. The sponge for the first consumable melt is pressed into 2 x 2 x 10-in. briquettes at 40 tsi. Briquettes are tack welded end to end to form an electrode which is consumably melted into a 3-in. diam ingot. The 3-in. ingots are scalped, faced, and tack welded end to end to form a final electrode for consumable melting into 5-in. diam ingots weighing 75 lb. The 5-in. ingots are

forged and rolled at 1050°C (1922°F) into 30.25 x 5.25 x 0.290-in. plates.

The material produced by direct melting hafnium sponge is referred to in this paper as sponge plate; that produced by melting crystal bar is referred to as crystal bar plate.

MATERIAL PROCESSING AT BETTIS

Ten plates made by this process were shipped to Bettis for evaluation. Upon receipt at Bettis, each of the plates was radiographed and visually examined for surface defects. Each plate was then hot rolled from 0.290 in. to 0.250 in. at 930°C (1706°F), given a 15-min. furnace anneal after the last pass, and allowed to cool in air prior to sectioning. The 10-in. sections from the ends of each 30-in. plate were machined to 0.200-in. thickness.

Sections of each plate were machined subsequent to a post fabrication heat treatment 1 hr at 700°C (1292°F). Process and test control were maintained by comparing the data with test results obtained from a section of cold rolled reactor grade crystal bar plate.

RESULTS

Preliminary Inspection

Secondary pipe, porosity, seams, cracks, and inclusions were not evident in the radiographs of any sponge plate. Visual examination of the sponge plates showed them to be free of pits and other surface blemishes that might affect mechanical test results. Plate flatness and camber were no problem.

Fabricability

The sponge and crystal bar ingots behaved similarly during forging and hot rolling. Cold rolling, however, split the sponge plate (see Fig. 1) and did not usually affect crystal bar plate.

No cracks were visible on the surface of any of the ruptured plates; however, metallographic examination showed some internal porosity. Figure 2A shows random type voids, and Fig. 2B shows porosity in the form of transgranular and grain boundary stringers.

Fig. 1 Typical Failure Encountered during the Cold Rolling of Direct Melted Sponge Plates. End Crop from Plate 267M after One Cold Roll Pass; 4% Reduction (0.250 In. to 0.241 In.).

A. Hot Rolled to 0.250 In. and Machined to 0.200 In.; Gross Porosity; 250X.

B. Hot Rolled to 0.250 In. and Machined to 0.200 In.; Equiaxed Grains with Pinhole Porosity Both Scattered and Aligned (Stringer-Type Defect that Does Not Follow Grain Boundaries); 250X.

Fig. 2 Porosity in Direct Melted Hafnium Sponge Plate.

Chemical Analyses

The chemical analysis of sponge plate is comparable with that of crystal bar plate with the notable exception of oxygen and nitrogen (see Table I). The oxygen content in crystal bar plate ranges between 300 and 450 ppm while sponge plate had an oxygen content approximately double that level. The nitrogen content of three of the sponge plates approached the maximum specified limit of 100 ppm.

Physical Properties

Corrosion

Corrosion results of sponge specimens tested 14 days in 750°F steam show weight gains comparable with those obtained on crystal bar plate; that is, 4 to 10.9 mg/dm² for crystal bar plate. Iridescent corrosion films, free of unacceptable corrosion products, were observed on all coupons.

Hardness

The average hardness of hot rolled and heat treated (700°C, 1292°F) plate was 57.9 R_a (range 57-60.5). Cold rolled and heat treated (700°C, 1292°F) sponge plate averaged 60.2 R_a (range 58-61.5). The average of cold rolled and heat treated crystal bar plate is 57 R_a (range 54-58 R_a). The specified hardness maximum for crystal bar plate is 58 R_a. The higher hardness recorded for sponge plate was probably due to the high oxygen and/or nitrogen content of the material.

Density

The density of crystal bar plate ranges between 12.90 and 13.00 g/cc. The density of the sponge plates averaged 12.82 g/cc. Samples from two of the plates were found to be below the 12.65-g/cc minimum specified. The microporosity noted in the sponge plates (Fig. 2) could account for the low densities; a study of plate chemistry gave no indication why such low values were obtained.

Weldability

Table II presents a comparison of the weld parameters for sponge vs crystal bar plates.

Grain Size

To determine the effect of heat treatment on sponge plates that were hot rolled from 0.290 in. to 0.250 in. and either machined or cold rolled to 0.220 in., specimens from both types of plate were selected for grain size studies.

No noticeable grain size difference existed between hot rolled sponge specimens annealed for the same time at either 700°C (1292°F) or 850°C (1562°F). Additional annealing for 1 or 3 hr caused slight, if any, additional grain growth.

Figure 3A shows that recrystallization in cold rolled sponge hafnium plate was not obtained after 1 hr at 700°C (1292°F). Heat treatment at 850°C (1562°F) for 1 hr induced recrystallization and removed all evidence of stressed structure (Fig. 3B).

Mechanical Properties

Impact Properties

Table III lists the room temperature impact values obtained from the sponge plates and compares them with those obtained from crystal bar plates. The sponge plates generally show higher impact values than those obtained with the crystal bar specimens. The cold rolled portions of the sponge plates exhibit slightly higher impact values than those obtained with hot rolled sponge plates.

The sponge plates possessing the lowest impact strength had the highest nitrogen level. The two plates displaying the highest impact strength have the lowest oxygen level. Statistical evaluation of the impact data shows that there is 80% correlation between the variation in the impact properties of sponge hafnium plate and the oxygen and nitrogen content. No correlation between grain size and impact strength is indicated.

TABLE I
RANGE OF CHEMICAL ANALYSIS OF HAFNIUM PLATE

Material	<u>N₂ (ppm)</u>	<u>O₂ (ppm)</u>
Sponge Plate		
Top	9-92	510-900
Middle	3-91	650-860
Bottom	6-94	590-930
Typical Crystal Bar Plate	14-25	300-450
Crystal Bar Control Plate	4	260

TABLE II

	<u>Amps</u>	<u>Volts</u>	<u>in. /min</u>
Butt Welds*			
Sponge	210	10-1/2	6-1/2
Crystal	250	10-1/2	6-1/2
Root Welds			
Sponge	300	10-1/2	6-1/2
Crystal	330	10-1/2	6-1/2

*0.200-in. plate to vacuum melted Zircaloy-2,
100% penetration

TABLE III
RANGE OF ROOM TEMPERATURE IMPACT STRENGTHS

<u>Material Condition</u>	<u>Impact Strength (ft-lb)*</u>	
	<u>Sponge Plate</u>	<u>Crystal Bar Plate</u>
Hot Rolled		
Vacuum H.T. — 1 hr 700°C	1.0-4.9	1.0-1.9
Vacuum H.T. — 1 hr 850°C	1.0-4.3	--
Cold Rolled		
Vacuum H.T. — 1 hr 700°C	1.4-4.8	1.3-2.6
Vacuum H.T. — 1 hr 850°C	1.4-4.7	--

* 8 lb hammer used for all tests

A. Cold Rolled Plate 266, Middle; Vacuum Annealed 1 Hr. at 700°C, Cold Rolled from 0.250 In. to 0.220 In. (12% Red.); Vacuum Annealed 1 Hr. at 700°C and Furnace Cooled; Worked Structure Evident throughout; Grain Size ASTM-65 (3-5); 35% (6-8); 250X.

B. Cold Rolled Plate 266, Middle; Vacuum Annealed 1 Hr. at 850°C, Cold Rolled from 0.250 In. to 0.220 In. (12% Red.); Vacuum Annealed 1 Hr. at 850°C and Furnace Cooled; Equiaxed Grains throughout; Grain Size 25% (3-5); 75% (6-8); 250X.

Fig. 3 Effect of Heat Treatment on Grain Size in Cold Rolled Sponge Hafnium Plate.

Tensile Properties

Table IV summarizes tensile data obtained on this sponge hafnium plate; included for comparison are typical crystal bar plate values. In general, both longitudinal and transverse strengths (yield and tensile) of sponge plate are significantly higher and ductility lower than those obtained on crystal bar hafnium plate.

The effectiveness of the higher heat treatment temperature evidences itself in a comparison of the tensile values obtained on cold rolled heat treated materials. There is a marked reduction in strengths with a similar increase in ductility following the 850°C, 1-hr heat treatment.

Regardless of heat treatment temperature, 5 out of 10 hot rolled heat treated plates and 2 of 5 cold rolled heat treated plates failed to meet specification.

The room temperature tensile values obtained for the sponge plate showed a wider range of values than for crystal bar plate. This may be attributed to microporosity and/or N₂ or O₂ content in the material.

SUMMARY

Fabricability

No difficulty was experienced in hot forging and rolling the ten sponge ingots to plate. Some difficulty, however, was experienced in cold rolling—

TABLE IV
SUMMARY OF TENSILE PROPERTIES

Condition	Test		Yield Strength (0.2% Offset)		Tensile Strength		% Total Elong		% Reduction in Area	
	Temp	No. of Samples	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$	Range
<u>700°C Vacuum H.T.</u>										
<u>Hot Rolled</u>										
Longitudinal	RT	18	30.6(34)*	19.6-40.7	73.8(64)	57.9-87.4	23.7(23)	8.6-30.5	29.1(37)	9.1-36.5
Transverse	RT	20	40.9(37)	24.9-53.7	70.5(60)	55.0-83.8	17.1(26)	5.5-26.0	22.4(38)	6.6-45.0
	260°C	20	23.6(26)	14.5-31.1	38.1(35)	29.4-44.7	47.2(36)	38-58.0	48.7(44)	38.0-59.0
<u>Cold Rolled</u>										
Longitudinal	RT	5	56.6(33)	53.6-61.7	79.6(62)	74.0-86.3	19.8(26)	8.0-26.0	32.2(37)	13.0-40.0
Transverse	RT	6	68.5(44)	59.0-79.2	82.9(58)	74.2-93.8	16.3(22)	10.9-19.0	34.7(40)	16.0-43.0
	260°C	9	44.8(34)	40.0-49.7	52.0(43)	47.6-56.5	28.6(40)	22.0-33.0	55.2(58)	43.0-61.0
<u>850°C Vacuum H.T.</u>										
Hot Rolled-Trans	RT	18	39.1(39)	24.3-50.7	69.9(63)	55.2-81.5	24.0(31)	13.3-28.9	32.9(35)	13.7-41.6
Cold Rolled-Trans	RT	5	39.4(34)	33.3-48.0	70.6(51)	65.4-76.9	22.4(28)	7.0-30.0	33.0(36)	9.0-66.0

*Values in parenthesis are values for crystal bar plate.

6 of the 9 cold rolled ingots split open after very small total reductions.

Corrosion Resistance—The corrosion resistance of sponge material is excellent; weight gain and corrosion films similar to those obtained on crystal bar plate were obtained.

Density—The average density of this sponge material is slightly less than that obtained on crystal bar material. It is believed, though not fully substantiated, that this lower density might result from internal porosity.

Weldability—The weldability of sponge hafnium plate is similar to that of crystal bar, requiring slightly less energy input to obtain the same penetration.

Recrystallization—The recrystallization temperature of sponge hafnium plate is lowered by 12% cold rolling to between 700°C (1292°F) and 850°C (1562°F). That is, 700°C heat treating up to 4 hr does not completely recrystallize hafnium cold rolled 12%.

Mechanical Properties

Sponge hafnium plate absorbs slightly higher input energy than crystal bar plate.

Yield and tensile strength are higher with ductility; they are lower for sponge plate hafnium than for crystal bar.

Chemical Analysis

Analysis of sponge hafnium plate shows that it is comparable with crystal bar hafnium plate with the exception that the oxygen in the sponge is approximately double that in crystal bar. Increased oxygen can account for the increased strengths and hardness noted above.

CONCLUSIONS

The material tested in this early evaluation fell below specification in some respects; however, by indicating product deficiencies, they served to define avenues for improvement. Subsequent work, based on the information established here, is still underway.

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Equations expressing the laws of conservation of mass, momentum, and energy are required for the study of hydrodynamics in reactor coolant channels. This article contains a discussion of these equations with an outline of assumptions involved in their derivations. Special emphasis is placed on developing the macroscopic quantities needed to describe the two-phase slip flow.

CONSERVATION LAWS IN ONE-DIMENSIONAL HYDRODYNAMICS

J. E. Meyer

The laws of conservation of mass, momentum, and energy are required to describe the transient thermal and hydraulic conditions in reactor coolant channels. Many presentations of these laws appear in the literature. However, in most cases, single phase flow is assumed; in others, two-phase, steady-state flow is utilized. Presentations including two-phase transient flow are often not in a form suitable for practical reactor calculations. This paper is aimed at developing these laws in a form particularly applicable to either one- or two-phase transient flow in reactor coolant channels.

Examples of the application of these laws in reactor design is furnished by the ART-04 and F002 programs for the IBM-704 (Ref 1-3). Other digital computer programs utilizing these laws are presently under development at the Bettis Atomic Power Laboratory and will be reported in future issues of the Bettis Technical Review.

The applications of chief interest here are in the turbulent flow regime. However, the statistical motion present in turbulent flow is not handled directly—for example, velocity at a point in the coolant channel is considered predominantly in

one direction. Random fluctuations of the velocity in all three coordinate directions are neglected. Therefore, processes such as the eddy diffusion of energy and momentum (see Ref 4, p 504) are not treated explicitly and must be handled by less detailed macroscopic quantities such as a mixing-cup enthalpy and an empirically-determined surface frictional stress.

Similarly, no effort is made to handle individual steam bubbles, and two-phase flow is represented by use of a macroscopic description. However, it is recognized that if the average vapor velocity in the coolant channel is significantly different from the average liquid velocity (slip flow), then the macroscopic quantities may be much different numerically than if the same flowrate were passing through the channel but vapor and liquid were moving with a common velocity (homogeneous flow). Therefore, macroscopic quantities are developed which allow one to account for the presence of slip flow. The development is in the form of general integral expressions. The reduction of these expressions to a homogeneous flow model and to the separated flow model postulated by Martinelli and Nelson (Ref 5) are also presented.

INTEGRAL FORMS FOR THE CONSERVATION LAWS

The following are considered basic statements of the laws of conservation of mass, momentum, and energy for an arbitrarily shaped but spatially fixed control volume, V , with a surface, S :

$$\frac{\partial}{\partial t} \left[\int_V \rho dV \right] + \int_S \rho \vec{u} \cdot d\vec{S} = 0, \quad (1)$$

$$\begin{aligned} \frac{\partial}{\partial t} \left[\int_V (\rho \vec{u}) dV \right] + \int_S (\rho \vec{u}) \vec{u} \cdot d\vec{S} \\ = \int_S (\vec{p}) d\vec{S} + \int_V \rho \vec{\Psi} dV, \end{aligned} \quad (2)$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \left[\int_V (\rho e) dV \right] + \int_S (\rho e) \vec{u} \cdot d\vec{S} = - \int_S \vec{\phi} \\ \cdot d\vec{S} + \int_V q''' dV + \int_S (\vec{u} \cdot \vec{p}) d\vec{S} + \int_V \rho \vec{u} \cdot \vec{\Psi} dV. \end{aligned} \quad (3)$$

Note that consistent units are used, and symbols are defined in the table of nomenclature. These equations are identical with the conservation laws of Liepmann and Roshko (Ref 6, Eqs 7.8, 7.12, and 7.17) with the following exceptions:

- 1) Notation has been changed. In particular, vector rather than tensor notation is used.
- 2) The surface forces, $\int_S (\vec{p}) d\vec{S}$, due to the medium adjacent to S may be composed of both normal pressure forces, $\int_S -p d\vec{S}$, and tangential friction forces.
- 3) The fluid may have both internal heat generation, $\int_V q''' dV$, and heat addition resulting from heat flowing across the surface S , $-\int_S \vec{\phi} \cdot d\vec{S}$.

CONSERVATION LAWS FOR A CLOSED VARIABLE AREA FLOW CHANNEL

Consider the channel geometry of Fig. 1. Cross sectional areas denoted by A (with elemental area

dA) are normal to the positive z -axis. The area A may vary with z , but the variation is small enough so that the flow may be considered to be predominantly in the positive z or axial direction (and through the areas A). The channel is closed by a solid surface surrounding the areas A .* The lines of contact between A and the surrounding surface are the wetted perimeter WP with an element $d\ell$. The velocity is assumed to be zero on the entire wetted perimeter. The conservation laws can be written in a simpler form for this geometry by the introduction of certain integrals. For example, the first term of Eq (1) may be replaced by

$$\int_V \rho dV = \int_z^{z+\Delta z} \left(\int_A \rho dA \right) dz.$$

Contributions to the second term of Eq (1) arise on surfaces at z and $z+\Delta z$, but there is no contribution from the zero velocity side walls:

$$\begin{aligned} \int_S \rho \vec{u} \cdot d\vec{S} = & \left(\int_A \rho u_z dA \right)_{z+\Delta z} \\ & - \left(\int_A \rho u_z dA \right)_z, \end{aligned}$$

where u_z is the component of $\vec{u}$ in the positive z -direction. The conservation of mass equation, Eq (1), can then be written (after dividing by Δz and taking the limit as Δz approaches zero) as

$$\frac{\partial}{\partial t} \left(\int_A \rho dA \right) + \frac{\partial}{\partial z} \left(\int_A \rho u_z dA \right) = 0. \quad (4)$$

If the pressure is considered constant over each plane normal to the z -axis [that is, $p = p(z)$], then

*Note that if significant flux variations exist across the width direction in the channel, flow in this direction could be quite important in boiling situations. However, this two-dimensional flow situation will not be discussed here.

Fig. 1 Flow Channel Geometry.

the pressure contribution to the surface force integral, $\int_S (\vec{p}) \cdot d\vec{S}$ of Eq (2), is

$$\begin{aligned} & - (pA)_{z+\Delta z} + (pA)_z + \int_z^{z+\Delta z} \left(p \frac{dA}{dz} \right) dz \\ & = - \int_z^{z+\Delta z} \left(A \frac{\partial p}{\partial z} \right) dz . \end{aligned}$$

The first two terms in this contribution are due to the pressure force at level $z+\Delta z$ and level z , respectively. The third term is due to the pressure force on the sloping side wall. An additional contribution to the surface force integral is due to the frictional resistance to flow offered by the side walls. If the frictional force acting in the negative z -direction per unit wetted perimeter and per unit axial length is denoted by τ , then this remaining contribution is

$$- \int_z^{z+\Delta z} \left(\int_{WP} \tau d\ell \right) dz .$$

Finally, if the body force per unit mass acting in the negative z -direction is a constant value, g (i. e., $\vec{\Psi}_z = -g$), then the body force integral in Eq (2) becomes

$$- \int_z^{z+\Delta z} \left(\int_A \rho g dA \right) dz .$$

Therefore, the z -component of the conservation of momentum equation [Eq (2)], after making similar substitutions to those of Eq (4), dividing by Δz , and taking the limit as Δz approaches zero, yields

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\int_A \rho u_z dA \right) + \frac{\partial}{\partial z} \left(\int_A \rho u_z^2 dA \right) \\ & = - A \frac{\partial p}{\partial z} - \int_{WP} \tau d\ell - \left(\int_A \rho dA \right) g . \end{aligned} \quad (5)$$

Finally, if φ_ℓ denotes the local heat flux from the wetted perimeter to the fluid, the conservation of energy equation [Eq (3)], after operations similar to those leading to Eq (5), becomes

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\int_A \rho e dA \right) + \frac{\partial}{\partial z} \left(\int_A \rho u_z e dA \right) = \int_{WP} \varphi_\ell d\ell \\ & + \int_A q''' dA - \frac{\partial}{\partial z} \left(\int_A \rho u_z dA \right) \\ & - \left(\int_A \rho u_z dA \right) g . \end{aligned} \quad (6)$$

Heat conduction in the positive z -direction has been neglected in this derivation. In addition, because of the zero velocity at the side wall, there is no contribution to this equation from pressure and shear forces operating at the side wall. Finally, only the portion $u_z \Psi_z$ of the product $\vec{u} \cdot \vec{\Psi}$ is considered important.

The last equation may be rewritten by letting

$$e = H - (p/\rho) + \frac{1}{2} u^2 .$$

This substitution results in

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\int_A \rho H dA \right) + \frac{\partial}{\partial z} \left(\int_A \rho u_z H dA \right) = \int_{WP} \varphi_\ell d\ell \\ & + \int_A q''' dA + \frac{\partial}{\partial t} (pA) - \left[\frac{\partial}{\partial t} \left(\int_A \frac{1}{2} \rho u^2 dA \right) \right. \\ & \left. + \frac{\partial}{\partial t} \left(\int_A \frac{1}{2} \rho u_z u^2 dA \right) + \left(\int_A \rho u_z dA \right) g \right] . \end{aligned} \quad (7)$$

Customary assumptions (see Ref 1, p 4) for transients of design interest are that the third term on the right-hand side of Eq (7) and the expression in brackets may be neglected. That is, kinetic and potential energy terms and the variation of pressure with time are assumed to have negligible effects on the energy balance.* Define the following for further simplification of Eqs (4), (5), and (7):

$$\bar{\rho} = \frac{1}{A} \int_A \rho dA, \quad (8)$$

$$G = \frac{1}{A} \int_A \rho u_z dA, \quad (9)$$

$$v' = \frac{1}{G^2} \left(\frac{1}{A} \int_A \rho u_z^2 dA \right), \quad (10)$$

$$\bar{H} = \left(\frac{1}{\rho} \right) \left(\frac{1}{A} \int_A \rho H dA \right), \quad (11)$$

$$H' = \frac{1}{G} \left(\frac{1}{A} \int_A \rho u_z H dA \right), \quad (12)$$

$$\varphi = \ell_1 \left(\frac{1}{A} \int_{WP} \varphi_\ell d\ell \right), \quad (13)$$

and

$$rq = \ell_1 \left(\frac{1}{A} \int_A q''' dA \right). \quad (14)$$

These substitutions result in

$$\frac{\partial(\bar{\rho}A)}{\partial t} + \frac{\partial(GA)}{\partial z} = 0, \quad (15)$$

$$\begin{aligned} \frac{\partial}{\partial t} (GA) + \frac{\partial}{\partial z} (v'G^2A) &= -A \frac{\partial p}{\partial z} \\ &- \int_{WP} \tau d\ell - \bar{\rho}gA, \end{aligned} \quad (16)$$

*With homogeneous flow in a constant area channel, this assumption may be shown equivalent to neglecting dissipation effects and the change of pressure with both time and distance.

and

$$\frac{\partial}{\partial t} (\bar{\rho} \bar{H}A) + \frac{\partial}{\partial z} (GH'A) = \frac{(\varphi + rq)A}{\ell_1}. \quad (17)$$

Therefore, Eqs (15), (16), and (17) are expressions of the laws of conservation of mass, momentum, and energy for a variable area channel. Equations (8)-(12) define the various macroscopic quantities needed to describe fluid conditions. Some possible simplifications of these laws and of the macroscopic quantities will now be discussed.

A CONSTANT AREA FLOW CHANNEL

In a constant area flow channel, if steady-state operation is assumed, if there is no change of $v'G^2$ with distance (no heat addition), and if gravity effects are neglected, then, from Eq (16),

$$\frac{dp}{dz} = -\frac{1}{A} \int_{WP} \tau d\ell. \quad (18)$$

However, a friction factor, f , is commonly used to represent this frictional pressure gradient; so, in this special case, the following is used:

$$\frac{1}{A} \int_{WP} \tau d\ell = \frac{(fv)}{2D_h} \frac{|G|G}{G}. \quad (19)$$

The product $|G|G$ is utilized in this equation to obtain a change in the sign of τ upon a reversal of flow through the channel. In the case of transient operation, with gravity effects and with heat addition, it is assumed that the wall shear stress may be represented by a friction-factor-like quantity by the use of Eq (19).

Therefore, with this empirical representation of τ , and with the assumption of constant area, the conservation laws [Eqs (15), (16), and (17)] become

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial G}{\partial z} = 0, \quad (20)$$

$$\frac{\partial G}{\partial t} + \frac{\partial}{\partial z} (v'G^2) = -\frac{\partial p}{\partial z} - \frac{(fv)|G|G}{2D_h} - \bar{\rho}g, \quad (21)$$

and

$$\frac{\partial}{\partial t} (\bar{\rho}\bar{H}) + \frac{\partial}{\partial z} (GH') = \frac{\varphi + rq}{\ell_1} \quad (22)$$

In some regions of heat transfer (such as sub-cooled nucleate boiling), the slip flow quantities $\bar{\rho}$, $\bar{H}$, etc. are probably functions of at least flux φ , mass flowrate G , mixing-cup enthalpy H' , and pressure p . However, if assumptions are made (such as evaluating all quantities at a reference value of pressure, flux, and flow) which permit the quantities $\bar{\rho}$, $\bar{H}$, etc. to be given as functions of only enthalpy H' , then considerable simplification can be obtained. Equation (20) becomes

$$\left(\frac{d\bar{\rho}}{dH'} \right) \frac{\partial H'}{\partial t} + \frac{\partial G}{\partial z} = 0, \quad (23)$$

and Eq (22) becomes

$$\left(\bar{\rho} \frac{d\bar{H}}{dH'} + \bar{H} \frac{d\bar{\rho}}{dH'} \right) \frac{\partial H'}{\partial t} + G \frac{\partial H'}{\partial z} + H' \frac{\partial G}{\partial z} = \frac{\varphi + rq}{\ell_1}. \quad (24)$$

Finally, substitute (23) into (24) to obtain

$$\left(\rho'' \frac{\partial H'}{\partial t} + G \frac{\partial H'}{\partial z} \right) = \frac{\varphi + rq}{\ell_1}, \quad (25)$$

where

$$\rho'' = \bar{\rho} \frac{d\bar{H}}{dH'} + (\bar{H} - H') \frac{d\bar{\rho}}{dH'}. \quad (26)$$

Therefore, in the simplified situation in which $\bar{\rho}$ and $\bar{H}$ are functions of H' only, the conservation of energy may be given in the simplified form of Eq (25), and a new macroscopic quantity, ρ'' , is introduced by Eq (26).

INLET AND EXIT REGIONS

To describe the channel inlet conditions, the original conservation laws [Eqs (1)-(3)] may be applied between a plane normal to the z -axis just outside

the channel inlet (denoted by the subscript I) and a plane normal to the z -axis just inside the channel inlet (denoted by subscript o). Assume that volume integrals such as $\int_V \rho dV$ are negligibly small since these planes may approach each other (for an abrupt inlet region). In addition, neglect any heat addition in this region. This process may be performed most readily by integrating Eqs (15)-(17) with respect to z from plane I to plane o. Note that Eq (16) should be divided by A prior to integration. Then,

$$(GA)_I = (GA)_o, \quad (27)$$

$$\int_{z_I}^{z_o} \left[\frac{1}{A} \frac{\partial}{\partial z} (v'G^2A) \right] dz = p_I - p_o - \int_{z_I}^{z_o} \left(\frac{1}{A} \int_{WP} \tau d\ell \right) dz, \quad (28)$$

and

$$(GH'A)_I = (GH'A)_o. \quad (29)$$

If σ_o is used to denote (A_o/A_I) , then Eq (27) becomes

$$G_I = \sigma_o G_o. \quad (30)$$

A possible empirical means* of evaluating Eq (28) in two-phase flow has been suggested by

*If homogeneous flow is assumed, then $v' = v$. If it is assumed that v is constant through the inlet section, then the left-hand side of Eq (28) becomes

$$v \int_{z_I}^{z_o} \left[\left(\frac{G}{A} \right) \frac{\partial(GA)}{\partial z} + G \frac{\partial G}{\partial z} \right] dz = v \left(\frac{1}{2} G_o^2 - \frac{1}{2} G_I^2 \right) = \frac{1}{2} v_o G_o^2 (1 - \sigma_o^2).$$

Therefore, a portion of Eq (31) can be derived directly.

LeTourneau* and is similar to the approach commonly used for single-phase flow:

$$p_I - p_O = \frac{1}{2} v_O G_O \left[K_O |G_O| + (1 - \sigma_O^2) G_O \right], \quad (31)$$

where K_O is an unrecoverable loss coefficient for abrupt change in area (such as those presented in Ref 7) and where the use of the absolute value indicates that this loss changes sign as the flow reverses. **Equation (17) becomes quite simple:†

$$H_I' = H_O' . \quad (32)$$

To describe the channel exit conditions, similar operations may be performed between the plane normal to the z -axis just outside the channel exit (denoted by the subscript E) and the plane normal to the z -axis just inside the channel exit (denoted by the subscript n). Therefore,

$$G_E = \sigma_n G_n , \quad (33)$$

$$p_E - p_n = \frac{1}{2} v_n G_n \left[-K_n |G_n| + (1 - \sigma_n^2) G_n \right], \quad (34)$$

and

$$H_E' = H_n' . \quad (35)$$

MACROSCOPIC QUANTITIES FOR DESCRIPTION OF TWO-PHASE FLOW

The macroscopic quantities needed to describe two-phase fluid conditions are $\bar{\rho}$, G , v' , $\bar{H}$, f_v , and

H' (and, in special cases, ρ'' which eliminates the need for $\bar{H}$). These are defined by Eqs (8) - (12) and by Eq (26). A further discussion of these quantities is presented below for two of the many possible two-phase flow models.††

1) The Martinelli-Nelson Separated Flow Model†—In this model the liquid and vapor are completely separated with the liquid all having a velocity V_ℓ , an enthalpy H_ℓ , and a density ρ_ℓ and the vapor all having a velocity V_v , an enthalpy H_v , and a density ρ_v . This model does not permit variations of velocity or enthalpy within an individual phase (such as would be present, for example, with a parabolic velocity profile). The effect of the zero velocity at the wall is assumed to extend over an extremely small portion of the fluid and is neglected.

2) Homogeneous (or Fog Flow) Model—In this model the liquid and vapor are completely mixed. This model is commonly used in the literature and is completely equivalent to the separated flow model with the further stipulation that $V_v = V_\ell$.

Separated Flow

Denote the fraction of the channel cross-sectional area occupied by vapor †† as R . Then, the above definitions for $\bar{\rho}$ and G yield

$$\bar{\rho} = \rho_\ell (1 - R) + \rho_v R , \quad (36)$$

and

$$G = \rho_\ell V_\ell (1 - R) + \rho_v V_v R . \quad (37)$$

* Unpublished work on exit coefficients by B. W. LeTourneau of Bettis. The approach would probably be satisfactory for inlet coefficients as well.

**The value of K_O will also change upon flow reversal.

†If flow is in the positive z -direction, then H_I' is the mixing-cup enthalpy of the fluid being supplied to the channel, and H_O' follows. If on the other hand, reverse flow exists, H_O' is determined from within channel conditions, and H_I' follows. Similar conditions exist at the exit. For forward flow, within-channel conditions are important, and H_E' follows; for reverse flow at the exit, plenum conditions control, and H_n' follows.

††Martinelli and Nelson (Ref 5) consider slip flow effects only on spatial acceleration terms in the momentum equation; and they suggest that these models represent two extremes and that the actual condition is probably between the two extremes.

†Ref 5, p 699.

‡‡Actually, this is a volume vapor fraction. However, the assumption is made here that over a small axial length, the area and volume fraction become the same. Therefore, flow patterns such as slug flow are not handled by this method if the slug spacing is large.

Now, introduce the mass flow fraction of vapor, X , by

$$X = \frac{\rho_v V_v R}{G} \quad (38)$$

Therefore, the phase velocities and the slip ratio are given by

$$\left. \begin{aligned} V_v &= \frac{XG}{R\rho_v} , \\ V_\ell &= \frac{(1-X)G}{(1-R)\rho_\ell} , \end{aligned} \right\} \quad (39)$$

and

$$\left(\frac{V_v}{V_\ell} \right) = \left(\frac{X}{1-X} \right) \left(\frac{1-R}{R} \right) \left(\frac{\rho_\ell}{\rho_v} \right)$$

These result in the following simplified expressions for the other quantities of interest:

$$v' = \frac{1}{G^2} \left[\rho_\ell V_\ell^2 (1-R) + \rho_v V_v^2 R \right] \quad (40)$$

$$= \frac{(1-X)^2}{\rho_\ell (1-R)} + \frac{X^2}{\rho_v R} \quad (41)$$

$$\bar{H} = \frac{1}{\rho} \left[\rho_\ell H_\ell (1-R) + \rho_v H_v R \right] \quad (42)$$

$$H' = \frac{1}{G} \left[\rho_\ell V_\ell H_\ell (1-R) + \rho_v V_v H_v R \right] \quad (43)$$

$$= H_\ell (1-X) + H_v X \quad (44)$$

and, where applicable,

$$\rho'' = (H_v - H_\ell) \left\{ \left[\rho_\ell X + \rho_v (1-X) \right] \frac{dR}{dH'} - X(1-R) \frac{d\rho_\ell}{dH'} + (1-X) R \frac{d\rho_v}{dH'} + \rho_v R \frac{dH_v}{dH'} + \rho_\ell (1-R) \frac{dH_\ell}{dH'} \right\} \quad (45)$$

Note that this last expression becomes especially simple if it is assumed, for some range of H' , that all vapor in the cross section is saturated vapor

(i.e., $H_v = H_g$ and $\rho_v = \rho_g$) and that all liquid in the cross section is saturated liquid (i.e., $H_\ell = H_f$ and $\rho_\ell = \rho_f$). For in this case, $d\rho_\ell/dH' = d\rho_v/dH' = dH_v/dH' = dH_\ell/dH' = 0$, and $H' = H_f + X(H_g - H_f)$.

Therefore, in this situation,

$$\rho'' = [\rho_f X + \rho_g (1-X)] \frac{dR}{dX} \quad (46)$$

So it may be seen that, for separated flow, three different densities— $\bar{\rho}$, $\rho' = 1/v'$, and ρ'' —may be defined and two different enthalpies— $\bar{H}$ and H' —may be used.

Homogeneous Flow

If a homogeneous flow model is used, then $V_v = V_\ell = V$ and, from Eq (39),

$$R = \frac{\rho_\ell X}{\rho_\ell X + \rho_v (1-X)} = \frac{v_v X}{v_\ell (1-X) + v_v X} \quad (47)$$

Therefore, Eqs (36), (37), and (40)–(45) become

$$\bar{\rho} = \rho = \frac{1}{v} = \frac{1}{v_\ell (1-X) + v_v X} \quad (48)$$

$$G = \rho V \quad (49)$$

$$\rho' = (1/v') = (1/v) = \frac{1}{v_\ell (1-X) + v_v X} \quad (50)$$

$$\bar{H} = H = H_\ell (1-X) + H_v X \quad (51)$$

$$H' = H = H_\ell (1-X) + H_v X \quad (52)$$

and

$$\rho'' = \rho = (1/v) \quad (53)$$

Now a single density, ρ , and a single enthalpy, H , can be used for a macroscopic description of homogeneous flow.

Experimental Determination of Macroscopic Quantities

In a steady-state experiment, several of these quantities may be obtained. The average mass

velocity, G , is the total mass flow through the channel per unit cross-sectional area and may therefore be obtained from inlet orifice measurements. The flux, φ , is determined by current and voltage measurements for an electrically heated test section. The density, $\bar{\rho}$, may be found by radiation attenuation methods (c.f. Ref 8). In addition, the static pressure gradient, dp/dz , may be measured by pressure taps. By use of the conservation of energy (Eq 22), the mixing-cup enthalpy, H' , may be determined for each cross section by the following steady-state relationship:

$$\frac{dH'}{dz} = \frac{\varphi + r q}{G \ell_1} \quad (54)$$

This equation results directly from combining Eqs (20) and (22) during the steady-state when derivatives with respect to time are zero. In this approach, if the density and enthalpy of the liquid are taken as saturated liquid values, if the density and enthalpy of the vapor are saturated vapor values, and if a separated flow model is used, then these quantities (G , H' , $\bar{\rho}$) are sufficient to calculate the additional quantities v' and $\bar{H}$ and, hence, fv at the particular cross section. If, however, the liquid enthalpy is unknown at the cross section, then some additional measurement or assumption is needed to predict v' and $\bar{H}$. For example, in Ref 8, when vapor is present during local boiling, if the assumption of homogeneous flow is made, then $v' = 1/\bar{\rho}$ and $\bar{H} = H'$. Similarly, if some single slip ratio other than one is assumed, then v' and $\bar{H}$ may be determined by the relationships of Eqs (36)-(44). But in either case, the determination of only G , H' , and $\bar{\rho}$ is not sufficient to determine the other macroscopic quantities of interest.

CONCLUSIONS

This paper has been devoted to a careful definition of one possible set of quantities needed to describe one-dimensional hydrodynamics on a macroscopic basis:

H' = a mixing-cup or flowing enthalpy,

$\bar{H}$ = a volume weighted mean or static enthalpy,

$\rho' = (1/v') =$ an effective density for momentum considerations,

$\bar{\rho}$ = a volume weighted mean density,

G = the mass velocity,

and

$\rho'' =$ an effective slip flow density used for energy considerations.

If homogeneous flow is assumed, the enthalpies H' and $\bar{H}$ are identical and the densities ρ' , ρ'' and $\bar{\rho}$ are identical. However, in the case of slip flow, such simplification is not possible. In addition, the case is even more complicated if $\bar{\rho}$, ρ' , and $\bar{H}$ are functions of mass velocity and heat flux at a given H' . In this latter case the simpler equation expressing conservation of energy (Eq 25) and the use of ρ'' is not applicable, and use of the more complicated Eq (22) is required.

NOMENCLATURE

Consistent units are used. Dimensions are denoted by M = mass, L = length, θ = time, T = temperature, $F = ML/\theta^2$ = force, and $H = FL = ML^2/\theta^2$ = energy.

Symbol	Description	Defining Equation	Dimensions
A, dA	The cross-sectional area of the coolant channel of Fig. 1 and an element of this area	--	L^2
D_h	Hydraulic diameter (4 flow area/wetted perimeter)	(19)	L
e	The internal energy per unit mass, including thermal intrinsic energy ($H-p/\rho$) and kinetic energy $1/2 u^2$	--	$H/M = L^2/\theta^2$
f	Friction factor	(19)	none
G	Mass flow in the positive z -direction per unit cross-sectional area	(9), (37), (49)	$M/L^2\theta$
g	Component of acceleration of gravity in the negative z -direction	--	$F/M = L/\theta^2$
H	Fluid enthalpy and enthalpy in homogeneous flow	(51)	H/M
$\bar{H}$	Volume weighted mean enthalpy	(11), (42), (51)	H/M
H'	Flow weighted or mixing-cup enthalpy	(12), (43), (52)	H/M
H_f, H_g	Enthalpy of saturated liquid and saturated vapor, respectively	--	H/M
H_v, H_l	Enthalpy of vapor and liquid phases, respectively	--	H/M
K_o, K_n	Unrecoverable loss coefficients at entrance and exit	(31), (34)	none
ℓ_1	The channel half-thickness	*	L
p	Static pressure	--	F/L^2
$\vec{p}$	The force per unit area acting on the surface elements dS — actually a tensor quantity since it depends on the orientation of dS	--	F/L^2
q	See rq	(14)	$H/L^2\theta$

*See Fig. 1

Symbol	Description	Defining Equation	Dimensions
q'''	Volumetric internal heat generation rate	--	$H/L^3\theta$
R	Fraction of cross-sectional area occupied by vapor	--	none
rq	Internal heat generation in fluid per unit heat transfer surface	(14)	$H/L^2\theta$
$S, dS, d\vec{S}$	The surface of V, the magnitude of a surface element of S, and a vector with magnitude dS and with direction along the outward normal to dS	--	L^2
t	Time after the start of the transient	--	θ
u_z	Velocity in the positive z-direction	--	L/θ
u	The local magnitude of the fluid velocity vector	--	L/θ
$\vec{u}$	The fluid velocity vector	--	L/θ
V, dV	A fixed control volume for writing conservation laws and a volume element of V, respectively	--	L^3
V	Velocity for homogeneous flow	(49)	L/θ
V_v, V_ℓ	Velocity of vapor and liquid phases, respectively	(39)	L/θ
v	Specific volume used in (fv) product and specific volume for homogeneous flow	(19), (48)	L^3/M
v'	Effective specific volume for momentum considerations	(10), (40), (50)	L^3/M
$WP, d\ell$	The wetted perimeter of the coolant channel of Fig. 1 and an element of this perimeter, respectively	*	L
X	Vapor flowrate/total flowrate of liquid and vapor	(38)	none

* See Fig. 1

<u>Symbol</u>	<u>Description</u>	<u>Defining Equation</u>	<u>Dimensions</u>
$z, \Delta z$	Position measured from the inlet end of the coolant channel of Fig. 1 and an increment of this length, respectively	--	L
ρ	Local mass density, or density in homogeneous flow	--	M/L ³
ρ'	$\rho' = (1/v')$	--	M/L ³
ρ''	Effective slip flow density for energy considerations	(26), (45), (53)	M/L ³
$\bar{\rho}$	Volume weighted mean density	(8), (36), (48)	M/L ³
ρ_f, ρ_g	Density of saturated liquid and vapor, respectively	--	M/L ³
ρ_v, ρ_ℓ	Density of vapor and liquid phases, respectively	--	M/L ³
σ_o, σ_n	Area ratio at inlet and exit (channel area/plenum area), respectively	--	none
τ	Component in the negative z-direction of wall friction force per unit perimeter per unit axial length	--	F/L ²
φ	Heat flux for a one-dimensional channel	(13)	H/L ² θ
$\vec{\varphi}$	The heat flux vector, positive in the direction of heat flow	--	H/L ² θ
φ_ℓ	Local wall heat flux directed from wall to fluid (heat per unit time per unit perimeter and per unit axial length)	--	H/L ² θ
$\vec{\Psi}$	The body force vector per unit mass	--	F/M = L/ θ^2
<u>Subscripts</u>			
E	Position just outside the channel exit		
f	Saturated liquid		
g	Saturated vapor		
I	Position just outside the channel inlet		
ℓ	Liquid conditions		
n	Position just inside the channel exit		
o	Position just inside the channel inlet		
v	Vapor conditions		

REFERENCES

1. J. E. Meyer, R. B. Smith, H. G. Gelbard, D. E. George, and W. D. Peterson, "ART - A Program for the Treatment of Reactor Thermal Transients on the IBM-704," WAPD-TM-156 (November 1959).
2. J. E. Meyer and W. D. Peterson, "ART-04 - A Modification of the ART Program for the Treatment of Reactor Thermal Transients on the IBM-704," WAPD-TM-202. (July 1960).
3. J. B. Callaghan and J. S. Williams, Jr., "F0020 - An IBM-704 Thermal Transient Analysis Code," WAPD-TM-145 (January 1959).
4. M. Jakob, Heat Transfer, Vol I (New York: John Wiley and Sons, Inc., 1949).
5. R. C. Martinelli and D. B. Nelson, "Prediction of Pressure Drop During Forced-Circulation Boiling of Water," Trans. ASME, Vol 70 (1948), pp 695-702.
6. H. W. Liepmann and A. Roshko, Elements of Gasdynamics (New York: John Wiley and Sons, inc., 1957).
7. W. M. Kays, "Loss Coefficients for Abrupt Changes in Flow Cross Section with Low Reynolds Number Flow in Single and Multiple Tube Systems," Trans. ASME, Vol 72 (1950), pp 1067-1074.
8. G. W. Maurer, "A Method of Predicting Steady-State Boiling Vapor Fractions in Reactor Coolant Channels," BETTIS TECHNICAL REVIEW, WAPD-BT-19 (April 1960).

Techniques are described for solving the spherical harmonics equations in various geometries. The spherical harmonics method is compared with the S_n method, and it is pointed out that the use of the spherical harmonics method is advantageous in many cases. In conclusion, an approximate form of the spherical harmonics equations is developed, and applications of this approximate form are discussed.

APPLICATION OF SPHERICAL HARMONICS METHOD TO REACTOR PROBLEMS

E. M. Gelbard

For some time, few-group diffusion theory has served as the basic tool for the analysis of light water moderated power reactors. As a result, very effective means have been developed to solve the diffusion equation. Recently, however, increasingly stringent design requirements have stressed the need for an improved computing system. While it seems unlikely that diffusion theory itself will be supplanted, the role of auxiliary transport calculations is becoming more and more important.

Many higher order transport approximations are available to fill this role. Of these, S_n (Ref 1) is probably the most widely used. Its versatility and precision are well known. Yet the spherical harmonics method, and the associated method of Yvon, have many advantages. In particular, the conventional first-order equations for the angular moments of the flux may be recast as second-order equations. In this form, they are amenable to solution by a rapidly convergent process which iteratively corrects the diffusion equations. Most of the apparatus used for solving diffusion equations may then be utilized for solving the spherical harmonics equations.

Of course, the complexity of the spherical harmonics equations varies strongly with geometry. Even the P-7 equations in slab geometry are rather simple. On the other hand, the P-3 equations for infinite cylinders, while tractable, are relatively complicated. In cylindrical and x-y geometries we treat only the P-3 equations exactly, relying on an approximate form of the spherical harmonics equations in higher orders. This form is simple in all geometries, to all orders.

The methods developed here will be used to attack some typical neutron transport problems. Through analysis of these test problems, the advantages and disadvantages of the subject approach will be brought out clearly. Generally, computing speed has been stressed over accuracy, and an adequate, rather than a nearly exact, solution has been the objective. In some cases the accuracy of the S_n method is not achieved. However, one important limitation of the S_n method is not present in the spherical harmonics method: anisotropic scattering, which is ignored or handled crudely in existing S_n codes, may be included without difficulty in spherical harmonics calculations. Anisotropic

scattering is a very important phenomenon in reactors containing large quantities of water. Unless it is treated correctly, other refinements may be superfluous.

SLAB GEOMETRY

It has been shown in Ref 2 that the one-energy P_L and double- P_L equations for slabs may be written in the form

$$-D^i \frac{\partial^2 \phi^i}{\partial x^2} + \Sigma_T^i \phi^i = A^i S + \sum_{j \neq i} \alpha^{ij} \phi^j. \quad (1)$$

Here, D^i , Σ_T^i , and α^{ij} are functions of the cross sections, while the A^i are position-independent numbers. The ϕ^i are linear combinations of the moments of the flux. If the sum on the right-hand side is deleted, the $i = 1$ equation becomes, simply, the diffusion equation generated in a P-1 approximation.

It is convenient and efficient to solve Eq (1) by a Gauss-Seidel iterative process. One may assume, initially, that $\phi^j = 0$ for $j \neq 1$. The first iterate of ϕ^1 will then be the P-1 scalar flux which is, generally, a good starting function. Furthermore, the rate of convergence is high and almost insensitive to the problem parameters. Comparisons in Ref 2 show that the method proposed here is much faster than the iterative solution of the slab equations at discrete ordinates.

The second-order form of the P_L and double- P_L equations lends itself well to reactor applications. With a computer program which solves coupled diffusion equations, it becomes possible to treat a wide variety of reactor problems. Fast fluxes may be calculated in P-1 or P-3; thermal fluxes in P-1 or double P-1. One or many fast groups may be used in conjunction with one or many thermal groups. Such a program has been written at Bettis by R. M. Cantwell (Ref 3), who has used it in the analysis of critical experiments. Its generality is restricted primarily by its inability to handle

anisotropic moderation explicitly. In this respect, it is quite similar to few-group codes such as WANDA (Ref 4).

Another, more elaborate, code has been written at Bettis to solve thermal multigroup problems. This code, called SLOP-1 (Ref 5), also uses the second-order form of the P-3 or double P-1 equations. Explicit provisions for anisotropic moderation are included in this program; P-0 through P-3 transfer matrices are stored in the program library. Though designed specifically for thermal neutron calculations, SLOP-1 will handle other problems if the transfer matrices are properly redefined.

OTHER GEOMETRIES

One-Dimensional, Cylindrical Geometry Problems

Like the slab equations, the P-3 cylindrical equations may also be written in second-order form. In both cases, the second-order equations are, simply, coupled diffusion equations, but the slab and cylindrical equations differ in many respects. There are four first-order P-3 equations in slab geometry, and these yield two second-order equations. In cylindrical geometry there are six conventional P-3 equations which coalesce into three second-order equations. While the D^i , Σ_T^i , and α^{ij} are not explicitly position-dependent in slab geometry, Σ_T^3 contains a $1/r^2$ term in cylindrical geometry. The most serious complication, however, occurs in the coupling terms. The slab equations are coupled only through the ϕ^j , but spatial derivatives of ϕ^j cannot be eliminated from the coupling terms in cylindrical geometry. Nevertheless, some important features of the method formulated here are common to both geometries. The $i = 1$ equation remains the P-1 diffusion equation, and the Gauss-Seidel iterative process remains quickly convergent.

It is instructive to compare P-3 and S-4 computations in selected test cases. Two test problems

are discussed below. The problem geometries are exhibited in Fig. 1, and the relevant parameters are listed in Table I. In both cases the scattering was assumed isotropic, and a constant, isotropic source appeared in Region II. All parameters are typical of slightly enriched fuel rods immersed in water, with cross sections appropriate to the thermal group. The water-to-metal volume ratio in Problem 1 is about 1. In Problem 2, this ratio is about 2.5 to 1.

Relative errors in the first problem are plotted in Fig. 2 which shows how errors in the S-4 and P-3 scalar fluxes vary with position. The S-8 results have been taken as a standard. It seems reasonable to neglect errors in the S-8 fluxes in view of the fact that the angular dependence of the S-8 flux is described in terms of 36 independent parameters.

It can be seen from Fig. 3 that the S-4 flux shape in the fuel is no better than the P-3 flux shape. In contrast, S-4 is much better than P-3 in the water region. Relative errors in the second problem appear in Fig. 3. Here the S-4 calculation is more accurate throughout the entire cell, although, again, it is better in the water than in the fuel.

Errors in the S-4 thermal utilization are negligible. In contrast, the P-3 thermal utilization is too

Fig. 1 Cylindrical Cell Configuration.

TABLE I
PARAMETERS IN S_n vs P-3 COMPARISON

	Region I	Region II
Σ_a	0.4943 cm ⁻¹	0.01955 cm ⁻¹
Σ_s	0.398 cm ⁻¹	2.18845 cm ⁻¹
r	Problem 1 0.762 cm ⁻¹	1.11264 cm
	Problem 2 0.762 cm	1.40484 cm

Fig. 2 Percent Error in S_4 and P-3 Fluxes ($V_W/V_M = 1$).

Fig. 3 Percent Error in S_4 and P-3 Fluxes ($V_W/V_M = 2.5$).

high by 0.17% in Problem 1 and by 0.25% in Problem 2.

The P-3 results, although not so accurate as S-4 results, appear to be adequate for most purposes.

Errors in the P-3 calculation are smaller than the uncertainties in measured activations and smaller than many other errors in reactivity calculations. The added accuracy of the S-4 calculation, however, is very costly. Problems 1 and 2 were run on General Atomics' S-4 and S-8 code and timed. They were then rerun on CLIP (Ref 6), which solves the P-3 equations in second-order form. The first problem converged in 135 seconds of computing time in S-4 and in 12 seconds in P-3. The second required 165 seconds in S-4 and 15 seconds in P-3. In both cases CLIP is about ten times faster than the S-4 code, despite the fact that it permits anisotropic scattering and the S-4 code does not. Quoted times exclude the time necessary to read cards or edit output and include only computing time. A factor of ten in computing time may not be important in one-group problems such as these, but it would be quite important in multigroup calculations.

The factor of ten may be separated into two components. First, the S-4 calculation required 48 iterations for convergence. With a very closely comparable convergence criterion, CLIP converged in only six iterations. In this connection, it is noteworthy that the General Atomics S-4 code uses Tchebycheff polynomials to accelerate convergence, whereas no accelerating technique is necessary in CLIP. Secondly, the S-4 code must solve ten coupled first-order equations, while CLIP solves the equivalent of six. The four additional parameters in an S-4 approximation probably account, in large measure, for its improved accuracy.

Two-Dimensional, x-y Geometry Problems

So far we have discussed only one-dimensional calculations, but the approach we have used is feasible in two dimensions also—for example, in the treatment of the P-3 equations in x-y geometry. It is convenient to start from the general tensor form of the P_2 equations—a form derived in Davison's book on transport theory (Ref 7). In

tensor notation, the P-3 approximation comprises four first-order differential equations. After elimination of the odd moments, two second-order tensor equations remain. At this point a rectangular mesh is introduced, and the second-order equations are integrated over mesh rectangles (as in Ref 8). The resulting equations are then expanded into their components, yielding four coupled second-order difference equations. Of these, the first is simply the P-1 diffusion equation, with coupling terms which introduce higher order corrections. Coupling terms contain the higher moments and their first two differences.

The solution of the x-y equations may be accomplished through the use of inner and outer iterations—a conventional procedure in multidimensional diffusion codes. This method of solution has been incorporated in the TRIP code (Ref 9), written for the IBM-704. Convergence of the outer cycle has been very rapid in all cases run at Bettis. The convergence rate of the inner iterative process depends on the problem parameters, as in the diffusion code PDQ (Ref 8) for example. As in PDQ, also, the inner iterations may be accelerated effectively through the use of overrelaxation. Because of all these similarities, large blocks of PDQ coding could be inserted, intact, into TRIP.

The TRIP code has been used to study thermal flux peaking problems in fuel cells. Results of the peaking calculations can be found in Ref 10. Little is known at this time regarding the range of validity of the P-3 approximation in x-y geometry.

DEEP PENETRATION PROBLEMS

Having touched on thermal utilization and flux peaking problems, we now focus on the opposite end of the neutron spectrum. In designing reactor shields, it is necessary to compute the neutron flux level and spectrum after decades of attenuation by both shield and reflector. If the reflector is water, it is the fastest neutrons (in the Mev range) which penetrate it most effectively. For

this reason the deep penetration of fast neutrons in water has been the subject of much study. It is easy to show that the fast neutron flux becomes more and more peaked forward as it traverses the reflector. Consequently, it has been felt that only the most refined transport methods are suitable for use in deep penetration problems. Yet our results seem to indicate that the fast flux may be computed with remarkable accuracy in a P-3 approximation, even after penetration of 90 cm of water.

To avoid slowing-down difficulties, we consider, first, the flux due to a plane fission source immersed in pure hydrogen. The number density of hydrogen will be taken to be the same as in pure water. Cross sections have been copied from the library of the MUFT-4 code (Ref 11), and the hydrogen scattering has been assumed isotropic in the center of mass. Multigroup flux calculations have been carried out in P-3 using SLOP-1 and in P-9 using RDR-5 (Ref 12). The SLOP-1 code has already been mentioned; RDR-5 is a multigroup transport code for the NORC computer. Figure 4 shows the scalar flux, at 1.2 Mev, as a function of position. Discrepancies between P-3 and P-9 results are quite small except in the immediate vicinity of the source plane. The error in the P-3 flux at 90 cm is negligible.

In the pure hydrogen calculation, hydrogen moderation was treated exactly (within limitations imposed by a finite lethargy mesh). The treatment of hydrogen moderation presents no difficulties because of the simple form of its scattering kernel. On the other hand, heavy element scattering kernels are considerably more complicated. It is possible to evaluate heavy element scattering integrals numerically with the aid of some appropriate quadrature formula. This is done in RDR-5, which thus treats heavy elements exactly in the limit of vanishing lethargy mesh width. In SLOP-1, we have chosen to use the Greuling-Goertzel approximation (Ref 13) in order to minimize computing time.

For the sake of simplicity we have not worked with water but with a mixture of mass 1 and mass 16 elements. All scattering was assumed isotropic in the center of mass; all cross sections were taken to be energy-independent, with values characteristic of hydrogen and oxygen at 10 Mev. Figure 5 shows P-3 and P-9 flux spectra 90 cm from the source. Both the P-3 and P-9 computations used a lethargy interval one-fourth as large as $q_{\max}$, the maximum lethargy change in an oxygen collision.*

In the mass 1 - mass 16 mixture, as in the case of pure hydrogen, the accuracy of the P-3 approximation would be more than adequate for shielding applications. Of course, no certain conclusions can be drawn from the results presented here. More realistic problems, with realistic cross sections and scattering kernels, have yet to be run. This will be done with a P-3 multigroup code which is now ready for programming. This code will be

Fig. 4 Comparison of P-3 and P-9 Fluxes in Pure Hydrogen.

* This work was done at Bettis in collaboration with J. A. Davis and R. C. Gast.

quite fast for two reasons. First, the slowing-down calculation has been kept very simple. In a Greuling-Goertzel approximation, heavy element slowing-down densities can be computed from recursion relations without explicitly summing the contributions of preceding groups. All P_ℓ components of the hydrogen slowing-down density can be treated in the same way. Secondly, a simple, approximate form of the P-3 equations is being used. With this code it should be possible to solve the simplified equations, in cylindrical geometry, in about one-third the machine time required by CLIP.

APPROXIMATE FORM OF SPHERICAL HARMONICS EQUATIONS

To motivate the following discussion, it is helpful to compare the treatment of P-3 equations in slab and x-y geometries. The slab equations coalesce into two diffusion equations, coupled through the moments of the flux. The x-y equations coalesce

into four second-order equations, coupled through the flux moments and their first two derivatives. Clearly the x-y equations are much more complicated than their one-dimensional analogues.

Now suppose that, in the slab P-3 equations, one were to substitute general three-dimensional Laplacians for the second derivatives. Equations (2) would result.

$$-D^i \nabla^2 \phi^i + \Sigma_T^i \phi^i = A^i S + \sum_{j \neq i} \alpha^{ij} \phi^j. \quad (2)$$

A simple analysis will show that these equations have some interesting, and perhaps useful, properties.

If, for example, the source strength and cross sections in a diffusing medium vary only in one direction, then, whatever its orientation, the scalar flux as determined by Eqs (2) will satisfy the true P-3 equations exactly. In a two-dimensional unit cell containing a long strip of absorbing material, the thermal flux near the absorber will vary predominantly in the direction normal to its surface. Equations (2) might, then, give much of the P-3 correction to the absorption in the strip. The coefficients of Eqs (2) could, as well, be derived from the double P-1 approximation. In this case, it is hoped, much of the double P-1 correction would be taken into account. The diffusion code PDQ-3 has been modified to test the value of this device. Output of the modified PDQ will be compared with P-3 and Monte Carlo results as soon as the necessary calculations have been completed.

Consider, next, an infinite medium of constant cross section containing any distribution of isotropic sources. Assume only that the source density can be Fourier analyzed. It follows that the source can be written as a superposition of one-dimensional components of the form $f(\vec{k})e^{i\vec{k} \cdot \vec{r}}$. For each component, Eqs (2) will be equivalent to the three-dimensional P-3 equations. By solving

Fig. 5 Comparison of P-3 and P-9 Flux Spectra after Penetration of 90 cm of Mass 1 — Mass 16 Mixture.

Eqs (2) for the given source distribution one has, in effect, solved the three-dimensional P-3 equations.

It can be shown that the range of validity of the approximate form may be extended somewhat. Equations (2) are exactly equivalent to the spherical harmonics equations under the following conditions.

- 1) If the source and scattering are isotropic, then, in any geometry, only the total cross section need be position independent. No restrictions are placed on the scattering and absorption cross sections individually.
- 2) In one-dimensional cylindrical or spherical geometry, the source need not be isotropic, but must be conically symmetric about the vector $\bar{\rho}$ or $\bar{r}$.
- 3) In such one-dimensional geometries, only the total cross section must be spatially independent, even if P-1 scattering is present.

Where the simplified form is rigorous, it can be used to provide reference solutions against which results obtained by other methods may be compared. Let it be required, for example, to find the leakage from a finite cylinder which is surrounded by vacuum. Assume that the source and the scattering are isotropic. Let the scattering, absorption, and total cross sections in the cylinder be represented by Σ_s , Σ_a , and Σ_T , respectively. Assume that the cylinder is embedded in a pure absorber (which is equivalent to a vacuum), and take the cross section of the absorber to be exactly equal to Σ_T . Now the total cross section is position independent, and the simplified form of the spherical harmonics equations is valid. Consequently, the two-dimensional P-7 equations, 36 first-order equations in 36 unknown functions, coalesce into four second-order equations. For the same problem an S-4 code must solve 18 first-order equations. Judging from the number of independent parameters available to describe the

flux, P-7 should be more accurate than S-4. Judging from the number and the nature of the equations to be solved, the P-7 calculation should also be faster. By the same means, reference problems could be constructed in other geometries for which no alternate high precision methods have yet been devised.

Where the simplified form is not rigorous, it may remain a good approximation. The case of an absorbing foil in a two-dimensional cell has been discussed earlier. With more insight into the nature of the approximation, it is now possible to cite an application to a broader class of problems.

Consider a one-group, one-dimensional problem in cylindrical or spherical geometry. Let the sources and cross sections be constant over specified regions, with arbitrary discontinuities at interfaces. Suppose, further, that the radius of curvature of each interface (as measured in mean free paths) is large, so that the interfaces are nearly planar. Many complexities of the true P-3 equations should, then, be irrelevant.

The requirement at interfaces is quite well satisfied in deep penetration and shielding problems. To illustrate the treatment of shielding problems, we choose, as a specific example, a cylindrical reactor configuration with a highly enriched core. The core, 40 cm in radius, is surrounded by a water reflector 100 cm thick. With the aid of the MUFT code, one may compute P-1 constants appropriate to the core and reflector, averaged over the range 10 Mev to 0.625 ev. From these one-group constants, rough P-3 cross sections can be constructed. It is then possible to calculate the one-group P-3 flux shape for fast neutrons. This has been done with CLIP. Equations (2), with corresponding parameters, have been solved with the SIMPL code (Ref 14). The CLIP and SIMPL scalar fluxes agree to within 0.3% at every mesh point. Isolating the range 10 Mev to 0.8 Mev, one may focus attention to the penetration of very fast neutrons. In this case,

CLIP and SIMPL fluxes agree to within 0.8%. It should be noted that, in the latter problem, the flux is attenuated by a factor 2×10^5 in traversing the reflector and that the P-3 and P-1 fluxes differ by a factor of 15 at its outer boundary. This is, then, a stringent test of the suggested approximation.

The method just described can be extended, without difficulty, to treat multienergy problems. Its use would permit the development of a single, fast, P-3 multigroup code for all one-dimensional geometries.

CONCLUSION

The approach outlined in this paper is designed for installations where diffusion codes are widely used. Insofar as possible, the techniques of diffusion theory have been applied to higher order transport calculations. It has been assumed that transport calculations will supplement, and not replace, diffusion theory. This point of view is based on experience with large, water moderated reactors—experience which indicates that for such reactors, transport corrections are only needed in limited and well defined areas of analysis. With this in mind, isolated classes of problems have been attacked, sacrificing generality for speed wherever necessary.

It is precisely for this reason that the S_n method and the methods developed here are not interchangeable. The spherical harmonics methods are fast. They constitute a simple and natural extension of computing systems based on diffusion theory. The S_n method, however, is easier to formulate in complicated geometries, and the S_n equations, once formulated, are valid to any desired order. Both methods are useful. The nuclear designer or reactor physicist should be familiar with both so that he can choose that computing tool best suited to his needs.

REFERENCES

1. B. G. Carlson, "The S_n Method and the SNG Code," LAMS-2201 (January 26, 1958).
2. E. Gelbard, J. Davis, and J. Pearson, "Iterative Solutions to the P-1 and Double P-1 Equations," Nuclear Sci. and Eng., Vol 5 (1959), pp 36-44.
3. Technical Progress Report for the Period December 1, 1959 to March 1, 1960, Reactor Physics and Math, WAPD-MRJ-9, p 17.
4. O. J. Marlowe, et al., "WANDA—A One-Dimensional Few-Group Diffusion Equation Code for the IBM-704," WAPD-TM-28 (November 1956).
5. H. Bohl, et al., "A Thermal Multigroup P-1 Code for the IBM-704," WAPD-TM-188 (To be published).
6. E. Gelbard, et al., "CLIP—An IBM-704 Code To Solve the Cylindrical P-3 Equations in One Dimension," WAPD-TM-207 (To be published).
7. B. Davison, Neutron Transport Theory (London: Oxford, Clarendon Press, 1957).
8. G. G. Bilodeau, et al., "PDQ—An IBM-704 Code To Solve the Two-Dimensional Few-Group Neutron-Diffusion Equations," WAPD-TM-70 (August 1957).
9. E. M. Gelbard, et al., "TRIP-1—A Two-Dimensional P-3 Code in x-y Geometry," WAPD-TM-217 (To be published).
10. J. A. Davis and E. M. Gelbard, "Transport Flux Peaking Calculation in a Fuel Cell," Trans. Am. Nuclear Soc., Paper 24-10, Vol 3, No. 1 (June 1960).
11. H. Bohl, Jr., E. M. Gelbard, and G. H. Ryan, "MUFT-4—A Fast Neutron Spectrum Code for the IBM-704," WAPD-TM-72 (July 1957).

12. R. C. Gast "A P-9 Multigroup Method for Solution of the Transport Equation in Slab Geometry," WAPD-232 (May 1960).
13. E. Grueling, F. Clarke, and G. Goertzel, "A Multigroup Approximation to the Boltzmann Equation for Critical Reactors," NDA-10-96 (1953).
14. L. M. Culpepper, et al., "The IBM-704 SIMPL Codes," WAPD-TM-107 (January 1958).

A solution is presented to the general problem of the transient behavior of a fixed bed ion-exchange system where the rate of exchange is determined by the combined effects of a liquid film, solid diffusion into spherical particles and radioactive decay. The solution enables one to predict the ratio of effluent to influent concentration of a radioactive nuclide as a function of time given this same functional relationship for the nuclide's nonradioactive isotope. Rosen (Ref 1) has developed equations which can be employed to describe this latter relationship provided the solid diffusion coefficient, liquid film resistance, and distribution coefficient are known, and methods are herein developed for evaluating these parameters from a series of simple experiments.

MATHEMATICAL DESCRIPTION OF THE TRANSIENT BEHAVIOR OF A FIXED BED ION-EXCHANGE SYSTEM FOR REMOVAL OF RADIOACTIVE MATERIAL

A. S. Kesten

The transient behavior of a fixed bed ion-exchange system is dependent upon the rate of exchange of ions between the solution and the ion-exchange resin. The steps which limit this rate might conceivably be any or all of the following three:

- 1) Mass transfer in the liquid phase to the surface of the exchanger particles.
- 2) Internal diffusion in the exchanger particles.
- 3) Chemical reaction of exchange at active sites.

In most ion-exchange cases the steps affording the principal resistance to exchange are mass transfer in the liquid phase together with internal diffusion. In the case of exchange of radioactive material, the rate of exchange is also dependent upon the decay rate of the material in question. It is the purpose of this paper to describe the transient behavior of a fixed bed ion-exchange system where the rate of exchange is determined by the combined effects of a liquid film, plus solid diffusion into spherical particles, plus radioactive decay.

It is believed that this is the first time equations have been derived to treat exchange and isotopic decay simultaneously. In addition, an extension is outlined in this article which allows one to treat those systems in which the influent concentration is a variable. Since this is a more realistic approach to the problem, a wider application should ensue.

The system considered consists of a bed of homogeneous spherical particles of uniform radius, through which the liquid solution flows with a constant linear velocity. The desired result is an expression for the effluent concentration as a function of time and bed length following a step increase in the influent concentration from zero to c_0 at zero time. This result has been obtained for the exchange of nonradioactive material by Rosen (Ref 1). A similar derivation for the exchange of radioactive material has been undertaken here, and Rosen's development has been extended to include a term for isotopic decay.

ASSUMPTIONS

The three primary assumptions made in the derivation are:

- 1) The liquid film coefficient and the solid diffusion coefficient are independent of position and of concentration over the range of its variation.
- 2) The system has a linear isotherm so that under equilibrium conditions the concentration, q_s , of adsorbed material at the surface of the solid is given by $q_s = Kc$, where K is an effective equilibrium constant which can be considered to be defined by this relation.
- 3) Any variations in concentration or velocity over a given cross-section of the bed can be neglected.

NOMENCLATURE

- b = radius of spherical particles (cm)
 c = $c(x, \theta)$ = concentration of material in fluid (meq/cc)
 c_o = $c(o, \theta)$ = concentration of input face of bed (meq/cc)
 D = solid diffusion coefficient (cm^2/sec)
 h = liquid film coefficient (cm/sec)
 K = effective equilibrium constant (distribution coefficient)
 m = void volume per unit volume of adsorbent
 q = $q(x, \theta)$ = average (over particle) of concentration of adsorbed material (meq/cc)
 q_i = $q_i(r, x, \theta)$ = internal concentration distribution of adsorbed material (meq/cc)
 q_s = $q_i(b, x, \theta)$
 r = radial distance from center of spherical particle (cm)
 R_f = $b/3h$ = effective surface film resistance (sec)
 t = time measured from instant of step input (sec)
 u = $u(x, \theta) = c(x, \theta)/c_o$
 v = linear flow velocity (cm/sec)
 x = z/mv = time required for fluid to flow distance z/m (sec)
 z = distance measured from input face of bed (cm)

$$\gamma = 3DK/b^2 (\text{sec}^{-1})$$

$$\theta = t - z/v = \text{time measured from instant point is reached by fluid (sec)}$$

$$\lambda = \text{decay constant of radioactive material} (\text{sec}^{-1})$$

$$\phi = \text{variable of integration}$$

DERIVATION OF EQUATIONS

Making use of Assumption (3), the concentration of trace material in solution depends only on the bed length, z , and time, t . A material balance around a differential element of bed length, dz , in an element of time, δt , gives

$$\begin{aligned} \frac{\partial c}{\partial z} dz + \frac{\partial c}{\partial t} \delta t + \lambda c \frac{dz}{v} \\ = - \frac{1}{m} \left[\frac{\partial q}{\partial t} \delta t + \lambda q \delta t \right]. \end{aligned} \quad (1)$$

Dividing through by δt and letting $x = z/mv$ and $\theta = t - z/v$, we get

$$\frac{\partial c}{\partial x} + \lambda mc = - \left[\frac{\partial q}{\partial \theta} + \lambda q \right]. \quad (2)$$

Letting $q^1 = qe^{\lambda\theta}$, Eq (2) becomes

$$\frac{\partial c}{\partial x} + \lambda mc = - \frac{\partial q^1}{\partial \theta} e^{-\lambda\theta}. \quad (3)$$

The rate at which material is taken up from solution by the solid particles is determined by the combined effects of a liquid surface film, solid diffusion into the particles, and radioactive decay. All material diffusing into the interior of a solid particle must first reach the surface of the particle by diffusing through a static layer of fluid surrounding the particle. To be able to take account of the effect of this layer, we assume that a uniform liquid surface film surrounds each solid spherical particle and that the concentration at the outer surface of the liquid film is that in the body of the fluid at that value of x and θ , i.e., $c(x, \theta)$. The rate at which the film diffusion takes place is then taken as proportional to the concentration change across the film, $c - q_s/K$. It is possible that, because of the flow pattern around the particle, the static layer of

fluid may not be of uniform thickness all around the particle. However, it may be possible to choose the value of the liquid film coefficient, h , so that $h(c - q_s/K)$ gives the average rate of flow of material across the surface film per unit of surface area. The effective film resistance, R_f , is then equal to the reciprocal of the surface to volume ratio of a particle multiplied by h , i.e., $R_f = b/3h$. Inside the particle the diffusion can be expected to follow Fick's second law.

With these conditions, the rate, $\partial q/\partial \theta$, is given in terms of the surface concentration, q_s , by solving Eqs (4) and (5):

$$\frac{\partial q}{\partial \theta} + \lambda q = \frac{\partial q_1}{\partial \theta} e^{-\lambda \theta} = \frac{1}{R_f} (c - q_s/K); \quad (4)$$

$$\frac{\partial q_1}{\partial \theta} + \lambda q_1 = \frac{D}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial q_1}{\partial r} \right]; \quad (5)$$

where $q_1 = q_1(r, x, \theta)$ is the concentration distribution of adsorbed material in the interior of the spheres, and $q_s(x, \theta) = q_1(b, x, \theta)$. The average concentration in the particles is given by

$$q(x, \theta) = \frac{3}{b^3} \int_0^b q_1(r, x, \theta) r^2 dr. \quad (6)$$

Equations (5) and (6) can be rewritten as

$$\frac{\partial q_1}{\partial \theta} = \frac{D}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial q_1}{\partial r} \right] \quad (5a)$$

and

$$q_1(x, \theta) = \frac{3}{b^3} \int_0^b q_1(r, x, \theta) r^2 dr. \quad (6a)$$

The initial and boundary conditions may be taken as the bed being initially free of adsorbed material and a step function in the influent concentration.

$$q_1(r, x, \theta) = q_1(r, x, 0) = 0, \quad 0 \leq r \leq b, \quad x \geq 0 \quad (7)$$

$$u(0, \theta) = c(0, \theta)/c_o = \begin{cases} 0, & \theta \leq 0 \\ 1, & \theta > 0 \end{cases} \quad (8)$$

By means of Duhamel's Theorem (Ref 2, p 20) we can obtain an expression for q_s^1 . For $q_s^1(r, x, 0) = 0$, we have

$$q_1^1(r, x, \theta) = \int_0^\theta q_s^1(x, \varphi) \frac{\partial}{\partial \theta} H(r, \theta - \varphi) d\varphi. \quad (9)$$

where $H(r, \theta)$ is the solution of the problem of solid diffusion into an initially empty spherical particle for a constant imposed surface concentration of unity for $\theta \geq 0$. The value of $H(r, \theta)$ is given (Ref 2, p 200) by

$$H(r, \theta) = 1 - 2 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{\sigma_n r} \cdot \sin(\sigma_n r) \exp[-D\sigma_n^2 \theta], \quad (10)$$

where $\sigma_n = n\pi/b$. Differentiation of Eq (10) with respect to θ gives

$$\frac{\partial H(r, \theta)}{\partial \theta} = 2D \sum_{n=1}^{\infty} (-1)^{n+1} \sigma_n \frac{\sin(\sigma_n r)}{r} \exp[-D\sigma_n^2 \theta]. \quad (11)$$

Substituting Eq (11) in Eq (9) and interchanging the order of integration and summation, we get

$$q_1^1(r, x, \theta) = 2D \sum_{n=1}^{\infty} (-1)^{n+1} \sigma_n \frac{\sin(\sigma_n r)}{r} \cdot \int_0^\theta q_s^1(x, \varphi) \exp[-D\sigma_n^2 (\theta - \varphi)] d\varphi. \quad (12)$$

If this expression is used in Eq (6a) and the order of integration and summation exchanged again, we get

$$q_1^1(x, \theta) = \frac{6D}{b^2} \sum_{n=1}^{\infty} \int_0^\theta q_s^1(x, \varphi) \cdot \exp[-D\sigma_n^2 (\theta - \varphi)] d\varphi \quad (13)$$

after performing the integration with respect to r . To get an expression for the rate, $\frac{\partial q_1^1}{\partial \theta}$, consider*

*Ref 3, p 220

$$\left. \begin{aligned} \frac{d}{dt} \int_{a(t)}^{b(t)} f(\varphi, t) d\varphi &= f[b(t), t] b'(t) \\ -f[a(t), t] a'(t) &+ \int_{a(t)}^{b(t)} \frac{\partial f}{\partial t}(\varphi, t) d\varphi. \end{aligned} \right\} (14)$$

We find, then, that

$$\left. \begin{aligned} \frac{\partial}{\partial \theta} \int_0^\theta q_s^1(x, \varphi) \exp[-D\sigma_n^2(\theta - \varphi)] d\varphi \\ = \int_0^\theta \frac{\partial q_s^1}{\partial \varphi} \exp[-D\sigma_n^2(\theta - \varphi)] d\varphi \end{aligned} \right\} (15)$$

after integrating by parts and making use of the fact that $q_s^1(x, 0) = 0$.

Combining Eqs (13) and (15), we have

$$\left. \begin{aligned} \frac{\partial q_s^1(x, \theta)}{\partial \theta} &= \frac{6D}{b^2} \sum_{n=1}^{\infty} \int_0^\theta \frac{\partial q_s^1}{\partial \varphi}(x, \varphi) \\ &\cdot \exp[-D\sigma_n^2(\theta - \varphi)] d\varphi. \end{aligned} \right\} (16)$$

We wish to obtain an equation involving only the single unknown function $c(x, \theta)$ and its derivatives. From Eqs (3) and (4), we get q_s^1 in terms of c :

$$q_s^1 = Ke^{\lambda\theta} \left[(\lambda m R_f + 1) c + R_f \frac{\partial c}{\partial x} \right]. \quad (17)$$

Combining Eqs (3), (16), and (17), we have the desired equation as a linear partial integro-differential equation:

$$\left. \begin{aligned} \left[\frac{\partial c}{\partial x} + \lambda m c \right] e^{\lambda\theta} &= -2\gamma \sum_{n=1}^{\infty} \int_0^\theta \frac{\partial}{\partial \varphi} \\ &\cdot \left\{ e^{\lambda\theta} [(\lambda m R_f + 1) c \right. \\ &\left. + R_f \frac{\partial c}{\partial x}] \right\} \exp[-D\sigma_n^2(\theta - \varphi)] d\varphi, \end{aligned} \right\} (18)$$

To solve this equation subject to the boundary conditions previously given, we use the Laplace transform, and transform Eq (18) with respect to θ . We will use the following relations:

$$\mathcal{L}[f(x, \theta)] = F(x, s) \quad (19)$$

$$\mathcal{L}\left\{ \frac{\partial}{\partial \theta} [f(x, \theta)] \right\} = sF(x, s) - f(x, 0) \quad (20)$$

$$\mathcal{L}\left[\frac{\partial}{\partial x} f(x, \theta) \right] = \frac{\partial F(x, s)}{\partial x} \quad (21)$$

$$\left. \begin{aligned} \mathcal{L}\left[\int_0^\theta f_1(x, \varphi) f_2(x, \theta - \varphi) d\varphi \right] \\ = F_1(x, s) F_2(x, s) \end{aligned} \right\} (22)$$

$$\mathcal{L}[\exp(-D\sigma_n^2 \theta)] = 1/(s + D\sigma_n^2) \quad (23)$$

$$\mathcal{L}[e^{\lambda\theta} f(x, \theta)] = F(x, s - \lambda) \quad (24)$$

$$\mathcal{L}\left[\int_0^\theta f(x, \varphi) d\varphi \right] = F(x, s)/s \quad (25)$$

If we transform Eq (18) using Relations (19) through (24), we get

$$\left. \begin{aligned} \frac{\partial C}{\partial x}(x, s - \lambda) + \lambda m C(x, s - \lambda) &= -2\gamma \sum_{n=1}^{\infty} \\ &\cdot \frac{s}{s + D\sigma_n^2} [(\lambda m R_f + 1) C(x, s - \lambda) \\ &+ R_f \frac{\partial C}{\partial x}(x, s - \lambda)], \end{aligned} \right\} (26)$$

or

$$\left. \begin{aligned} \frac{\partial C}{\partial x}(x, s - \lambda) + \lambda m C(x, s - \lambda) \\ = -Y_D(s) \left[(\lambda m R_f + 1) C(x, s - \lambda) \right. \\ \left. + R_f \frac{\partial C}{\partial x}(x, s - \lambda) \right], \end{aligned} \right\} (27)$$

$$\text{where } Y_D(s) = 2\gamma \sum_{n=1}^{\infty} \frac{s}{s + D\sigma_n^2}.$$

Solving for $\frac{\partial C}{\partial x}(x, s - \lambda)$, we get

$$\frac{\partial C}{\partial x}(x, s - \lambda) = -C(x, s - \lambda) [\lambda m + Y_T(s)], \quad (28)$$

where

$$Y_T(s) = \frac{Y_D(s)}{1 + R_f Y_D(s)}.$$

The solution of Eq (28), satisfying the initial condition $\frac{C(0, s - \lambda)}{c_0} = \frac{1}{s - \lambda}$, is

$$\left. \begin{aligned} U(x, s - \lambda) &= \frac{C(x, s - \lambda)}{c_0} \\ &= \frac{1}{s - \lambda} e^{-Y_T(s)x} e^{-\lambda mx}. \end{aligned} \right\} \quad (29)$$

The desired result, $u(x, \theta)$, may be obtained by taking the inverse transform of Eq (29):

$$e^{\lambda \theta} u(x, \theta) = \mathcal{L}^{-1} \left[\frac{1}{s - \lambda} e^{-Y_T(s)x} \right] e^{-\lambda mx}; \quad (30)$$

$$u(x, \theta) = \mathcal{L}^{-1} \left[\frac{1}{s - \lambda} e^{-Y_T(s)x} \right] e^{-\lambda(mx + \theta)}. \quad (31)$$

It is desired to express the solution to the problem, $u(x, \theta)$, as a function of the result obtained by Rosen (Ref 1) for the exchange of nonradioactive material. Rosen's result, $u^+(x, \theta)$, may be written as

$$u^+(x, \theta) = \frac{c^+}{c_0}(x, \theta) = \mathcal{L}^{-1} \left[\frac{1}{s} e^{-Y_T(s)x} \right]. \quad (32)$$

Letting $F(x, s) = e^{-Y_T(s)x}$ and applying Relation (25), we obtain

$$u^+(x, \theta) = \mathcal{L}^{-1} \left[\frac{F(x, s)}{s} \right] = \int_0^\theta f(x, \varphi) d\varphi. \quad (33)$$

From Relation (22), we have

$$\mathcal{L}^{-1} \left[\frac{F(x, s)}{s - \lambda} \right] = \int_0^\theta f(x, \varphi) e^{\lambda(\theta - \varphi)} d\varphi. \quad (34)$$

Differentiating Eq (33) with respect to θ , we get

$$f(x, \theta) = \frac{\partial u^+(x, \theta)}{\partial \theta}. \quad (35)$$

Substituting this in Eq (34), we find

$$\mathcal{L}^{-1} \left[\frac{F(x, s)}{s - \lambda} \right] = \int_0^\theta \frac{\partial u^+(x, \varphi)}{\partial \varphi} e^{\lambda(\theta - \varphi)} d\varphi. \quad (36)$$

Integrating Eq (36) by parts and recalling that $u^+(x, 0) = 0$, we get

$$\left. \begin{aligned} \mathcal{L}^{-1} \left[\frac{F(x, s)}{s - \lambda} \right] &= u^+(x, \theta) \\ &+ \lambda \int_0^\theta u^+(x, \varphi) e^{\lambda(\theta - \varphi)} d\varphi. \end{aligned} \right\} \quad (37)$$

Combining Eqs (31) and (37), we get, finally,

$$\left. \begin{aligned} u(x, \theta) &= \left[u^+(x, \theta) + \lambda \int_0^\theta u^+(x, \varphi) \right. \\ &\quad \left. \cdot e^{\lambda(\theta - \varphi)} d\varphi \right] e^{-\lambda(mx + \theta)}, \end{aligned} \right\} \quad (38)^*$$

where Rosen's solution, $u^+(x, \theta)$, is given by

$$\left. \begin{aligned} u^+(x, \theta) &= \frac{1}{2} + \frac{2}{\pi} \int_0^\infty e^{-\gamma x H_1(\varphi, \nu)} \sin \\ &\quad \cdot [\sigma \theta \varphi^2 - \gamma x H_2(\varphi, \nu)] \frac{d\varphi}{\varphi}, \end{aligned} \right\} \quad (39)$$

in which

$$\begin{aligned} \sigma &= 2D/b^2, \\ \nu &= \gamma R_f, \\ \gamma &= 3DK/b^2, \end{aligned}$$

*The efficacy of Eq (38) has not been tested with experimental data. Some qualitative support for the over-all approach is available in Ref 4; however, the mathematical approach in Ref 4 is somewhat different from that used here.

$$H_1(\varphi, \nu) = \frac{\left[H_{D1} + \nu(H_{D1}^2 + H_{D2}^2) \right]}{\left[(1 + \nu H_{D1})^2 + (\nu H_{D2})^2 \right]},$$

$$H_2(\varphi, \nu) = H_{D2} / \left[(1 + \nu H_{D1})^2 + (\nu H_{D2})^2 \right],$$

$$H_{D1} = \varphi (\sinh 2\varphi + \sin 2\varphi) / (\cosh 2\varphi - \cos 2\varphi) - 1,$$

and

$$H_{D2} = \varphi (\sinh 2\varphi - \sin 2\varphi) / (\cosh 2\varphi - \cos 2\varphi).$$

SOLUTION FOR THE CASE OF VARIABLE INFLUENT CONCENTRATION

Equation (38) was derived for a constant influent concentration. For the case of a variable input, the boundary condition which must be satisfied by Eq (28) is $C(0, s - \lambda) = C_0(s - \lambda)$. Equation (29) then becomes

$$C(x, s - \lambda) = C_0(s - \lambda) e^{-Y_T(s)x} e^{-\lambda mx}. \quad (40)$$

The desired result, $c(x, \theta)$, may be obtained by taking the inverse transform of Eq (40):

$$c(x, \theta) = \mathcal{L}^{-1} \left[C_0(s - \lambda) e^{-Y_T(s)x} \right] e^{-\lambda(mx + \theta)}. \quad (41)$$

Applying Eq (35) and Relations (22) and (24), we find

$$c(x, \theta) = \left[\int_0^\theta \frac{\partial u^+(x, \varphi)}{\partial \varphi} c_0(\theta - \varphi) \cdot e^{\lambda(\theta - \varphi)} d\varphi \right] e^{-\lambda(mx + \theta)}. \quad (42)$$

For the case of a variable influent concentration then, Eq (42) may be employed to compute $c(x, \theta)$ using numerical or graphical methods to evaluate the integral.

APPLICATION OF EQUATIONS TO THE ANALYSIS OF EXPERIMENTAL DATA

Determination of $u(x, \theta)$ from $u^+(x, \theta)$

It has been shown that the values for the ratio of effluent to influent concentration of a radioactive nuclide, $u(x, \theta)$, can be calculated from the ratios determined for its nonradioactive isotope, $u^+(x, \theta)$, using Eq (38). With a plot of $u^+(x, \theta)$ versus θ and a knowledge of the decay constant of the nuclide in question, values of $u(x, \theta)$ can be obtained from Eq (38) using numerical or graphical methods to evaluate the integral Rosen has computed and plotted values of $u^+(x, \theta)$ as a function of a time parameter for selected values of bed length and film resistance parameters (Ref 5). A typical plot is shown in Fig. 1. Here, $u^+(x, \theta)$ is plotted versus θ for the case where

$$\beta = \frac{3DKz}{mvb^2} = 20.0,$$

$$\nu/\beta = \frac{mvR_f}{z} = 0.1,$$

and

$$\frac{mv}{Kz} = 3 \times 10^{-4} \text{ min}^{-1}.$$

Values of $u(x, \theta)$ were computed for the above parameters using a value of $5 \times 10^{-4} \text{ min}^{-1}$ for the decay constant, λ . Equation (38) was employed to calculate $u(x, \theta)$ as a function of θ from λ and

Figure 1

$u^+(x, \theta)$. The term $u(x, \theta)$ has been plotted, along with $u^+(x, \theta)$, in Fig. 1.

Determination of the Distribution Coefficient, K, from $u^+(x, \theta)$

For a fixed bed ion-exchange system in which there is no resistance to exchange (i.e., $D = \infty$, $R_f = 0$), a plot of $u^+(s, \theta)$ versus θ would exhibit a step change in $u^+(x, \theta)$ from 0 to 1 at time θ_B . It is apparent that the value for this inflection point in such a system is given by

$$\theta_B = \frac{Kz}{mv}. \quad (43)$$

Rosen's graphs indicate that, even for ion-exchange systems with some resistance to exchange, the inflection point in the typical S-shaped plot of $u^+(x, \theta)$ versus θ is still given approximately by Eq (43). If such plots are obtained for systems in which $\beta = 3DKz/mvb^2 \geq 1$ and $\nu/\beta \cdot mvR_f/z \leq 0.2$, Eq (43) can be used to predict the distribution coefficient, K, to within a few percent. Since β and ν/β satisfy these conditions in most ion-exchange systems, the distribution coefficient can be determined by the above method for the majority of cases.

Determination of the Solid Diffusion Coefficient, D, and the Liquid Film Resistance, R_f , from $u^+(x, \theta)$

Rosen has plotted $u^+(x, \theta)$ versus α/β with β and ν/β as parameters, where $\beta = 3DKz/mvb^2$, $\nu/\beta = mvR_f/z$, and $\alpha/\beta = (2mv/3Kz)\theta$. These curves have been replotted in Fig. 2 as $u^+(x, \theta)$ at $\alpha/\beta = 0.5$ versus erf N with ν/β as a parameter, where $N = 0.125/\sqrt{1/5\beta + \nu/\beta}$. Plots of $u^+(x, \theta)$ versus α/β , representing a series of experiments run at different velocities with all other parameters constant, can be employed, with the aid of Fig. 2, to determine D and R_f . The procedure makes use of the facts that the solid diffusion coefficient, D, is independent of velocity and that the liquid film resistance, R_f , approaches zero with increasing vel-

ocity. At sufficiently high velocities, then, $1/5\beta \gg \nu/\beta$, and

$$N = 0.125 \sqrt{5\beta} = 0.125 \sqrt{15 \frac{DKz}{mb^2}} \sqrt{\frac{1}{\nu}} \left\{ \begin{aligned} &= 0.483 \sqrt{\frac{DKz}{mb^2}} \sqrt{\frac{1}{\nu}} \end{aligned} \right\} \quad (44)$$

If N is calculated at each velocity from the value of $u^+(x, \theta)$ at $\alpha/\beta = 0.5$ and from the curve $\nu/\beta = 0$ in Fig. 2, a plot of these calculated values of N versus $1/\nu$ should approach a straight line (passing through the origin) asymptotically with increasing velocity. The slope of this asymptote, given by Eq (44) as $0.483/\sqrt{DKz/mb^2}$, may be used to calculate the solid diffusion coefficient, D. With a knowledge of D, R_f can be obtained at each velocity by (1) assuming a value of ν/β and determining N from this assumed value and from the value of $u^+(x, \theta)$ at $\alpha/\beta = 0.5$ using Fig. 2, and (2) calculating ν/β from $N = 0.125/\sqrt{1/5\beta + \nu/\beta}$. When the assumed and calculated values of ν/β check, R_f is calculated from $\nu/\beta = mvR_f/z$. The entire procedure may be summarized as follows:

- 1) Plot $u^+(x, \theta)$ versus α/β at each velocity. From each of these plots, determine $u^+(x, \theta)$ at $\alpha/\beta = 0.5$.
- 2) Determine erf N for each velocity from Fig. 2 using the value of $u^+(x, \theta)$ at $\alpha/\beta = 0.5$ and the curve $\nu/\beta = 0$. Calculate N.
- 3) Plot these calculated values of N versus $\sqrt{1/\nu}$. At high velocities the curve should approach a straight line which passes through the origin. Determine the slope of this line and calculate the solid diffusion coefficient, D, from

$$D = \frac{mb^2}{Kz} \left[\frac{\text{slope}}{0.483} \right]^2 = 4.28 \frac{mb^2}{Kz} (\text{slope})^2. \quad (45)$$

- 4) Assume a value of ν/β at each velocity. Determine N from this assumed value and from the

Figure 2

value of $u^+(x, \theta)$ at $\alpha/\beta = 0.5$ using Fig. 2. Calculate ν/β from

$$\frac{\nu}{\beta} = \left[\frac{0.125}{N} \right]^2 - \frac{1}{5\beta} \quad (46)$$

If the assumed and calculated values of ν/β do not agree, use the calculated value for the next assumption and repeat this step.

5) Calculate R_f at each velocity from

$$R_f = \frac{z}{mv} \frac{\nu}{\beta} \quad (47)$$

SUMMARY

Summarizing, then, Eq (38) enables one to predict the ratio of effluent to influent concentration of a

radioactive nuclide as a function of time given this same functional relationship for the nuclide's non-radioactive isotope. To describe this latter relationship, Rosen's equations can be employed provided the solid diffusion coefficient, liquid film resistance, and distribution coefficient are known. These parameters can be evaluated from a series of simple experiments using the methods developed above.

REFERENCES

1. J. B. Rosen, "Kinetics of a Fixed Bed System for Solid Diffusion into Spherical Particles," J. Chem. Phys., Vol 20 (1952), pp 387-394.
2. H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids (London: Oxford University Press, 1947).
3. W. Kaplan, Advanced Calculus (Reading, Massachusetts: Addison-Wesley Publishing Co., Inc., 1952).
4. G. P. Simon, C. S. Abrams, and W. T. Lindsay, Jr., "The Performance of Base-Form Ion Exchangers for pH Control and Removal of Radioisotopes from a Pressurized Water Reactor System," WAPD-TM-215 (July 1960).
5. J. B. Rosen, "General Numerical Solution for Solid Diffusion in Fixed Beds," Ind. Eng. Chem., Vol 46, pt 2 (1954), p 1590.

The effects of eliminating the pickling operation normally employed on PWR Seed 1, Zircaloy-2 components prior to corrosion testing were investigated. Corrosion weight gains, hydrogen analysis, and metallographic methods were employed to evaluate the corrosion resistance of the three prior-to-welding surface conditions investigated. A black lustrous corrosion film proved to be the most satisfactory component condition for welding.

ELIMINATION OF PWR SUBASSEMBLY AND CLUSTER PICKLING

J. C. Helbling

An undesirable white corrosion product was found on many PWR Seed 1 type clusters following the standard corrosion test—3-1/2 days in 650°F water, employed to prove the integrity of the Zircaloy-2 cladding and welds in the cluster. The white corrosion in these cases was caused by acid staining resulting from acid drying on the surfaces before they could be adequately rinsed. This problem had not arisen earlier because subassemblies and clusters were considerably shorter than the 97-in. long PWR Seed 1 clusters.

The long PWR Seed 1 cluster length also enabled the temperature of the pickling acid to increase approximately 40°F from the bottom to the top of the pickling bath. Acid temperatures as high as 145°F were recorded. Channel surfaces could be expected to be even hotter.

The undesirable corrosion results on these Zircaloy-2 clusters pointed out the need for improving or eliminating the pickling operation. The possibility of eliminating the pickling of PWR subassemblies and clusters prior to corrosion testing appeared encouraging. Machined surfaces exhibited normal weight gains following satisfactory surface

cleaning without resorting to a pickling operation. Corrosion tests performed on PWR fuel elements that had been previously welded into subassemblies with pickled surfaces and also with prior black corrosion surfaces produced a lustrous black film in all areas except the heat affected zone of the welds. Since the white corrosion at the heat affected zone (HAZ) could be eliminated by a pickling operation that removed approximately 0.0015 in. of surface metal, it was believed that the corrosion in this area would be limited to a depth of less than 0.0015 in. Earlier experiments of this nature were all performed on atmosphere melted Zircaloy-2, and no actual evaluation of this heat affected zone corrosion, either by metallographic, weight gain, or hydrogen analysis, had been made.

Although the shop practices and equipment have since been improved to eliminate acid staining of Zircaloy-2 and the resultant white corrosion product, there are many additional advantages to eliminating the pickling operation. These include:

- 1) a savings of from 6 to 8 mils in cladding material, depending upon the method of fuel element preparation, because only one fuel

element pickling operation is necessary,

- 2) better control of subassembly and cluster channel dimensions,
- 3) elimination of the acid staining encountered in PWR Seed 1,
- 4) greater confidence in the cladding thickness of fuel elements in finished clusters, and
- 5) elimination of three annealing operations.

The use of corrosion tested elements, cited above, offers two additional advantages in that it makes it possible to examine the actual heat transfer surface of the fuel elements before welding into a subassembly, and it minimizes surface contamination from the Ti-Namel steel spacers.

The only major disadvantages in the utilization of either the pickled surfaces or the corrosion tested surfaces are the white or gray corrosion at the HAZ of the weld, the decrease in thermal conductivity in this area, and the incomplete stress relief produced by the proposed 750°F corrosion test. Data, as yet unpublished, performed on beta-quenched Zircaloy indicates that a complete stress relief cannot be accomplished by a 24-hr corrosion test in 750°F steam. These data show that residual stress as high as 14,000 psi can remain after such a treatment.

Dummy fuel elements of double vacuum melted Zircaloy-2 were fabricated for this investigation by rolling and machining to PWR Seed 1 fuel elements. Fuel elements, prepared by three different fabrication procedures which previously had shown promise of success, were welded into three nine-plate subassemblies. The fuel elements were prepared for welding by three methods: (1) corrosion testing, vapor blasting, and pickling, (2) corrosion testing, vacuum annealing, and pickling, and (3) corrosion testing only. The subassemblies welded with these elements are identified as EP-1, EP-2, and EP-3, respectively. All element pickling

was performed in a 3.5% HF, 39% HNO₃, balance H₂O solution. The effects of these three methods of element preparation upon corrosion were evaluated by metallographic examination, corrosion weight gain data, and hydrogen analysis.

Ti-Namel channel spacers of the same dimensions as those used on production subassemblies were employed during welding to duplicate production welding conditions. However, all spacers were vacuum annealed 2 hr at 700°C prior to assembly to remove volatile gases that might be trapped within or on the surfaces of the spacers.

The effect of subassembly annealing upon corrosion results and channel spacing was also included as part of this investigation.

EXPERIMENTAL PROCEDURE

The 27 dummy fuel elements employed in the fabrication of the three test subassemblies were made from the same ingot of vacuum melted Zircaloy-2. To expedite fabrication, the material was hot and cold rolled to a thickness suitable for machining into fuel elements. Subsequent to machining, the dummy elements were pickled and corrosion tested for 3 days in 680°F water.

The corrosion tested dummy elements were divided into three groups of nine plates each. The first group was vapor blasted to remove the black oxide film and pickled 0.0015 in. per surface in the HF-HNO₃-H₂O solution prior to assembly and welding. The second group of elements was vacuum annealed 4 hr at 750°C to dissolve the oxide film and then pickled in the same manner as the first group prior to assembly and welding. The third group was assembled and welded with the corrosion film still intact.

The nine-plate dummy subassemblies were assembled and welded from fuel elements prepared according to the three fuel element preparation procedures cited above. The channel spacers used

in the welding of these subassemblies were made of Ti-Namel, vacuum annealed 2 hr at 700°C prior to assembly.

All three subassemblies were welded in a helium atmosphere by identical welding procedures. The welding current was increased from that employed in the production of PWR Core 1 Seed 1 because of the increased welding currents required for vacuum melted material. Welding conditions were 190 amp, 16 v, and 8 in./min travel.

Following welding, each of the three subassemblies was cut into three equal lengths of approximately 26 in. The Ti-Namel spacers were removed by pickling from one length, Section A, of each subassembly immediately after cutting. A second length, Section C, of each subassembly was annealed 1 hr at 600°C with the channel spacers in place. The spacers were then removed by pickling and the length given a second anneal for 4 hr at 760°C to dissolve spacer contamination. The spacers were also removed from the third length, Section B, of each subassembly immediately after cutting and the section held for possible future tests. All channel spacers were removed by pickling in a hot solution of 50% HNO_3 - 50% H_2O .

Corrosion Testing

A 2-in. section was cut from each of the six test lengths for corrosion weight gain tests. The remaining portions (approximately 24 in.) were subjected to a 3-day corrosion test in 650°F water. The only surface preparation employed prior to corrosion test was a cleaning operation in a hot (160° - 180°F) detergent (Penn Salt A27) solution, followed by hot water and Grade A water* rinses. The detergent solution employed in this case was 6 oz/gal of Penn Salt A27 in water.

The 2-in. lengths of each test section mentioned above were machined to remove the weld metal

*Grade A water is deionized water with an electrical resistivity of 500,000 ohm-cm and a pH value of 7.0 ± 1.0 .

and free the web sections of the elements for preparation into corrosion coupons. Six of the seven inner plates were selected for machining into coupons. The two coupons identified as A and C were taken near the edges of elements and included the entire HAZ of the weld. The B section, from the center of the element, was unaffected by the welding operation.

The A, B, and C coupons from three plates of each 2-in. length were corrosion tested in 680°F water for total test periods of 3, 14, 28, 42, 66, 94, 122, and 140 days. The coupons of the other three plates were similarly tested through 140 days in 750°F steam. A set of reference coupons representative of element conditions EP-1 and EP-2 was inserted into the corrosion tests under each condition for comparison. Three standard weight gain coupons were also inserted into each test to check the operation of the autoclaves. All weight gain coupons were detergent cleaned and rinsed in the same manner as employed on the subassembly sections. The average weight gain data are presented in Table I.

Metallographic Examination

Metallographic examination of the corrosion film was performed on the samples taken from the 24-in. subassembly lengths after the 3-day, 650°F water corrosion test and on the C weight gain coupons after 14 days test and again after each succeeding test period in both 680°F water and 750°F steam. The as-welded element was also examined metallographically to compare and explain the observations noted on the corrosion coupons. Photomicrographs of the various corrosion films are presented in Figs. 1-9.

Effect of Annealing

The 24-in. subassembly sections were included in the investigation to determine if annealing is needed to stabilize channel spacing and to afford a visual observation of the corrosion that may

TABLE I

EFFECT OF FUEL ELEMENT CONDITION UPON CORROSION WEIGHT GAIN (mg/dm²)

As-Welded Subassemblies A Sections

680°F Water Corrosion Test

Time (days)	<u>EP-1</u>		<u>Element Condition</u>		<u>EP-3</u>		<u>Reference Samples</u>		Prior Corrosion Film
	UA*	HAZ**	UA	HAZ	UA	HAZ	Calc	Pickled	
3†	10.9	9.4	11.1	9.8	1.4	9.5	37.0	12.6	1.4
14	16.6	15.9	16.8	9.9	7.4	19.7	56.5	19.4	6.6
28	19.5	19.3	23.6	15.2	9.8	23.6	74.6	20.4	8.3
42	22.0	21.1	24.2	15.1	11.2	29.0	95.4	24.7	12.9
66	27.1	26.4	29.5	20.5	16.5	34.9	102.1	30.6	18.4
94	30.6	31.1	34.8	26.6	21.2	42.0	118.8	33.1	20.3
122	35.7	42.8	44.1	39.3	24.7	49.3	118.8	41.8	25.2
140	49.9	51.8	55.2	47.3	36.8	59.6	144.5	53.5	37.8

750°F Steam Corrosion Test

3	22.8	18.8	26.0	23.1	7.4	24.5	112.7	25.3	9.4
14	33.4	30.3	38.9	36.8	17.6	39.6	153.1	39.3	22.7
28	42.1	39.7	45.9	43.8	24.9	50.6	174.5	45.4	28.5
46	57.9	57.1	62.5	61.0	39.8	66.6	197.0	62.6	46.0
66	72.8	73.6	77.7	78.9	54.5	84.3	228.1	76.8	59.8
94	84.9	89.2	89.4	95.0	64.2	102.0	286.7	93.2	73.3
122	105.4	113.1	98.0	118.0	82.8	123.5	320	106.2	92.3
140	118.6	128.7	112.8	135.2	97.5	142.2	355.7	123.8	109.7

Annealed Subassembly (C Sections)680°F Water Corrosion Test

3	9.8	9.4	11.7	10.5	14.0	14.7
14	15.0	14.4	17.6	15.9	21.5	22.1
28	18.2	18.8	21.9	21.8	36.4	37.6
42	24.3	24.3	26.0	25.7	48.4	58.5
66	37.9	37.6	41.3	36.3	69.1	79.3
94	54.2	54.7	59.1	56.7	91.6	100.0
122	70.1	70.5	76.3	73.1	113.3	119.9
140	79.8	80.7	86.5	83.5	127.6	132.3

750°F Steam Corrosion Test

3	18.0	18.3	19.9	21.3	21.3	22.5
14	32.3	32.2	36.0	34.9	49.9	63.3
28	50.1	49.4	52.5	49.9	108.8	136.6
46	65.2	65.3	68.6	66.3	174.5	161.0
66	87.9	87.8	90.3	88.6	226.3	208.5
94	98.3	101.2	103.4	102.0	258	237.5
122	125.1	128.2	125.6	123.3	310.5	303.1
140	141.4	146.8	146.5	143.8	360.9	332.1

* UA coupons taken from area unaffected by weld heat.

** HAZ coupons taken from edge of elements containing the heat affected zone.

† Weight gain data for the HAZ area are the average of six coupons (A and C coupons) for 3-day test period. All others are average of three coupons.

Fig. 1 Oxide Layer Produced on an As-Welded Subassembly Section A Containing Element EP-1, Corrosion Tested in 650°F Water for 3 Days. (A) White Corrosion Layer in Heat Affected Zone (HAZ) of the Weld. (B) Black Lustrous Corrosion Layer in Area Unaffected by Weld Heat (UA). 1000X.

Fig. 2 Oxide Layer Produced on As-Welded Subassembly Section A Containing Element EP-2, Corrosion Tested in 650°F Water for 3 Days. (A) White Corrosion Layer in Heat Affected Zone (HAZ) of the Weld. (B) Black Lustrous Corrosion Layer in the Area Unaffected by Weld Heat (UA). 1000X.

Fig. 3 Oxide Layer and Microstructure Produced on As-Welded Subassembly Section A Containing Element EP-3 before Corrosion Testing. (A) Microstructure in the Heat Affected Zone (HAZ) of the Weld Showing Complete Solutions of the Oxide Layer into the Surface Metal. A Layer of Alpha-Zircaloy Exists near the Surface with a Transformed Beta Structure below. (B) Microstructure at the Edge of the HAZ Showing Partial Diffusion of the Oxide Layer. (C) Microstructure of an Area Unaffected by the Welding Heat Showing the Prior-to-Welding Corrosion Film. 1000X.

occur on larger sections. Many corrosion tests performed on small samples indicate that a possible size effect may exist.

Channel spacing was employed to measure the effect of annealing upon channel stability. These data were obtained on the six test sections after removing the channel spacers and again after corrosion testing for 3 days in 650°F water. The data were then analyzed statistically to show what effect the elimination of annealing (which is a necessity if corrosion tested surfaces are employed) would have upon the stability of the subassembly. All standard annealing procedures would dissolve or partially dissolve the "prior-to-weld" corrosion film and negate its existence.

Hydrogen Analysis

Hydrogen analyses were obtained on the subassembly sections after 3 days in 650°F water and on the C weight gain coupons (see Figs. 10 and 11) after 14 days and each succeeding test period to 140 days total testing time in both 680°F water and 750°F steam. Samples for hydrogen analysis were obtained by punching a 3/16-in. diam sample from the lustrous black corrosion area and from the white corrosion area of the HAZ. The results of these analyses are listed in Table II.

Fig. 4 Oxide Layer and Microstructure Produced on As-Welded Subassembly Section A Containing Element EP-3 Corrosion Tested in 650°F Water for 3 Days. (A) Corrosion Film in the Area Adjacent to the Weld where the Corrosion Film Was Completely Dissolved into the Zircaloy upon Welding. (B) Thick Tenacious Oxide Film Which Formed in the Alpha-Zircaloy Layer Shown in Fig. 3 (A). (C) Oxide Film Still Farther Away from Weld. The Alpha-Zircaloy Layer Is Evident in the Microstructure. (D) Oxide Film in an Area Unaffected by the Weld Heat. 1000X.

Fig. 5 Oxide Layer and Microstructure Produced on As-Welded Subassembly Section A Containing Element EP-3 Corrosion Tested in 680°F Water for 140 Days. (A) Corrosion Film Adjacent to Weld. (B) Corrosion Film in Heat Affected Zone of Weld where Alpha-Zircaloy Layer Had Been. Note Tenacious Thick Oxide Layer. (C) Corrosion Film Farther from the Weld Showing a Heavy Oxide Layer. Cracks in Oxide Layer Were Apparently Producing during Polishing. (D) Corrosion Film in Area Unaffected by Weld Heat. Note Similarity to Film Found Adjacent to Weld. 1000X.

DISCUSSION

Visual Examination

Examination of the fuel element surfaces representing the three conditions tested revealed a black lustrous corrosion in the center portion of all elements which had been tested without subassembly annealing. Some over-all white corrosion was noted on the elements that had been vacuum annealed and pickled prior to welding. This may have been caused by incomplete pickling to remove the surface layer containing the dissolved oxide film. Some tenacious spacer contamination was evident on elements welded using either of the "pickled element procedures". The spacer contamination was less evident and could be easily wiped off the surfaces of elements which were welded from corrosion tested elements.

Figures 10 and 11 show the heavy white corrosion band which existed parallel with the edge of the plate that had been pickled prior to welding (EP-1 and EP-2 conditions). The corrosion along the edge of the "prior-to-welding corrosion tested" plate (Specimen EP-3 of Figs. 10 and 11) was gray in color and occurred closer to the edge of the plate. A possible explanation of this observation is presented in the metallographic results. Similar observations were made on the coupons tested 14 and 140 days in 750°F steam as shown in Fig. 11.

Examination of all annealed subassembly sections (identified C) indicated that the surfaces had become contaminated as evidenced by the over-all gray oxide which formed as early as 14 days in 680°F water. This contamination is indicative of

Fig. 6 Oxide Layer Produced on Weight Gain Coupons from As-Welded Subassembly Section A Containing Element EP-1. Coupons Corrosion Tested in 750°F Steam for 14 Days. (A) Area of White Corrosion in Heat Affected Zone (HAZ). Note the Early Evidence of Spalling. (B) Area Unaffected by Weld Heat (UA). 1000X.

Fig. 7 Oxide Layer Produced on Weight Gain Coupons from As-Welded Subassembly Section A Containing Element EP-2. Coupons Corrosion Tested in 750°F Steam for 14 Days. (A) Area of White Corrosion in Heat Affected Zone (HAZ). Note Depth of Penetration and Spalling. (B) Area Unaffected by Weld Heat (UA). 1000X.

Fig. 8 Oxide Layer Produced on Weight Gain Coupons from As-Welded Subassembly Section A Containing Element EP-3. Coupons Corrosion Tested in 750°F Steam for 66 Days. (A) Corrosion Film in Heat Affected Zone (HAZ) of the Weld. Note the Thick, Solid Corrosion Layer. (B) Corrosion Film in Area Unaffected by Weld Heat (UA). 1000X.

Fig. 9 Oxide Layer Produced on Weight Gain Coupons from As-Welded Subassembly Section A Containing Element EP-3. Coupons Corrosion Tested in 750°F Steam for 140 Days. (A) Corrosion Film in Heat Affected Zone (HAZ) of the Weld. Note Cracks in Thick Corrosion Layer and Irregularity of Metal Interface. (B) Corrosion Film in Area Unaffected by Weld Heat (UA). 1000X.

the difficulty in obtaining suitable vacuums for annealing large components.

Metallographic Examination

Sample preparation for metallographic examination of the corrosion films required careful handling during metallographic preparation and polishing to preserve the oxide films. The thicker oxide layers were brittle and prone to crack during polishing; however, a layer of epoxy resin painted on the surface of each sample prior to mounting

Fig. 10 Corrosion Weight Gain Coupons from As-Welded Subassembly Section A with Element Conditions Noted. Corrosion Tested in 680°F Water. (A) After 14 Day Test and (B) After 140 Day Test.

was successful in holding the layer intact in the event of cracking. Many samples contained oxide layer cracks which were believed to have originated during specimen preparation. Metallographic evaluation of the corrosion produced with each element condition and subassembly condition are discussed below.

As-Welded Subassemblies (Condition A)

Element Condition EP-1—Elements designated EP-1 were fabricated by pickling, corrosion testing, vapor blasting, and pickling. Metallographic examination of the corrosion layer produced on the as-welded elements with this conditioning revealed an irregular and deep corrosion penetration at the HAZ as early as 3 days in 650°F water. Pronounced spalling was evident in this area even in these early tests; however, a heavier corrosion

layer did develop with increased time, but spalling was still evident. The oxide layers adjacent to the welded sidewall and also in the area unaffected by weld heat were uniform and thin. The corrosion thicknesses in the HAZ and in the area unaffected by weld heat are listed in Table III. Good agreement exists in the thickness of the corrosion layer found in the unaffected area and in the reference samples pickled prior to corrosion testing. Photomicrographs of the oxide layer found in the unaffected area and the HAZ for the 650°F water and 750°F steam tests are presented in Figs. 1 and 6. In all cases pronounced spalling was evident in the HAZ. Extensive corrosion was evident for the 140-day test in 750°F steam.

Element Condition EP-2—Elements designated EP-2 were fabricated by pickling, corrosion testing, vacuum annealing, and pickling. Metallographic

Fig. 11 Corrosion Weight Gain Coupons from As-Welded Subassembly Section A with Element Conditions Noted. Corrosion Tested in 750°F Steam. (A) After 14 Day Test and (B) After 140 Day Test.

examination of these samples revealed corrosion layers similar to those found on samples of element condition EP-1. Photomicrographs of the corrosion films found in the HAZ and in an area unaffected by weld heat are presented in Figs. 2 and 7 for both corrosion test conditions. The thicknesses of the corrosion layers found in each area are listed in Table III. Actual corrosion thickness in the heat affected zone could not be measured because of spalling. The corrosion thickness in the area unaffected by weld heat shows good agreement with the reference samples that had been pickled prior to corrosion testing in spite of the white corrosion visible on the samples tested in 750°F steam.

Element Condition EP-3—Elements designated EP-3 were fabricated by pickling and corrosion testing. Metallographic examination of the pre-

weld corrosion film revealed complete solution of the oxide into the transformed beta structure in the vicinity of the weld heat. Approximately 1/16 in. away, where the temperature was lower, the diffusion of the oxide was complete at the surface, but it dissolved only into the surface metal to a depth of approximately 3×10^{-4} in. as shown by the retained alpha-Zircaloy layer at the surface. Somewhat farther from the weld, where a still lower temperature was experienced, the oxide was partially dissolved. Still more distant from the weld heat, the oxide was unaffected. These conditions can be seen in the first series of photomicrographs in Fig. 3.

Photomicrographs taken after 3 days in 650°F water and 14 days in 680°F water show that increased corrosion occurs in this alpha-Zircaloy layer. Longer tests in 680°F water and tests in

TABLE II

EFFECT OF FUEL ELEMENT CONDITION AND CORROSION TEST ENVIRONMENT UPON HYDROGEN CONTENT (ppm H₂)As-Welded Subassemblies (A Sections)680°F Water Corrosion Test

Time (days)	Element Conditions						Reference Samples	
	EP-1		EP-2		EP-3		Pickled	Prior Corrosion Film
	UA*	HAZ**	UA	HAZ	UA	HAZ		
0†	21	--	23	--	25	--	23	25
3††	34	35	30	33	28	33	--	--
14†	36	36	35	35	34	36	41	36
28†	40	41	38	39	41	42	50	40
66	48	45	44	45	45	48	66	45
94	76	51	45	54	42	53	56	43
122	57	58	48	51	65	60	66	55
140	85	67	64	65	62	65	83	69

750°F Steam Corrosion Test

0	21	--	23	--	25	--	23	25
14†	39	40	38	35	43	46	50	36
28†	47	48	46	48	49	54	56	47
66	79	81	72	74	81	89	78	62
94	93	83	89	99	88	81	80	58 and 65
122	114	113	116	118	99	100	84	111
140	120	121	138	138	161	113	93	110

Annealed Subassemblies (C Sections)680°F Water Corrosion Test

0**	12	--	11	--	12	--		
14†	21	21	21	22	22	22		
28†	23	26	31	25	31	31		
66	34	35	37	38	47	55		
94	41	49	50	50	69	46		
122	55	58	59	51	64	62		
140	72	72	71	71	84	81		

750°F Steam Corrosion Test

0	12	--	11	--	12	--		
14†	25	26	24	25	38	42		
28†	38	40	40	40	89	87		
66	79	81	79	78	124	120		
94	96	90	86	102	100	108		
122	103	106	123	123	234	233		
140	146	141	146	149	70	161		

* UA Samples from area unaffected by weld heat.

** HAZ Samples from heat affected zone of weld.

† These data are the average of two tests.

†† These tests taken from samples corrosion tested three days 650°F.

‡ These data are the average of three tests.

TABLE III
CORROSION FILM THICKNESS

Element Condition EP-1

	<u>As-Welded Subassembly</u>		<u>Annealed Subassembly</u>	
	Max Corr Layer			Pickled Reference
	<u>HAZ</u>	<u>UA</u>		
<u>680°F</u>				
14	0.0002	0.00004	0.00010	0.00002
28	0.00035*	0.00006	0.00008	0.00006
42	0.00028*	0.00008	--	--
66	0.00030*	0.00014	0.00015	0.00008
94	0.00040*	0.00014	0.00036	0.00010
140	0.0006*	0.00016	0.00035	0.00016
<u>750°F</u>				
0	0.00010	0.00002	--	--
14	0.00025	0.00010	0.00010	0.00008
28	0.00030*	0.00020	0.00015	0.00020
46	0.00040*	0.00022	--	--
66	0.00040*	0.00022	0.00035	0.00035
94	0.00045*	0.00040	0.00055	0.00040
140	0.0028*	0.0006	0.0005	0.0005

Element Condition EP-2

<u>680°F</u>				
14	0.00032*	0.00005	0.00008	0.00002
28	0.00052*	0.00004	0.00008	0.00006
42	0.00045*	0.00010	--	--
66	0.00055*	0.00014	0.00018	0.00008
94	0.00055*	0.00016	0.00040	0.00016
140	0.0005*	0.00016	0.0045	0.00016
<u>750°F</u>				
14	0.00050*	0.00004	0.00010	0.00008
28	0.00040*	0.00010	0.00018	0.00020
46	0.00070*	0.00020	--	--
66	0.0006*	0.00028	0.00035	0.00035
94	0.00050*	0.00028	0.00050	0.00040
140	0.0009*	0.00045	0.00055	0.0005

Element Condition EP-3

	<u>As-Welded Subassembly</u>		<u>Corrosion Tested Reference</u>	<u>Annealed Subassembly</u>	<u>Pickled Reference</u>
	<u>HAZ</u>	<u>UA</u>			
<u>680°F</u>					
3 650°F	0.00022	0.0004			
14	0.00020	0.00002	0.00004	0.00010	0.00002
28	0.00030	0.00010	0.00005	0.00014	0.00006
42	0.00040	0.00012	--	--	---
66	0.00060	0.00014	0.00012	0.0008	0.00008
94	0.00060	0.00014	0.00012	0.00035	0.00016
140	0.00060	0.00016	0.00016	0.0012	0.00016
<u>750°F</u>					
14	0.00040	0.00004	0.00005	0.00015	0.00008
28	0.00055	0.00010	0.00012	0.00045	0.0002
46	0.00070	0.00016	--	0.00065	--
66	0.00080	0.00025	0.00030	0.00110	0.00035
94	0.00085	0.00035	0.00025	0.00120	0.0004
140	0.00090	0.0004	0.0006	0.0013	0.0005

*Spalling

750°F steam show that this thick corrosion layer is tenacious but brittle. Except for the local oxide penetration found after 66 days in 680°F water, there does not appear to be any deep erosion or spalling in the HAZ.

The thickness of the corrosion layer adjacent to the weld, where the oxide was completely dissolved into the transformed beta-Zircaloy, was similar to that found in the area unaffected by weld heat. Both areas are shown in the last series (140 days) of photomicrographs presented in Figs. 3-5, 8, and 9.

The thickness of the oxide layer found in the photomicrographs of Figs. 3-5, 8, and 9 were measured by optical methods. These data are listed in Table III. The thickness of the oxide found in the areas unaffected by weld heat are similar to the films found on the two reference samples. The subassembly welding and fabrication operations did not affect post-weld corrosion of the elements which had a pre-weld corrosion film (element condition EP-3). Corrosion film thickness in the heat affected zone increased rapidly at the beginning of test but became slower as the time progressed as shown in Fig. 12. The decreasing rate of corrosion film thickness and the increasing weight gain in the HAZ indicates an increase in corrosion film density for the corrosion produced in the HAZ of these elements.

The metallographic results presented here show that element condition EP-3 has better resistance to corrosion than the two pickled fuel element conditions (EP-1 and EP-2). The thicker corrosion layer in the HAZ is tenacious and not subject to catastrophic failure. Corrosion films in the areas unaffected by weld heat are normal and show no effects of welding on the prior corrosion film.

Annealed Subassemblies (Condition C)

Element Conditions EP-1 and EP-2—Metallographic examination of the elements from the annealed subassemblies of element conditions EP-1

Fig. 12 Corrosion Film Thickness vs Time of Test for Element Condition EP-3.

and EP-2 which had been pickled prior to welding revealed similar corrosion films throughout the 140-day, 680°F water and 750°F steam corrosion tests. However, the thicknesses of the corrosion films produced in 680°F water tests were approximately twice those found on the pickled reference samples. The film thicknesses formed by the 750°F steam tests were approximately the same as those of the pickled reference samples (see Table III). It should be pointed out, however, that visual observation of the element surfaces did not reveal the normal lustrous black corrosion film, and the outer surfaces of these subassemblies were contaminated sufficiently to form a white corrosion product after only a 3-day, 650°F water corrosion test. The photomicrographs of both series of tests appear in Figs. 13, 14, 15, and 16. The deep local penetration of corrosion film shown for the 66-day, 750°F steam corrosion test for element condition EP-3 may have been caused by local contamination.

Element Condition EP-3—Contrary to the excellent corrosion results observed on elements of condition EP-3 in the as-welded subassembly, heavy irregular corrosion films were observed on the metallographic samples prepared from the annealed subassembly having elements in the EP-3 (prior corrosion film) condition. The photomicrographs shown in Figs. 17 and 18 were taken from

Fig. 13 Typical Corrosion Film Produced on Annealed Subassembly Section C Containing Element EP-1. Corrosion Tested in 680°F Water for 140 Days. 1000X.

Fig. 14 Typical Corrosion Film Produced on Annealed Subassembly Section C Containing Element EP-2. Corrosion Tested in 680°F Water for 140 Days. 1000X.

Fig. 15 Corrosion Film Produced on Weight Gain Coupons from Annealed Subassembly Section C Contained Element EP-1. Corrosion Tested in 750°F Steam for 140 Days. 1000X.

areas of greatest corrosion film thickness. The thicker irregular corrosion films shown here were apparently the result of inhomogeneous solution of the oxide film during the annealing treatments employed. Calculations by A. E. Oaks and D. B. Scott of Bettis from their data show that two mils of surface metal must be removed by pickling to eliminate the high oxygen concentrations found

Fig. 16 Corrosion Film Produced on Weight Gain Coupons from Annealed Subassembly Section C Containing Element EP-2. Coupons Corrosion Tested in 750°F Steam. (A) Corrosion in Heat Affected Zone (HAZ) of Weld after 140 Day Test. (B) Corrosion in Area Unaffected by Weld Heat (UA) after 140 Day Test. 1000X.

near the surfaces of material annealed with a prior corrosion film. The results reported here are in agreement with their work.

Corrosion Weight Gain Data

The average corrosion weight gain data for the three coupons representing the center area of the plate (B coupons) and the coupons containing the HAZ (A and C coupons) are listed in Table I. The values for the two reference conditions are also presented for comparison. These same values are plotted in Figs. 19-25 along with the 2σ limits for the standard corrosion weight gain data of Zircaloy-2. In many cases the weight gain data obtained here are misleading, and metallographic examinations must be relied upon.

As-Welded Subassemblies (Condition A)

Element Condition EP-1—The B coupons from the center area (unaffected by weld heat) showed

Fig. 17 Corrosion Films Produced on Annealed Subassembly Section C Containing Elements EP-3 Corrosion Tested in 680°F Water for 140 Days. (A) Corrosion Film in Heat Affected Zone (HAZ). (B) Corrosion Film in Area Unaffected by Weld Heat (UA). Note Even in this Area the Annealing Has Caused Erratic Corrosion. 1000X.

normal weight gains in both 680°F water and 750°F steam as seen in Figs. 19 and 22, respectively. Metallographic examinations substantiate these data by showing a tenacious black oxide on these samples through 140 days in 680°F water. Coupons tested in 750°F steam showed evidence of a gray oxide after 122 days, but the oxide still appears to be tenacious after 140-day tests.

Weight gain data for the A coupons, which were obtained from the area of the element nearest the weld, also appear to be normal; however, metallographic examination revealed spalling after only 3 days in 650°F water. Weight gain data for tests performed in 750°F steam show greater weight

Fig. 18 Corrosion Film Produced on Weight Gain Coupons from Annealed Subassembly Section C Containing Elements EP-3. Coupons Corrosion Tested in 750 F Steam. (A) Corrosion Film at Heat Affected Zone (HAZ) of Weld after 140 Day Test. (B) Corrosion Film at an Area Unaffected by Weld Heat (UA) after 140 Day Test. 1000X.

gains for the reference coupons of the same material. These weight gains are greater than the 2σ corrosion limits. It is apparent that the "normal" weight gain observed on the A coupons from the area nearest the weld heat was caused by the large area unaffected by the weld heat offsetting the spalling in the HAZ on the same coupons tested.

Fig. 19 Corrosion Weight Gain and Hydrogen Content of Coupons from As-Welded Subassembly EP-1A after 680 F Water Corrosion Test.

Fig. 21 Corrosion Weight Gain and Hydrogen Content of Coupons from As-Welded Subassembly EP-3A after 680 F Water Corrosion Test.

Fig. 20 Corrosion Weight Gain and Hydrogen Content of Coupons from As-Welded Subassembly EP-2A after 680 F Water Corrosion Test.

Fig. 22 Corrosion Weight Gain and Hydrogen Content of Coupons from As-Welded Subassembly EP-1A after 750 F Steam Corrosion Test.

Figures 10 and 11 clearly show the areas which were affected by the weld heat.

Element Condition EP-2—Corrosion weight gain data for these samples are similar to data for coupons from condition EP-1. This was to be ex-

pected as metallographic evidence was also similar. Corrosion weight gains for test coupons from the center area of the elements welded with this condition (B coupons) agree very well with the

Fig. 23 Corrosion Weight Gain and Hydrogen Content of Coupons from As-Welded Subassembly EP-2A after 750 F Steam Test.

corrosion data of the pickled reference samples shown in Figs. 20 and 23. The B coupons and the reference coupons are within the 2σ corrosion limits for tests in 680°F water but are greater than the 2σ limits in 750°F steam. The increased weight gain in the latter case was evident after only 3 days in 750°F steam. The area of the corrosion coupons unaffected by weld heat showed a white corrosion after only 14 days in 750°F steam; this oxide can be seen in Fig. 11. This may have been caused by insufficient pickling or improper vacuum annealing of the fuel elements. The hydrogen content of a representative sample of the annealed elements did not show any appreciable reduction in hydrogen from the corrosion tested element condition.

Weight gain data for coupons containing the HAZ (A coupon) were quite erratic because of the increased corrosion and spalling in the HAZ. This spalling is evident in the photomicrographs of Figs. 2 and 7. Weight gain data for the 750°F steam corrosion tests agree with the pickled reference sample. However, again, metallographic examination revealed a thick but somewhat more adherent corrosion film than the oxide formed in 680°F water. The surfaces of these samples displayed a

Fig. 24 Corrosion Weight Gain and Hydrogen Content of Coupons from As-Welded Subassembly EP-3A after 750 F Steam Corrosion Test.

Fig. 25 Corrosion Weight Gain and Hydrogen Content of Coupons from Annealed Subassemblies (C Section) EP-1, EP-2, and EP-3 after 680 F Water Corrosion Test.

white oxide after only 14 days in 750°F steam (see Fig. 11).

Element Condition EP-3—Corrosion weight gain data for the B coupons (area unaffected by weld heat) were less than the 2σ limits for

standard weight gain tests in 680°F water throughout the 140-day test period. Similar results were found through 28 days in 750°F steam. The weight gain data listed in Table I for these coupons are plotted in Figs. 21 and 24. The lower weight gains found for elements tested in this condition were attributed to the prior-to-welding corrosion film that existed on these samples reducing the initial corrosion rate after welding. The corrosion film was tenacious and black with flecks of tan appearing after 122 days in 750°F steam. The tenaciousness and general appearance of the film has already been shown in the metallographic samples (Figs. 3-5, 8, and 9) and the photographs (Figs. 10 and 11).

Corrosion weight gain data for coupons from the HAZ were along the upper 2 σ weight gain limit for tests in 680°F water and were slightly higher than the upper 2 σ limit for tests in 750°F steam. The higher weight gains are understandable in both cases as metallographic examination showed the oxide in the HAZ to be thicker than in the unaffected area and tenacious through 140 days in 680°F water and 750°F steam. The weight gain for these coupons does not represent the true weight gain in the HAZ as these areas represent only approximately 25% of the A coupon. An approximation of the weight gain in the HAZ was obtained by calculation and is also shown in Figs. 21 and 24. These curves show the calculated weight gain in 680°F water and 750°F steam to be three and five times greater, respectively, than the normal weight gains. The discolored areas did not show signs of spalling until 122 days in 750°F steam. This spalling was probably caused by the brittle nature of the oxide at this point as it appeared to be "glassy" when viewed under low power magnification. The discolored areas of element conditions EP-1 and EP-2, on the other hand, appeared to be a white powder.

Annealed Subassemblies (Condition C)

The effect of subassembly annealing upon corrosion weight gain was determined on corrosion

coupons from the three subassembly sections of condition C (annealed by standard subassembly annealing procedures). These weight gain data are listed in Table I and plotted in Figs. 25 and 26. The average weight gain for the A and B coupons for element conditions EP-1 and EP-2 were also plotted in these figures because of the similarity in both the data and appearance of the coupons. These data appeared to be normal through 46 days of test in 680°F water, at which point an inflection in the weight gain curve occurred. Similar data in 750°F steam did not show the pronounced inflection of Fig. 25; nor were the data as precise as most weight gain data. The weight gains for these two conditions were surprisingly normal in view of the nonuniform surface appearance of the samples.

Fig. 26 Corrosion Weight Gain and Hydrogen Content of Coupons from Annealed Subassemblies (C Sections) EP-1, EP-2, and EP-3 after 750°F Steam Corrosion Test.

The corrosion weight gain data for coupons taken from prior-to-welding corrosion tested elements (condition EP-3) which had been annealed in the subassembly stage are also listed in Table I and plotted in Figs. 25 and 26. Corrosion weight gains were several times greater than the standard

corrosion data. However, unlike the unannealed samples, the corrosion film was not tenacious and in many cases was quite thick and irregular. This increased corrosion was caused by incomplete solution of the oxide by the two subassembly annealing operations. Oaks and Scott also found that pickling had to be employed prior to corrosion testing if a previous oxide film had been dissolved by vacuum annealing.

Hydrogen

The hydrogen analysis listed in Table II revealed little difference in hydrogen content between the HAZ and the unaffected area of the samples. This was apparently caused by the rapid diffusion of hydrogen throughout the small samples being tested. In view of this, the average hydrogen values for the two areas were plotted in Figs. 18-25 along with the corrosion weight gain data.

The hydrogen concentrations were independent of element conditions, the 750°F steam corrosion test yielding higher hydrogen values than the 680°F water test. The 23-ppm initial hydrogen concentration of element condition EP-2 was higher than normal for vacuum annealed Zircaloy-2. Hydrogen concentrations for the reference pickled samples appear slightly higher than the three element conditions for 680°F water tests and for the first 65 days of test in 750°F steam. The hydrogen concentrations for the prior-to-weld corrosion film reference sample and element condition EP-3 (which also had a prior-to-weld corrosion film) are similar for the 680°F water test, but the reference samples appear to be considerably less for tests in 750°F steam.

Hydrogen concentrations for coupons from the annealed subassembly sections welded from elements in the EP-1 and EP-2 conditions showed less hydrogen pickup in the 680°F water test than coupons from the unannealed subassemblies. This was also true up to 65 days in 750°F steam. Beyond this time, the hydrogen concentrations became slightly higher.

Hydrogen values for coupons from the annealed section of subassembly EP-3 became higher than the as-welded subassembly after only 45 days in 680°F water and 15 days in 750°F steam. This would be expected in view of the higher corrosion rate and thicker corrosion film noted for the annealed sections of subassembly EP-3.

If hydrogen were the only basis of selecting a satisfactory fuel element process, all three conditions would be satisfactory provided subassembly annealing were not employed. If subassembly annealing were necessary, only conditions EP-1 and EP-2 would appear satisfactory; however, improved methods of vacuum annealing are necessary to prevent contamination of the outer subassembly surfaces.

Effect of Annealing Subassemblies Before Corrosion Test

Visual examination of sections of subassemblies which had been vacuum annealed prior to corrosion testing revealed excessive surface contamination on the outside of the subassembly during the annealing operation. Internal surfaces were contaminated approximately 2 in. from each end of the subassembly. These results indicate that satisfactory control of the annealing operation would be very difficult from the standpoint of preventing surface contamination during annealing.

Statistical analysis was performed on the channel spacing data of the six subassembly sections by comparing the channel spacing data both before and after corrosion testing. The σ value for differences in channel measurements taken before and after corrosion testing is slightly less for the unannealed sections. A slight decrease in the mean channel spacing was noted after corrosion testing for both subassembly conditions. However, these differences are not statistically significant. Results indicate that the omission of the annealing operation would not be detrimental to the dimensional stability of a subassembly.

SUMMARY

An investigation was conducted to determine a means of eliminating the pickling operation normally employed prior to the final corrosion test of subassemblies and clusters. Early tests showed that properly machined Zircaloy-2 surfaces cleaned with detergent corrode in a normal manner. It was also known that welding produces a contaminated area at the HAZ of the weld and that this area has to be removed by pickling to avoid excessive corrosion. This program was aimed at investigating this HAZ and determining the effects of three different fuel element surface conditions on the corrosion that forms in this area. The three surface conditions investigated were (1) corrosion tested surfaces; (2) corrosion tested, vapor blasted, and pickled surfaces; and (3) corrosion tested, vacuum annealed, and pickled surfaces. The effects of subassembly annealing were also included.

The variables were evaluated by corrosion weight gain, hydrogen pickup, and metallographic examination over 140 days of corrosion testing in 750°F steam and 680°F water.

The corrosion tests showed that a black corrosion film on the fuel elements prior to welding substantially reduces the accelerated corrosion in the HAZ forming a tenacious layer of increased corrosion which, even after 140 days in 750°F steam, was only 0.0009 in. thick.

Tests on pickled fuel elements revealed considerable oxide spalling in the heat affected zone. Vacuum annealing of the two subassemblies containing pickled fuel elements appears to eliminate this accelerated corrosion; however, the black lustrous corrosion film was absent from samples treated in this manner, which indicates that an investigation of methods to improve vacuum annealing may be warranted.

CONCLUSIONS

PWR subassembly and cluster pickling and annealing can be eliminated by applying a black corrosion film to the fuel elements before welding. Subsequent corrosion tests after welding were normal except in the HAZ of the weld. The increased corrosion film in the HAZ was tenacious and did not show signs of catastrophic failure. However, the effects of residual weld stresses should be considered before utilizing this process.

Detergent cleaning of the Zircaloy-2 subassemblies prior to corrosion test produces satisfactory corrosion results in all areas of the element unaffected by welding heat for all three element conditions tested.

The corrosion film formed in the heat affected zone of the weld on elements with a prior black corrosion film was tenacious throughout the tests. The oxide appears "glassy" in comparison with the powdery white oxide found in the HAZ of the elements welded with a pickled surface.

Solution of a black corrosion film by annealing will cause excessive corrosion. However, past experience with PWR, Zircaloy-2 subassemblies and clusters has proven that a pickling operation prior to the final corrosion testing will eliminate this excessive corrosion.

Vacuum annealing of PWR Zircaloy-2 subassemblies welded with pickled fuel element surfaces (conditions EP-1 and EP-2) eliminates the excessive corrosion found at the HAZ and produces normal corrosion weight gain, hydrogen pickup, and corrosion film thickness. However, visual examination of these films does not reveal the black lustrous corrosion normally considered a good corrosion film.

The apparent normal weight gain data at 680°F for element conditions EP-1 and EP-2 were caused by the spalling which compensated for the excessive corrosion in the HAZ.

RECOMMENDATIONS

The effects of residual weld stresses should be analyzed before utilizing components with a pre-corrosion film since these stresses cannot be fully eliminated by thermal treatments at temperatures below 1450°F.

In view of the encouraging results on annealed subassemblies with element conditions EP-1 and EP-2, an investigation to determine means of reducing surface contamination as the result of

vacuum annealing might prove profitable. The use of a gettering material around the PWR subassembly during annealing should be considered in such an investigation.

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The use of copper eutectic diffusion bonding for the manufacture of plate-type, oxide bearing fuel elements (investigated for use in the manufacture of PWR Core 2 fuel elements but abandoned in favor of the pressure bonding process) necessitated the placement of a copper bonding agent at the diffusion bonding interface. A program to establish methods of achieving this by electroless deposition of copper on pilot-run quantities of fuel receptacle plates and to establish methods of inspection of the copper deposit was undertaken. The required aims were achieved by establishing methods to control all pertinent surface preparation and plating variables and by the use of an X-ray fluorescence inspection instrument.

DEVELOPMENT OF TECHNIQUES FOR LARGE-SCALE ELECTROLESS COPPER PLATING OF ZIRCALOY PLATE-TYPE FUEL RECEPTACLE COMPONENTS

V.V. DeGeorge

In conjunction with the development of the copper eutectic diffusion bonding process* for the fabrication of plate-type oxide bearing fuel elements (Ref 1), the development of a process to place the required copper bonding agent at the bonding interface was undertaken. Feasibility studies conducted at Bettis indicated that a violently agitated aqueous solution of cupric nitrate and hydrofluoric acid deposited copper on the surface of zirconium alloys immersed in the solution (Ref 2). Subsequent investigations were undertaken at the Armour Research Foundation to determine the variables of this copper plating process and at Bettis to develop pilot-plant-scale plating methods for various types of receptacle components.

The general requirements of the process are (1) to deposit the required copper on fuel receptacles, (2) to locate the copper only on the bonding surfaces, and (3) to develop a satisfactory method of

inspection of the copper deposit.** Initial diffusion bonding studies indicated that a copper deposit in the thickness range of 0.15 to 0.18 mils was required to produce satisfactory bonds. However, with the development of accurate copper inspection methods it was found that this thickness range was actually 0.15 to 0.25 mils.

The method of achieving the quality and quantity requirements of the copper deposit was to first determine the required plating parameters, then determine all pertinent variables of the operation, and, finally, control these variables to produce plated receptacles in pilot-run quantities. In addition, various physical and chemical masking techniques were investigated to control the location of the copper deposits.

The establishment of adequate nondestructive inspection methods involved a survey of the commercial instruments for this purpose and their application to this problem.

*Early in the investigation of possible methods for manufacturing PWR Core 2 fuel elements, the copper eutectic diffusion bonding process, devised by R. A. Wolfe of Bettis, was examined in detail. The process has been abandoned, however, in favor of pressure bonding.

**See the article entitled "The Thin Copper Film Gage" in this issue.

The major portion of the development program involved the establishment and control of operational variables. These variables were found to include not only the plating parameters, but also the pre-plating surface preparation. This article presents the results of this development program and a discussion of the plating process, including the related pre-plating surface preparation and nondestructive inspection of the plated deposit.

DESIGN OF RECEPTACLE PLATE

From a copper plating standpoint, there were two general types of receptacles under consideration for the plate-type, oxide bearing fuel element. They were the machined-integral receptacle and the machined- or punched-through receptacle. Figure 1 is a section of a machined-integral receptacle showing its general configuration, the single bonding surface, and the integral cover plate. The machined- or punched-through receptacle has a similar configuration except for a second bonding surface necessitated by the absence of the integral cover plate.

Fig. 1 Section of Machined-Integral Receptacle Plate.

PROCEDURE, RESULTS, AND DISCUSSION

Selective Deposition of Copper Deposit

To produce a diffusion bonded fuel element having acceptable chemical and physical properties, the

location of the copper bonding agent must be restricted only to the surfaces to be bonded. Two general methods of achieving this are either the removal of the copper deposit from the undesired areas, or the restriction of copper deposition by masking the areas in question during the plating operation. Because removal of the copper after plating was found to be laborious and time-consuming, the development of a masking technique was stressed.

The application of mechanical masking devices such as tape, Teflon, and rubber inserts was generally time-consuming and presented difficulty in achieving complete masking. The use of films such as plastics or ink offered serious problems in both accurate application and complete removal.

The most satisfactory method developed for either type of receptacle was the use of an adherent, non-porous oxide film which rendered the areas coated by this film inert to the plating solution. Such a suitable oxide film was applied to the entire surface of the receptacle plate by autoclaving in demineralized water at 650°F for 2 hr at saturation pressure. The oxide was then removed from the surfaces to be plated by one of the approved flat surface machining operations. During the plating operation only those surfaces free from oxide film received a copper deposit (see Fig. 2). The remaining oxide film does not require removal since it is dissolved into the receptacle during the diffusion-bonding, heat-treating cycle and is not of sufficient quantity to adversely affect the physical and chemical properties of the Zircaloy.

Surface Preparation

To produce a uniform copper deposit, all areas to be plated must react with the copper plating solution at a uniform rate. To achieve this, the surface of the sample is prepared to present a chemically and metallurgically uniform surface to the plating solution. In addition, the surface

Fig. 2 Photograph of a Section of a Processed Machined-Integral Receptacle Plate Showing Copper Deposit (Light Area) and Oxide Masking (Dark Areas).

preparation adjusts the receptacle dimensions to fuel element design requirements and removes the oxide masking film from the surfaces to be plated.

The surface preparation operations are divided into three general classifications. They are, in the usual order of their use, mechanical surface forming, surface cleaning, and chemical surface forming. Mechanical surface forming refers to operations that remove material from the surface or drastically change the surface profile by mechanical means. The function of surface cleaning operations is the removal of contamination from the metal surface without attacking or altering the metal itself. The chemical surface forming operations are those which alter the sample surface by means of a chemical attack.

The following is a description of the various pre-plating surface preparations investigated during the development of the plating process, their effects on the receptacle surface, and their application to the plating process.

Mechanical Surface Forming

Vapor Blasting—This operation alters the receptacle surface by impingement of a vapor

stream containing abrasive particles. The abrasive used was 220 grit Burr-Al*. The use of semi-automatic equipment yielded a uniform surface having a roughness of approximately 35–50 μ in. rms without significant alteration of the dimensions of the receptacle. A serious objection to the use of vapor blasting is that it introduces contamination on the sample surface in the form of embedded vapor blasting grit, the main contaminant being alumina. Because of this excessive contamination, and also because of the difficulty in preventing removal of the oxide masking film from those areas requiring masking, this operation is not applicable to the manufacture of plate-type, oxide bearing fuel elements.

The vapor blasted surface, however, does receive a uniform and highly adherent copper film and is recommended for all uses where selective plating and control of surface contamination are not required.

Grinding—The main purpose and function of a grinding operation is to remove material. However, by adjustment of grinding parameters, properties desirable for copper plating can be imparted to the surface. Final surface roughness is dependent on the roughness of the grinding abrasive, applied pressure, and cleanliness of the grinding surface. Liberal quantities of coolant are required to avoid oxidation and distortion of the ground surface and to aid in the maintenance of surface cleanliness. Because this operation involves harsh abrasion with friable materials, it is inherently capable of contaminating a metallic surface with embedded grit.

The grinding investigations were essentially applications of earlier grinding studies which resulted in the use of silicon carbide abrasive grinding wheels with high pressure water as a

*Pressure Blast Manufacturing Co., Inc., Manchester, Conn.

coolant. Although this operation is theoretically capable of being applied to production of the plate-type elements, great difficulty was encountered in controlling receptacle dimensional tolerances. Particular problems existed in clamping of samples to allow for precision grinding and in controlling the applied pressure to prevent warpage, fracture, and burning of the Zircaloy surface. The behavior of the ground surface during the plating operation was also unreliable, resulting in copper deposits unpredictable in both thickness and uniformity.

Because of these uncontrolled variables, additional development is required before this process can be recommended as a satisfactory surface preparation operation.

Abrading—Abrading is similar to grinding except that it involves lower speeds, pressures, and coolant quantities. It is generally a gentler and slower operation than grinding and, as such, offers more promise of precision control.

Abrading of receptacle components was performed by manual and semiautomatic methods. The method most applicable to production was a semiautomatic method utilizing a flat finisher with coated silicon carbide abrasive belts and an oil-base coolant. The main difficulty encountered with this operation again involved maintenance of dimensional tolerances. Areas having small surface contact with the abrasive belt (longitudinal ribs) invariably had more metal removed than the larger solid areas (edge strips and end plates). Any warpage of the receptacle plate, such as transverse bow or waviness, also added to the non-uniform metal removal. The use of a rigid backup wheel and multiple passes of extremely small metal removal (less than 0.0005 in. per pass) reduced this condition of non-uniformity. However, abraded receptacles normally exhibited rib areas that were 0.001 to 0.002 in. thinner than the frame areas.

The manual operation utilized a rotary sander with coated silicon carbide abrasive paper. This method did not produce the above mentioned non-uniformity, mainly because it was incapable of rapid metal removal. This fact, however, made it too time consuming for production practice.

Machining—Machining is a cleaner and more precise method of removing metal from a receptacle surface than either grinding or abrading. By varying the depth of cut and speed of pass, the surface roughness of the sample can be varied and controlled from 10 to 500 μ in. rms. The greatest difficulty encountered in machining is that it required rigid and accurate clamping or jiggling of the receptacle. Once this is accomplished, dimensional tolerances of ± 0.001 in. are easily achieved.

The specific machining operations investigated were climb milling and fly cutting. Of the two, climb milling, removing 0.003–0.005 in. per pass, offered the least problems, and consistently produced a surface suitable for copper plating. The operation was performed with a water soluble coolant using a hardened steel helical cutting knife. There was little apparent contamination of the surface, and therefore the sample required only a light degreasing operation prior to plating. Clamping of the machined integral receptacle plate was achieved by use of a vacuum chuck or by the use of double backed masking tape.

This method of surface preparation is most applicable and recommended as a production operation for plate-type, copper diffusion bonded fuel elements.

Surface Cleaning

Vapor Degreasing—Vapor degreasing as employed at Bettis utilizes the vapors of perchloroethylene at a temperature of 258°F to remove grease and oil films from metal surfaces. Samples

degreased in this matter generally receive a non-uniform, spotty copper film during the copper plating operation. This is attributed to residual films of perchloroethylene that remained on the metal surface and could not be removed during subsequent rinsing cycles. For this reason this operation is not applicable to the copper plating process.

Detergent Degreasing—This degreasing is performed by soaking the sample to be plated in a 2% solution of Penn Salt A-27 at 180°F. Required soaking times are 15-30 min, and a 15-min rinse in cold flowing tap water removes all trace of the detergent. This procedure consistently produces a surface readily applicable to copper plating and, as such, is very satisfactory and recommended as the degreasing operation following machining in the copper plating process.

Chemical Surface Forming

The investigation of chemical surface forming was undertaken with the intention of producing a contamination-free surface capable of receiving a copper deposit satisfactory for diffusion bonding. However, since the use of the machining and detergent degreasing operations produced such a surface, the chemical forming operation was no longer required. The results of the investigations of chemical surface forming are reported here only to acquaint the reader with the effects of these operations on the plating properties of the Zircaloy surface.

Flash Pickling—Flash pickling is the immersion of the sample to be plated in a 39.5% HNO_3 , 2.5% HF * aqueous solution for 5-30 sec. The purpose of this operation is to remove minute oxide films from the surface of the Zircaloy just prior to plating and to chemically condition the surface. No appreciable metal removal results,

so no dimensional adjustment occurs. When applied to vapor blasted samples it reduces the surface contamination level by approximately 50%. When applied to machined surfaces it conditions the surface to result in a more macroscopically uniform copper deposit. This operation is performed after degreasing. A 15-min rinse in flowing tap water is required after pickling to remove acid traces before plating.

Bright Etching—Bright etching is the term applied to the pickling of a Zircaloy surface with a 39.5% HNO_3 , 2.5% HF acid solution until a shiny metallic surface results (usually 0.001-0.002 in. metal removal per surface required). This operation removes surface films and embedded contamination (provided contamination is less than 0.002 in. below the surface) but does not usually result in uniform, adherent copper deposits upon subsequent plating. This operation can also result in passivated areas or surfaces, thereby preventing and deposition of copper during the plating operation. A removal of more than 0.004 in. of material per surface usually results in pitting of the surface.

Chemical Polishing—This term applies to the pickling of a Zircaloy surface with a 45% HNO_3 , 10% HF acid solution, generally resulting in a shiny surface with a removal of as little as 0.0005 in. of material per surface. This operation can be used to remove embedded surface contamination but will cause pitting upon removal of 0.004 in. of material per surface. It produces a surface better suited for chemical plating than bright etching but has been known to passivate certain areas (particularly welded areas), thereby preventing the deposition of copper. Dimensional control of samples is difficult to maintain in this solution because of the rapid rate of metal removal generally encountered.

* HNO_3 - Commercial Grade, Sp Gr - 1.42
HF - 52, Conc Technical Grade

HCl-HF Etchant—An etchant consisting of 99% HCl , 1% HF was used in an attempt to produce a

roughened contamination-free surface for copper plating. The etchant is capable of producing a microscopically pitted surface with removal of 0.002 in. of material (Ref 3). This operation is satisfactory on Zircaloy-2 surfaces but results in poor copper adherence when employed with Zircaloy-4. The extreme slowness (15-30 min for 0.001 in. metal removal), the unpredictable nature, and the short life of the solution itself were other disadvantages encountered when using this solution.

Copper Plating

Plating in the operation under consideration occurs as a result of the difference in solution potential between the zirconium base metal and the metallic cupric ion in solution. Since, as indicated by their electrode potentials (see Ref 2), copper is a more noble metal than zirconium, its ability to plate out of solution onto the Zircaloy without an applied DC voltage is theoretically possible.

Investigations of this plating operation using the aqueous cupric nitrate, hydrofluoric acid solution recommended by Ref 2 indicate that the concentration of hydrofluoric acid has a marked effect on the rate of deposition of copper and that the rate of deposition decreases with the use of the plating bath. Chemical analysis of spent solutions indicated that zirconium is being taken into solution during the plating operation. The following are possible reactions describing these occurrences:

Reaction (1) is the reaction by which the deposition of copper occurs. It is due solely to the difference in solution potential between zirconium and copper. This reaction, however, cannot occur unless the passive surface layer, common on all Zircaloy surfaces, is first removed to present an active surface to the solution. This removal of the passivated surface is achieved by Reaction (2). The

depletion of the fluoride ion by the formation of $\text{ZrF}_6^{=}$ is the probable reason why the rate of copper deposition decreases with use of the plating bath. It is recognized that other reactions may also occur; however, detailed studies of the chemistry of the plating process were not undertaken.

The copper, as deposited by this chemical plating process, is a series of discontinuous, irregularly shaped granules with areas of exposed Zircaloy between some of the copper granules. The shape, size, and orientation of these granules depend on a number of variables including the solution temperature, agitation, and composition; the plating time; and the pre-plating surface preparation of the sample. Figure 3 shows the differences in copper deposition achieved by variation of the pre-plating surface preparation alone. It is probably because of the porosity of the copper deposit that the plating operation progresses to the thicknesses achieved, since, normally, chemical plating operations of this type deposit only minute, microscopic films of metal. This type of copper deposit is normally more resistant to gross peeling, flaking, or chipping than comparable foil-type deposits, and, as indicated by bonding experiments, the porosity does not affect the quality of the diffusion bond.

The principal variables affecting the quantity or quality of copper deposit are:

- Solution temperature,
- Solution agitation,
- Plating time,
- Concentration of cupric ion in solution, and
- Concentration of fluoride ion in solution.

During the development of the plating operation, each of the above variables was investigated to establish its optimum condition, allowable limits, and controls to produce reproducible copper deposits. Following is a summary of these investigations.

- A. Pre-Plating Surface Preparation
 1. Vapor Blast
 2. Detergent Degrease
 3. Flash Pickle
- B. Pre-Plating Surface Preparation
 1. Abrade (Flat Finisher)
 2. Detergent Degrease
- C. Pre-Plating Surface Preparation
 1. Climb Mill
 2. Detergent Degrease
- D. Pre-Plating Surface Preparation
 1. Climb Mill
 2. Detergent Degrease
 3. Flash Pickle
- E. Pre-Plating Surface Preparation
 1. Climb Mill
 2. Detergent Degrease
 3. Bright Etch
- F. Pre-Plating Surface Preparation
 1. Climb Mill
 2. Detergent Degrease
 3. Chemical Polish

Fig. 3 Photographs of Copper Plated Zircaloy Surfaces Showing Variations in Porosity and Granular Characteristics of Copper Deposit (Gray and Dark Areas) due to Variations in Base Metal Pre-Plating Surface Preparation; 250X.

Solution Temperature

Unpublished work by the Metals Research Department of the Armour Research foundation has established that the plating rate is directly proportional to the temperature of the plating solution. Observations from additional experiments at Bettis indicated that the porosity of the copper deposit decreases as the solution temperature decreases. Early studies utilized a solution temperature of 100°F; however, to produce a less porous deposit and to gain additional control of the copper deposition, a solution temperature of 80°-85°F was found to be more satisfactory. Solution temperatures lower than this require a method of cooling to prevent the temperature from rising out of tolerance during extended use.

The temperature of the solution is controlled by automatic thermostatic controls. Stainless steel sheathed electric immersion heaters were used in

the development facility. The facility installed for large-scale production of fuel elements employed a less complicated, heated water jacket.

Solution Agitation

To achieve a satisfactory copper deposit, the solution must be violently agitated while the samples are immersed in it. This agitation is to combat polarization by mechanically replacing the spent solution near the plating surface with fresh solution. Also, because the rate of deposition is directly proportional to the rate of agitation and the porosity of the copper decreases with increased agitation, uniform agitation is required over the entire sample being plated in order to achieve a uniform copper deposit. To control this, an agitation system is built into each tank, and agitation is maintained constant during all plating operations.

The initial agitation system consisted of compressed air passed through three perforated tubes attached to the bottom of the plating tank. The perforations and tubing were sized and located to achieve uniform agitation over the length of the tank. Samples to be plated were suspended between the agitation tubes out of the direct stream of air bubbles. An improved, more uniform, and more violent agitation was achieved by pumping and recirculating the plating solution through two perforated tubes located at the bottom of the tank. These tubes and perforations were sized and directed to impart a rapid axial swirling motion to the solution. Recirculation systems in the development facility utilized a pumping rate of 13 gpm. For the large-scale facility the more rapid rate of 50 gpm was found to be advantageous. The receptacles were suspended in the swirling solution at locations where they received uniform agitation over all areas to be plated. These locations were determined initially by trial and error placement of the receptacle plates and by adjustment of the agitation system until the desired plating capacity was achieved.

Another type of agitation investigated involved the use of a closed plating chamber. The receptacles

were rigidly clamped, and the solution was pumped longitudinally through the chamber over them. This system offered more control of the agitation, and, when solution speeds of 4-6 fps were used, a more adherent and less porous copper deposit than that deposited by other agitation methods was achieved. Control of the plating thickness within the allowable range of 0.15 to 0.25 mils, however, was difficult due to a rapid plating rate. Required deposit thicknesses were achieved in 4-5 min as compared with the 15-20 min required for the swirling agitation systems. This method of agitation was discarded, however, because the increase in quality of the copper deposit did not warrant the increased clamping and control problems.*

Plating Time

The optimum plating time is one short enough to allow a high production capacity and long enough to allow easy achievement of the required deposit thickness range. To do this an average plating rate of approximately 0.01 mil/min was chosen. This results in a plating time of 20 min to achieve the required 0.15-0.25 mil copper deposit. The rate of deposition is governed mainly by the solution temperature and the degree of agitation. Slight variations in plating time are also used to allow for variation of the plating strength of the solution due to depletion of the fluoride ion as discussed below. Figure 4 shows the relationship of plating time vs copper deposit thickness for a full-strength plating bath using the recommended parameters of surface preparation, solution temperature, and agitation.

Control of Cupric Ion Concentration

The concentration of the cupric ion is not critical unless it is below 0.50%. Below this value the rate

Fig. 4 Relationship of Copper Thickness to Plating Time.

*A detailed study has recently been completed at Bettis regarding the effects of agitation on copper plating of Zircaloy. Rates as high as 15 fps have been found to offer some decided advantages. The complete report of the findings of this study will be published in the future as WAPD-238.

of deposition and quality of copper deposit decreases. In practice, this variable is eliminated by adding an excess of cupric nitrate upon initial mixing of the plating solution. Barring excessive solution spillage, the 5% cupric nitrate (1.3% cupric ion) and the volume of solution used (approximately 120 gal) is sufficient to maintain the concentration of cupric ion above the critical level during the useful life of the plating bath.

Control of Fluoride Ion Concentration

To achieve both a desirable rate of copper deposition and a deposit of satisfactory quality, a concentration of $0.125 \pm 0.025\%$ fluoride ion must be maintained in the plating solution. Higher concentrations result in a rapid rate of deposition making it difficult to control the thickness of copper to the prescribed limits. Concentrations of fluoride ion below 0.10% usually result in a poor quality copper deposit. Because, as noted in Reaction (2), the fluoride ion combines with zirconium during the plating operation, periodic additions of this ion in the form of hydrofluoric acid are required to maintain the necessary concentration.

The method by which this variable is controlled involves the use of the relationship between the thickness of the copper deposit and the concentration of the fluoride ion in the solution (calculated from the initial concentration of hydrofluoric acid). During the mixing of each new plating solution, a number of standard plating runs are performed at various concentrations of hydrofluoric acid. When the thickness of the copper deposit is determined, a curve showing the relationship of copper thickness to hydrofluoric acid concentration is plotted (see Fig. 5). During the life of the plating bath, test samples are plated periodically at conditions similar to those used to construct the above curve. By determining the thickness of copper on these samples and consulting the above mentioned curve, the amount of hydrofluoric acid required to completely rejuvenate the plating solution can be determined.

Fig. 5 Relationship of Fluoride Ion Concentration to Copper Thickness.

By utilizing the above mentioned method of control of the cupric and fluoride ion concentrations, the life of a plating bath can be extended indefinitely. In practice, however, plating baths are discarded when they become contaminated by extended use or when nonadherent and out-of-tolerance copper deposits consistently occur. This uncontrollable behavior depicts the end of the useful life of the plating solution. It usually occurs after 7% of the original content has been removed from the bath and is probably caused by a buildup of dissolution products in the solution.

Inspection of Copper Deposit

Determination of Copper Thickness

The porosity and granular nature of the copper deposit make measurement of its literal thickness both difficult and meaningless. Instead, the value that is actually determined and referred to as "thickness" reflects the weight or amount of copper per unit area of plated surface. For expression in terms of thickness, the weight of copper is divided by the theoretical density (8.95 g/cc) to determine

the volume and then by the number of square centimeters plated to determine the theoretical copper thickness per square centimeter of plated surface area. This thickness is, therefore, the actual thickness that would result if the copper were deposited as a nonporous, uniform film having the theoretical density. Because the amount of copper required for satisfactory diffusion bonds was originally determined using this type of thickness value, the "thicknesses," as determined by all inspection methods to date, have been calibrated according to this method.

The method of determining copper thickness most used during the development investigations was the gravimetric analysis of test coupons. This method involves the destructive determination of the amount of copper deposited on test coupons plated along with the receptacles in question. Since these coupons are to represent the receptacles, they must be of the same material and be treated by the same pre-plating surface preparation. The thickness of copper is determined by the weighing of the plating coupon before and after removal of the copper in nitric acid and calculating the thickness as noted above. The disadvantages of this method are: (1) it does not directly inspect the receptacles that will be used for fuel elements, (2) it assumes that the copper is uniformly deposited on the coupon, (3) it assumes that the copper deposited on the coupon is exactly similar to that deposited on the receptacles, and (4) it is destructive. Because of these disadvantages, this method cannot be used to inspect fuel element receptacles; however, it is used for periodic checks on the plating solution to determine any discrepancy in its behavior.

Investigations were undertaken to develop a nondestructive inspection method for measuring copper thicknesses on fuel element receptacles. Instruments for this purpose, operating on the principle of induced eddy-current, were determined to be too unstable. This instability was caused

mainly by the porosity of the deposit. An X-ray fluorescent instrument was finally determined to be most applicable to this problem.

After tests at the Denver Research Institute and at Bettis proved the feasibility of the X-ray fluorescence inspection method, an instrument for the inspection of receptacles in production quantities was procured and assembled*. The general function of this instrument is to excite the copper film on a plated sample and measure the intensity of the resultant copper $K\alpha$ radiation. The thickness of copper is then determined by referring to a curve correlating this intensity with copper thickness as determined by gravimetric analysis. Figure 6 shows such a calibration curve. The instrument procured consists of an X-ray source, collimators to locate the sample and direct the rays, a detector to measure the intensity of fluoresced copper $K\alpha$ radiation from the sample, a scaler to record the intensity of this radiation, and a timer to control the recording interval of the scaler. Figure 7 shows the relationship of these components schematically.

Fig. 6 Relationship of Copper Thickness to Fluoresced Radiation Intensity.

*For a more detailed description of this instrument, see the article entitled "The Thin Copper Film Gage" in this issue.

Fig. 7 Schematic Drawing of X-Ray Fluorescent Instrument Components Showing Relationship to Sample.

Inspection for three types of copper uniformity is required. These are:

- Uniformity related to copper porosity,
- Uniformity related to spotty deposits, and
- Uniformity related to different copper thicknesses on various locations of plated receptacles.

The porosity of the deposit is not critical in the diffusion bonding application. For standardization purposes, however, a porosity of less than 50% is specified. This porosity is controlled by the pre-plating surface preparation, the solution temperature, and solution agitation during plating. Control of these variables makes the deposit porosity essentially constant. As such, an occasional visual comparison with prepared standards is adequate production inspection.

Spotty deposits, consisting of small unplated areas, may be caused by faulty pre-plating surface preparation. Like porosity, these unplated areas do not affect the quality of a diffusion bond as long as they are not excessively large or numerous. Experiments and experience along these lines during this development program have indicated that such unplated areas as large as 1/8 in. in diam per sq in. of bonding area and having not less than

1/2 in. between unplated areas are acceptable. A visual inspection is used to determine this type of nonuniformity.

Variations in copper thickness are not critical as long as the requirement of 0.15 to 0.25 mil is maintained. Inspection for this nonuniformity is performed by use of the X-ray fluorescent instrument described above. With this instrument the receptacle component is surveyed to determine the copper thickness at various locations. These surveys indicate that the copper on the rib areas of a receptacle plate is generally 0.01 to 0.04 mil thicker than that on the edge strips and 0.01 to 0.05 mil thicker than that on the more solid end plates. These variations are due mainly to preferential attack by the plating solution caused by differences in geometric structure within the receptacle. Again, they are not critical as long as the copper thickness requirement of 0.15 to 0.25 mil is maintained.

Determination of Adherence of Copper Deposit

Since the purpose of the copper deposit is to provide a bonding agent, the only adherence requirement is that it remain in place until bonding. As such, only visual inspections of the copper plated receptacles are required to prevent the use of those whose copper deposit has flaked or peeled during handling. This condition is not generally a major problem because such flaking and peeling, if it does occur, will occur during drying of the receptacle after plating. When occurring, this condition is indicative of a faulty surface preparation or spent plating solution, and the cause can then be rapidly corrected before too many such plates are produced.

Determination of Plated Surface Contamination

The composition of the copper deposit is governed by the plating operation. Wet chemical and spectrographic analysis of copper deposits have indicated that this composition is essentially constant and

greater than 98% Cu (major contaminant < 1% ZrO). As such, no problem with this property is anticipated.

The contamination of the base material is controlled by proper pre-plating surface preparation. No detailed inspection is required; however, if desired, a measure of contamination of the surface can be made by ignited AC surface spectrographic analysis and comparison of these results with similarly analyzed control samples. This method, however, is not good for all surface contaminants, and the accuracy of quantitative results is questionable.

The final source of surface contamination is that introduced in storage and handling of the components after copper plating. This is controlled by close adherence to the general Bettis rules of "clean handling" of components. Wrapping with clean, waxless Kraft paper and storing in a dry box or desiccator is sufficient protection from normal atmospheric contaminants.

SUMMARY

A process capable of depositing copper on production pilot run quantities of receptacle plates was successfully developed. In this process the control of quantity and quality of the copper deposit was achieved by rigid control of pertinent variables of the receptacle surface preparation and of the copper plating operation. Selective deposition of copper was achieved by masking those areas where copper is not desired with a nonporous oxide film.

An outline of the recommended procedure for this copper plating process is presented in the Appendix.

APPENDIX: COPPER PLATING PROCEDURE

Surface Preparation

- 1) Pickle machined receptacle component in HNO_3 -HF solution to prepare it for the

application of oxide masking film (minimum removal—1 mil/surface).

- 2) Rinse in cold flowing tap water and cold flowing distilled water (10 min each minimum).
- 3) Autoclave in distilled water at 650°F for 2 hr at saturation pressure to deposit oxide film on all surfaces of the receptacle component.
- 4) Climb-mill surface to be bonded to remove oxide masking film, attain final thickness dimensions, and prepare surface for plating.
- 5) Detergent degrease receptacles by immersion in 2% solution of Penn Salt A-27 at 180°F to remove oil films from the surface of the receptacle.
- 6) Rinse in cold flowing tap water for a minimum of 15 min.

Copper Plating

- 1) Immerse prepared receptacles in solution observing the following parameters:
 - a) Solution composition -
 - (1) Cupric nitrate (crystalline purified grade) - 5 w/o (nom)
 - (2) Hydrofluoric acid (52% tech grade) - 0.25 v/o (nom)
 - (3) Tap water
 - b) Solution temperature - 80°-85°F
 - c) Plating time - 17-23 min (depending on thickness of copper required and strength of plating solution)
 - d) Agitation - forced recirculation of plating solution through perforated tubing (50 gpm)
- 2) Rinse in cold flowing tap water - 5 min

- 3) Dry - blot and blow dry with filtered air or immerse in hot deionized water for 5 min and allow to air dry

Inspection of Plated Surface

1) Thickness

- a) Gravimetric analysis of test coupons (determine average thickness of copper for the plating bath)
- b) X-ray fluorescence measurement of copper on plated receptacles

2) Uniformity

- a) Visual inspection to determine unplated areas and porosity
- b) X-ray fluorescence survey of receptacle to determine deposit thicknesses at various locations

3) Adherence

Visual inspection during subsequent processing to observe any chipping or peeling of copper deposit

4) Contamination

Periodic wet chemical and spectrographic analysis of copper deposit

REFERENCES

1. E.F. Losco, R.L. Fischer, N.T. Saunders, and R.A. Wolfe, "Plate-Type, UO_2 Bearing Fuel Elements for the PWR Core 2 Blanket," BETTIS TECHNICAL REVIEW, WAPD-BT-10 (October 1958), pp 57-72.
2. F.M. Cain, Jr., "The Chemical Displacement Plating of Zirconium and Zircaloy," BETTIS TECHNICAL REVIEW, WAPD-BT-6 (January 1958), pp 48-57.
3. S. Kass, D.J. Fontanese, A.E. Oaks, and D.B. Scott, "Pickling of the Zircaloys Prior to Corrosion Exposure," WAPD-TM-141 (September 1958).

One of the methods investigated for the fabrication of fuel elements for PWR Core 2 was a eutectic diffusion bonding process which required a thin copper film on one of the two surfaces to be bonded. A gage, employing the X-ray fluorescence technique, was developed to measure the critical thickness of this film. A statistically established accuracy of ± 0.000004 in. is possible with this gage, which is more than adequate in the range of interest.

THE THIN COPPER FILM GAGE

R. A. Betz

The second core being built for insertion in the Pressurized Water Reactor (PWR) is to be made of plate-type elements loaded with small rectangular uranium oxide wafers. The wafers will be put into a receptacle plate consisting of small compartments as shown in Fig. 1.

The process finally decided upon for the manufacture of PWR Core 2 plate-type fuel elements is pressure bonding. However, one of the methods investigated for the fabrication of fuel elements was a eutectic diffusion bonding process.* This process requires a thin copper film on the receptacle plate. The receptacle plate, fuel wafers, and cover plates are assembled into a fuel element which is placed in a furnace under pressure for several hours. The copper and the zirconium form a low melting eutectic which distributes itself evenly over the mating surfaces and then diffuses into the matrix. When bonding is completed, all evidence of a bond line has disappeared.

In the eutectic diffusion bonding process, the thickness of the copper film is fairly critical. If the film is too thin, poor bonds result; if it is too thick, the Zircaloy becomes copper enriched, and its corrosion resistance is impaired. Consequently, the film thickness is required to be in the range 0.00015 to 0.00018 in. To insure that the film thickness requirements are being met, a gage had to be developed to nondestructively measure the film thickness to within ± 0.00001 in.

X-RAY FLUORESCENCE MEASUREMENTS

The X-ray fluorescence technique, used in the steel industry to measure the thickness of thin tin plate, was suggested by L. H. Sherwin of Bettis as a promising method for measuring the critical copper film thickness.

Fig. 1 Portion of One Type of Compartmented Receptacle Plate. Compartment and Rib Widths Are Typical. Plating Is on Top Surface Only.

*See the article entitled "Development of Techniques for Large-Scale Electroless Copper Plating of Zircaloy Plate-Type fuel Receptacle Components" in this issue.

X-Ray fluorescence analysis depends essentially upon the emission of secondary X-rays by a material when it is placed in a suitable beam of primary X-rays. These secondary (fluorescent) X-rays have a specific energy or wave length that is different for each element, and a certain minimum energy of the primary beam is required to excite the secondary radiation of each element.

Once the secondary X-rays have been obtained, there are two methods of working with them. The first (and most common) is the dispersive technique. Here, the secondary X-rays fall on a suitable analyzing crystal where they are diffracted just as light is diffracted by a grating. Each wave length leaves the analyzing crystal at a specific angle, and, by setting a detector at the proper place, the radiation emitted from a particular element can be detected. For film measurement, the dispersive technique can be used to measure either the total radiation from the plated element or the attenuation of the radiation from the base element as it passes through the plating.

The second method, called the nondispersive technique, measures the total radiation leaving the sample. This method is applicable only under a rather special condition—the base material must have a higher atomic number than the plating. In this method the energy of the primary beam is set to excite the plating material only. Most of the radiation measured by the detector is then emitted from the coating material, with a small portion resulting from scattering of the primary beam from the sample and the structural parts of the gage.

Since the atomic number of zirconium is 40 and that of copper is 29, the conditions for using a nondispersive technique are met; consequently the gage was built using this technique.

DESCRIPTION OF THE GAGE

Since the nondispersive technique was to be employed, equipment needed for the gage was

simplified because a goniometer—the device for holding and manipulating an analyzing crystal and detector—was not needed. A standard spectrographic X-ray generator, tube, and detection system were selected. The detector is an argon filled proportional counter tube whose maximum counting efficiency occurs just at the energy of copper radiation. Output of the detector tube is a series of pulses which are amplified and counted on a decade scaler. When these pulses are counted for a predetermined length of time, the total number of counts accumulated becomes a direct measure of the total amount of copper in the area being irradiated.

As originally planned, the X-ray tube and detector were to be housed below the sample table and aimed at a small aperture in the table top. This soon proved inadequate because of the extreme amount of scattered radiation that was picked up by the detector. Consequently, a collimator was designed and built which totally enclosed both the primary and secondary beams from source to destination (see Fig. 2). The collimator is made of aluminum to minimize secondary radiation since the detector has a very low efficiency for radiation of this energy. For radiation protection through the aperture, a solenoid operated steel shutter was incorporated in the collimator. Closing an interlocked cover over the sample opens the shutter. Details of the collimator are shown in Fig. 3, and mounting of the X-ray tube, collimator, and detector are shown in Fig. 4. The whole unit is shown in Fig. 5.

The gage had to be able to measure both narrow ribs and the larger edge clad area of the receptacle plate. Consequently, the opening at the top of the collimator, shown in Fig. 2, is 0.030 x 0.250 in., the width being dictated by the necessity of inspecting ribs only 0.042 in. wide. To inspect the larger flat areas with the same collimator, the rib positioning pins are spring loaded and can retract into the collimator body.

Fig. 2 Top of Collimator. Pins Are Retractable and Spring Loaded. Circular Item at Left Is Secondary Standard.

Fig. 3 Details of Collimator Design.

Fig. 4 Interior of Gage Showing Mounting of X-Ray Tube, Collimator, and Detector.

Fig. 5 Over-All View of Thin Copper Film Gage. Large Cabinet Contains the X-Ray Generator. Unit in Pedestal Is DC Power Supply.

In operation, the gage is set up with a tube potential of 19 kvp and a tube current of about 34 ma. Actual tube current is set so that a secondary standard—made of copper dust imbedded in plastic—reads a prescribed number of counts. With the conditions described above, a sample with 0.00015 in. of copper will count at the rate of about 3190 c/sec. Counts are accumulated for a 10-sec interval which is ample for good counting statistics.

Evaluation of the gage was made on a statistical basis. A set of test coupons was run daily over a 10-day period, and from the data acquired the precision was calculated to be equivalent to ± 0.000004 in. of copper at a 95% confidence level. For calibration purposes a number of sample coupons were run, and the average of readings at twenty different locations was taken as the average for the sample. The average copper thickness was then determined by the gravimetric analysis method. The values thus calculated and the average counting rate are plotted as the calibration curve shown in Fig. 6. The curve is linear over the range shown but would flatten out at somewhat

higher copper thicknesses because of self-absorption of the copper fluorescent radiation within the film.

Fig. 6 Calibration Curve of X-Ray Fluorescence Gage for Copper Thickness Plated on Zircaloy-2 Coupons with Mat-Etched Edges. Counting Rate Is Plotted as a Function of Copper Thickness.

The method which has been selected for PWR Core 2 fabrication is pressure bonding. Therefore, although the gage has been successfully used to

inspect critical experiment plates,* it will not be used during core production. However, by using a different counter tube, the unit can be used for any film meeting the requirements for a nondispersive technique.

CONCLUSIONS

A simple and accurate gage for measuring the amount of copper deposited on a Zircaloy-2 base has been developed which utilizes a nondispersive X-ray fluorescence technique. The gage has a statistically established precision of ± 0.000004 in. of copper in the range of interest which is more than adequate.

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*See the article entitled "Development of Techniques for Large-Scale Electroless Copper Plating of Zircaloy Plate-Type Fuel Receptacle Components" in this issue.