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HEAVY WATER
ORGANIC COOLED REACTOR
SCREENING TESTS
OF
HYDROGEN DIFFUSION BARRIERS
FOR
ZIRCONIUM

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By
W. R. KERR

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ATOMICS INTERNATIONAL—COMBUSTION ENGINEERING

A Joint Venture for Heavy Water Organic Cooled Reactors

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ABSTRACT

Screening tests in gaseous hydrogen were conducted at 399°C (750°F) to determine the efficacy of hydrogen barrier coatings for zirconium alloys for use in Heavy Water Organic Cooled Reactor (HWOCR) organic coolant. Plasma sprayed aluminum coatings were extremely porous and hence ineffective. Zirconium oxide, zirconium nitride, and diffused aluminum coatings were found to be effective hydrogen barriers but subject to progressive, catastrophic failure because of their inherent brittleness. It is concluded that further investigation should consider primarily a ductile coating, such as pure aluminum, or coatings which can be continuously repaired in service, such as oxide coatings.

I. INTRODUCTION

Consideration of zirconium base alloys for pressure tube or fuel cladding applications on HWOCR will require that hydrogen pickup from the organic coolant be controlled or retarded to prevent serious degradation of the zirconium alloy properties, especially ductility. One approach to retardation of hydriding is the use of barrier coating on the zirconium alloy surfaces exposed to the organic. Barrier candidates considered were zirconium oxide, zirconium nitride, zirconium-aluminum intermetallics, and aluminum applied by plasma spraying.

Screening tests in gaseous hydrogen were performed to determine the efficacy of the various coatings as hydrogen barriers without extensive testing in organic coolant. Because the concentration of free hydrogen available in such tests can be much greater than that available in the organic coolant, the screening tests are considered accelerated tests to compare relative effectiveness of barriers. Such factors as pyrolytic and radiolytic decomposition of the coolant, solubility of hydrogen in the coolant, and impurities in the coolant are not well defined, and a quantitative correlation between the screening tests and HWOCR environment is therefore not possible.

This report describes the apparatus and testing procedure used for hydrogen screening tests and summarizes the results of these tests.

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Figure 1. Schematic of Hydrogen Retort

II. APPARATUS

Figure 1 shows schematically the arrangement of one of the hydrogen retort tubes. A total of six such tubes were attached to the manifold. The vacuum system consisted of a cold trap, mercury diffusion pump, and mechanical pump.

In order to permit determination of the amount of hydrogen absorbed by the specimens as a function of pressure drop in the retort, it was necessary to determine the average temperature in the retorts (only part of the retort containing the specimen was heated to the test temperature), as well as the volume of the retorts. The volume of the manifold was determined by measuring the pressure change when air at a known pressure in the calibrated volume was admitted to the evacuated manifold. Use of the ideal gas law indicated the volume of the manifold was 1560 cc. Using the manifold as a secondary calibrated volume, the volume of each of the retorts was determined by the same method. Each of the retorts was found to have a volume of 573 cc.

The average temperature of the retort was also determined from the ideal gas law. The retort was filled with hydrogen at ambient temperature and the pressure was recorded as the furnace was heated to 399°C (750°F). The average temperature in the retort was calculated from the pressure increase at 81°C (178°F).

Using the volume and temperature thus determined, the relationship between pressure decay and hydrogen absorption was determined as 2.59×10^{-5} mole (5.18×10^{-5} g) of hydrogen per mm Hg decrease in pressure.

III. PROCEDURE

The following procedure was used to set up and conduct tests. The retort tubes were removed from the system at the ground glass joints and specimens were suspended within them by a 0.003-in.-diameter nickel wire. The joints were reclosed and the system was evacuated and purged with hydrogen three times. The system was again evacuated overnight. The furnaces were heated to 399°C (750°F) as measured by the thermocouples in the bottoms of the retorts. Vacuum pumping was continued during heating. When the specimens had reached the test temperature, the vacuum valve and manometer and retort valves were closed. Hydrogen at approximately 710 mm Hg was admitted to the manifold and calibrated volume. One of the retort valves was then opened for 5 sec to admit hydrogen. The manifold was refilled to 710 mm Hg and a second retort was filled. This procedure was repeated until all the retort tubes were filled. The initial pressure in the retorts was 600 to 610 mm Hg. The pressure in each of the tubes was measured and recorded initially at 5-min intervals, then at varying intervals depending upon the rate of pressure decay.

The above procedure was established as a result of a number of preliminary tests and trial runs. Blank runs, in which the nickel wire without a specimen attached was suspended in the retort, showed no significant pressure change in 7 hr. Preliminary specimens of uncoated zirconium alloys, tested without the hydrogen purging operation, showed a light oxide film on their surfaces after testing. The purging operation was then introduced to eliminate all oxygen from the system prior to heating; specimens tested subsequently showed no evidence of oxidation. It was desired to keep the time during which the retort valve was open as short as possible to prevent absorption by the specimens of hydrogen from the manifold. Tests showed that 5 sec was adequate to permit equalization of pressure between manifold and retort.

Hydrogen pressure in the system was kept slightly below atmospheric pressure so that any failure would result in an implosion rather than an explosion. (Normal atmospheric pressure at the location of the tests is 715 mm Hg.) Operation at less than atmospheric pressure also provided a check against leaks in the system. At pressures above atmospheric, a leak might be misinterpreted as hydrogen absorption by the specimen; operating at lower pressures, a leak would result in an increase in pressure within the retort.

IV. SPECIMENS

With the exception of one specimen of 3Z1 (1.25% Al, 1.00% Si, 1.00% Mo), all specimens were Zircaloy-2 obtained from Wah Chang, Heat Number 37413-Zr-2. This material was 0.050 in. thick, as received, and was cold rolled to 0.030 in. and vacuum annealed to provide suitable stock for the test specimens. Specimens 3/4 by 4 by 0.030 in. were sheared from this material and holes 1/8 in. in diameter were punched in each end to be used to support the specimen during coating and testing.

Coatings tested were similar to those applied to samples inserted in the U-305 Experiment. Available data on the coatings is shown in Table 1.

Coatings applied by oxidation in air and in oxygen were done in a thermal balance. An attempt was made to control coating thickness by continuously measuring specimen weight gain during oxidation. Based on the assumption that the weight gained by the specimens was oxygen which formed ZrO_2 at the surface, a weight gain of 0.148 mg/cm^2 would result in a coating thickness of 1μ . Because the samples were attached to the balance in groups of five, and because oxidation was not uniform on all specimens, the desired weight gain was not always attained. Therefore, the desired as well as the actual thickness (based on weight gain calculations and the assumptions that all oxygen formed ZrO_2 and that the coating is uniform) is shown in Table 1. Specimens oxidized in air gained weight at a much higher rate than those oxidized in pure oxygen. The coatings produced in air probably contain some nitrogen. Lustman and Kerze⁽¹⁾ show that the rate at which zirconium gains weight in air at 500°C is approximately twice the rate in oxygen. This difference would account for the shorter times required for an equivalent weight gain in air as in oxygen.

Assumptions with respect to stoichiometry were not possible for nitride layer as with oxide layer. Samples were therefore nitrided for a fixed time at temperature.

Specimens oxidized in steam were sealed in an autoclave with an amount of water calculated to produce the indicated pressure (1500 psi). The autoclave was then heated to 427°C (800°F) for 96 hr. Weight gains and oxide thicknesses were estimated from data on specimens treated similarly.

TABLE 1
SPECIMEN COATING DATA

Specimen No.	Coating				Specimen Weight Gain (mg/cm ²)	Coating Thickness (μ)
	Type	Medium	Temperature	Time		
Zr-2	Pickled	—	—	—	—	—
3Z1	Pickled	—	—	—	—	—
521	Oxide	Air	450°C	23 hr, 15 min	0.152	1.03
525	Oxide	Air	450°C	23 hr, 15 min	0.175	1.18
501	Oxide	Air	500°C	2 hr, 50 min	0.150	1.01
503	Oxide	Air	500°C	2 hr, 50 min	0.150	1.01
514	Oxide	Air	500°C	13 hr, 51 min	0.338	2.28
515	Oxide	Air	500°C	13 hr, 51 min	0.364	2.46
506	Oxide	O ₂	450°C	35 hr, 42 min	0.214	1.45
507	Oxide	O ₂	450°C	35 hr, 42 min	0.182	1.23
544	Oxide	O ₂	500°C	5 hr, 25 min	0.201	1.35
545	Oxide	O ₂	500°C	5 hr, 25 min	0.181	1.22
529	Oxide	O ₂	500°C	27 hr, 10 min	0.315	2.13
530	Oxide	O ₂	500°C	27 hr, 10 min	0.323	2.18
51	Oxide	Steam	800°F, 1500 psi	96 hr	0.230	1.55
52	Oxide	Steam	800°F, 1500 psi	96 hr	0.230	1.55
532	Nitride	N ₂	800°C	8 hr	0.132	—
535	Nitride	N ₂	800°C	8 hr	0.150	—
517	Nitride	N ₂	800°C	16 hr, 10 min	0.201	—
520	Nitride	N ₂	800°C	16 hr, 10 min	0.201	—
537	Nitride	N ₂	850°C	8 hr	0.243	—
540	Nitride	N ₂	850°C	8 hr	0.287	—
546	Nitride	N ₂	900°C	8 hr	0.303	—
549	Nitride	N ₂	900°C	8 hr	0.276	—
1	Aluminum coated by plasma spray					
12	Aluminum coated by plasma spray					
374-10	Aluminized	Na	1400°F	6 hr	10.44	40
374-5	Aluminized	Na	1400°F	6 hr	9.95	40
375-1	Aluminized	Na	1400°F	6 hr	9.92	40*
374-6	Aluminized	Na	1400°F	6 hr	10.25	40†
374-7	Aluminized	Na	1400°F	6 hr	10.19	40§
374-9	Aluminized	Na	1400°F	6 hr	10.04	40**

*Additional aluminum by plasma spray

†3 hr oxidation in air at 800°F

§1 hr oxidation in air at 900°F

**26-1/4 hr oxidation in air at 850°F

Difcoated specimens were aluminized by Atomics International's proprietary process. The coating consisted of Zr-Al intermetallics. Page and Sneesby⁽²⁾ indicated that coatings produced by this method consist primarily of $ZrAl_3$ and $ZrAl_2$. Several Difcoated specimens were also subjected to oxidation treatment in an air furnace in an attempt to form a heavier oxide coating than that which occurs naturally at ambient temperature.

The plasma sprayed aluminum was applied in air and was extremely porous. These samples were tested only because they duplicated specimens in the U-305 Experiment.

TABLE 2
RESULTS OF PRESSURE DECAY TESTS — 600 mm

Specimen No.	Coating				Time of Initiation of Failure	Time to Absorption of Available H ₂ (~3000 ppm)
	Type	Medium	Temperature (°C)	Time (hr)		
Zr-2			None		0	24 min
3Z1			None		0	2 hr, 55 min
525	Oxide	Air	450		7 hr	24 hr
501	Oxide	Air	500		7-1/2 hr	24 hr
515	Oxide	Air	500		7-1/2 hr	24 hr
506	Oxide	O ₂	450		1 hr	7 hr
544	Oxide	O ₂	500		7 hr, 25 min	24 hr
530	Oxide	O ₂	500		6 hr, 55 min	24 hr
51	Oxide	Steam			7 hr, 30 min	24 hr
535	Nitride	N ₂	800	8	3 hr, 53 min	4 hr, 5 min
520	Nitride	N ₂	800	16	0	25 min
540	Nitride	N ₂	850	8	25 hr, 41 min	25 hr, 53 min
549	Nitride	N ₂	900	8	551 hr, 20 min 6 hr, 15 min after cool down and reheat	- 24 hr
546	Nitride	N ₂	900	8	1 hr	1 hr, 50 min
1	Plasma Spray Aluminum				0	35 min
12	Plasma Spray				0	47 hr
374-10	Aluminized by Difcoat				30 hr, 37 min	47 hr
374-5	Aluminized				24 hr	43 hr
375-1	Difcoat and Plasma Spray				0	4 hr
374-6	Difcoat and Oxidation				7 hr, 30 min	24 hr
374-7	Difcoat				7 hr, 20 min	23 hr
374-9	Difcoat				7 hr, 20 min	24 hr

V. RESULTS

Results of the screening tests are shown in Table 2. Pressure decay data were recorded during the normal work day, although the specimen exposure continued on an uninterrupted basis. With three exceptions, all specimens absorbed all the hydrogen available (1.55×10^{-2} moles, approximately 3000 ppm for a 10-g specimen) in less than 24 hr. Because of the shape of the pressure decay curves and the condition of the specimen upon removal from the retorts, the mode of failure is considered more significant than the time for hydrogen absorption.

Figure 2 shows typical pressure decay curves. The uncoated specimens and the plasma spray-coated specimen began to absorb hydrogen immediately and at a relatively rapid rate. Oxide coated specimens began to absorb hydrogen at a relatively low rate and then at a gradually accelerating rate. Nitride coated specimens were characterized by no detectable hydrogen absorption for some period of time, followed by rapid absorption. All of the pressure decay curves show evidence of decreasing absorption rate at pressures below 100 mm Hg. [Smith⁽³⁾ indicates that absorption rate is independent of pressure only at pressures greater than 100 mm Hg.]

Figure 2. Typical Hydrogen Pressure Decay Curves

Figure 3. Typical Failure of an Oxidized Specimen 6643-2-2

Figure 4. Typical Failure of a Nitrided Specimen 6643-1-2

Figures 3 and 4 show the typical condition of specimens after removal from the retort. In all instances, even for uncoated specimens, failure was localized, occurring at or near an edge, a corner, or at the hanger hole. The localized failure was attributed to small defects in the coatings. Such defects, whether initially present or formed by cracking of the brittle coating during heating or holding at temperature, would absorb hydrogen at a very low rate initially. However, as the hydride content in the area of the defect increased, the resulting volume change (density of ZrH is 5.6 g/cc, density of Zr is 6.4 g/cc) caused cracking of the coating, which exposed more uncoated metal, and resulted in an accelerating catastrophic failure.

Metallographic examination of specimens showed very high concentrations of hydride in the area of the failure. Figure 5 shows a typical microstructure in such an area. A sharp gradient exists between the severely hydrided area and the area where little hydride is present. Figure 6 shows the microstructure of the same sample, some distance from the failed area. The sharp gradient is taken as an indication that the rate of absorption of hydrogen is much greater than the rate of diffusion away from the defect area. This difference in rates greatly accentuates the localization of hydriding and the progressive catastrophic failure.

Localized attack was not observed on Specimen No. 374-10, which was aluminized by the Difcoat process. The pressure decay curve for this sample showed a gradual decrease in pressure with no acceleration of absorption during the 43 hr in the retort. Metallographic examination of this specimen showed a uniform distribution of hydride throughout. Figure 7 shows the microstructure of this specimen. Hydrogen had apparently been absorbed at the cracks in the coating, as well as through the coating itself, but the rate of absorption at the defects was presumably sufficiently slow to permit diffusion away from the area and prevent excessive volume changes.

Sample No. 549, nitrided 8 hr at $900^{\circ}C$ ($1652^{\circ}F$) and presumably free from defects, was exposed for more than 550 hr with no detectable hydrogen absorption. After this time the specimen was removed from the retort and scratched with a steel knife blade. The specimen was then retested to determine the effect of an

6518-1-1

Figure 5. Hydride Formation at a Failed Area —
Specimen No. 530 Oxidized at 500°C

6518-1-2

Figure 6. Microstructure of Specimen No. 530
at an Area Some Distance From Failure

6518-2-1

Figure 7. Typical Microstructure of Specimen
No. 374-5, Aluminized by Difcoat
(Note hydride precipitate at
crack in coating)

artificially introduced defect on material with this coating. Failure occurred in less than 24 hr. Subsequent examination revealed that the specimen failed not at the intentional defect but near an edge. Metallographic examination indicated that the scratch had not penetrated the coating and the failure probably resulted from a crack in the coating as a result of cooling the specimen from test temperature to remove it from the retort, or reheating when the specimen was tested the second time.

TABLE 3
RESULTS OF PRESSURE DECAY TESTS - 100 mm

Specimen No.	Coating				Time to Initiation of Failure (hr)	H ₂ Absorbed Prior to Initiation (mg)
	Type	Medium	Temperature (°C)	Time (hr)		
503	Oxide	Air	500	8	52	5.02 (566 ppm)
514	Oxide	Air	500		244	4.66 (518 ppm)
521	Oxide	Air	450		73	4.77 (592 ppm)
52	Oxide	Steam			168	4.92 (- -)
545	Oxide	O ₂	500		167	4.87 (603 ppm)
529	Oxide	O ₂	500		544*	16.4 (1970 ppm)
507	Oxide	O ₂	450		191	5.34 (6.06 ppm)
532	Nitride	N ₂	800	8	464*	0
537	Nitride	N ₂	850	8	272*	0
517	Nitride	N ₂	800	16	104	0

*Removed from test, no failure. Hydrogen absorbed at time of removal is recorded.

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Figure 8. Typical Hydrogen Pressure Decay Curve

VI. LOW PRESSURE TESTS

The amount of hydrogen available in the retorts at 600 mm Hg pressure, and therefore the rate of hydrogen absorption in the tests described in Section V, is much greater than that anticipated in organic coolant. Metallographic examination indicated that the catastrophic failure resulted because hydrogen was absorbed at defects faster than it could diffuse away. In an attempt to provide a less severe test, a number of specimens were tested with only 100 mm Hg pressure in the retorts. The specimens were permitted to absorb hydrogen until pressure in the retort was reduced to 10 mm Hg or less; the retort was then refilled to 100 mm Hg pressure. This procedure was repeated until a rapid drop in pressure, indicating failure, was observed.

Results of the lower pressure tests are summarized in Table 3. Figure 8 shows a typical pressure decay curve. Although the time required for absorption of the initial charge of hydrogen varies, all but one of the oxidized specimens failed soon after addition of the second charge. All specimens failed after absorption of approximately 5×10^{-3} g H₂ (500 ppm for a 10-g specimen). However, specimens subjected to this test failed by the same mode, localized hydriding, as those subjected to the high pressure tests. The hydrogen contents at the defects are therefore much higher than that calculated for uniform distribution. Specimen No. 529, which absorbed nearly 2000 ppm without failure, is presumed to have had a uniform coating with no defects. Figure 9 shows the microstructure of the specimen indicating a uniform distribution of hydride.

Figure 10 shows the microstructure of Specimen No. 503 in the area of the failure. The gradient between the severely hydrided area and the base material appears to be less sharp than the gradient in specimens subjected to the 600 mm Hg test. This difference may indicate that hydrogen absorption at the lower pressure was sufficiently slow to permit some diffusion away from the defect. Because of the complex geometry at the failed area, no attempt was made to assess this effect quantitatively.

No pressure decay or failure was observed for any of the nitrided specimens tested. Testing of these specimens and of Specimen No. 529 was discontinued to permit relocation of the apparatus.

6633-2-1
Figure 9. Microstructure of Specimen No. 529
Which Absorbed Nearly 2000 ppm
Hydrogen Without Failure

6633-1-3, -4

Figure 10. Hydride Formation Near a Failed Area — Specimen No. 503
Tested in 100 mm Hg Hydrogen

VII. DISCUSSION

The most significant result of the screening tests is the mode by which coatings failed. Because of the susceptibility of the brittle coatings to fail progressively and catastrophically as a result of defects, the screening tests are more indicative of the integrity of coatings than of their efficacy as hydrogen barriers. With the exception of the plasma sprayed aluminum, all coatings tested impede hydriding of zirconium. The fact that the "uncoated" specimens failed locally rather than generally indicates that the thin, naturally occurring oxide layer retards hydriding sufficiently so that hydriding occurs preferentially at the fresh metal surfaces exposed at defects. Paradoxically, the effectiveness of the coatings as hydrogen barriers causes the catastrophic failure by concentration of hydriding.

In considering uncoated specimens, it should be noted that the 3Z1 specimen absorbed hydrogen at a slower rate than the Zircaloy-2 specimens. This difference may result from differences in the naturally occurring oxide film on the two materials or from a difference in the mode of precipitation or in the rates of absorption for the two alloys. Metallographic examination, for example, revealed that hydride in the 3Z1 were nodular (see Figure 11) as compared with the acicular hydrides (Figure 5) in Zircaloy-2. This observation should not be overlooked, and suggests that further work be pursued on alloy systems which will form nodular hydrides.

Because the results of the tests were influenced primarily by coating integrity, it is not possible to assess, quantitatively, the effectiveness of the various coatings (aluminides, oxides, and nitrides) or of various coating parameters (time, temperature, or coating thickness). Qualitatively, some differences have been observed. Within the limits of the test sensitivity, nitride coatings do not appear to permit absorption of hydrogen prior to occurrence or growth of a significant defect. Some absorption of hydrogen occurs through the oxide coating prior to rapid absorption at a defect. The permeability of ZrO_2 coatings on zirconium has been investigated by Smith⁽³⁾ and by Shannon⁽⁴⁾ who attribute hydrogen diffusion through the ZrO_2 to the presence of vacancies in the structure. Shannon⁽⁴⁾ indicates that in the absence of an oxidant, an oxide coating used as

6518-4-1

Figure 11. Failed Area in 3Z1 Specimen.
Note That Hydride Precipitate is Nodular

a hydrogen barrier will degrade with time, presumably a result of vacancies formed by diffusion of small quantities of oxygen into the base metal. Such a mechanism could result in defects by accelerated hydriding at thin areas in an oxide coating.

The data obtained at low pressure appear to indicate that thicker oxide coatings are more effective than thin ones. This observation is in agreement with the conclusions of Smith⁽³⁾ who found the rate of permeation to be inversely proportional to film thickness. Sawatsky,⁽⁵⁾ however, indicates that thick oxide coatings ($\sim 3\mu$) are subject to cracking.

The mechanism by which the tested coatings failed, spalling of the coating due to volume changes resulting from hydride formation, indicates that brittle coatings are not suitable hydrogen barriers unless the integrity of the coatings can be assured initially and throughout their expected residence time in organic coolant. While inspection techniques which would assure the initial integrity of coatings might be developed, assurance of the integrity of thin brittle coatings during the life of a reactor is difficult.

Oxide coatings are also subject to the brittle type of failure as well as to gradual degradation resulting from vacancy formation. Boulton,⁽⁶⁾ however, has indicated that continual repair of oxide coatings is possible if 50 to 150 ppm water are present in the organic coolant. For this reason, future investigations of the efficacy of oxide coatings for this application should be concerned with the relationship between the chemistry of the organic coolant (specifically hydrogen and water content) and the rate of hydrogen pickup by zirconium exposed to this coolant.

VIII. CONCLUSIONS

1. Because progressive failure may occur, brittle coatings are considered unreliable for use as hydrogen barriers for zirconium in organic coolant unless some means of continuously regenerating the coating in situ is possible.
2. Within the limits of detection of these experiments, an undamaged zirconium nitride coating is impervious to hydrogen at 750°F.
3. While zirconium oxide and zirconium aluminide coatings impede hydrogen diffusion, these coatings are less impervious than nitride coatings. The permeability of oxide coatings is dependent upon the availability of an oxidizing agent.

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Topical

Duke Power Company
P. O. Box 2178
Charlotte, North Carolina 28201

Mr. E. C. Fiss

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E. I. du Pont de Nemours and Company
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Wilmington 98, Delaware 19898

Dr. D. F. Babcock, Director
Reactor Engineering Section

1

E. I. du Pont de Nemours and Company
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Aiken, South Carolina 29801

Dr. J. L. Crandall

1

Mr. S. W. O'Rear, Supervisor
Technical Information Service

2

Massachusetts Institute of Technology
77 Massachusetts Avenue
Room 24-109
Cambridge 39, Massachusetts 02139

Dr. Manson Benedict, Head
Department of Nuclear Engineering

1

Oak Ridge National Laboratory
Union Carbide Corporation
AEC Operations
P. O. Box X
Oak Ridge, Tennessee 37831

Mr. D. A. Douglas

1

Mr. D. E. Ferguson

1

Mr. J. A. Lane (ORNL P. O. Box Y)

1

Dr. I. Spiewak

1

Pacific Northwest Laboratory
P. O. Box 999
Richland, Washington 99352

Dr. J. J. Cadwell, Manager
Metallurgy Department

1

Topical

Puerto Rico Water Resources Authority
Box 4267
San Juan, Puerto Rico

Dr. Modesto Iriarte, Jr., Sr. Electrical and Nuclear Power Engineer (after patent clearance) 1

Rensselaer Polytechnic Institute
Troy, New York

Dr. P. B. Daitch, Department of Nuclear Science and Engineering 1

Tennessee Valley Authority
303 Power Building
Chattanooga, Tennessee 37401

Mr. C. H. Waugaman, Chief Power Research Staff 1

Mr. Harold L. Falkenberry 1

U. S. Atomic Energy Commission

Brussels Office
U. S. Mission to the European Communities
APO, New York, New York 09667

Theodore J. Iltis, Acting Sr. USAEC Representative 1

California Patent Group
P. O. Box 808
Livermore, California 94551

Mr. F. A. Robertson, Chief 1

Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439

Mr. D. E. Simpson, Director 2

Division of Compliance, Region 111
Suite 410 Oakbrook Professional Building
Oak Brook, Illinois 60523

Mr. H. D. Thornburg 1

U. S. Atomic Energy Commission (Continued)

Oak Ridge Operations Office
P. O. Box E
Oak Ridge, Tennessee 37830

Mr. H. W. Behrman 1
Mr. R. L. Philippone 1

Richland Operations Office
P. O. Box 550
Richland, Washington 99352

Mr. P. G. Holsted, Director 2
Research and Development Division

Savannah River Operations Office
P. O. Box A
Aiken, South Carolina 29801

Mr. R. J. Crosson, Acting Director, 2
HWOCR Division
Mr. R. G. Erdley, Chief Patent Branch 1
Mr. N. Stetson, Manager, SROO 1

Headquarters, Washington, D.C. 20545

Mr. R. M. Forssell, Chief 1
Advanced Development Branch
Division of Naval Reactors

Division of Reactor Development and Technology

Mr. Milton Shaw, Director 1
Mr. R. W. Bean 1
Mr. M. Booth 1
Mr. J. W. Crawford 1
Mr. D. E. Erb 1
Mr. R. Feit 1
Mr. A. Giambusso 1
Mr. P. A. Halpine 1
Mr. F. Kerze 1
Mr. J. A. Lieberman 1
Mr. W. M. McVey 1
Mr. B. T. Resnick 1
Mr. M. Rosen 1
Mr. E. E. Sinclair 1
Mr. F. R. Standerfer 1
Mr. A. N. Tardiff 2
Mr. K. A. Trickett 1
Mr. W. W. Ward 1

TopicalDivision of Reactor Development and Technology (Continued)

Mr. M. J. Whitman	1
Mr. W. A. Williams	1
Mr. I. F. Zartman	1

RDT Site Offices

RDT Program Office (AI-CE)
CPAO
Canoga Park, California

Mr. R. L. Morgan RDT Sr. Site Representative	4
---	---

RDT Site Office
P. O. Box 500
Windsor, Connecticut

Mr. A. J. Alexander, RDT Sr. Site Representative	2
--	---

RDT Site Office
P. O. Box A
Aiken, South Carolina

Mr. J. H. Kruth, RDT Site Representative	1
--	---

United States Department of the Interior
Bonneville Power Administration
P. O. Box 3621
Portland, Oregon 97208

Mr. E. C. Starr, Consulting Engineer	1
--------------------------------------	---

Washington Public Power Supply System
P. O. Box 166
130 Vista Way
Kennewick, Washington

Mr. Owen W. Hurd, Managing Director	1
-------------------------------------	---

Westinghouse Electric Corporation
Atomic Power Department
P. O. Box 355
Pittsburgh 30, Pennsylvania 15230

Mr. S. Bartnoff, CVTR Project Manager	1
---------------------------------------	---

Mr. Hood Worthington
Devon Apartments, No. 1512
2401 Pennsylvania Avenue
Wilmington, Delaware 19806

1

Atomics International
 P. O. Box 309
 Canoga Park, California 91304

S. O. Arneson	D/782	C001	1
R. Balent	D/716	C002	1
A. Bennett	D/799	C002	1
G. D. Calkins	D/745	C001	1
E. M. Chandler	D/782	C001	1
J. C. Cochran	D/784	C001	1
D. J. Cockeram	D/731	C002	1
J. Falcon	D/716	C002	1
J. J. Flaherty	D/797	C002	1
D. C. Fulton	D/710	C002	1
S. Golan	D/793	C002	1
R. B. Gordon	D/782	C002	1
J. Hume	D/717	C002	1
R. T. Keen	D/741	C004	1
G. Koris (Patent Office)	GO	C002	1
J. R. Lewis	D/782	C001	1
J. E. Mahlmeister	D/793	C002	1
W. E. Parkins	D/740	C002	1
T. G. Parker	D/782	C001	1
D. Saxe	D/797	C002	1
S. Siegel	D/793	C002	1
C. Starr	D/797	C002	1
B. J. Thomas*	D/782	Canada	1

Combustion Engineering, Inc.
 Nuclear Division
 P. O. Box 500
 Windsor, Connecticut 06095

C. Andrea	1
F. Bevilacqua	1
W. P. Bigler	1
H. Cahn	1
W. P. Chernock	1
A. W. Cope	1
J. R. Dietrich	1
J. S. Greacen	1
R. S. Harding	1
H. V. Lichtenberger	1

*Atomics International Representative at Chalk River, Canada.

Combustion Engineering, Inc. (Continued)

E. H. Luther (Patent Office)	1
D. McLaughlin	1
H. Oslick	1
B. J. Selig	2
S. H. Shippenberg	2
P. Sontaro	1
W. Taylor	1
J. C. Tobin	1
R. P. Varnes*	1
S. Visner	1
J. M. West	1
R. H. Young	1
W. H. Zinn	1
CE HWOOCR File (G. Basu)	5
CEND File, W. Simon	1

HWOOCR Program Office
 c/o Atomics International
 P. O. Box 309
 Canoga Park, California 91304

V. E. Adler	1
L. E. Anderson	1
M. G. Andrews	1
D. P. Cary†	1
W. S. Flinn	1
D. Graf	1
K. S. Helm	1
B. L. Hoffman	1
D. A. Huber	1
J. Jacobson	1
B. Katz	1
R. W. Keaten†	1
S. Miner	1
W. A. Muller	1
W. B. Murray	1
P. G. Parr	1
R. Quantock	1
M. K. Sanders	1
P. F. Shaw	1
H. I. Starr	1
F. M. Stern	1

*HPO Representative at Combustion Engineering. Use CE mailing address.

†HPO Representative at Pinawa, Canada.

HWOOCR Program Office (Continued)

C. L. Storrs	1
D. S. Thompson	1
C. A. Trilling	1
R. H. Vollmer	1
H. VonSteiger	1
W. B. Wolfe*	1
HPO Central File	1

*HPO Representative at Douglas Point, Canada.