QUARTERLY TECHNICAL PROGRESS REPORT
FUELS, MATERIALS, AND COOLANT
CHEMISTRY PROGRAMS
JANUARY-MARCH 1971

The preceding Quarterly Progress Report was AI-AEC-12987

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Atoms International
North American Rockwell

P.O. Box 309
Canoga Park, California 91304

CONTRACT: AT(04-3)-824
ISSUED: APRIL 30, 1971

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

isrl

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONTENTS

<u>AEC Task No.</u>	<u>Program and Project Title</u>	<u>Page</u>
	<u>Sodium Technology</u>	
1	A. FFTF Component Qualification	5
	B. Special Compatibility (Sodium Frost)	17
	C. Coolant Related Mechanical Properties.	28
	<u>Radiation Effects</u>	
2-A	Irradiation Damage in Cladding and Core Structural Material.	43
	<u>Fuel Cladding and Structural Materials</u>	
2-B	Integral (n, α) Cross Section Measurements.	57

TABLES

1.	Summary of Test Results for the Packed Bed Vapor Trap	12
2.	Sodium Mass Balances on Filters for Packed Bed Vapor Trap	14
3.	Characters Used in the Analytical Expressions	22
4.	Biaxial Stress-Rupture Tests - 12 Specimens per Retort.	30
5.	Biaxial Stress-Rupture Data on Annealed Type 304 Stainless Steel - Heat 20013, 1200°F Sodium, Retort 17.	31
6.	Biaxial Stress-Rupture Data on Annealed Type 304 Stainless Steel - Heat 20303, 1200°F Sodium, Retort 134.	32
7.	Biaxial Stress-Rupture Tests on Cold-Worked Type 316 Stainless Steel Tubing in 1000°F Sodium Under 46,000-psi Hoop Stress.	33
8.	Length Changes - ΔT Test 2.	37
9.	Summary of Creep Tests at 700°C in Vacuum at an Initial Stress of 10 kg/mm ²	51
10.	Average Values of Creep Data	51
11.	Contents of Eight Capsules for Second Dosimetry Test	60
12.	Alloys Included in Front Capsules for Second Dosimetry Test	62

FIGURES

	<u>Page</u>
1. Packed Bed Vapor Trap	6
2. Multiple Baffle Vapor Trap	8
3. Controlled Temperature Profile Vapor Trap	9
4. Test Rig No. 1	10
5. Oxidation Rate of Sodium Exposed to Streamline Flow of Argon Containing Oxygen and Water Vapor.	24
6. Biaxial Stress-Rupture Strength of Annealed Type 304 Stainless- Steel Tubing in 1200°F Sodium	31
7. Longitudinal Cross Section of As-Received Low Carbon (0.011 wt %) 2-1/4 Cr - 1 Mo Tubing - Tubing Contained ~45% Cold Work.	34
8. Longitudinal Cross Section of Annealed Low Carbon (0.011 wt %) 2-1/4 Cr - 1 Mo Tubing Annealed 1850°F, 10 Minutes, Slow Furnace Cool	36
9. Comparison of Bulk Carbon Measurements on Type 316 Stainless- Steel Controls and Static and Flowing Sodium Tests	40
10. Swelling at 500°C as a Function of Damage for Proton-Irradiated Type 316 Stainless Steel Containing Helium.	44
11. Void Density as a Function of Displacement Rate for Proton- Irradiated Type 316 Stainless Steel Containing Helium	46
12. Transmission-Electron Micrograph Showing Voids in Sample 59 Where the Damage Was 100 Displacements/Atom.	47
13. Micrograph of Sample Seen in Figure 12 at Higher Magnification . . .	48
14. Transmission-Electron Micrograph Showing Voids and Ferrite in Sample 38 Where the Damage Was 18 Displacements/Atom	50
15. Strain as a Function of Time at 700°C for Type 316 Stainless Steel With and Without Helium	52
16. Replica-Electron Micrographs of Type 316 Stainless Steel Interrupted During Creep at 700°C	55
17. Sample Identification Macrographs	58

Program:	Sodium Technology		
AEC Task:	1, A. FFTF Component Qualification		
Project Manager:	G. W. Meyers		
Reporting Period:	January - March 1971		
General Order:	06507	Subaccount:	39600
		AEC Category:	04-01-61-03.1

Principal Investigator(s): J. L. Ballif, J. Guon

I. PROGRAM OBJECTIVES

The general objective of this work is to provide component testing services and/or ordering information on FFTF component vapor traps, freeze vents, and filters. Specifically, the objectives are: (1) construct and evaluate the performance of 5-scfm versions of three existing vapor trap designs, while maintaining the space restrictions imposed by FFTF applications, and issue evaluation reports; (2) revise and issue the RDT Standard for vapor traps, and prepare an RFP (Ordering Data) for the FFTF static and dynamic vapor traps; (3) construct and evaluate the performance of one freeze vent, and issue an evaluation report; (4) participate in the revision of the RDT Standard for the freeze vent, and prepare an RFP (Ordering Data) for the FFTF freeze vent; and (5) prepare an RDT Standard for filters for the FFTF sodium charging system, and prepare an RFP (Ordering Data) for these filters.

II. MAJOR ACCOMPLISHMENTS DURING FISCAL YEAR 1971

Three vapor trap assemblies were detailed and fabricated. Two of the traps were installed in test rigs and testing has started.

Drafts of RDT Standards for vapor traps and freeze vents have been submitted for review according to project milestones.

III. PROGRESS DURING REPORT PERIOD

A. VAPOR TRAPS

In the testing and qualifying program for vapor traps, it was agreed with HEDL to test three vapor trap concepts as candidates for the FFTF application

4-14-71

6507-5122

Figure 1. Packed Bed Vapor Trap

and to qualify them. The HEDL selections were made from among known vapor trap designs representing systems like EBR-II, Fermi, SRE, and loop-operation programs. The design relating to the FFTF application poses two problems. The first is a scale-up problem. In the case of two of the three candidate traps, neither had been intended for use at continuous flow rates of 2 to 5 scfm or intermittent flows of 15 scfm as required for FFTF use. As a consequence, none of these trap concepts has thus far been subjected to a stringent performance evaluation either for the total throughput or for the outlet gas quality standards necessary to meet the FFTF requirements.

A second problem imposed on the program was a space limitation. The device size was constrained by previously-made space allocations, which stipulated the envelope for containing the vapor traps to be 24 in. in diameter by 48 in. in height. If space were not a limitation, oversize components could be used in the system. Thus, in order to meet the FFTF needs, it is necessary not only to make an extension of the state-of-the-art design, but also to measure the performance characteristics of the vapor traps.

The vapor trap assembly, in the terminology adopted for the FFTF, consists of a vapor trap unit, such as that shown in Figure 1, and a backup filter unit. The trap itself is intended to remove the major fraction of the sodium vapor, fog, and aerosols from the argon stream, and the filter unit is intended to be a final clean-up unit to ensure that the exit gas is indeed free of sodium impurities. In practice, therefore, the argon stream leaving the vapor trap unit must be sufficiently low in sodium vapor, fog, and aerosol content that the filter does not plug within the specified service cycle time. This time is set at three months for FFTF service. If one could establish the maximum sodium contaminant concentration at the exit of the trap, one could select a filter area which would collect that amount over a 3-month period without exceeding its allowable pressure drop.

The test program is, therefore, designed to measure the total sodium content of the gas leaving the trap unit, and to measure the times required to develop pressure differences of 10 and of 20 in. of water across the system.

Three vapor traps (packed bed, multiple baffle, and controlled temperature profile) have been fabricated in the AI Shops and delivered for test (Figures 1, 2, and 3). The packed bed vapor trap has been installed in Test Rig No. 1. Sodium

4-14-71

6507-5124

Figure 2. Multiple Baffle Vapor Trap

4-14-71

6507-5125

Figure 3. Controlled Temperature Profile Vapor Trap

AI-AEC-12993

Figure 4. Test Rig No.1

was added and argon circulated in mid-February. Figure 1 shows a cross-section through the packed bed vapor trap and Figure 4 shows the schematic drawing of the test arrangement. The argon is pumped by the blowers through the argon flowmeter, and enters the sodium saturator above the level of the sodium pool. It passes upward through the packed bed down which a flow of liquid sodium is maintained by the EM pump. The argon leaves the saturator and passes through an injector section, whose purpose is to inject hydrogen and oxygen into the sodium saturated argon stream to form a highly contaminated test gas mixture (when such tests are to be performed). A sample station is located near the exit of the saturator and is used to analyze the sodium content of the argon stream as it leaves the saturator. The argon, with its impurities then enters the vapor trap unit. The effluent gas is analyzed by withdrawing a sample at the sample station. The gas then passes to the filter bank which consists of two units each having a 4-ft² area of 5-micron Type 304 stainless-steel frit. One filter is used per test run. The gas leaving the filter is analyzed by withdrawing a sample from the line leading to the blower intake manifold.

Table 1 shows the test sequence and a summary of the results of the tests made on the packed bed vapor trap. Eleven separate tests were run, three at 5 scfm continuous flow, six at 2 scfm continuous flow and two at 15 scfm intermittent flow. Run No. 1 (5 scfm) was made during the heating-up period when the sodium temperature in the saturator was increasing from 700 to 800°F. The sodium was not circulated during this period. The filter was plugged in 4-1/2 hours with the system operating with argon gas whose hydrogen, oxygen, and nitrogen levels were initially at the levels shown. Runs 2 and 3 were made at a saturator temperature of ~800°F, with circulating sodium and the filter plugged in a half-hour or less. The analysis of the argon stream leaving the trap and entering the filter showed 1700 and 1600 wppm sodium, respectively. These values are now thought to be high because later experience with the test rig indicates that deposited material is loosened and carried over when the flowrate through the system is changed. In these early tests, one sample was taken, beginning about 25 min into Run No. 2. Because plugging occurred shortly thereafter, the sampling operation was continued into Run No. 3. However, the fact that the filter did plug in a very short time is strong evidence of a high sodium concentration in the effluent argon in those tests.

TABLE 1
SUMMARY OF TEST RESULTS FOR THE PACKED BED VAPOR TRAP

Run Number	Date	Argon Flow Rate (scfm)	Saturator Conditions		Vapor Trap Temperature (°F)		Filter Performance – Time to ΔP (hr·min)		Argon Gas Analysis for Sodium (wppm)				Argon Gas Analysis (vppm)		
			Sodium Flow Rate (gpm)	Sodium Temperature (°F)	Upper 1/3 of Packing	Lower 1/3 of Packing	ΔP = 10 in. H ₂ O	ΔP = >20 in. H ₂ O	Outlet of Saturator	Outlet of Trap	Inlet to Filter	Outlet of Filter	H ₂	O ₂	N ₂
Circulate argon at ~5 scfm for two days with sodium temperature in saturator of ~500°F, no sodium circulation. Start heatup to 800°F continuing argon circulation and no sodium circulation.															
1	2/17/71	5.0	0.0	700 to 800	275 to 290	360 to 370	~4.00*	~4:30*	-	-	-	-	60	10	450
Clean and replace filters.															
2	2/19/71	5.0	1.4	800	180	260	0:28	0:32	780 to 1400	1700	1600	<30 [†]	40	<10	90
		5.0	1.4	805	210 to 225	280	0:10	0:12	-				40	<10	90
Clean and replace filters.			Purge line between vapor trap and filter with argon.												
4	2/23/71	2.0	1.3	800	170	160	-	0:05	-	-	-	-	-	-	-
5		2.0	1.3	800	160 to 170	150 to 160	2:35	2:50	830 to 1400	450	540	<3 [†]	5	<10	<30
Clean and replace filters.			Purge vapor trap and line between vapor trap and filter with argon, ~30 scfm for 3 min. Bypass filter element at 2 scfm for ~20 min prior to start of run.												
6	2/25/71	2.0	1.3	800	180 to 195	245 to 270	2:25	2:45	700 to 1100	240	250	<4 [†]	4	<10	<30
Bypass filter element at 2 scfm for ~20 min prior to start of run.															
7		2.0	1.3	800	180	260	0:20	0:35 [§]					4	<10	<30
Clean and replace filters.			Purge vapor trap and line between vapor trap and filter with argon, ~30 scfm for 3 min. Bypass filter element at 2 scfm for ~20 min prior to start of run.												
8	3/1/71	2.0	1.1	800	230 to 240	315 to 360	1:45	2:00	1500 to 2000	280	260	<3 [†]	1	<10	<30
Bypass filter element at 2 scfm for ~20 min prior to start of run.															
9	3/1/71	2.0	1.1	800	230 to 250	370	2:00	2:15	-	-	-	-	2	<10	<30
Clean and replace filters.			Purge vapor trap and line between vapor trap and filter with argon, ~30 scfm for 3 min.												
10	3/3/71 to 3/5/71	15**	0.7	490	145 to 250	150 to 305									
11	3/8/71 to 3/9/71	15**	0.7	520	110 to 270	130 to 305									

*Time sodium above 700°F.

†Based on blank correction of 0.0001 gm

§Appears to have been a plug of sodium at inlet to filter, rather than a plugged filter that caused excessive pressure drop.

**Intermittent flow.

Table 2 shows the sodium mass balances on the filters for these tests. The data for Run 2 suggest that sodium had been removed from the gas stream and had deposited in the trap and/or the line between the trap and the filter. In Run 3, (10 min duration), a good mass balance was found (4.7 gm found vs 5.0 gm transported from saturator), although it might be fortuitous.

Runs 4 through 9 are the 2-scfm tests made with the trap. In Run 4, the entrance to the filter developed a plug within 5 min. This was attributed to having loosened material in the unit during the purging operation and then having it carried to the filter during the test. Run 7 showed a similar problem. This points up a basic difficulty with a "dry" system in that when flow conditions are changed, particulate material which is lightly adhering to a trapping surface is subjected to a different set of flow-induced forces, and may become dislodged.

Runs 5, 6, 8, and 9 are similar and characteristic of 2-scfm operation in that the time to develop the 20 in. of water across the system was 2 to 3 hours, and the gas leaving the trap had 250 to 500 ppm sodium. Table 2 shows that more sodium was found in the filter parts in Run 5 than in Runs 6, 8, or 9, and this is consistent with the higher impurity analysis found in Run 5.

In terms of the trap's effectiveness in removing sodium vapor, fog, and aerosol, one can compare the impurity content of the gas leaving the saturator (entering the trap) with that of the gas leaving the trap. Table 1 shows the analyses at the saturator outlet to be 780 to 1400 ppm, 830 to 1400 ppm, 700 to 1100 ppm, and 1500 to 2000 ppm. The reason for showing two figures is that an operational difficulty developed in the sampling station at the top of the saturator. This sample was a "grab" sample in that an evacuated valved bulb was attached to the sampling valve, and the sample taken by opening the valve on the bulb, and then the sampling valve. The sample was removed after closing both valves. The first (lower) quoted analysis value is that corresponding to the sodium taken into the bulb. The second value includes the sodium which collected in the tube section between the two valves. The operating difficulty that was uncovered was that the sampling valve developed a small leak sometime during the test series. The consequence of this is that some gas and sodium would leak into the tube section between the valves before the formal sampling occurred. Because of this, the lower value quoted is considered the better of the two. In every case, that value is greater than the value corresponding to complete saturation with sodium vapor at 800° F.

TABLE 2

SODIUM MASS BALANCES ON FILTERS FOR PACKED BED VAPOR TRAP

Test Number	Date	Vapor Trap Temperature (°F)		Weight of Sodium on Filter* (gm)	Weight of Sodium on Filter Can (gm)	Weight of Sodium in Plug at Filter Inlet (gm)	Total Weight of Sodium Found After Test (gm)	Sodium Content of Argon Exiting Trap (wppm)	Calculated Sodium Transport During Test (gm)	Gas Flow (scfm)
		Upper 1/3 of Packing	Lower 1/3 of Packing							
2	2/19/71	180	260	1.0*	0.6	0.04	1.6	~1650	13.4	5 [†]
3	2/19/71	210 to 225	280	2.2*	1.3	1.2	4.7	~1650	5.0	5 [†]
4	2/23/71	170	160	0.0	0.0	Not Analyzed	-	~500	0.3	2 [†]
5	2/23/71	160 to 170	150 to 160	4.0*	1.9	Not Analyzed	>5.9	~500	8.9	2 [†]
6	2/25/71	180 to 195	245 to 270	2.2*	1.5	0.7	4.4	~245	4.1	2 [†]
7	2/25/71	180	260	0.06	0.2	1.6	1.9	~245	0.9	2 [†]
8	3/1/71	230 to 240	315 to 360	1.3*	2.0	0.0	3.3	~270	3.3	2 [†]
9	3/1/71	230 to 250	370	0.4	1.3	2.5	4.2	~270	3.7	2 [†]
10 [§]	3/3/71 to 3/5/71	145 to 250	150 to 305	0.11	0.01	0.0	0.12	-	0.12	15 ^{**}
11 ^{††}	3/8/71 to 3/9/71	110 to 270	130 to 305	0.25	0.01	0.0	0.26	-	0.31	15 ^{§§}

*Filter plugged.

†Saturated with sodium at 800°F.

§Cycles for intermittent operations - number/minutes. 6/4, 2/10, 2/7, 4/17.

**Saturated with sodium at 490°F.

††Cycles for intermittent operations - number/minutes. 3/35, 1/17.

§§Saturated with sodium at 520°F.

By comparing the impurity levels entering and leaving the trap, then, one can infer that this unit under the 2-scfm operating condition removes from 1/2 to 4/5 of the sodium impurity from the argon stream, but the packed bed vapor trap still allows a nominal 250 ppm sodium in its effluent stream. This amount of sodium will plug about 1.5 ft² of 5-micron, stainless-steel filter frit per hour. The filter size necessary to collect this amount of sodium over a 3-month period is nominally 3000 ft². Therefore, the packed bed vapor trap is considered too ineffective for continuous service at either 2 or 5 scfm on an argon stream saturated with sodium at 800°F.

Runs 10 and 11 were made at 15 scfm intermittent flow with a nominal 500°F saturator temperature. Table 2 shows the flow cycle patterns used, and indicates that the filters collected nominally as much sodium as was carried into the trap, assuming the argon gas leaving the saturator to be saturated with sodium vapor (no fog or aerosol). Based upon the sodium loading factor at plugging as determined in the 2 and the 5-scfm tests, the filters were considered 10% (at 0.11 gm sodium) and 20% (at 0.25 gm sodium) plugged at the conclusion of these tests.

By linear extrapolation, plugging of the 4 ft² filter would have occurred in about 10 to 12 hours. Although this time may be acceptable for FFTF system requirements, the packed bed vapor trap is only operating as a gas temperature reducer under these conditions. Therefore, concepts other than the packed bed are recommended for sodium removal of intermittent high flowrate and low temperature sodium-saturated argon.

The multiple baffle trap was installed in Test Rig No. 2. After insulation, instrumentation, and pre-operational tests, the sodium was loaded into the system on March 17, 1971, and testing activities commenced. There are no data to report for this reporting period.

B. FREEZE VENT

The freeze vent device was fabricated, delivered, and installed in its test rig. The final tests of the instrumentation are being carried out in preparation for the initiation of the test program.

During a technical project review, the means for measuring the height of the sodium plug was chosen to be a PVT measurement. This technique will utilize a commercially available pressure transducer in conjunction with known gas volumes to determine the sodium plug height. The instrumentation and the test setup have been completed and are now being calibrated.

C. FILTER

The only requirements relating to filters are the preparation of standards and ordering data. During this report period, a first draft of a standard was generated and is undergoing final internal review.

D. STANDARDS AND ORDERING DATA

1. Vapor Trap

A draft standard was forwarded to AEC, LMEC, and HEDL for review on February 15, 1971. A formal review meeting was held at AI on March 15, 1971 from which a second draft was to result. The preparation of the second draft is now underway. The ordering data package is being assembled.

2. Freeze Vent

A draft standard for the freeze vent was prepared and issued by LMEC for review. This standard has been reviewed by AEC, AI, ANL, HEDL, and LMEC. It is acceptable for FFTF needs and it will be unnecessary for this project to expend further effort here. The ordering data package is being prepared.

IV. IMPACT ON LMFBR PROGRAM

The data obtained on the packed bed vapor trap indicate that it does not meet the FFTF needs. Testing of the multiple baffle vapor trap and of the controlled temperature profile vapor trap must proceed as quickly as possible. If the presently-quoted FFTF needs for cover gas recirculation cannot be met by either of these two traps, it will be necessary to either review and modify the flowrates, or search out an alternate vapor trap system having adequate capacity.

V. NEXT REPORT PERIOD ACTIVITIES

- 1) The multiple baffle vapor trap will be tested.
- 2) The controlled temperature profile vapor trap will be installed and testing will commence.
- 3) The freeze vent tests will commence.
- 4) Draft standards for the vapor trap, the freeze vent, and the filter will be issued.
- 5) Drafts of appropriate ordering data will be issued.

Program: Sodium Technology

AEC Task: 1, B. Special Compatibility (Sodium Frost)

Project Manager: G. W. Meyers

Reporting Period: January - March 1971

General Order: 06507

Subaccount: 39810

AEC Category: 04-01-61-03.1

Principal Investigators: L. G. Kellogg, T. T. Shimazaki

I. PROJECT OBJECTIVES

The objectives of this work are:

- 1) Develop an analytical model of sodium-oxide deposition on surfaces exposed to simulated FFTF reactor cover gas (argon) based on a typical LMFBR reactor operating cycle. This effort consists of the following parts:
 - a) Develop an analytical expression for the rate of formation and distribution of sodium oxide layers on a surface due to reaction of a sodium film with free oxygen in the cover gas.
 - b) Develop an analytical expression for the rate of removal of the sodium oxide deposit by refluxing sodium during reactor operation.
- 2) Verify the conclusions of the analytical model by experimental test.
- 3) Relate the verified model to design application of FFTF components susceptible to the sodium frost phenomenon, viz., vapor trap, rotating plug annuli, IVHM, and instrument tree.

II. MAJOR ACCOMPLISHMENTS DURING FISCAL YEAR 1971

An analytical model describing the oxidation rate of sodium exposed to inert gas containing low concentrations of oxygen and water vapor has been formulated during this report period. The model has yet to be experimentally verified. Investigation of various techniques for this has started. A conceptual design of the most promising apparatus has been completed and a test plan to support the experimental effort has been drafted.

Work was also initiated on the second phase of the analytical effort, namely, development of the model for the dissolution of sodium oxide by refluxing sodium which occurs during reactor operation.

III. PROGRESS DURING REPORT PERIOD

A description of the problem was formulated and the analytical effort initiated. The following discussion presents these data.

1. Description of the Problem

During reactor operation, sodium will condense on surfaces which are at a lower temperature than the dew point of the gas-sodium vapor mixture flowing past such surfaces. There will be very little oxygen contamination of the sodium condensing on these surfaces from the gas side, during reactor operation, inasmuch as any oxygen and/or water vapor that leaks into the cover gas will tend to combine with the abundant sodium vapor present, to form sodium oxide aerosol, rather than to diffuse to the sodium wetted surfaces. The sodium oxide aerosol, being generally too large to diffuse, is not readily transported to the surfaces. (A possible exception is upward facing surfaces on which the aerosol could settle by gravity.) Upon shutdown, a film of sodium is left on the surfaces on which sodium had been condensing. During the reduced temperature shutdown period, free oxygen and water vapor (from air in-leakage) in the cover gas diffuse to, and react with, the sodium (liquid or frozen) film on the surfaces to form a sodium oxide deposit. Upon resumption of reactor operation, refluxing sodium flows over that part of the sodium oxide deposit which is located in the temperature region higher than the freezing point of sodium and dissolves and removes at least a part of the sodium oxide deposit. Upon shutdown, a new layer of sodium film is left on such surfaces, and the cycle is repeated. Consequently, during each shutdown period a new layer of sodium oxide is formed. Eventually, such deposits on surfaces of mechanisms could build up to the extent that the mechanisms cannot function properly.

An approach to the solution of this problem is to design surfaces and annuli such that the amount of sodium "frost" formed in these areas during the lifetime of the plant would be insufficient to cause a problem. Hence, a proven analytical

model of sodium oxide deposition and dissolution is needed to permit determination of adequate design and/or required operating conditions (purge rate, shutdown temperature, etc.) for avoidance of the sodium frost problem.

2. Description of the Model

An analytical model for the oxidation rate of quiescent sodium exposed to an inert gas containing low concentrations of oxygen and water vapor is described as follows:

The system under consideration assumes a quiescent sodium surface exposed to flowing inert gas, e.g., argon, containing low concentrations of oxygen and water vapor. The ratio of the water vapor partial pressure to the oxygen partial pressure is assumed to be that typical for air, namely, of the order of 10^{-2} . The sodium temperature is assumed to be less than about 500°F, so that the sodium vapor pressure is small compared to the partial pressure of oxygen.

The reaction of sodium with oxygen is given by

The reaction of sodium with water vapor is either

or, if the concentration of water vapor is sufficiently low,⁽¹⁾

The latter reaction is expected to occur for the conditions assumed.

It has been observed that when the oxygen is sufficiently dry, the oxidation rate of sodium is very slow.⁽²⁻⁵⁾ For example, Longton,⁽²⁾ found no detectable reaction at temperatures up to 1020°F (his maximum test temperature) when the ratio of the partial pressure of H₂O to the partial pressure of O₂ is less than 2×10^{-6} . Longton further found that when the ratio of the partial pressures is in the range of 2.5×10^{-6} to 1.1×10^{-4} , no reaction occurs below a certain temperature, defined as the ignition temperature, but above this temperature, a vigorous combustion process develops; and, that when the ratio of the partial pressures is in the range of 1.4×10^{-4} to 2.5×10^{-2} , reaction occurs readily and smoothly at 220°F (his minimum test temperature).

On the basis of these results, it is hypothesized that in the absence of sufficient water vapor, the sodium oxide layer formed on the sodium surface is quite impervious to gases, but that when there is sufficient water vapor present, the sodium oxide layer is rendered porous by the hydrogen evolved as the oxide is formed. With a porous oxide layer, the oxygen, as well as the water vapor, can diffuse readily through the pores in the oxide. Inasmuch as it is assumed that the amount of water vapor present is about two orders of magnitude smaller than the amount of oxygen present, the amount of oxide formed by the sodium water vapor reaction is assumed to be negligible, compared to that formed by the sodium-oxygen reaction.

As a consequence of the reactions described by Equations 1 and 3, a layer of Na_2O tends to form and grow on the sodium surface. Once this layer is formed, the contact of the sodium with the oxygen and water vapor is assumed to be effected by the diffusion of oxygen and water vapor through the pores of the Na_2O layer as indicated in the sketch below. If the Na_2O is wetted by the sodium, the sodium surface could be within the Na_2O layer rather than at the lower side of the oxide layer as shown in the sketch. Simultaneously, some, or even all, of

the Na_2O being formed could be dissolving into the sodium. The conditions under which no Na_2O would be dissolving into the sodium include the following:

- 1) When the sodium is saturated with O_2
- 2) When the Na_2O layer is not in contact with, or not wetted by the sodium.

In view of the low concentrations of oxygen and water vapor, it is assumed that the heat of the reactions will have a negligible effect on the system temperature.

Based on the above assumptions, the following analyses describe the model for the case of contact between the sodium and oxide layer, but it assumes the oxide layer is not wetted. The attached Table 3 defines the characters used in the analytical expressions.

In this analysis, the contribution of the water vapor to the total amount of sodium oxide formed is neglected inasmuch as the oxide formed from the water vapor is a small fraction of the total oxide formed.

The rate of diffusion of oxygen from the gas stream to the gas oxide layer interface is, for small values of B,⁽⁶⁾

$$\frac{dW''_{O_2}}{d\theta} = g^*B \quad , \quad \dots (4)$$

where

$$B = \frac{m_{O_2,b} - m_{O_2,l}}{m_{O_2,l} - m_{O_2}^T} \quad \dots (5)$$

in which $m_{O_2}^T$ can be taken as equal to 1 since essentially only one substance is transferred.⁽⁶⁾ In the present case, $m_{O_2,l} \ll m_{O_2}^T = 1$, so the expression for B may be written

$$B = m_{O_2,b} - m_{O_2,l} \quad , \quad \dots (6)$$

but

$$m_{O_2} = \frac{\rho_{O_2}}{\rho_g} = \frac{P_{O_2}}{\rho_g R_{O_2} T} \quad . \quad \dots (7)$$

Substituting Equations 7 and 5 into Equation 4,

$$\frac{dW''_{O_2}}{d\theta} = \frac{g^* (P_{O_2,b} - P_{O_2,l})}{\rho_g R_{O_2} T} \quad . \quad \dots (8)$$

In the oxide layer, there is flow of hydrogen from the sodium-oxide layer interface. We assume that by virtue of the small amount of hydrogen that is generated that its velocity will be sufficiently low to have a negligible effect on the diffusion

TABLE 3
CHARACTERS USED IN THE ANALYTICAL EXPRESSIONS

b	= quantity defined by Equation 18
B	= mass transfer driving force, defined by Equation 5
c	= quantity defined by Equation 19
d _e	= equivalent diameter
D	= diffusion coefficient
D _{eff}	= effective diffusion coefficient in porous media
g*	= mass transfer conductance = $\lim_{B \rightarrow 0} \left(\frac{1}{B} \frac{dW''}{d\theta} \right)$
K	= equilibrium constant
l	= oxide layer thickness
m	= mass fraction
P	= pressure
q	= tortuosity factor
R	= gas constant
T	= absolute temperature
W''	= weight reacted per unit surface area
ε	= porosity
ρ	= density
θ	= time
Subscripts not defined elsewhere:	
b	= in bulk gas
g	= gas
H ₂	= hydrogen
l	= at gas-oxide layer interface
Na	= sodium
Na ₂ O	= sodium oxide
o	= at sodium surface
O ₂	= oxygen
T	= inside the neighboring phase, i.e., in the oxide layer

of oxygen through the oxide layer. Then, if the partial pressure of the oxygen is small compared to the total pressure, the rate of diffusion of oxygen through the oxide layer can be expressed as⁽⁷⁾

$$\frac{dW''_{O_2}}{d\theta} = \frac{D_{O_2-H_2,eff} (P_{O_2,l} - P_{O_2,o})}{\ell R_{O_2} T} \quad \dots (9)$$

in which, for normal diffusion through a porous media⁽⁸⁾

$$D_{O_2-H_2,eff} = \frac{\epsilon}{q} D_{O_2-H_2} \quad \dots (10)$$

According to Equation 1,

$$\frac{dW''_{Na}}{d\theta} = \frac{46}{16} \frac{dW''_{O_2}}{d\theta} \quad \dots (11)$$

We also have, by mass balance,

$$W''_{Na_2O} = \rho_{Na_2O} (1 - \epsilon) \ell \quad \dots (12)$$

But, from Equation 1,

$$W''_{Na_2O} = \frac{62}{46} W''_{Na} \quad \dots (13)$$

Combining Equations 12 and 13,

$$\ell = \frac{31 W''_{Na}}{23 \rho_{Na_2O} (1 - \epsilon)} \quad \dots (14)$$

If Equations 8, 9, 10, 11, and 14 are combined, we obtain

$$\frac{8}{23} \left[\frac{\rho_g}{g^*} + \frac{31 W''_{Na} q}{23 \rho_{Na_2O} (1 - \epsilon) \epsilon D_{O_2-H_2}} \right] \frac{dW''_{Na}}{d\theta} = \frac{P_{O_2,b} - P_{O_2,o}}{R_{O_2} T} \quad \dots (15)$$

Integrating Equation 15, we have

$$\frac{31 q (W''_{Na})^2}{46 \rho_{Na_2O} (1 - \epsilon) \epsilon D_{O_2-H_2}} + \frac{\rho_g W''_{Na}}{g^*} = \frac{23 (P_{O_2,b} - P_{O_2,o}) \theta}{8 R_{O_2} T} \quad \dots (16)$$

Figure 5. Oxidation Rate of Sodium Exposed to Streamline Flow of Argon Containing Oxygen and Water Vapor

from which the amount of sodium reacted per unit surface area is

$$W''_{\text{Na}} = \frac{-b + \sqrt{b^2 - 4c\theta}}{2}, \quad \dots (17)$$

where

$$b = \frac{46}{31} \left[\frac{\rho_{\text{Na}_2\text{O}} (1 - \epsilon) \epsilon D_{\text{O}_2 - \text{H}_2}}{q} \right] \frac{\rho_g}{g^*}; \quad \dots (18)$$

$$c = -\frac{(23)^2}{124} \left[\frac{\rho_{\text{Na}_2\text{O}} (1 - \epsilon) \epsilon D_{\text{O}_2 - \text{H}_2}}{q} \right] \frac{(P_{\text{O}_2,b} - P_{\text{O}_2,o})}{R_{\text{O}_2} T}. \quad \dots (19)$$

The oxidation rate is obtained by differentiating Equation 17.

$$\frac{dW''_{\text{Na}}}{d\theta} = \frac{-c}{\sqrt{b^2 - 4c\theta}}. \quad \dots (20)$$

To solve Equation 17, $P_{\text{O}_2,o}$, the partial pressure of oxygen at the sodium surface must be known, unless it is small relative to $P_{\text{O}_2,b}$, the partial pressure of oxygen in the cover gas. Inasmuch as the magnitude of the equilibrium constant for the reaction given by Equation 1 is large, it appears reasonable to assume that $P_{\text{O}_2,o}$ will be small relative to $P_{\text{O}_2,b}$, i.e., the oxidation rate is diffusion rate limited. The validity of this assumption decreases as the magnitude of $P_{\text{O}_2,b}$ decreases, i.e., as $P_{\text{O}_2,b}$ becomes smaller, the predicted oxidation rate will tend to be increasingly greater than the true oxidation rate.

Figure 5 shows a plot of Equation 17 for the following conditions:

- 1) Gas is argon containing oxygen and some water vapor.
- 2) Gas is in streamline flow between parallel surfaces covered with sodium.
- 3) Pressure is 1 atm.

The abscissa is the product of the concentration of O_2 in argon and the exposure time.

It is seen that for a fixed oxygen concentration, the oxidation is initially linear with time (slope = 1). However, as time increases, oxidation becomes

proportional to the square root of time (slope = 0.5). The reason for this is that initially the oxide layer formed on the sodium surface is so thin that it offers negligible resistance. With time, however, it becomes the dominant resistance. Inasmuch as the thickness of the oxide layer, and therefore its resistance, increases with time, the oxidation rate now follows the parabolic law. The curves shown in this figure are based on the following estimated properties of the oxide layer:

Porosity = 0.8

Tortuosity factor* = 4.0

If the tortuosity factor is taken to be 2 instead of 4, the curves in Figure 5 in the region where they have a slope of 0.5 would be raised by a factor of $\sqrt{2}$.

IV. IMPACT ON LMFBR PROGRAMS

These studies relate directly to design of LMFBR components which are exposed to sodium vapor environments. Typically these include rotating plug annuli, shield plug annuli, and other penetrations such as IVHM and instrument trees. In addition, floor valves, vapor traps, and CLEM need this design support. Verification of the models is needed to supply design information on these critical components.

V. NEXT REPORT PERIOD ACTIVITIES

The experimental apparatus to verify the sodium oxide deposition model will be designed and fabricated.

Work will continue on the analytical model that described the removal of sodium oxide by refluxing of sodium. A preliminary report that describes both the deposition model and the removal model should be available for issue at the end of the next reporting period.

*The square of the ratio of effective path length through the oxide layer to the thickness of the layer.

REFERENCES

1. C. C. Addison and J. A. Manning, "The Reactor of Water Vapor With Liquid Sodium, Sodium Peroxide, Sodium Monoxide, and Sodium Hydride; Vapor Pressure in the Sodium Hydroxide-Water System," Chem. Soc. (December 1964)
2. P. B. Longton, "Alkali Metal-Gas Reactions, Part IX: The influence of Moisture on the Reaction of Sodium With Oxygen," IGR-TN/C-535 (April 1957)
3. J. V. Cathcart, L. L. Hall, and G. P. Smith, "The Oxidation Characteristics of the Alkali Metals - I," Acta Metallurgica, Vol 5 (May 1957)
4. W. Holt and W. E. Sims, J. Chem. Soc., Vol 65, p 432 (1894)
5. J. W. Moyer, Phys. Rev. 83, p 877 (1951)
6. W. M. Kays, Convective Heat and Mass Transfer, McGraw-Hill, 1966
7. E. R. G. Eckert and R. M. Drake, Jr., Heat and Mass Transfer, McGraw-Hill, 1959
8. R. B. Evans, III and G. M. Watson, "Gaseous Diffusion in Porous Media at Uniform Pressure," J. Chem. Physics, Vol 35, No. 6 (December 1961)

Program: Sodium Technology		
AEC Task: 1, C. Coolant Related Mechanical Properties		
Project Manager: G. W. Meyers		
Reporting Period: January-March 1971		
General Order: 06507	Subaccount: 39130	AEC Category:

Principal Investigators: D. F. Atkins and J. H. Shively

I. OBJECTIVES OF SUBTASK

The objectives of this work are:

- 1) Determine the effects of mass transport on the mechanical behavior of cladding and structural alloys under LMFBR system conditions.
- 2) Study the influence of interstitial compositional changes (initially carbon) on the engineering design properties of structural alloys to be used in high temperature sodium service.
- 3) Determine the individual and combined effects of environment, strain rate, and stress mode on the creep and stress-rupture behavior of Types 304 and 316 stainless steel for LMFBR cladding and structural applications.

II. MAJOR ACCOMPLISHMENTS DURING FY 1971

Studies of the influence of heat to heat effects on the biaxial stress rupture properties of 316 stainless steel were concluded. Three heats of tubing were tested in static sodium in both the cold-worked and annealed conditions. As discussed later in this report, the results were used as base-line comparison data for similar tests in flowing sodium.

The flowing sodium tests were conducted in the second ΔT leg experiment in the 2-in. loop. The experiment consisted of: a heat-to-heat study on the effects of flowing sodium on creep behavior of Type 316 and 304 stainless steels, and a repeat of stress-rupture of cold-worked Type 316 stainless steel but without wire wrap.

A series of cold-worked Type 316 stainless-steel specimens were thermally aged for 2000 hours in 1000 and 1200°F sodium. The specimens were then removed from the sodium, cleaned, and stored. Several cleaning and storage techniques were employed and subsequent biaxial stress rupture tests were used to evaluate the effects of these treatments on the mechanical performance of the thin wall tubing.

A carburized case was placed on cold-worked Type 316 stainless-steel tubing and the tensile, stress rupture, and fatigue properties of these specimens were evaluated. The carbon case was applied using rotating sodium retorts and methane gas on the carbon source.

Specimens of bulk-carburized annealed Type 304 stainless steel were prepared for mechanical testing. The specimens were exposed for 3000 hours in an agitated sodium retort. The carbon source was 2-1/4 Cr - 1 Mo steel.

III. PROGRESS DURING REPORT PERIOD

A. STATIC SODIUM TESTS

Long-term biaxial stress-rupture tests were continued in multiple specimen static sodium retorts. Thin-wall tubing of both Type 304 and Type 316 stainless steel (0.275 in. ID by 0.010 in. wall) are internally pressurized to produce a 2:1 biaxial stress. The status of the retorts is given in Table 4.

One of these long-term tests (Retort No. 17) containing twelve specimens of annealed Type 304 stainless-steel tubing was completed in 1200°F sodium. The stress levels imposed on the tubular specimens produced ruptures over the range of 3000 to 25,000 hours. The stress rupture data for this retort are listed in Table 5. The rupture strengths are plotted in Figure 6, together with data obtained on the same heat from a previous retort test. It is observed that there is a slope change in the stress rupture curve occurring in the vicinity of 3000 hours. A similar change in slope, though more subtle, was reported⁽¹⁾ on the same material at 900 and 1000°F. At these lower temperatures, the break in the curves did not appear until about 9000 hours. It is postulated that this long-term strength loss is due to structural changes associated with carbide and sigma formation. Diametral strain measurements, calculated from profilometer readings, show that the annealed Type 304 stainless-steel tubing exhibited over 3.5% rupture strain after 25,000 hours in 1200°F sodium (Table 5).

TABLE 4
BIAXIAL STRESS-RUPTURE TESTS - 12 SPECIMENS PER RETORT

Retort Number	Test Temperature (°F)	Alloy	Cladding Condition*	Environment	Life Span (hr)	Status		Remarks	Date Start/Completed
						Test	Examination		
17	1200	304 SS	Ann	Na	5000 to 10,000	Completed	-	Extension of Data	2-22-68/12-21-70
22	1000	304 SS	Ann	Na	5000 to 10,000	Completed	-	Extension of Data	2-29-68/7-23-70
25	900	304 SS	Ann	Na	1000 to 10,000	Completed	-	Extension of Data	10-8-68/8-10-70
26	900	304 SS	AR	Na	1000 to 10,000	Completed	-	Extension of Data	3-27-69/8-21-70
110	1000	316 SS	AR	Na	1000 to 10,000	3/4 Complete	-	Extension of Data	4-23-68
113	900	316 SS	AR	Na	100 to 10,000	In Progress	-	Extension of Data	8-16-68
115	1000	316 SS	AR	He	100 to 5000	Completed	-	Effect of Sodium	10-18-68/11-9-70
116	1000	316 SS	AR + Aged	Na	100 to 5000	Completed	-	Effect of Thermal Aging	11-5-68/7-31-70
120	900	316 SS	Ann	Na	1000 to 10,000	3/4 Complete	-	Extension of Data	12-20-68
126A	1200	316 SS	AR	Na	1000	Completed	-	Cleaning Study	8-20-70/10-8-70
127A	1000	316 SS	AR	Na	2000	Completed	-	Cleaning Study	10-22-70/3-5-71
130	1200	316 SS	AR	Na	200 to 3000	Completed	-	Lot to Lot Study	4-27-70/8-31-70
133	1200	316 SS	Ann	Na	200 to 2000	Completed	-	Heat 03574	9-15-70/10-27-70
134	1200	316 SS	Ann	Na	200 to 2000	Completed	-	Heat 20303	9-17-70/12-14-70

*AR = As-received tubing containing 10 to 15% cold work
Ann = Annealed tubing

TABLE 5
BIAXIAL STRESS-RUPTURE DATA ON ANNEALED TYPE 304 STAINLESS
STEEL - HEAT 20013, 1200°F SODIUM, RETORT 17

Specimen Number	Hoop Stress (psi)	Rupture Time (hr)	Diametral Strain (%)	Average Strain Rate (%/hr)
A4-1	13,000	24,752	3.70	1.49×10^{-4}
A4-2	13,000	21,608	3.30	1.53×10^{-4}
A4-3	13,000	21,896	3.53	1.61×10^{-4}
A4-4	15,000	16,449	5.55	3.37×10^{-4}
A4-5	15,000	15,432	5.12	3.32×10^{-4}
A4-6	15,000	14,296	4.27	2.98×10^{-4}
A4-7	17,000	9,728	5.28	5.43×10^{-4}
A4-8	17,000	11,460	7.98	6.96×10^{-4}
A4-9	17,000	9,768	6.89	7.05×10^{-4}
A4-10	22,000	3,106	7.90	2.54×10^{-3}
A4-11	22,000	2,234	4.17	1.87×10^{-3}
A4-12	22,000	2,984	7.37	2.47×10^{-3}

Figure 6. Biaxial Stress-Rupture Strength of Annealed Type 304 Stainless-Steel Tubing in 1200°F Sodium

In another long-term stress rupture test, a cold-worked (10 to 15%) Type 316 stainless-steel specimen failed under 60,000-psi hoop stress after 22,546 hours in 900°F sodium. The extremely long rupture life under such a high stress emphasizes the high quality of the thin wall (0.010 in.) tubing and the high creep strength benefits of cold work in this temperature regime.

The 12 annealed Type 316 stainless-steel specimens of Heat 20303 were profilometered after biaxial stress-rupture testing to determine the biaxial rupture strains. The test conditions and results on each specimen are listed in Table 6. Three of the specimens were used as biaxial creep specimens under 21,257-psi stress for 200, 500, and 1000 hours. The creep results were compared directly with the flowing sodium data of ΔT Test No. 2. It was found that the static sodium vs flowing sodium environments had no effect on the creep strain of the material over the 1000-hour test time at 1200°F.

TABLE 6
BIAXIAL STRESS-RUPTURE DATA ON ANNEALED TYPE 316
STAINLESS STEEL - HEAT 20303, 1200°F SODIUM,
RETORT 134

Specimen Number	Hoop Stress (psi)	Rupture Time (hr)	Diametral Strain (%)	Average Strain Rate (%/hr)
AT6-1	28,000	333	7.21	2.16×10^{-2}
AT6-2	28,000	362	8.04	2.22×10^{-2}
AT6-3	28,000	321	7.47	2.33×10^{-2}
AT6-4	26,000	801	5.87	7.33×10^{-3}
AT6-5	26,000	825	5.97	7.24×10^{-3}
AT6-6	26,000	959	6.74	7.03×10^{-3}
AT6-7	24,000 to 25,000*	1859	6.71	3.61×10^{-3}
AT6-8	24,000	No Rupture	4.61	2.37×10^{-3}
AT6-9	24,000	2074	6.97	3.36×10^{-3}
AT6-10	21,257	200-hr creep	1.37	-
AT6-11	21,257	500-hr creep	1.57	-
AT6-12	21,257	1000-hr creep	1.83	-

*Stress increased to 25,000 psi after 1458 hours.

Further studies were performed on the effect of sodium cleaning and handling on the stress rupture behavior of cold worked (10 to 15%) Type 316 stainless steel. Twelve specimens which were exposed to 1000°F sodium for 2000 hours were subjected to various treatments as described in a previous report.⁽¹⁾ All 12 specimens were stressed to 46,000 psi in 1000°F sodium. The rupture times, given in Table 7, show considerable scatter. Based on previous tests without cleaning treatment, it seems that the scatter is related to the cleaning and storage treatments. However, there is no consistent pattern to relate with the various treatments imposed on the specimens. A similar series of specimens exposed to 1200°F sodium did not exhibit this scatter in stress-rupture life. Perhaps when the current specimens are removed from the test retort, examination and strain measurements will yield further insight into the causes for the high scatter in data.

TABLE 7
BIAXIAL STRESS-RUPTURE TESTS ON COLD-WORKED TYPE 316
STAINLESS-STEEL TUBING IN 1000°F SODIUM UNDER
46,000-psi HOOP STRESS
(Specimens Pre-Exposed 2000 Hours in 1000°F Sodium)

Specimen Number	Pre-Stress-Rupture Test Treatment				Rupture Life (hr)
	Sodium Solvent	Handling	Storage	Stress (psi)	
6-165	Butyl Alcohol	Gloves	Air	16,000	2795
6-166	Butyl Alcohol	Gloves	Air	16,000	817
6-167	Butyl Alcohol	Bare Hands	Air	16,000	3202
6-168	Butyl Alcohol	Bare Hands	Air	16,000	2360
6-169	Butyl Alcohol	Gloves	Air	0	275
6-170	Butyl Alcohol	Gloves	Air	0	1994
6-171	Butyl Alcohol	Bare Hands	Air	0	1896
6-172	Butyl Alcohol	Bare Hands	Air	0	2453
6-173	Butyl Alcohol	Gloves	Dry N ₂	0	1281*
6-174	Butyl Alcohol	Gloves	Dry N ₂	0	151*
6-175	Dowanol EB	Gloves	Air	0	2604
6-176	Dowanol EB	Gloves	Air	0	1151

*Specimen contained a very slight dent incurred during handling. Based on experience, it was felt that the dent should not influence the results. Specimens have not been examined after test to determine cause of failure.

Unetched 9515-1 250X
(a) Unidentified Phase (arrows)

Nital Etch 9515-1 250X
(b)

Figure 7. Longitudinal Cross Section of As-Received
Low Carbon (0.011 wt%) 2-1/4 Cr - 1 Mo Tubing -
Tubing Contained ~45% Cold Work

B. INTERSTITIAL TRANSPORT

The bulk carburization retort, containing twelve annealed Type 304 stainless-steel specimens has completed the intended 3000-hour exposure. The specimens were exposed to 1100°F sodium with a carbon source of 2-1/4 Cr - 1 Mo steel. The retort was equipped with a pneumatically operated agitation device to homogenize the sodium. This device operated without problems for 27,000 cycles during the test.

Metallographic examination of the exposed Type 304 stainless-steel specimens indicated a uniform structure across the 0.010-in. wall with heavy carbides concentrated at the grain boundaries. Three specimens were under stress during the sodium exposure to determine whether there is an influence of stress on carburization. These specimens, together with an unstressed specimen, have been submitted for chemical analyses. Tensile and biaxial stress rupture tests are planned to evaluate the mechanical behavior of the carburized material.

A heat of low carbon (0.011 wt %) Croloy 2-1/4 Cr - 1 Mo tubing, melted by Bureau of Mines (Albany) and drawn into tubing by PNL, has been examined metallographically. In the as-polished condition, the tube wall was found to be sound and free of nonmetallic stringers and other structural defects. As shown in Figure 7a, the structure did contain some fine particles of a hard phase which stood out in relief. This phase was found mainly in the grain boundaries. At first, this phase was believed to be retained austenite, but the phase persisted after annealing and slow cooling. This phase is unidentified but nitrides or carbides are suspect. The etched structure of the as-received tubing is shown in Figure 7b. The elongated grains and flow lines are the result of about 45% cold work in the as-received tubing.

An annealing cycle of 1850°F for 10 min followed by a slow furnace cool was selected for this low carbon 2-1/4 Cr - 1 Mo material. Figure 8 shows that this treatment produced recrystallization and resulted in a somewhat smaller grain structure than in the starting material. It was concluded that this annealing treatment would be adequate to use on test specimens prior to mechanical test studies.

Nital Etch

9526-1

250X

Figure 8.. Longitudinal Cross Section of Annealed
Low Carbon (0.011 wt %) 2-1/4 Cr - 1 Mo Tubing
Annealed 1850° F, 10 Minutes, Slow Furnace Cool

C. POST-TEST EXAMINATION OF ΔT LEG TEST SPECIMENS

1. Tube Shrinkage

All tests in flowing sodium are completed using the ΔT leg on the 2-in. flowing sodium loop. Data from the second ΔT leg test continue to be evaluated. The results of length measurements on "piggy-backed" pins and long tubes are presented in Table 8.

The first ΔT leg experiment revealed an unexpected phenomenon which resulted in a slackening of wires around the pins.⁽²⁾ The most plausible explanation for the slackening of wires is that the tubes shrank during creep. This explanation requires that the material be anisotropic because, for the 2:1 stress state used in these tests, the tubes should not change length during plastic strain. Other reasons for slackening such a twisting of tubes, creep of wires, density changes of tubes, and yielding are possible. Unfortunately, no gage marks were placed on the tubes prior to testing. It was, therefore, difficult to prove the exact amount that the tubes actually shrank during testing. However, a gross comparison of the length of tested tubes to untested tubes showed that

TABLE 8
LENGTH CHANGES - ΔT TEST 2

Specimen Number	Pressure (psi)	Time at Pressure (hr)	Length Changes for Various Materials and Heats (mils)					Specimen Length (in.)	Full Pin ΔL (mils)
			CW316 65808	A316 20303	A316 03574	A316 65808	A304 20013		
30	1440	1525	-5	0	-5	-20	-10	4.1	-40
31	1440	1532	-5	+5	-5	-25	0	4.1	-40
32	1440	1433	0	0	-15	-15	-5	4.1	-30
33	1440	1001	-5	-5	-10	-15	0	4.1	-25
34	1440	600	-5	-5	0	-10	0	4.1	-20
36	1440	305	0	-5	0	-20	+10	4.1	-15
37	1440	114	+5	-5	-5	-5	0	4.1	-10
38	1540	114	0	-5	-5	0	-5	4.1	-15
39	1540	194	-5	-5	+5	-5	0	4.1	-10
45	1540	305	0	-5	0	-15	+5	4.1	-15
46	1540	500	0	0	-10	-5	-5	4.1	-20
47	1540	762	0	-5	-5	-10	0	4.1	-20
48	1540	1001	-5	+5	-10	-15	0	4.1	-25
49	1540	1200	0	0	-010	-15	0	4.1	-30
50	2117	2110	40					19.1 [†]	40
51	2117	2110	25					19.1 [†]	25
8	2117	1897	40					20.1 [†]	40
43	Ramp	2107	30	+5*	-5*	-5*	0*	4.1	35
44	Ramp	1250	15	Corrosion Rings				4.1	15

*Specimens were not pressurized

†Specimens were long tubes

all tested tubes had shrunk with the amount of shrinkage increasing with time under stress and the amount of diametral plastic strain.

The absence of gage marks in the first ΔT leg test left the results uncertain. To clarify the shrinkage question, axial gage marks were placed on the end caps and between the piggy-back specimens in the second ΔT leg test. In this way, the length of each biaxial creep specimen from three heats of annealed and one heat of cold-worked Type 316 stainless steel and one heat of annealed

Type 304 stainless steel could be measured. Long tubes had gage marks on each end and were from the same lot and heat as first ΔT leg specimens. These tests constitute a direct comparison to the first ΔT leg test and the observed wire slackening.

The results of the changes in length for the second ΔT leg experiment are shown in Table 5. The precision of the length changes is 5 mils. Most of the "piggy-backed" creep specimens from annealed Heat 65808 (Column 7) and the highly strained specimens of cold-worked Heat 65808 (Column 4) decreased in length significantly. Other heats or slightly strained specimens did not change length within experimental accuracy.

The long tubes (Specimens 50, 51, and 8) corroborated the supposition that the length changes during creep explained the wire slackening. Furthermore, the magnitude of the change agreed with those in the first test based on a comparison of tested and untested tubes. As seen in the previous ΔT test, the length decreased progressively with time under stress following a hypothetical creep curve. The amount of shrinkage increased with the creep strain.

From these results, it is concluded that the wire slackening observed in the first ΔT leg test can be completely explained by a tube shortening during creep. The other reasons suggested earlier may occur but are not necessary to explain the wire slackening. The shortening means that Heat 65808 is anisotropic either from cold work, grain orientation, or residual stress patterns. Since both cold-worked and annealed tubes from this heat exhibited shortening, some anisotropy is intrinsic to this heat. However, the degree of anisotropy is greater in the cold-worked steel than in the annealed steel.

Other conclusions were made on the basis of the tube length measurements. These are:

- 1) Small creep strains produce the same shrinkage in cold-worked steel as do large creep strains in annealed steel.
- 2) Two of the Type 316 stainless-steel heats did not exhibit anisotropy effects, perhaps as a result of less creep strain.

- 3) The annealed Type 304 stainless steel did show large creep strain but no evidence of shrinkage. Hence Type 304 stainless steel is apparently not anisotropic.

2. Bulk Carbon Measurements on ΔT Leg Cladding

Early bulk carbon measurements on specimens from the first ΔT -leg experiment indicated a large reduction in bulk carbon content from exposure to flowing sodium.⁽³⁾ In reviewing these early carbon data, it was suspected that a small analytical error could have led to a large error in the measured value of bulk carbon. As a result of the uncertainty additional measurements of bulk carbon were made on cladding which was exposed to flowing sodium, static sodium, and unexposed (controls).

The data were evaluated to determine if the losses in carbon were statistically significant. Histograms were made of the new carbon measurement data. These are presented in Figure 9. As can be seen, the distributions for the control and static sodium samples were almost identical. The mean of each distribution as well as the spread (S_x) are the same. The distribution for the flowing sodium data overlaps and is shifted to lower carbon levels relative to the other two distributions.

The student "t" ratio statistical test applied to the shift indicates that there is greater than 0.9975 confidence that the mean of the flowing sodium carbon data is different from the mean of the control carbon data or of the static sodium carbon data. This can be interpreted to signify that about 10% of the bulk carbon was removed during exposure of the steel to flowing sodium.

The 10% average decrease in carbon content is consistent with microstructural observations seen in an optical microscope previously reported.⁽⁴⁾ There was little evidence of massive sigma phase particles or enhanced recovery processes as observed in specimens exposed to zirconium-gettered sodium at higher temperatures.⁽⁵⁾

The mechanism of reduced rupture strain in 1200°F flowing sodium has not been clearly established. It is postulated that sigma particles too small to be seen optically or by x-ray diffraction are responsible for the effect. Also, the carbon loss is associated with grain boundary diffusion rather than bulk decarburization of the grains as seen in Zr-gettered tests. Hence the grain boundaries

4-14-71

6507-5137

Figure 9. Comparison of Bulk Carbon Measurements on Type 316 Stainless-Steel Controls and Static and Flowing Sodium Tests

would have less carbon relative to the grains. This should increase the tendency for sigma phase in the boundary and would be expected to lead to a reduction in the amount of tertiary creep.⁽²⁾ Additional work beyond the present scope of this program would be required to resolve the mechanism of the loss in rupture strain.

IV. IMPACT ON LMFBR PROGRAM

Tube shrinkage observed in the first and second ΔT leg experiments indicate that cold-worked Type 316 stainless steel can be mechanically anisotropic. The degree of anisotropy cannot be determined from this single stress-state

test but its existence is substantiated by the fact that failure correlates with the largest principal stress rather than an effective stress. The anisotropic effect on wire wrapped tubes was to cause the wires to slacken during thermal creep. This could only happen in an LMFBR fuel rod if steel swelling and irradiation creep were exactly balanced during burnup. Since both phenomena are sensitive to temperature, stress, and the degree of cold work, it is not likely that the anisotropic effect should be considered important. Components built of cold-worked Type 316 stainless steel which experience high enough temperature to creep but fluxes too low to cause swelling or irradiation creep may have to consider anisotropy in design evaluations.

The bulk carbon measurements from the cladding exposed in the ΔT leg indicate that amount of carbon loss was small relative to that observed at higher temperatures. While the time of the tests was short relative to the life of a fuel element, the results indicate that a 10% reduction in bulk carbon can reduce the rupture ductility. It is believed that most of the carbon was removed from grain boundaries causing them to be weakened. During third-stage creep, cracking was assisted by the presence of an additional amount of sigma phase and less carbide precipitation. If this mechanism is correct, additional enhancement of radiation embrittlement from helium at temperatures above or equal to 1200°F could be expected. Additional work will be required to define the mechanism of embrittlement from decarburization. For the present fuel rod, designers will have to include some effect on ductility or rupture life for decarburization in their analysis of fuel pin life expectancies.

A second implication of the carbon loss data is that the amount of carbon removed in equal times decreases rapidly with temperature. This means that carbon loss from cladding may be considered to be insignificant at lower temperatures and perhaps disappears below 1200°F. This significantly reduces the potential for carburizing long-term components in the LMFBR primary system from decarburized cladding. While additional work is needed to determine a temperature threshold for decarburization of cladding, it would appear that only cladding at 1200°F and higher will significantly lose carbon to the primary sodium.

Biaxial stress rupture testing in static sodium has yielded some of the first long-term information available on the performance of cold-worked austenitic stainless steel at FFTF operational temperatures. Tests extending beyond 20,000 hours have demonstrated the stability of the cold-worked materials at 900 and 1000°F.

V. NEXT REPORT PERIOD ACTIVITIES

1. Long-term biaxial stress-rupture testing will be continued.
2. Specimens from the bulk carburization retort will be analyzed for carbon content. Mechanical property tests on these specimens will be initiated.

REFERENCES

1. "Quarterly Technical Progress Report — Fuels, Materials and Coolant Chemistry Programs, October-December 1970," AI-AEC-12987
2. J. H. Shively, "Biaxial Stress-Rupture of Wire-Wrapped Cladding in 1200°F Sodium Under ΔT Conditions," Interim Report, AI-AEC-19244, April 15, 1970
3. "Quarterly Technical Progress Report — Fuels, Materials and Coolant Chemistry Programs, July-September 1970," AI-AEC-12980, p 6
4. "Annual Technical Progress Report — Fuels, Materials and Coolant Chemistry Program, GFY 1970," AI-AEC-12970, p 19
5. W. T. Lee, "Biaxial Stress-Rupture Properties of Austenitic Stainless Steels in Zr-Gettered Sodium," NAA-SR-12353, October 1, 1967

Program:	Radiation Effects		
AEC Task:	Task 2-A, Irradiation Damage in Cladding and Core Structural Material		
Project Manager:	G. W. Meyers		
Reporting Period:	January-March 1971		
General Order:	06506	Subaccount:	29621 and 29622
		AEC Category:	

I. PROJECT OBJECTIVES

The objectives of this task are: (1) study the process of void formation and helium embrittlement in fuel cladding and core structural alloys by means of accelerator irradiations and reactor irradiations; (2) determine the effects of fluence, temperature, helium concentration, and microstructure on void formation and helium embrittlement; and (3) perform preliminary evaluations of modified and new alloys developed by other laboratories.

II. MAJOR ACCOMPLISHMENTS DURING FISCAL YEAR 1971

Swelling as a function of damage for proton-irradiated Type 316 stainless steel (annealed) has been measured up to 50 displacements/atom with estimates of swelling for 100 displacements/atom. No limit on swelling with increasing damage has been observed. The irradiation caused a progressive transformation of austenite to ferrite with increasing damage.

Six capsules containing Type 316 stainless steel and a variety of other alloys were inserted into the EBR-II core in ORNL subassembly X100.

III. PROGRESS DURING REPORT PERIOD

A. VOID FORMATION IN TYPE 316 STAINLESS STEEL

The final value for the swelling of Sample 56B where the damage was 50 displacements/atom was determined to be 21%. Voids were present at a density of $6 \times 10^{15}/\text{cm}^3$ with an average size of 370 Å. A least-squares fit of a straight line to the swelling-damage data was made on a fully logarithmic plot as shown in Figure 10.

4-14-71

6507-5126

Figure 10. Swelling at 500°C as a Function of Damage
for Proton-Irradiated Type 316 Stainless
Steel Containing Helium

The equation for the straight line is:

$$\text{volume increase (\%)} = 0.17 N^{1.2}$$

where N is the damage in displacements per atom. The equation differs slightly from that reported previously which was not computed by the least-squares technique. The vertical bars in Figure 10 represent uncertainties in obtaining void size and number distributions as well as actual inhomogeneities in void distribution within an electron-microscope foil. The horizontal bars represent the variation in calculated number of displacements introduced by uncertainty in the depth from which an electron-microscope foil is extracted. This uncertainty is estimated to be $\pm 1000 \text{ \AA}$. An additional error in the swelling values arises from estimating the thickness of the electron-microscope foil. Equipment is being assembled to measure accurately foil thickness by stereoscopic techniques.

The density of voids as a function of displacement rate is given in Figure 11 for samples whose swelling data is shown in Figure 10. Void nucleation increases with the displacement rate but it is not affected by the total number of displacements.

Sample 59, which received a very high proton fluence of $1.3 \times 10^{20} \text{ p/cm}^2$ at 500°C , was examined in cross-section with the light microscope while still bonded to the copper block used during irradiation. The sample was quite distorted and there was some separation at the steel-copper interface as a result of the irradiation. Large increases in the thickness of the foil were obvious.

After removal from the copper block, the sample was found to be attracted to a magnet and x-ray diffraction showed 10% of the sample had transformed to ferrite. This value is an average over the whole 0.0005-in. thickness of the sample whereas the amount of transformation is probably greatest in the regions that experienced the most damage and could exceed 10% there.

Figures 12 and 13 show void formation in Sample 59 at two magnitudes where the damage is 100 displacements/atom. Voids larger than $1500 \text{ \AA}$ are present. The very large voids have resulted in much void overlap and impingement which produced larger irregularly shaped voids. It is not possible to obtain an accurate void count and present estimates place the swelling at greater than 30%. Electron diffraction also showed the presence of ferrite.

4-14-71

6507-5127

Figure 11. Void Density as a Function of
Displacement Rate for Proton-
Irradiated Type 316 Stainless
Steel Containing Helium

Figure 12 Transmission-Electron Micrograph Showing Voids in Sample 59
Where the Damage Was 100 Displacements/Atom

Figure 13. Micrograph of Sample Seen in Figure 12 at Higher Magnification

The existence of ferrite in Sample 59 prompted us to test with a magnet other samples previously irradiated at 500°C. A sample with 0.5 displacements/atom (maximum) was not attracted whereas those with 10 or more displacements/atom (maximum) were attracted, and the strength of attraction increased with damage.

Examination of Sample 38 with 5.8 appm helium that was proton irradiated at 600°C has begun. A preliminary estimate of the swelling where the damage was 18 displacements/atom is between 20 and 25%. The void density and average void size are about $2 \times 10^{15}/\text{cm}^3$ and 600 Å. At 500°C, the same damage produced only 6% swelling.

The appearance of the voids is shown in Figure 14 where much linking of them is evident. Ferrite was detected in the sample by electron diffraction and some is resolved in the figure as a distinct region growing from the grain boundary.

Two papers have been submitted for technical meetings as follows:

- 1) "Void Formation in Proton-Irradiated Type 316 Stainless Steel," by D. W. Keefer, A. G. Pard, and D. Kramer, "Conference on Radiation-Induced Voids in Metals," to be held in Albany, New York, in June 1971.
- 2) "A Comparison of Void Formation in Types 316 and 321 Stainless Steel by Proton Irradiation," by D. W. Keefer, A. G. Pard, C. G. Rhodes, and D. Kramer, American Nuclear Society Meeting, to be held in Boston, Massachusetts, in June 1971.

B. CREEP OF TYPE 316 STAINLESS STEEL AT 700°C

Interrupted creep tests are being continued. The results of recent tests as well as those from previous tests are presented in Table 9. Average values for the duration of the creep stages, the associated strain, and the secondary creep rate are given in Table 10. A plot of strain as a function of time for two samples, with and without helium, is given in Figure 15.

The major effects of helium are a reduction in rupture time and strain at rupture. Third stage creep is greatly diminished and the secondary creep rate shows a small increase. A significant portion of the measured strain is merely due to intergranular cracking.

Figure 14. Transmission-Electron Micrograph Showing Voids and Ferrite in Sample 38 Where the Damage Was 18 Displacements/Atom

TABLE 9
SUMMARY OF CREEP TESTS AT 700°C IN VACUUM
AT AN INITIAL STRESS OF 10 kg/mm²

Sample	Helium (appm)	Time (hr)	Creep Strain (%)				Secondary Strain Rate (10 ⁻⁴ /hr)
			Primary	Secondary	Tertiary	Total	
C-5	0	645	3.0	11	38	52	4.4
C-6	0	561	3.5	11	17	32	4.2
C-19	0	120(i) [†]	3.0	3.6	none	6.6	4.5
C-20	0	120(i)	3.5	3.3	none	6.8	4.9
C-21	0	190(i)	3.2	7.1	none	10.3	4.8
C-22	0	25(i)	2.0	none	none	2.0	none
C-23	0	303(i)	3.5	12	none	16	4.7
C-24	0	70(i)	-	-	none	4.2	-
19-8	30*	148	1.5	7.0	2.0	11	6.3
19-9	30	218	2	6.5	5.5	14	5.5
19-16	30	70(i)	-	-	-	5.0	-
19-17	30	70(i)	-	-	-	4.7	-
19-20	30	120(i)	1.0	6.4	none	7.4	5.8
19-21	30	120(i)	0.0	6.7	none	6.7	5.3
19-24	30	25(i)	0.9	0.8	none	1.7	5.6
19-25	30	190(i)	1.2	6.0	3.8	11	5.0

*All concentrations of helium are nominal.

†(i) Means creep test was interrupted at indicated time.

TABLE 10
AVERAGE VALUES OF CREEP DATA

Helium (appm)	Duration of Stages (hr)			Strain in Stages (%)			Secondary Creep Rate (10 ⁻⁴ /hr)
	1	2	3	1	2	3	
0	47	280	276	3.2	11	28	4.6
30	12	118	46	1.1	6.5	3.8	5.6

Figure 15. Strain as a Function of Time at 700°C for Type 316 Stainless Steel With and Without Helium

Samples with helium failed in an intergranular manner whereas those without failed transgranularly. The intergranular cracks begin as small voids on grain boundaries and these have been found after 25 hours, which is early in the second stage of creep. The sequence of Figures 16a, 16b, and 16c shows how the voids become more numerous and link to form a crack. Figures 16a and 16b are of samples interrupted in the second stage of creep, and Figure 16c shows a sample interrupted early in the third stage. Intergranular cracking proceeds very rapidly in this stage.

Transmission-electron microscopy of the helium-containing sample interrupted after 25 hours revealed helium bubbles on grain boundaries and within the grains. The dislocation density was low and no cells were observed. Cell formation was still absent after 120 hours; the beginning of cell formation was seen after 190 hours (11% strain). In samples without helium, cell formation began after 120 hours (7% strain); it appears that helium retards cell formation.

A paper was published titled, "The Effect of Helium on the Stress-Rupture Behavior of Type 316 Stainless Steel," by K. R. Garr, D. Kramer, and C. G. Rhodes, *Met. Trans.*, 2, 269 (1971).

C. STAINLESS STEELS FROM OTHER LABORATORIES

Tensile samples and foil of Type 316 stainless steel that we sent to BMI-Columbus for shock hardening have been returned to us. The tensile samples were deformed and cannot be used for testing. The foil has become rippled and is unfit for proton irradiation.

D. EBR-II IRRADIATIONS

The AI capsules were removed from subassemblies X034A and X035 and are ready to be sent back. A shipping container has been sent to ORNL for their return.

IV. IMPACT ON LMFBR PROGRAM

No limit has yet been reached for the amount of swelling that occurs in proton-irradiated Type 316 stainless steel (annealed) even at high amounts of damage. The greatest swelling that we have produced exceeds 30% on a volume

basis, far above any tolerable amount for a fuel cladding or other core component. Present results lead to the concern that swelling will continue with high exposures for reactor-irradiated stainless steel.

The unexpected transformation of austenite to ferrite due to proton irradiation may have important consequences for the behavior of a fuel clad, especially after high-neutron fluences. Although no examples of such a transformation have yet been reported in neutron-irradiated Type 316 stainless steel, routine attempts should be made to detect ferrite during post-irradiation examination.

V. NEXT REPORT PERIOD ACTIVITIES

1. The sixth proton irradiation and seventh helium injection will be performed.
2. A topical report on creep will be written.
3. Samples of annealed Type 316 stainless steel, proton irradiated at 600 and 400° C will be examined.
4. Creep testing at 700° C but at lower loads will continue.

4-14-71

(a) After 70 hou

(c) After 190 hours

6507-5134

Figure 16. Replica-Electron Micrographs of Type 316 Stainless Steel Interrupted During Creep at 700°C

Program: Fuel Cladding and Structural Materials		
AEC Task: 2-B, Integral (n, α) Cross Section Measurements		
Project Manager: G. W. Meyers		
Reporting Period: January-March 1971		
General Order: 06506	Subaccount: 29623	AEC Category: 04-40-02-01.1

Principal Investigator: H. Farrar IV

I. PROJECT OBJECTIVES

The objectives of this task are: (1) determine which elements in commonly used alloys are contributing to the high production of helium in fast neutron irradiations so that their use might be eliminated or minimized, (2) determine the spectrum integrated (n, α) cross sections of 50 elements in various fast reactor neutron spectra, (3) make estimates of the differential (n, α) cross sections of the same elements by correlating the integral cross sections in the different neutron energy spectra by using unfolding techniques, and (4) use this information to predict with some confidence what helium production might be expected from any present or new alloy contemplated for fast reactor use.

II. MAJOR ACCOMPLISHMENTS DURING FISCAL YEAR 1971

Advantage is being taken of the forthcoming second EBR-II dosimetry test to irradiate additional pure elements for (n, α) cross-section determinations. Capsules containing a total of over 1000 specimens of elements, compounds, and separated isotopes have been prepared for inclusion at eight different locations in the core and blanket regions. Each capsule also contains 9 metal wires and 43 alloys. New lots of most of the elements and compounds were obtained with the highest purities available. Additional capsules containing ^{10}B specimens sealed in vanadium were also prepared in conjunction with WADCO and ORNL to make sure the helium production rate of this isotope is determined with maximum absolute accuracy.

Approximately 150 specimens of several elements and compounds irradiated at 5 locations in EBR-II during Run 31F have been prepared for mass spectrometric helium analysis and 32 determinations have been made. Some

NaCl CRYSTALS

STAINLESS STEEL SPECIMENS

1 cm

Figure 17. Sample Identification Macrographs

preliminary experiments have been conducted to vaporize high-melting-point-temperature specimens using an available ruby laser. Evaluation on the best method to vaporize such specimens continued.

III. PROGRESS DURING REPORT PERIOD

The second EBR-II dosimetry test will give the high accuracy neutron spectral data so necessary for cross section determinations, providing an ideal opportunity to radiate a very wide range of specimens in several different neutron fluxes. A considerable amount of time and effort was therefore taken to prepare for this test.

Eight capsules containing pure elements, isotopes, compounds, and alloys have been shipped to WADCO for inclusion at selected locations in the core and blanket regions of EBR-II adjacent to flux-spectral dosimetry sets. The 8 locations were chosen from earlier results to give a maximum expected variation in neutron spectrum shape so that the integrated (n, α) cross sections can be correlated with spectral change to give differential (n, α) cross sections using unfolding techniques. Twenty-eight pure elements and 30 crystalline compounds were taken from supplies of high purity materials for inclusion in some or all of the capsules. In all, 50 elements are represented, many of these several times in the form of different compounds. Also included are the complement of highly enriched separated isotopes of nickel (5), copper (2), and boron (2), all of which have been converted from powder to metallic form under high vacuum at either ORNL or AI.

Each element and compound was either cut up or broken, and pieces weighing generally between 1 and 5 mg were selected and macrophotographed twice in groups of 20 as shown in Figure 17, for later identification. Several important materials were included more than once when separate heats were available. Each heat is expected to contain different trace impurities which could be useful if even these small amounts were to contribute significantly to the helium production. Also included were several 2-cm long Ti, Fe, Ni, Cu, and Mo high purity wires which will provide specimens whose helium content will give the flux gradient across each capsule.

TABLE 11
CONTENTS OF EIGHT CAPSULES FOR SECOND DOSIMETRY TEST

Element or Compound	Melting Point (° C)	Element or Compound	Melting Point (° C)	Element or Compound	Melting Point (° C)
LiF*	842	Cr	1930	Y	1490
Be	1278	CrP	>1930	SrF ₂	1450
B	2300	Mn	1220	Zr	1857
¹⁰ B	2300	MnF ₂ *	856	ZrC	3540
¹¹ B	2300	Fe	1535	Nb	2415
C	3500	Fe ₃ C	1837	Mo	2620
NaF	988	FeF ₂	>1000	Ru	2450
NaCl*	801	Co	1495	Pd	1549
Mg [†]	651	Ni	1455	Ag	961
MgF ₂	1266	⁵⁸ Ni	1455	CdS	1750
Al [†]	660	⁶⁰ Ni	1455	InP	1070
Al ₂ O ₃	2045	⁶¹ Ni	1455	SnTe*	780
Si	1410	⁶² Ni	1455	Sb [†]	631
SiC	2700	⁶⁴ Ni	1455	NdF	1410
KCl*	776	Cu	1083	Hf	2230
CaF ₂	1360	⁶³ Cu	1083	HfN	3305
Sc	1539	⁶⁵ Cu	1083	Ta	2996
Ti	1725	Cu ₂ S	1100	TaN	3360
TiC	3140	ZnO	1975	W	3410
TiN	2930	Ga ₂ P ₃	1455	Re	3167
TiP	>1725	GaAs	1238	Au	1063
V	1710	RbI [†]	642	PbS	1114
V ₂ O ₅ [†]	690				

*Element or compound not included in capsule K1

†Element or compound not included in capsules K1, K2, or K4.

Although the elements and compounds are not expected to react with each other, they were grouped nevertheless into similar types, e. g., high melting-point metals, low melting-point materials, fluoride and chloride compounds etc., and loaded into separate subcapsules. Table 11 lists the elements, isotopes, and compounds in each capsule. Nearly every material was placed in duplicate in each capsule and the most important elements were sometimes in triplicate. In the previous EBR-II dosimetry test (Run 31F), several of the lower melting-point elements and compounds melted in the Row 4 and 6 capsules, presumably from gamma heating. As a result, capsules K1, K2, and K4 do not contain all the lower melting-point materials but instead contain additional specimens of others.

Also included in each capsule is the stack of well-characterized alloys listed in Table 12. These include 13 heats of modified Type 316 stainless steel with minor alloying variations, 13 alloys of LMFBR interest, and 17 NBS standard reference materials. Each alloy was rolled to a 0.010-in. foil, punched-out, and identified by scratching its designated number on its face, as shown in Figure 17. These alloys not only will give useful helium generation rates in the eight EBR-II locations but also will give important data that must be reconciled with the helium production data obtained from the pure elements.

Loading over 1000 small specimens, 72 wires, and 350 alloy foils into eight capsules each with a volume of only 1.2 cm^3 was an intricate and time-consuming task. Each specimen was wrapped individually in gold foil and placed in the appropriate subcapsule in known order so that their exact spatial locations in the reactor will be known. All 56 subcapsules, and later the 8 loaded capsules were evacuated to 1×10^{-5} torr and baked at 500°C before being sealed by EB welding.

A knowledge of the helium production rate of ^{10}B in fast neutron spectra is sufficiently important that two additional experiments to measure this quantity have been undertaken in cooperation with WADCO and ORNL. Crystals of enriched ^{10}B have been sealed in very small vanadium capsules for irradiation in 3 separate EBR-II locations during the second dosimetry test, and 5 similar capsules are being prepared for inclusion in the Controls Materials Experiment. Later mass spectrometric analysis of the entire capsules and their contents will ensure that all the helium is measured. Identical sealed capsules without boron

TABLE 12
ALLOYS INCLUDED IN FRONT CAPSULES FOR SECOND DOSIMETRY TEST*

Alloy	Type	Alloy	Type	Alloy	Type
316	316 SS	S-1	316 modified	NBS 409B	Fe base
316 + Ti	316 SS	S-2	316 modified	NBS 461	Fe base
316 (FFTF heat)	316 SS	S-3	316 modified	NBS 462	Fe base
304	304 SS	S-5	316 modified	NBS 463	Fe base
12R72 HV	Stainless	S-6	316 modified	NBS 465	Fe base
19-9 DL	Fe base	S-9	316 modified	NBS 439	Fe base
18-8 + Ti	Stainless	S-12	316 modified	NBS 445	Stainless
321	Stainless	S-13	316 modified	NBS 1152	Stainless
405	Ferritic	S-14	316 modified	NBS 1154	Stainless
430	Ferritic	S-15	316 modified	NBS 1194	Stainless
IN-744X	Stainless	S-28	316 modified	NBS 1091	Stainless
IN-718	Ni base	S-29	316 modified	NBS 1092	Stainless
T-111	Ta base	S-45	316 modified	NBS C1102	Brass
NBS 442	Stainless	NBS 447	Stainless	NBS 1215	Zircaloy 2F

*All alloys with S- designation are Type 316 stainless steel with minor alloying variations, obtained from J. L. Straalsund and J. J. Holmes (WADCO). All NBS designations are National Bureau of Standards Standard Reference Materials (NBS Special Publication 260, July 1970 edition). Each alloy was included as a 0.01-in.-thick disc weighing approximately 8 mg.

are being used for blanks, and unsealed capsules containing ^{10}B are being included in the dosimetry test to measure the helium retained in the crystals themselves.

The next most important elements and compounds to be studied: B, Al_2O_3 , TiN, HfN, TaN, SiC, TiC, and ZrC all have melting points well above 2000°C and therefore require a higher temperature method of helium extraction. New methods are being tried and it is hoped that one can be devised that displays a 100% helium recovery which might then replace the existing system for all specimens. Other important elements and compounds with lower melting points, such as Be, V, Mn, Co, and MnF_2 have been prepared for analysis with the existing method of helium extraction.

The high sensitivity gas mass spectrometer spiking volumes were refilled with exactly known amounts of ^3He and ^4He . After this was completed the mass spectrometer calibration was verified by several independent methods using various combinations of spikes and standard samples.

A paper entitled "Determination of Nitrogen and Hydrogen at Parts per Million Levels in Milligram Steel Samples," was published in Analytical Chemistry 43, 439 (1971).

IV. IMPACT ON LMFBR PROGRAMS

The measurements of helium in Al, Si, Cr, Fe, Ni, and Type 304 stainless steel resulting from irradiation during Run 31F at five widely differing EBR-II locations have given rather precise values of the integrated (n, α) cross sections of these elements. Comparison with the steel results moreover, has shown that up to 70% of the helium generated in the stainless steel cannot be attributed to the major steel components, and must therefore have come from (n, α) reactions with trace constituents with evidence pointing to nitrogen, with its high (n, α) cross-section being the major source. Measurements in EBR-II structural components and sodium loop steels have shown, moreover, that nitrogen can become highly redistributed. The combination of these two phenomena points to the conclusion that some effort should now be directed to the study of nitrogen mobility and the importance of nitrogen as a producer of helium in fast neutron energy spectra. The effects of nitrogen could become even more important in future LMFBR's because these reactors will operate at higher temperatures than those in EBR-II so that any temperature-dependent phenomenon could well be enhanced.

V. NEXT REPORT PERIOD ACTIVITIES

1. Continue preliminary experiments to melt high melting-point materials under vacuum.
2. Modify the mass spectrometer rough vacuum system to provide improved between-sample evacuation.