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INVESTIGATIONS OF MATERIALS COMPATIBILITY
RELEVANT TO THE EBR-II SYSTEM

by

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EBR-II Project

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INVESTIGATIONS OF MATERIALS COMPATIBILITY RELEVANT TO THE EBR-II SYSTEM

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ABSTRACT

Components removed after years of service in the primary sodium tank of EBR-II showed little evidence of direct interaction with liquid sodium or sodium vapor. The only significant deterioration (of a labyrinth pump-shaft seal) was caused by abrasion of aluminum bronze by an adherent mixture of sodium and sodium oxide rotating with the shaft.

Components removed from the seal troughs of the rotating plugs showed no interaction between the bismuth-tin alloy and Types 405 and 304 stainless steel.

The cracking of a feedwater-heater relief valve was attributed to a combination of inadvertent sensitization of the Type 325 stainless steel during improper welding and oxygen contamination of the feedwater at that location.

Ex-reactor exposure of irradiated, deliberately defected mixed-oxide fuel elements to sodium at temperatures up to 1200°F for 87 days resulted in a maximum diameter increase of 10.3 mils at the defect. Other experiments indicated that no extensive contamination of EBR-II equipment would occur through inadvertent washing of a sodium-logged defected fuel element.

Ex-reactor exposure of irradiated boron carbide pellets to 1000°F sodium resulted in the penetration of the pellet by sodium and subsequent loss of material in washing. Unirradiated control pellets were not penetrated in the same exposures.

No adsorption-desorption effects were detected on the walls of a 100-ft Type 304 stainless steel sampling line for either oxygen or hydrogen impurities in sodium.

A series of experiments showed that pure sodium at 1200°F did not penetrate structurally sound Type 304 stainless steel.

Vacuum distillation and flowing water were effective in removing sodium from simulated deep crevices. Anhydrous liquid ammonia and moist argon were not.

I. INTRODUCTION

This report is the third in a yearly series^{1,2} devoted to investigations of components removed from service in the EBR-II complex and to ex-reactor experiments that pretest materials or techniques before they are used in the EBR-II system. Wide ranges of materials, circumstances, and evaluation techniques are involved. For this reason, each investigation is reported as a self-contained unit. General information concerning the configuration of the EBR-II plant, sodium chemistry, and sodium-removal techniques was presented in Ref. 1 and will not be repeated here.

Additional information concerning mechanical properties and compatibility of materials exposed in the blanket region of EBR-II is contained in a separate series of reports on the three materials-surveillance sub-assemblies examined to date.³⁻⁵

In several instances, ex-reactor investigations in cooperation with other staff members this past year have resulted in separate topical reports. In these instances, abbreviated summaries from the other reports are included here to indicate the scope of the activities.

II. DATA AND RESULTS

A. Examination of Reactor Components

Components removed from EBR-II for maintenance or replacement are examined as completely as possible consistent with reactor scheduling requirements. Residual radioactivity of the components examined during the past year is analyzed in a companion report.⁶ The examinations reported here relate to the physical changes in the component materials.

1. Evacuation Tube from the Intermediate Heat Exchanger (IHX)

In the original design of the IHX (see Fig. 1), a 1-in.-dia evacuation tube (since removed) entered the elbow of the secondary-sodium inlet pipe and extended downward about 21 ft to a terminal piece welded to the diffuser troughs at the bottom of the IHX. This tube provided a means for removing sodium from the secondary side of the IHX, if this should have become necessary. The tube was supported by a weldment at the top, where the tube penetrated the elbow; two support clips 6 and 19 ft, respectively, from the top (these held the tube against the pipe wall); and the lower terminal piece to which the tube was welded. The upper end of the tube extended a few inches out of the pipe elbow and had been capped and welded shut since the IHX was built.

Fig. 1. EBR-II Intermediate Heat Exchanger, Showing Location of Evacuation Tube

In November 1970, a rattling noise developed in the IHX. Investigation of this noise ultimately required draining of the secondary sodium system, pumping out of secondary sodium from the IHX through the evacuation tube, and cutting of an access port into the elbow of the secondary-sodium inlet pipe.⁷ Subsequent examination of the interior of this pipe showed that the upper support clip for the evacuation tube was loose and that the lower support clip was broken off. Although the tube was still supported by the upper clip and by the top and bottom welds, it had evidently begun to impact against the inner wall of the inlet pipe when the secondary-sodium flow exceeded some critical velocity. Following this assessment, the tube was permanently removed from the IHX. Portions of the tubing were returned to ANL-East for examination.

Markings, still visible after nearly eight years in sodium service, identified the tubing as SPEC-ASTM-A213 TMI HEAT W93899 1 OD x 0.065. This specification is for Type 304 stainless steel seamless tube made from an electric furnace melt. Secondary sodium at temperatures of 610-650°F had flowed past the outside of the tube while static sodium at the same temperature contacted the inside. The sections of tube received for examination were dark in color, but no obvious corrosion product was noted on the outside surface.

Fig. 2. Appearance of Dark Flakes from Inside of IHX Evacuation Tube. Mag. 85X.

that the material was amorphous. The flakes disappeared without leaving a residue when heated on white aluminum oxide.

Ultrasonic treatment in a degreasing solution of methanol-benzene released a small quantity of black flakes, as shown in Fig. 2, from the inside of the tube. These flakes were collected and examined. It cannot be determined whether a similar deposit was on the outside surface, because the tube, after sodium removal, had been wiped down with lintless cloths containing a mild cleaning agent. The flakes analyzed 51% carbon. A spectrographic survey showed no strong metallic lines; traces of uranium and thorium were the major metallic constituents. An x-ray diffraction analysis showed

A section of the tube was mounted in a lathe, and its outside surface was machined off in 0.002-in.-thick cuts. The turnings were collected and analyzed for carbon and nitrogen; Table I gives the results. The surface cut resulted in the occasional release of a fine, black powder into the air, similar in appearance to the sooty airborne particles from an improperly adjusted acetylene flame.

TABLE I. Chemical Analyses of Turnings
from IHX Evacuation Tube

Depth from Original OD, in.	Carbon, wt %	Nitrogen, wt %
0-0.002	0.148	0.034
0.002-0.004	0.039	0.036
0.004-0.006	0.029	0.035
0.006-0.008	0.028	0.034
0.008-0.010	0.028	0.034

Metallographic specimens of the tube wall showed a nonsensitized structure, as expected from the service temperature. The outside surface of the tube had a "case" of about 0.0004 in., as shown in Fig. 3, which polished differently from the rest of the tube. No such case was found on the inside surface. The chemical analyses (see Table I) strongly suggest that the "case" was caused by the higher carbon content near the surface. It seems unlikely that the carbon enrichment at the outside surface was caused by the presence of the carbonaceous flakes. The thickness of the case was over twice the maximum depth that the data of Agarwala *et al.*⁸ would predict for carbon diffusion at this temperature. Further, no case was discernible on the inside surface, even though the carbonaceous flakes were present there.

Fig. 3

Transverse Section of Outer Surface
of IHX Evacuation Tube. (Electro-
etched 15 sec in 5 wt % oxalic acid.)
Mag. 325X.

It is also unlikely that the source of the carbonaceous residue was carbon transported from the ferritic-alloy steam generator. Further, carbon deposited on the tube surface from the sodium would be expected to be 100% carbon, not about 50%. Thus, the tube probably acquired this case during fabrication heat treatment, when the temperature was much higher. Similar "cases" have been observed frequently on other as-received tubing. The carbonaceous residue may have resulted from the decomposition of a lubricant or preservative on the tube as installed.

The overall condition of the tube was excellent. No significant deterioration was observed.

2. Labyrinth Seal from Primary Pump No. 1

The EBR-II primary pumps are vertically mounted, single-stage, centrifugal-type mechanical pumps. They are driven by variable-speed, totally enclosed, gastight electric motors. Labyrinth-type shaft seals, as shown in Fig. 4, minimize the diffusion of sodium vapor into the motor enclosure. Capscrews hold the baffle section to the pump case and the shield section. When primary pump No. 1 was removed for maintenance during the winter shutdown of 1970-1971, the lower labyrinth seal and the capscrews were replaced. Specimens were returned to ANL-East for evaluation.

The lower labyrinth seal was fabricated from Ampco 18-13 aluminum bronze, which has a chemical composition of Cu-10.3 wt % Al-3.7 wt % Fe, with nickel (0.16 wt %) as the major impurity. It had an ID of approximately 9.75 in. The stationary horizontal rings of the labyrinth originally had projected approximately 1/8 in. from the body. All but three labyrinth rings had been eroded and abraded severely during about 7 yr of operation. The maximum change in the 9.5-in. OD of the stainless steel shaft was less than 0.005 in.

A portion of the inner face of the labyrinth, including a ring, was examined with a scanning electron microscope (SEM) equipped with the energy-dispersive X-ray analyzer attachment. A band less than 5 μ m thick at the bronze/sodium interface was depleted in aluminum, but the corrosion film on the surface of the bronze was enriched in aluminum, probably as aluminum oxide. Two types of second-phase particles were noted deeper in the metal. The first type, the larger of the two, was enriched in aluminum and, to a lesser extent, iron. The second, smaller, particles contained a small amount of chlorine. No way of estimating the total chlorine content of the labyrinth was available, but it undoubtedly was very low. Chlorine could be detected only in the tiny particles that could be analyzed individually by the electron beam.

Ampco 18-13 alloy has proved satisfactory¹ in sodium as bushing rings for control-rod subassemblies, so the loss of the labyrinth rings cannot be attributed to a dissolution problem. The presence of an abrasive mixture of sodium "frost," sodium oxide, and aluminum-bronze corrosion products adhering to the rotating shaft presumably wore the rings away.

3. Capscrews from Primary Pump No. 1

One capscrew from the upper and one from the lower flange of the baffle section (see Fig. 4) were examined to evaluate the extent of

Fig. 4. EBR-II Primary Pump, Showing Locations of Lower Labyrinth Bushing and Baffle Section. ANL Neg. No. 103-N5097 Rev. 1.

material/coolant interaction after exposure to liquid sodium or sodium vapor for nearly seven years. The capscrews (1-in. size) were forged from Type 316 stainless steel.

Transverse sections of the capscrew heads were polished and examined metallographically. No interaction zone or deposit was noted over most of the surface. However, the tops of the heads had areas of embedded oxide particles extending about 1 mil deep by 1-20 mils laterally,

Fig. 5. Embedded Particles in Capscrew Head Exposed to Sodium Vapor for Seven Years in Upper Baffle Flange of Primary Pump. Mag. 300X.

as shown in Fig. 5. These areas are not uncommon in the surfaces of objects formed by high-temperature forging. Some of the areas were porous, as indicated by the continued slow release of the polishing lubricant after initial cleanup of the surface. These porous areas were probably responsible for the retention of radioactive compounds by the lower capscrew, which had been immersed in the liquid primary sodium.⁶

The SEM was used as before to compare the composition of the surface with the bulk composition of the capscrews. In the capscrew exposed to liquid sodium at 700°F, only the spot examined closest to the edge (0.0004 in. from the edge) showed any significant compositional change. As compared with the bulk metal, this spot was richer in molybdenum and nickel and was depleted in chromium. The surface of the capscrew exposed to argon and sodium vapor at 700°F also was depleted in chromium, but to a lesser extent.

Finally, a pocket of mixed metal and oxide was examined with the electron beam and showed significant enrichment in chromium and depletion in iron as compared with the bulk metal.

It was concluded that the capscrews had reacted to a maximum depth of about 0.001 in. with the liquid primary sodium and with the sodium vapor in the gas phase. The actual interaction zone may have been less than this value if allowance is made for changes in surface composition the capscrew heads may have undergone during forging.

4. Heaters and Thermocouple from Fusible Seal

a. Heaters. Fuel handling in EBR-II is made possible by two rotatable plugs in the top of the primary tank. The gas seal on each of these plugs is maintained by immersing a stainless steel circular blade,

attached to the plug, in a trough of liquid bismuth-tin alloy that is attached to the primary tank. The heat required to keep the alloy liquid is supplied by tubular heaters inserted in holes drilled in the circular blade. The heater sheaths contact the alloy.

Three tubular heaters were examined for possible attack by the liquid alloy on their Type 405 stainless steel sheaths. Two of the heaters, No. 205 and 314, had failed in service owing to leakage of the alloy into their electrical connections. The third heater, No. 317, had obviously never been hot and was included to provide a standard wall thickness for comparison.

The heaters were sectioned at the midpoint with a water-cooled, abrasive-wheel cutoff machine. Pieces approximately 0.3 in. long were mounted for metallurgical examination. Figure 6 shows sections from heaters 314 and 317.

Fig. 6. Transverse Sections through Axial Centers of Heaters 314 and 317 from Seal Trough of EBR-II. Mag. 2.6X.

The granular ceramic between the Nichrome heater wire and the sheath had been discolored outwardly from the heater and made more friable by the temperature of operation. The nickel support wires and the solid ceramic heater mandrel were unaffected by the high temperature.

The relative thicknesses of the three sheaths were determined by measuring the polished sections. Surprisingly, the sheath of the unheated heater (No. 317) was about 0.001 in. thinner than those of the heated heaters (No. 205 and 314). The very slight difference in sheath thickness probably represents different manufacturing batches.

Figure 7 shows transverse section of the outer surface of heated heater No. 314 at higher magnification than in Fig. 6. An etchant was used to darken the adhering bismuth-tin alloy. The lack of attack on the Type 405 stainless steel sheath is evident.

Fig. 7. Interface between Sheath and Bismuth-Tin Alloy: Heater No. 314. Mag. 400X.

b. Thermocouple. Thermocouple No. 13, which had a 0.125-in.-OD sheath, was installed in the fusible seal of the small rotating plug late in 1969 and removed in December 1971. The bismuth-tin alloy wiped off, leaving the Type 304 stainless steel sheath apparently untouched. For further verification of the compatibility, longitudinal sections of the sheath were taken at the end (which had been in the alloy) and 12 in. from the end (not in contact with the alloy).

Figure 8 compares transverse sections of the sheath at the two sampling points. The thickness is the same for both, and the outer sheath

Fig. 8. Comparison of Transverse Sections of Thermocouple Sheath. Mag. 175X.

surface is smooth and unetched for both specimens. No evidence of bismuth-tin was developed in an etch that darkens the fusible alloy. Although the stainless steel contains many small inclusions, its corrosion resistance would not be impaired, because the inclusions apparently are not interconnected.

5. Feedwater-heater Relief Valve

Type 325 stainless steel relief valves manufactured by Crosby-Ashton are used on feedwater heaters No. 3 and 4 in the EBR-II steam plant. The original units were threaded into place, but the need for routine maintenance of the valves made it desirable that they be flanged. New valves were welded to carbon steel nipples and flanges by the manufacturer. The welding procedure used was not recommended for stainless steel. The valve and nipple were preheated to red heat, the joint was TIG-welded, and then the assembly was reheated to red heat.

The valve for heater No. 4 subsequently leaked in service through cracks in the threaded portion of the body. Ultrasonic examination of both valves showed cracks. Half the valve for heater No. 3 was returned to ANL-East for metallurgical examination. This valve had operated at about 475°F. Figure 9 shows a cross section of the valve at approximately actual size. Two areas of cracking were noted upon inspection, one in the threaded portion and the other in the tapered section, as shown in Figs. 10 and 11. The depth of the cracks in the threaded section may be judged from the composite of Fig. 12. The voids on the crack result from loss of encircled metal grains in polishing. Figure 13 shows the mouth of the crack

Fig. 9. Section through Relief Valve from Feedwater Heater No. 3. Mag. ~1X.

Fig. 10. Cracks Running at Right Angle to Threads of Relief Valve. Mag. ~3X.

Fig. 11. Cracks in Tapered Section of Relief Valve. Mag. $\sim 3X$.

Fig. 13. Mouth of Crack in Threaded Section of Relief Valve after Electroetching for 40 sec in 5 wt % Oxalic Acid. Mag. 175X.

Fig. 12. One Crack in Threaded Portion of Relief Valve (composite of two exposures). Mag. 50X.

after etching. The view shows that (1) the penetration is along grain boundaries, (2) adjacent grain boundaries are not attacked, and (3) the curvature of the grain boundaries at the surface is typical of surface-worked (in this case, by threading) metal. Microhardness indentations were smaller at the edge, confirming the presence of coldworking.

Examination of the cracks in the tapered section showed similar characteristics, including an increase in hardness adjacent to the surface. The cracks in this section were less than half as deep as those in the threaded section. Difficulty in sawing through the hardened surface of the tapered section had been reported.

Since Type 325 stainless steel, which contains 20% Ni, 8% Cr, and 0.4% C, is a relatively rare alloy, data on its response to heat treatment were not readily obtained. A portion of a nonwelded valve was obtained to determine whether the peculiar welding technique could cause carbide precipitation at the grain boundaries. A heat treatment of 40 min at 1200°F was arbitrarily chosen as representative of the maximum that the welded valve body might have undergone. Figure 14 shows the microstructure before and after the treatment: the etch times are the same as those for Fig. 13. Comparison of Figs. 13 and 14 shows that the grain boundaries are approximately as heavily populated with carbides in the cracked valve body as in the heat-treated specimen. Thus, the valve body had been sensitized by the welding procedure.

As Received

HT 40 min at 1200°F

Fig. 14. Effect of Heat Treatment on Microstructure of Type 325 Stainless Steel (both etched 40 sec in 5 wt % oxalic acid). Mag. 190X.

Information concerning the solution in contact with the valve was also sought, because the usual cases of stress-corrosion cracking involve specific cracking agents. The plant feedwater is carefully controlled and monitored. During operation of the steam generators, it typically contains a residual hydrazine content of about 10 ppb and a chloride content less than 0.1 ppm. Traces of recirculated corrosion products are also

present. (Note that the valves are on a "dead-leg," so the concentrations within the valve might be substantially different than those in the bulk feedwater.) The most likely contaminant was considered to be oxygen. This could result from air diffusing back through the valve seat during nonoperating periods or from the oxygen level frequently being much higher in the feedwater during startup than after operation has been stabilized. The lack of flow through the valve might allow the oxygenated water at startup to remain in contact with the valve body for extended periods of time.

No specific corrosion-cracking data were found in the literature for Type 325 stainless steel. However, both Type 304 stainless steel and Incoloy 800 have been observed⁹⁻¹¹ to crack intergranularly in the sensitized condition in pure water containing oxygen at a somewhat higher temperature (550°F). The compositions of these two alloys bracket that of Type 325 stainless steel. Further, the reported cracking nucleated in plastically deformed areas on the surface,¹¹ a feature that was also observed in the relief valve. Thus, it appears probable that the observed cracks were caused by a combination of stress, metal sensitization (improper welding), and locally high oxygen concentration in the feedwater.

B. Testing in Sodium in Support of EBR-II

In many cases, it is advantageous to investigate the effects of sodium exposures on materials to be used in the EBR-II. The results of these ex-reactor exposures permit a realistic evaluation of the risk, if any, involved to the reactor in a subsequent in-reactor experiment. Five such investigations have been completed during the past year.

1. Exposure of Irradiated Mixed-oxide Fuel

A breach of the cladding of experimental, helium-bonded, mixed-oxide fuel elements irradiated in EBR-II would expose the fuel to primary sodium at temperatures ranging from ~1200°F in the core to 700°F in the temporary storage baskets. No information on compatibility was available for the lower temperature, but limited data available for the higher temperature had suggested that the oxygen level in the sodium was important. Since EBR-II operates at a low oxygen level--0.4-1.8 ppm (as determined by mercury-amalgamation analysis)--a few experiments were performed to determine whether exposure of the fuel to sodium of low oxygen concentration would pose problems in reactor operation or interfere with the evaluation of experiments. The results of the initial exposures at 700°F were described previously;² those data have been incorporated into this report.

The experiments were carried out in the compact (2 x 2 x 0.8 ft) test loop shown schematically in Fig. 15. The loop was in an alpha-gamma

Fig. 15. Sodium Test Loop in Alpha-Gamma Cave

checked out initially outside the cave. Distillation analysis of the sodium for oxygen demonstrated that the oxygen concentration of the sodium could be predictably controlled by setting the temperature of the cold trap. For the tests of the fuel elements, the cold trap was operated at 237-248°F.

The oxygen concentration of the sodium was checked again, this time with the vanadium-wire equilibration technique, after the first series of experiments had been completed. Values of ~0.3 ppm oxygen were obtained; these were at the low end of the desired range.

The effects of the exposures were evaluated by determining changes in dimensions and weights, by visual observation, and by metallographic examination. Except when the presence of sodium was desired for subsequent tests, all sodium on the exterior of the specimens was removed by brushing with a brass-bristle brush. The cave atmosphere was dry nitrogen, so the exposed sodium remained bright for an appreciable time.

The characteristics of the specimens are shown in Table II. These specimens were selected from the limited variety available on the

TABLE II. Characteristics of Defected Samples from Helium-bonded Fuel Elements Used for Studying Effects of Exposure of UO_2 -20 wt % PuO_2 to Sodium

Element No.	Fabricator	Method of Fabrication	Burnup, at. %	Initial O/M Ratio	% TD		Type of SS Cladding and (thickness, in.)	Defect Dimensions, in. ^a	
					Pellet	Smear		Length at Surface	Depth into Fuel
007	ANL	Coprecipitation	5.8	1.98	79.4	76.5	304 (0.020)	0.80	0.020
C15 (top)	NUMEC	Mech. Mixing	9.6	2.00	84 ^b	82.4	316 (0.015)	0.83	0.028
C15 (bottom)	NUMEC	Coprecipitation	9.6	1.99	84 ^b	83.0	316 (0.015)	0.66	0.013
SOV-15G	ANL	Dynapak	3.5	1.98	c	79.5	304 (0.020)	0.77	0.017
SOVG-17	ANL	Spherepak (Sol-gel)	3.5	1.99	c	80.0	304 (0.015)	0.73	0.019

^aDefect made by 0.015-in.-wide, 4-in. OD abrasive wheel.

^bBy specification.

^cNot in pellet form.

cave during the experiments. Sodium velocity past the specimens was 0.5-1.0 fpm. Samples were deliberately defected sections, about 2 in. long, of fuel pins that had been irradiated in EBR-II. The defects, axial slits about 3/4 in. long and penetrating up to 0.028 in. into the fuel, were produced by a 0.015-in.-thick abrasive wheel. The cut ends were capped by press-fit stainless steel end pieces.

The loop, with several grams of sodium oxide in the cold trap, was

Fig. 16. Effect of Fuel Burnup on the Swelling of Defected Fuel Elements Exposed to Sodium at 700°F. Both fuels fabricated by coprecipitation.

basis of their (as-fabricated) high O/M ratios and relatively low densities. It was expected from the limited information available that these properties would lead to maximum sensitivity to sodium exposure.

Figure 16 shows the relatively small effect of fuel burnup on diametral swelling (measured normal to the slit) for two specimens of similar manufacture. The solid lines of Fig. 17 show the effect of the method of fuel fabrication on the swelling of two specimens from the same fuel element.

The dashed lines show, for comparison, the effect of the other two fabrication methods. Those lines were determined from the results of irradiation of the Spherpak and Dynapak fuels (in other elements), subject to the following assumptions: (1) Variation in O/M ratio over the range of 1.98-2.00 is not significant to fuel swelling in sodium; (2) fuel burnup has relatively small effect on diametral swelling during exposure to sodium (see Fig. 16); and (3) the defected cladding would be unable to restrain the chemical reactions causing swelling.

Fig. 17

Effect of Method of Fuel Fabrication on Swelling of Defected Fuel Elements Exposed to Sodium at 700°F

The relatively large effect of temperature of exposure is shown in Fig. 18. For this comparison, sections of the same element were used to minimize the effects of other variables.

Figure 19 shows the effect of sodium temperature on microstructure. No gross differences are obvious in the sections exposed to the two temperatures. The reaction product at the grain boundaries was

difficult to retain during ordinary polishing (see Fig. 20). Backfilling the polished specimen with epoxy and regrinding with anhydrous ethyl alcohol retained the reaction product well enough for examination in the electron microprobe.

A specimen with 9.6 at. % burnup, which had been exposed to high-temperature sodium for 87 days (42 days at 700-1050°F, 45 days at 1200°F), was chosen for examination in the electron microprobe. Well-defined areas of reaction phase were observed. The composition ($\pm 1\%$) of the reaction phase was as follows: 60% U, 15% Pu, 12% Na, and 13% O. Sodium concentration was relatively constant with time; this indicated that the sodium was not there as a metal, because the energy of the beam would have caused free metal to vaporize. There was no detectable amount ($<0.1\%$) of cesium or tellurium in the reaction phase, but cesium was

Fig. 18

Effect of Temperature of Sodium Exposure on Swelling of Defected Fuel Element. Fuel fabricated by coprecipitation; burnup, 5.8 at. %.

Fig. 19. Effect of Temperature of Sodium Exposure on Microstructure of Defected Fuel Element. Fuel fabricated by coprecipitation; burnup, 5.8 at. %. Mag. 115X. ANL Neg. No. 104-533.

As Irradiated (Etched)

Exposed to 1200°F Sodium (Not etched)

Fig. 20. Effect of Sodium Exposure Shown at High (210X) Magnification.
Mechanically mixed fuel; burnup, 9.6 at. %.

detected in many locations in the fuel/cladding gap. There was no apparent relation, however, between the presence of cesium and the cladding defect. There was no detectable ($<1\%$) oxygen gradient in the fuel in the region of the defect. This specimen had the largest diameter increase of all the specimens: 10.3 mils, which is equivalent to $3.9\% \Delta D/D$. As with the other samples, the rate of increase in diameter was very slow at 87 days.

Figure 21 shows the appearance of this sample after 63 days of exposure. Cracks had developed in the stainless steel cladding, emanating from the ends of the milled defects. In addition, fine cracks appeared generally over the surface after 68 days of exposure. The cause of the fine

Fig. 21

Appearance of a Specimen with 9.6 at. %
Burnup after 63 days of Exposure to High-
temperature Sodium. Mag. 1.5X.

cracks, originating from the outside of the cladding, is not known. Incomplete cleaning at an interim examination may have caused the residual sodium hydroxide to crack the stressed cladding upon reinsertion into the hot sodium.

In most cases, the central voids and other porosity were completely filled with sodium as a result of the exposures. For observation of the effect this sodium would have after removal from the reactor, a sample exposed to sodium for 26 days at 700°F was subsequently held in moist nitrogen and then in moist air. No increase in diameter or cracking of the cladding occurred as a result of the exposure to the moist gases. The sample was covered with a thick crust, presumably sodium hydroxide, and a small amount of black material was found in the container in which the sample was exposed. The surface of the crust was black. This black material contained fuel and fission products. However, no gross fuel loss was observed. Figure 22 compares the microstructures of the fuel as irradiated, as exposed to 700°F sodium, and as exposed to 700°F sodium plus the moist gases. Slight grain-boundary etching is evident in the last example.

Present EBR-II operating procedures do not include the deliberate water washing of defected mixed-oxide fuel elements. Two short experiments were performed to determine if any hazard to EBR-II equipment or to the defected element would result from the inadvertent washing of such elements. Deliberately defected samples from vibratorily compacted elements SOV-15G and SOVG-17 had been exposed to flowing sodium at 700°F for a month. As a result of this exposure, the central voids were filled with sodium. The sections of the fuel had press-fit end caps, so the only access to this sodium was through the defect slits. The sample from SOVG-17 was immersed in water for 3 hr, and that from SOV-15G for 6 hr. A very brief surge of bubbles at the defects was noted upon immersion, followed by very slow trickles of bubbles throughout the rest of the exposure. The sample exposed for 3 hr lost 17 mg, and the one exposed for 6 hr lost 113 mg. No diametral changes were noted, nor did the defect change in any visible fashion. The water in which the samples were immersed was checked for radioactivity after the exposure. The 3-hr water showed 300 mR at 2 in., and the 6-hr water showed 500 mR.

The results of this experiment indicate that no extensive contamination of the EBR-II equipment would occur through the inadvertent washing of defected fuel elements and that no serious distortion of the fuel would take place.

Temperature of exposure and method of fuel fabrication were clearly the most important of the limited number of variables studies. Exposure of mixed-oxide fuel to sodium at storage temperature (700°F) should cause no reactor operational problems. No rapid attack occurred

at 1200°F, but the effect of high sodium velocity (which could not be evaluated in the experimental equipment used) might cause significantly greater fuel loss than was observed in our study.

Fig. 22. Effect of Exposing a Defected Fuel Element to Moist Gases. Mag. 115X. ANL Neg. No. 104-534.

Interpretation of the results of test irradiations in EBR-II may be compromised somewhat by exposure of fuel to sodium, especially, if the defected element is exposed to moisture after it has been removed from the reactor.

2. Exposure of Irradiated Boron Carbide Pellets

Knowledge of the compatibility of boron carbide with high-temperature sodium was required for evaluation of potential hazards in the use of EBR-II high-worth control rods (which contain the carbide) and in certain other proposed irradiations in EBR-II.

Separate tests of unirradiated cylindrical pellets of boron carbide (0.54-in. OD, 1.0 in. long) from two commercial sources (Cerac Co.

TABLE III. Weight Loss (mg/cm²) of Unirradiated Boron Carbide Pellets Exposed to 1110°F Sodium^a

Manufacturer	Days of Exposure	
	1	8
Cerac Co.	0.12	0.45
Carborundum Co.	0.17	0.86

^a Cold-trap temperature, 230°F; velocity, ~0.1 fpm.

and Carborundum Co.) showed that the pellets had only a slight weight loss during short sodium exposures at 1110°F (see Table III). A sample of the sodium taken at the end of the test of the Carborundum pellet contained 0.17 ppm boron.

Irradiated boron carbide pellets made by Cerac were available after the initial testing of the concept

of the high-worth control rod. Pellets 13 and 14 from capsule E of subassembly L-4008S, the test subassembly, were obtained. These pellets had been fabricated from natural boron carbide (which contains 19.8 at. % ¹⁰B) and had been irradiated to a burnup of approximately 1.6 at. % (of the ¹⁰B). During the irradiation, they had been exposed in stainless steel capsules for 1946 hr at power (62.5 MWt) in EBR-II. The estimated temperature range of the irradiation was 830-940°F.

Pellet 13 was used in a 16-day test exposure at three temperatures: 1 day at 700°F, 1 day at 850°F, and 14 days at 1000°F. The pellet was exposed to sodium in the same sodium test loop (see Fig. 15) in which the mixed-oxide fuel was exposed. After the test, adherent sodium was removed by washing the pellet first in ethyl alcohol and then in water. The overall loss of weight was 30 mg/cm² (4.5% of the postirradiation weight). This was substantially larger than anticipated from the preirradiation test results (see Table III).

Pellet 14 was exposed only to 1000°F sodium. An unirradiated boron carbide pellet was included in the same test, as a control, to determine if some abnormal sodium impurity was causing the large weight loss noted for pellet 13. The pellets were removed and examined at six days and again at 13 days. In both examinations, the sodium was removed by washing in alcohol and then by water. The irradiated pellet (No. 14) released a large cloud of black particles into the liquid at each cleaning (as did irradiated pellet No. 13). A few particles were also released by the unirradiated control pellet. The black particles from both pellets remained in suspension for several hours in the alcohol; this suggests that they were almost colloidal. Even after extensive washing, the irradiated pellet

retained enough sodium beneath its surface to continue to show tiny bubbles of hydrogen forming in wet areas. Figure 23 compares the appearance of the irradiated pellet No. 14 with that of the unirradiated control.

Fig. 23. Effect of Exposure of Irradiated and Unirradiated Boron Carbide Pellets to 1000°F Sodium for 13 days. Mag. 2X.

The weight loss of the unirradiated pellet (see Table IV) for the first six days of exposure was greater than previously obtained (see Table III). It is suspected that an error was made when weighing this pellet initially (in the cave).

TABLE IV. Weight Loss (%) of Boron Carbide upon Exposure to 1000°F Sodium^a

Specimen	Days of Exposure	
	6	13
Irradiated (Pellet No. 14)	5.2	11.2
Unirradiated Control	0.75	0.75

^a Cold-trap temperature, 265-275°F; velocity, 0.5 fpm.

The high-temperature sodium apparently found paths available for penetrating deeply into the irradiated pellets. In this low-velocity test (low velocity in relation to flow rate in EBR-II), the pellet did not disintegrate to any extent in the sodium. The gentle bubbling in the alcohol and the dissolution of the metallic sodium "gluing" the particles together caused most of the observed loss of material. The fragile nature of the sodium-penetrated pellet suggests that it would be eroded quickly in rapidly flowing sodium.

3. Investigation of Possible Effects of Line Length in the Measurement of Oxygen and Hydrogen Impurities in Sodium

The sodium-sampling stations at EBR-II (and other proposed LMFBR systems) are separated from the reactor by lengths of stainless steel tubing. A series of experiments was conducted to establish whether interaction of oxygen and hydrogen impurities in the sodium with the walls

of the line would invalidate the sodium sample. A separate ANL report¹² has been issued to describe those experiments, so only the abstract of that report is presented here, as follows:

"The response of on-line impurity meters to step changes in oxygen and hydrogen activities of flowing sodium were measured before and after the sodium had passed through 100 ft of Type 304 stainless steel tubing. Tests were conducted at sodium temperatures of 350, 450, and 565°C with electrochemical oxygen meters and at 450 and 565°C with diffusion-type hydrogen meters at sodium flow rates of 2.5 and 5 gpm. Both increasing and decreasing step changes in the activities of oxygen and hydrogen were introduced in separate experiments. The levels of these impurities were chosen to simulate those expected in an LMFBR. No absorption-desorption effects on the walls of the 100 ft of tubing could be detected by the on-line meters. The uncertainty on the meter readings was ~4% for the oxygen meters and ~6% for the hydrogen meter. Thus, no loss of sampling accuracy would be encountered by locating the sampling or monitoring station 100 ft from the main sodium system of a liquid-metal-cooled fast breeder reactor."

4. Exposure of Seat Materials of Ball Valves

A proposed modification of the argon-gas supply of the EBR-II fuel-unloading machine (FUM) created a need for information on the compatibility of available seat materials with sodium vapor and liquid sodium. The actual application was for a flowing stream of hot argon gas (at 650°F max) that might contain sodium vapor. Metallic sodium could conceivably collect by condensation during the cooler phases of the operation.

A series of short experiments was completed in which samples of available seat materials were exposed to either liquid sodium at 250, 350, and 450°F or mixtures of inert gas and sodium vapor (just over the surface of liquid sodium) at 250, 350, 450, 550, and 650°F. The materials tested were:

- No. 1. Graphite ball seals designated EK3059 (black)
- No. 2. "Fire Seal" reinforced TFE ball seal (grey)
- No. 3. Hills-McCanna reinforced TFE ball seal (black)
- No. 4. Hills-McCanna reinforced TFE steam packing washer (black)
- No. 5. Hills-McCanna TFE bonnet seal gasket (white)
- No. 6. Pure Teflon.

Small pieces of the various materials were cut to approximately $1/4 \times 1/4 \times 1/8$ in., and a $1/32$ -in. hole was drilled through them. They were then weighed, and one of each kind was strung on a stainless steel wire, with stainless steel washers separating each piece. The groups were then wired to a sample rod so that the specimens were either immersed in liquid sodium or just above the surface of the sodium in a small (~1-liter) materials-exposure system. After exposure, the specimens were cleaned in ethyl alcohol and distilled water, dried, and reweighed. They were then sectioned with a sharp blade to evaluate the depth of attack.

Tables V-VII give the results of the exposures.

TABLE V. Results of Exposing Seat Materials to Liquid Sodium

Exposure	Observations
250°F, 0.7 day	Graphite sample gone; others unchanged in appearance and weight.
350°F, 0.8 day	Graphite sample gone; others now dark on surface, but unchanged in weight (<0.001 g).
450°F, 1.0 day	Graphite sample gone; others dark and crumbling.

TABLE VI. Results of Exposing Seat Materials to Sodium Vapor and Inert Gas

Exposure	Observations
250°F, 0.7 day	All samples unchanged in appearance and weight (<0.001 g).
350°F, 0.8 day	
450°F, 1.0 day	
550°F, 2.8 days	All samples black; weight changes, ± 0.002 g.
650°F, 6.5 days	All samples black, but not crumbling; graphite sample absorbed sodium.

TABLE VII. Relative Performance of Seat Materials

Material No.	Weight Loss, %	
	In Vapor; 6.5 days at 650°F	In Liquid; 1 day at 450°F
1	1.5	100
2	0.4	2.0
3	1.5	5.9
4	2.3	5.8
5	2.8	5.8
6	1.4	28

The only cases of severe attack occurred in the liquid sodium. The graphite (No. 1) material was lost completely at all test temperatures, and a corner of the sample of pure Teflon (No. 6) was carbonized at 450°F. In all other cases, the cross sections after exposure showed essentially untouched material under a thin carbonized layer.

Figure 24 shows the sections of the six specimens exposed to inert gas and sodium vapor at 650°F for 6.5 days.

Fig. 24. Sections through Specimens of Seat Materials after 6.5 days at 650°F in Inert Gas and Sodium Vapor. Mag. ~2.5X.

5. Evaluation of Seal for Delayed-release Capsule

A HEDL experiment in EBR-II to identify the characteristics of a fission-product release from a low-burnup fuel element did not give the expected signal after a much longer exposure than was originally anticipated. While EBR-II was shut down for scheduled maintenance, an ex-reactor test of the deliberate delayed-failure defect was undertaken to determine the approximate time required for sodium to penetrate the prepared defect.

HEDL supplied two sample capsules for the ex-reactor test. In both, the deliberate defect was a 0.005-in. hole drilled through the wall of the 0.230-in.-OD stainless steel capsule tube. The hole was filled with a silver brazing alloy, and the defect and the adjacent area of the tubing were plated with copper and then with nickel. In the HEDL developmental testing in sodium at higher temperature, the copper dissolved and the nickel plating peeled off, thereby exposing the silver brazing alloy directly to the sodium. Sodium penetration occurred after about 100 hr.

The sample capsules were prepared for testing by inserting a "spark plug"-type leakage indicator directly under the known defect. The capsules were then exposed to rapidly flowing sodium on their outer surfaces to simulate their exposure in EBR-II. Oxygen level in the sodium was maintained at ~1 ppm by a cold trap.

No leakage signal was received in a 1500-hr exposure (940 hr at 740°F and 12 fps, plus 560 hr at 700°F and 6 fps). The capsules were removed and examined. The nickel plating was still in place on both capsules, and both passed a helium leaktest with a Veeco detector. Small bumps were noted, however, in the nickel plating over the location of the 0.005-in. holes, so one capsule was sectioned. It was determined that sodium had penetrated the hole, but had formed a corrosion plug with residual oxygen in the capsule. No detectable amount of metallic sodium had entered the capsule, even though a 4-psi differential pressure favored its entry.

The nickel plating was pried back with a sharp knife. The copper underplating had been dissolved, but only for a distance of about 0.03 in. from the edge of the nickel overplate. When water was present, the prying off of the nickel was accompanied by the release of tiny hydrogen bubbles as fresh copper plate was exposed. This suggests that lateral diffusion through a porous plating had allowed sodium to reach and react with the silver brazing alloy in the hole.

The second capsule was not sectioned; inspection of the interior of the defect revealed a telltale bump of corrosion product, however, which indicated that the capsule had also been penetrated.

The same sort of corrosion-product plug may have been responsible for the lack of response in the reactor experiment. Small quantities of residual oxygen and moisture were probably present in the experimental fuel element.

C. Sodium Removal and Component Cleaning

The removal of sodium for the interim examination of experiments is a continuing subject of concern and discussion among the experimenters and members of the EBR-II Project. The techniques currently in use at EBR-II (described in Ref. 1) have proved satisfactory. However, the possibilities of (1) physical damage of experimental components by heat and pressures developed in reaction of sodium masses with water and (2) penetration of stainless steel surfaces by sodium not adequately removed have continued to be areas of interest.

In addition, the possibility in the future of removing and repairing a major component of the reactor plant has sharpened the need for developing a sodium-removal technique suited to this circumstance. The crux of this

problem would be sodium-filled crevices. Inadequate cleaning of the crevices would probably leave sodium hydroxide residues in the crevices, which would cause cracking when the component is reinserted into the high-temperature sodium.

Information pertinent to these problems was obtained during the last year in the three series of experiments described here.

1. Subassembly Draining

Some experiments in EBR-II that require a low sodium flow have much smaller than usual orifice holes in the inlet to the subassembly. When the subassembly is removed from the reactor, the sodium inside the subassembly drains through these orifices. If a subassembly were not completely drained, the possibility for a damaging sodium-mass reaction in the subsequent water-wash cycle would be greatly increased. To ensure that the standard holding time during in-reactor draining provided an adequate safety factor, a series of short experiments was performed to measure the drain times and amount of sodium holdup for several typical orifice plates.

The experiments were performed at 580 and 700°F to simulate EBR-II operating conditions. A 7-in.-long cup made from 1-in.-OD, 7/8-in.-ID Type 304 stainless steel tubing was fitted with orifice plates on the bottom. The cup held approximately the same sodium volume per inch of length as a typical experimental subassembly.

The cup was weighed and then completely immersed in the sodium in a small circulating loop system operating with a cold trap set at 250°F. The sodium temperature was raised to 1200°F, to ensure wetting of the cup, and then lowered to 580°F. The cup then was rapidly withdrawn into a length of Pyrex pipe, where the draining could be viewed under an argon atmosphere. Several drain cycles were made and timed. Then, the temperature was raised to 700°F, and the drain tests were repeated. The cup was allowed to cool undisturbed after the last drain cycle at 700°F. It was then reweighed. Table VIII summarizes the results of the experiments.

TABLE VIII. Results of Experiments on Sodium Draining

Orifice	Temperature, °F	Average Drain Time, sec	Sodium Holdup, g
Two 0.045-in.-dia holes; 1/8-in. plate	580	52	-
	700	51	1.8
Two 0.060-in.-dia holes; 1/8-in. plate	580	28	-
	700	25	2.1
Two 0.090-in.-dia holes; 1/8-in. plate	580	11	-
	700	11	2.0
One 0.125-in.-dia hole; 1/4-in. plate	580	10	-
	700	10	1.8
Two 0.063-in.-dia holes; 3/4-in. plate	580	23	-
	700	21	1.4

The relationship between the drain times for the 7-in.-long cup and a full-length subassembly is established by a total energy balance, which in this case simplifies to

$$h = \frac{v^2}{2g},$$

or

$$v = (2gh)^{1/2}, \quad (1)$$

where

h = height of sodium in cup,

v = velocity through orifice,

and

g = gravitational constant.

Also,

$$A_o(v) = A_c \frac{dh}{dt},$$

or

$$dt = \frac{A_o}{A_c} \frac{dh}{v}, \quad (2)$$

where

A_o = cross-sectional area of orifice,

and

A_c = cross-sectional area of cup.

Substituting Eq. 1 for v in Eq. 2,

$$dt = \frac{A_o}{(2g)^{1/2} A_c} \frac{dh}{h^{1/2}}.$$

Integrating, we obtain

$$\left[t \right]_0^{t_d} = - \frac{2A_o}{(2g)^{1/2} A_c} \left[h^{1/2} \right]_{h_0}^0,$$

$$t_d = \frac{A_o}{g^{1/2} A_c} h_0^{1/2},$$

and

$$t_d \propto h^{1/2},$$

where

t_d = time to drain cup,

and

h_0 = initial height of sodium in cup.

The length of a subassembly that can drain may be considered to be about 80 in., so the drain times for the 7-in.-long cup should be multiplied by $(80/7)^{1/2}$, or ~ 3.4 , to convert to subassembly drain times. (This relationship was verified with the actual cup and an added length of 1-in. tubing. Distilled water was used as the fluid.)

The results of this experiment indicate that even the two 0.045-in. holes would drain a subassembly in less than 3 min, which is much less than the usual waiting period.

The inside of the cup drained completely in all cases. Except for a very thin adherent film on the walls, the measured sodium holdup was concentrated in a globule suspended from the bottom of the cup. It would be difficult to extrapolate this data to a full-size subassembly, because the relationship would depend on the area of exposed metal and the number of possible ledges or drip points in the particular subassembly. The orifice size, however, does not appear to be a significant factor in sodium holdup.

2. Interaction of Stainless Steel Surfaces with High-temperature Sodium

A series of experiments was performed to evaluate previous reports¹³ of high-temperature sodium penetrating deeply into grain boundaries of structurally sound Type 304 stainless steel. A separate ANL report¹⁴ has been issued describing the results of these experiments. Only the abstract of that report is given here, as follows:

"Several experiments contradict the hypothesis postulating the deep grain-boundary penetration of structurally sound Type 304 stainless steel by high-temperature sodium. The rapid disintegration in subsequent Strauss testing reported by earlier investigators has taken place only with specimens exposed to the sodium in their test equipment and with those samples deliberately carburized during other sodium exposures. Chemical analyses of the surface layers of specimens exposed in their equipment confirmed the presence of increased carbon. In the absence of a carburizing source, specimens

exposed to sodium behaved equivalently in Strauss testing to those exposed in vacuum to the same heat treatment. No detectable amount of sodium diffused through a thin-walled capsule at 650°C. No significant grain-boundary attack on Types 304, 304L, 316, and 316L stainless steels was noted in experiments lasting 1 yr at 650°C. These experiments included three intermediate washings and inspections of the specimens. Microimperfections in ordinary surfaces have retained sodium or sodium compounds after washing, but electropolished surfaces did not. Finally, the deep penetration of sodium along sulfide and oxide inclusion-stringers in austenitic stainless steel has been demonstrated."

3. Sodium Removal from Deep Crevices

The intermediate heat exchanger (see Fig. 1) of EBR-II contains many deep crevices. Any attempt to clean, repair, and requalify such a component requires information on techniques for removing sodium from these crevices. Preliminary experiments were performed last year to provide a basis for evaluating alternative cleaning procedures.

A crevice between a tube and a tube sheet was simulated by inserting a machined rod in a machined tube and welding the two together at one end. The crevice created was 5/8 in. in diameter and had a 0.006-in. radial width. The crevice was filled by plunging the specimen (open end up) into sodium at 300°F while the entire system was evacuated. Gas pressure was then applied to the sodium to force it into the crevice. The sodium temperature was raised to 930°F, to aid wetting, and then lowered to 700°F (the temperature of removal).

Four procedures were tried for removing the sodium from the crevice. The effectiveness of each was determined by change in specimen weight with time. Table IX shows the results.

TABLE IX. Comparison of Methods of Removing Sodium from a Deep Crevice

Method	Result
Vacuum distillation at 750°F	100% removed in <80 min
Running water ^a	99% removed in 3.5 hr
Moist argon ^b	<1% removed in 4 hr
Anhydrous liquid ammonia ^a	No detectable amount removed in 1 hr

^aCrevice up, facing stream of cleaning fluid.

^bCrevice down, from stream of argon.

The good result obtained with vacuum distillation in a relatively short time is impressive. Unfortunately, this method might be difficult to apply to many components. Therefore, the only practical effective method appears to be the water wash.

Moist argon and anhydrous liquid ammonia were totally ineffective in removing sodium from the crevice. The results with the anhydrous liquid ammonia were poor because a thin film formed over the mouth of the crevice and blocked the dissolution of the metallic sodium.

III. DISCUSSION

EBR-II operated during 1971 without any problem directly attributable to interaction of material and coolant. An earlier problem of sticking of primary pump No. 1--a result of an accumulation of sodium, sodium oxide, and aluminum-bronze corrosion product in the normal clearance between the pump shaft and the labyrinth--was corrected before the start of the year's operation.

Surveillance of materials removed from the entire reactor system continues to be encouraging. The only serious failure was the cracking of an improperly heat-treated relief valve of a feedwater heater.

A wide variety of ex-reactor testing was performed in support of EBR-II. The exposure of irradiated and defected mixed-oxide fuel elements to sodium indicated that no serious interaction would occur during storage periods, even at temperatures as high as 1200°F, and that no serious contamination of the reactor facility would result from the inadvertent washing of a sodium-logged defected fuel element.

The observed penetration of irradiated boron carbide by high-temperature sodium is not surprising, since each reaction of ^{10}B with a neutron forms a helium atom and a lithium atom. Accommodating the helium in the brittle ceramic pellet could lead to cracking. The high solubility of lithium in sodium further aids the penetration.

The limited number of crevice-cleaning experiments performed clearly indicated the most useful techniques to be used if reconditioning of a major component is required.

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