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CORROSION OF URANIUM, THORIUM, AND URANIUM ALLOYS IN SODIUM AND ORGANICS

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ABSTRACT

CORROSION OF URANIUM, THORIUM, AND URANIUM ALLOYS IN SODIUM AND ORGANICS

Sodium and sodium-potassium alloys and the polyphenyl class of organic compounds possess certain advantages over water for use as reactor coolants. There are no reactions between uranium and the pure liquid metals; however, thermodynamic data predict that formation of uranium carbide and uranium hydride is possible in reactions with organics, and with their pyrolytic and radiolytic products.

In this paper, available experimental data are reviewed for uranium and uranium alloys exposed both to sodium and sodium-potassium alloys in static and dynamic systems. Effects of irradiation on corrosion rate do not appear to be significant. The observed corrosion rate of uranium and uranium alloys depends very strongly on the impurity (especially oxygen) content of the liquid metal. In capsule-type static corrosion experiments, made with liquid metal with oxygen content near 0.01 weight percent (100 ppm), corrosion rates are of the order of 10 mg/cm^2-mo, at temperatures up to 750°C. UO_2 and UO have been identified as corrosion products. In dynamic systems, corrosion rates of more than 600 mg/cm^2-mo have been observed at 500°C, with oxygen content ranging near 0.005 weight percent (50 ppm).

Corrosion rates of uranium and uranium alloys in purified biphenyl are of the order of 1 mg/cm^2-mo at temperatures up to 400°C in static systems. Under dynamic conditions in loop experiments, rates are perhaps five times greater. Formation of uranium monocarbide, through UH_3 as an inferred intermediary, has been observed in mono-isopropyl biphenyl under hydrogen gas pressures of the order of 100 psi. Impurities dissolved in the organic, such as air, oxygen, or water, greatly accelerate the corrosion rate.

It is concluded that the corrosion rate of uranium and its alloys in liquid sodium and NaK is low enough to permit the use of a static liquid metal bond between the fuel and a cladding of some other metal.

Exposure of relatively large surfaces of fuel to circulating liquid metal coolant appears to be not feasible because of the difficulty of adequate control of oxygen in a large volume liquid metal system. There would be no advantage in reactor performance in direct exposure of unclad fuel to an organic coolant, but in case of accidental exposure by way of a cladding failure, the corrosive attack would be relatively very slow.

1. INTRODUCTION

One of the principal attractions in pursuing development of non-aqueous reactor technology has been the possibility of achieving high temperature without an accompanying high pressure. Sodium and sodium-potassium alloys as well as certain high boiling point organic compounds, have accordingly received considerable attention in power reactor development programs in the United States. Sodium and its alloys with potassium, in addition to having relatively wide liquid ranges and high boiling points, possess other advantages such as excellent heat transfer characteristics, good pumping efficiency, and acceptable nuclear properties. Also, because of their elementary nature, they are free from chemical effects induced by ionizing radiation.

In the last ten years in the United States, many experimental investigations have been made on numerous organic compounds of different chemical types in order to evaluate their resistance to radiation and to high temperature. Although all compounds show some tendency to undergo radiation-induced chemical change, the polyphenyl compounds, such as biphenyl and the terphenyls, appear to possess adequate chemical stability for use as reactor coolants. Their nuclear properties are excellent for reactors operating with neutrons of thermal energies. Their heat transfer capability falls far short of sodium and is in some ways inferior to water; however, it is possible that bulk temperatures in the neighborhood of 325°C (620°F) may be attained with them without excessive pyrolysis, and adequate overall plant thermal efficiency appears assured.

To the advantages mentioned above for these non-aqueous coolants there can be added the fact that catastrophic chemical reaction between them and uranium is high improbable. Table 1[1] summarizes in survey fashion the thermodynamic data for certain chemical reactions of uranium metal, and also of sodium and potassium. It may be seen that per mol of uranium metal, the largest free energy change, by far,

TABLE 1

THE EFFECT OF TEMPERATURE ON THE FREE ENERGY OF VARIOUS CORROSION REACTIONS

Reaction	Standard Free Energy Values (kcal)		
	25°C	225°C	400°C
$U_{(s)} + 3/2H_{2(g)} \longrightarrow UH_{3(s)}$	—17.7	—9.0	—1.6
$Th_{(s)} + H_{2(g)} \longrightarrow ThH_{2(s)}$	—22.1	—13.4	—5.8
$U_{(s)} + 8/3H_2O_{(1)} \longrightarrow 1/3U_3O_{8(s)} + 8/3H_{2(g)}$	—131.3	—129.0	—127.0
$U_{(s)} + C_{(s)} \longrightarrow UC_{(s)}$	—43.6	—44.0	—44.3
$Th_{(s)} + C_{(s)} \longrightarrow ThC_{(s)}$	—25.1	—26.6	—27.9
$U_{(s)} + 1/6C_6H_{6(g)} \longrightarrow UC_{(s)} + 1/2H_{2(g)}$	—48.8	—49.5	—50.1
$U_{(s)} + 3C_6H_{6(g)} \longrightarrow UH_{3(s)} + 3/2C_{12}H_{10(1)}$	—23.9	—15.2	—7.8
$U_{(s)} + O_{2(g)} \longrightarrow UO_{2(s)}$	—246.6	—238.2	—230.9
$Th_{(s)} + O_{2(g)} \longrightarrow ThO_{2(s)}$	—279.2	—269.7	—261.4
$4Na_{(s)\ or\ (1)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)}$	—179.8	—166.0	—153.9
$4K_{(s)\ or\ (1)} + O_{2(g)} \longrightarrow 2K_2O_{(s)}$	—152.6	—137.8	—124.9
$4Na_{(s)\ or\ (1)} + 2/3Cr_2O_{3(s)} \longrightarrow 2Na_2O_{(s)} + 4/3Cr_{(s)}$	—11.1	—5.8	—0.7

attends the reaction with oxygen. The table further shows what is already well known, that on thermodynamic criteria alone, uranium will reduce any oxide of sodium or potassium. The free-energy change for reaction with water is relatively large, although not so large as with oxygen. In organic media it is seen that, at least on the basis of free energy considerations, the production of uranium monocarbide is favored over the formation of uranium hydride.

Observations from corrosion experiments, performed both with sodium and its alloys and with polyphenyls, in direct contact with uranium, have generally borne out the expectation that there would be little reaction between the metal and the pure coolant. In almost every case, the observed corrosion has reflected the chemical reactions between uranium and the impurities present in the coolants including, in the case of the polyphenyls, pyrolysis products. Deliberate use in a reactor of unclad fuel in direct contact with coolant is not considered desirable, even if corrosion were not a factor—perhaps primarily because of inevitable contamination of the primary coolant loop by fission product recoils from the fuel surface. Nevertheless, relative inertness to coolant is a highly useful property in minimizing the consequences of cladding failure.

2. CORROSION IN SODIUM AND NaK

The impurity contributing principally to corrosion of uranium in sodium is oxygen, present in the metal as Na_2O. To reduce the oxygen content of elementary sodium as received from the chemical suppliers, procedures such as chemical gettering, distillation, and filtration have been utilized. The last, carried out through stainless-steel mesh (or glass) filters at temperatures only slightly above the melting point (97.8°C), supplies sodium with an oxygen content low enough for many uses.

The sodium-potassium alloy compositions most frequently used are approximately 44 weight percent K (m.p. 18°C) and the eutectic (approximately 78 weight percent K, m.p. —12°C). These are usually purified by distillation by the supplier and further purified by filtration at room temperature.

2.1 *Solubility in Sodium*

Pure uranium is virtually insoluble in sodium. An upper limit of the order of 0.01 weight percent U (100 ppm) is estimated at 97.8°C.[2] At 300°C a value of 0.005 weight percent U (50 ppm) has been quoted.[3] It appears correct to conclude that solubility is of negligible importance in the corrosion of uranium in sodium.

2.2 *Corrosion in Static Systems*

Early experiments[4] on small cylinder or sheet specimens of uranium, in rather pure NaK enclosed in a mild steel container, yielded a weight change rate of +0.009 mg/cm^2-hr (6.5 mg/cm^2-mo) at 600°C. This is an initial rate value from short-time tests (6 days). The coating was qualitively identified as oxide. Other experiments[5] performed in a Type 347 stainless-steel container, and using NaK of very high purity, gave weight gains at about 400°C ranging from 0.002 to 0.01 mg/cm^2-hr (1.4 to 7 mg/cm^2-mo). Again, these are initial values for short exposures (7 days). In this case, the coating on the uranium appeared from chemical evidence to be UO_2.

Table 2 summarizes available early data on static corrosion. The results show considerable scatter. This probably reflects the variations in oxygen content of the liquid metal, in outgassing procedures carried out on the container, in metallurgical soundness of the specimens, and also in ratios of specimen surface/volume, and of liquid metal volume/specimen surface. All tests are of relatively short duration, carried out in the absence of radiation.

The data in the table are for weight changes only, on specimens whose post-exposure treatment consisted usually of rinsing in alcohol to remove adherent liquid metal. Metallurgical history of the metals was not known in all cases. Specimens were not stripped to bare metal (nor were they in any of the subsequent liquid metal work reported here). Chemical analysis for oxygen in the liquid metal was usually not made, although the deleterious effects of oxygen on the fuel metal were clearly recognized.[4] In one series of tests at Argonne National Laboratory, the static corrosion rate of uranium in purified NaK

TABLE 2

STATIC CORROSION IN PURIFIED SODIUM AND NaK[3, 4, 5]

Material	Argonne National Laboratory			Knolls Atomic Power Laboratory		
	T (°C)	Time (hr)	$\frac{\text{mg}}{\text{cm}^2\text{-mo}}$	T (°C)	Time (hr)	$\frac{\text{mg}}{\text{cm}^2\text{-mo}}$
Uranium	200	144	—0.08(a)	500	166	—0.1(e)
	600	144	+3.1(a)			
	405	160	+7(b) (d)			
	396	160	+1.4(c) (d)			
U-10wt. %Pu	350	160	—216(d)			
U-10wt. %Pu	405	160	—288(d)			
U-60wt. %Al	. . .	. . .	. . . . .	450	124	—30
				500	170	+8
				660	164	—720
U-60wt. %Al	. . .	. . .	. . . . .	500	167	—220
Thorium	600	144	+4.5			

(a) In NaK of 44 wt. %K, purified by gettering with U

(b) Small wire specimen

(c) Standard ANL corrosion specimen, 0.97 in. by 0.61 in. by 0.106 in.

(d) In double-filtered NaK. Plutonium alloy specimens showed evidence of flaking into the liquid metal.

(e) In Na purified by gettering with Be or Ca

(44 weight percent K) was found to be +3 mg/cm^2-mo at 600°C. In another (capsule) test, similar except that 1.7 weight percent oxygen as O$_2$ gas had been added to the system, the rate was +29 mg/cm^2-mo. Both tests were of 6-day duration.[6]

In the course of development work for the Sodium Reactor Experiment (SRE) at Atomics International, samples of uranium-thorium alloys and also of pure thorium were exposed to sodium and eutectic NaK in Type 304 stainless-steel capsules at 750°C for a month.[7] Results of weight change observations are summarized in Table 3, and are seen to be lower than the range of static corrosion values from earlier work. The sodium was purified by filtration, but the NaK was used as-received. The estimated oxygen content was ~ 0.025 weight percent in the sodium, and ~ 0.02 weight percent in the NaK. The capsule atmosphere was purified argon gas. The specimen surface after test showed only slight discoloration. Surveys made after test indicated negligible alpha activity in the liquid metal. The composition of the coating was not determined in the above experiment, but it was very probably a mixture of thorium oxide and uranium oxide.

There is some reason to expect thorium to be more resistant than uranium to oxygen impurity in liquid metal. The adherence of oxides to the base metals is governed by, among other factors, the ratio:[8]

TABLE 3

STATIC CORROSION OF THORIUM-URANIUM ALLOYS IN SODIUM AND NaK AT 750°C[a]

Material	Fabrication Method	Weight Change Rate $\left(\frac{\text{mg}}{\text{cm}^2\text{-mo}}\right)$	
		In Sodium	In NaK
Th	Rolled Plate	+2	+2
Th-3wt. %U	Cast	+1	+2
Th-4wt. %U	Powder Metallurgy	−40, +3[b]	−12

[a] All exposures one month duration. Metal specimens had volume of ~ 0.5 cm^3 and 1-2 cm^2 surface area. Liquid metal volume was about 10 cm^3. Nak contained 78wt. %K.

[b] Duplicate samples.

$$E = \frac{V_{ox}}{V_m} = \frac{\text{volume per metal atom in oxide}}{\text{volume per atom in metal}}$$

Maximum adherence would be expected in systems where E = 1. For both UO_2 and ThO_2, the ratio is given by

$$E = \frac{\text{molecular wt. oxide}}{\text{atomic wt. metal}} \times \frac{\text{density metal}}{\text{density oxide}}$$

For ThO_2, E is about 1.4; for UO_2, it is about 2. On this criterion, oxide should be more adherent on thorium than on uranium and should, in fact, compare favorably with such well-known protective oxides as Al_2O_3 (E = 1.3-1.5).

2.3 *Wetting of Fuel Metals by Sodium and NaK*

Wettability is a quality of the metal-liquid metal interface that is determined by surface attractive forces. It is related to corrosion, although the latter is usually controlled by chemical processes (solution, reaction). Wetting is of importance in determining the heat transfer rate from fuel to coolant.

The effect of surface film on heat transfer may be illustrated by consideration of the SRE fuel element, which consists of a cluster of seven thin-walled stainless-steel fuel tubes.[9] Each tube contains twelve beta-heat-treated uranium slugs, ¾ inch in diameter by 6 inches long (1.9 by 15.3 cm). The slugs are stacked along the length of the tube to form a six-foot-long active fuel zone (183 cm); and about 7.3 cubic inches (120 cm^3) of NaK are added to provide a 10 × 10^{-3} inch (2.5 × 10^{-2} cm) thick bond between uranium and steel. The fuel element is shown in Fig. 1. It is estimated that if the NaK contained 0.01 weight percent oxygen, and if all the oxygen reacted with the uranium surface, an oxide layer 2 × 10^{-3} inch (5 × 10^{-3} cm) thick would form, which at the peak SRE heat flux of 340,000 Btu/hr-ft^2 (107 watts/cm^2) would cause an increase in the temperature drop from slug center to surface of 12°C.[10]

The above estimate assumes that the oxide layer is interposed between metal and liquid metal. Experimental results[10] indicate, however, that direct contact between metal and liquid metal is achieved rather readily. Tests were made to determine the "wetting temperature." At this temperature, a drop of liquid metal begins to spread freely over the surface of the metal; that is, the contact angle is less than 90°.

Using metal specimens that had been outgassed at 350°C in a vacuum of 10^{-5} mm of mercury, in an atmosphere of carefully purified argon, the results summarized in Table 4 were obtained.

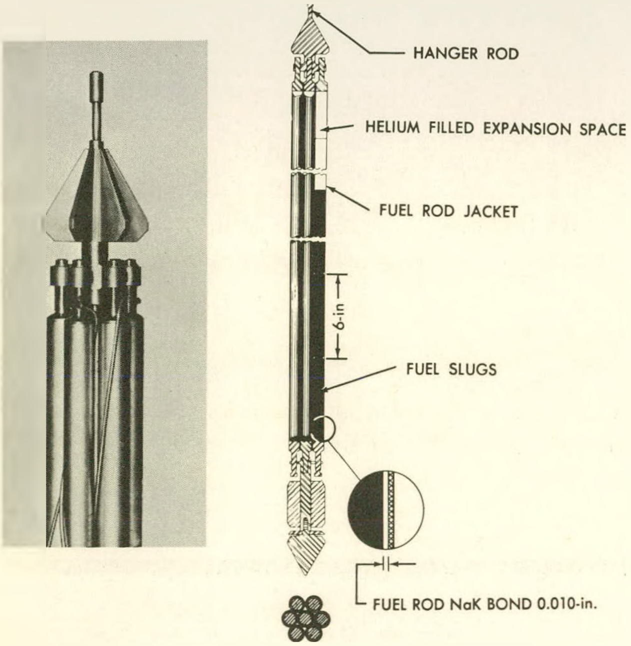

Figure 1. SRE Fuel Element

TABLE 4

WETTING TEMPERATURE AS FUNCTION OF WETTING FLUID

Material[a]	Fluid	Range of Wetting Temperature (°C)
Cast Thorium	Sodium	240 - 250
Cast Thorium	NaK[b]	235 - 245
Th-4wt. %U	Sodium	190 - 225
Th-4wt. %U	NaK	198 - 228
Th-5wt. %U	Sodium	200 - 223
Th-5wt. %U	NaK	202 - 215

[a] All specimens were metallographically polished

[b] NaK contained 78wt. %K

These results indicate that there is no significant difference between sodium and NaK. Other tests showed that there was essentially no difference in wetting temperatures among different metals. Thorium, thorium-uranium alloys, uranium, and even stainless steels all wet near 200°C. It was established that previous wetting reduces subsequent wetting temperatures, but that surface roughness increases the wetting temperature, as does heavy oxidation.

If the oxide coating is very thin, as would be the case on an electropolished surface briefly exposed to

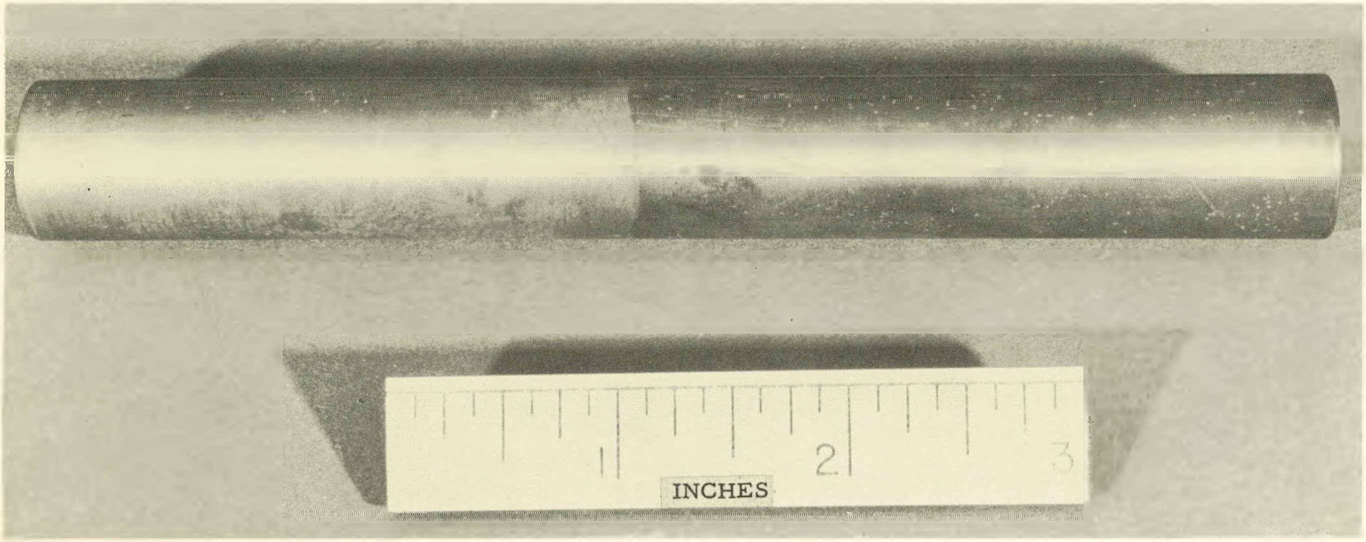

Figure 2. Nak Adherence to Uranium

air, wetting is attained simply by dipping. The wetting temperatures noted in practice were frequently observed to be below those observed in the controlled experiments. Figure 2 shows an SRE fuel slug, partly coated by immersion in NaK at 175°C very shortly after the slug had been electropolished. Adherence was excellent.

2.4 Corrosion in Dynamic Systems

Corrosion data are available from three types of test made with flowing sodium.

2.4.1 Rocking Capsule Tests

Dynamic corrosion tests[11] have been made at Oak Ridge National Laboratory in a rocking-type apparatus, shown in Fig. 3. The uranium used was alpha-rolled material, electropolished prior to test. Specimens were retained in the hot zone during test. The sodium was once-filtered just above the melting point. Oxygen content was not measured, but was probably between 0.02 and 0.025 weight percent (200 to 250 ppm). Capsules were made of Type 347 stainless steel, stringently purified by hydrogen firing and evacuating prior to loading.

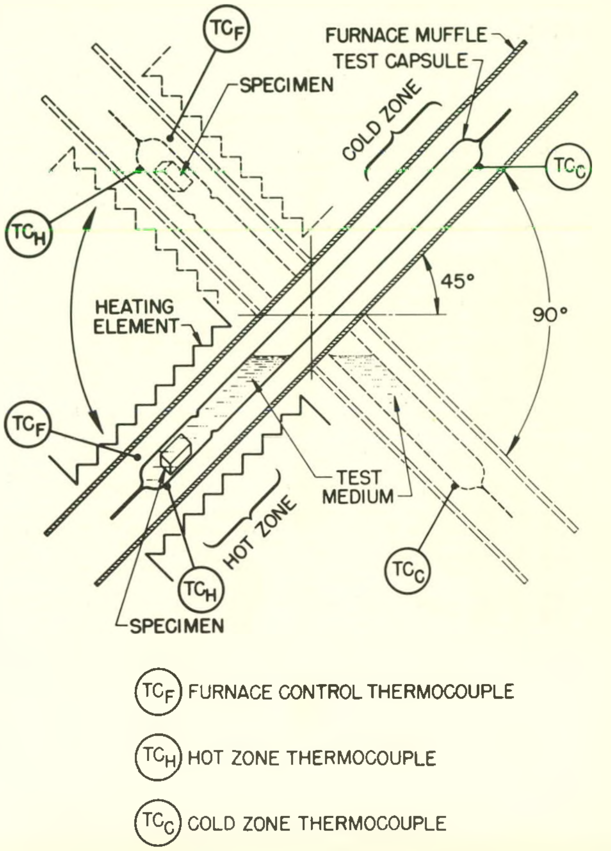

Figure 3. **Uranium Specimen in Stainless Steel Rocking Test Capsule**

TABLE 5

"ROCKING" CORROSION TESTS ON SYSTEM U-Na-347 SS(a)

Test Code Number	Temperature Hot Zone/Cold Zone °C	(°F)	Weight U In Sodium After Test(b) (mg)	Specimen Weight Change Rate $\left(\frac{mg}{cm^2\text{-hr}}\right)$	U Plated On Container $\left(\frac{microgram}{cm^2}\right)$	Total U Plated (microgram)
SS-188	676 565	(1250) (1050)	16.1	+0.047 mg/cm^2-hr		
SS-189	648 526	(1200) (980)	24	+0.065 mg/cm^2-hr	700 2940	1.05 4.4
SS-190	538 400	(1000) (752)	26.2	—0.029 mg/cm^2-hr	10,000 470	15.0 0.7
SS-191	538 396	(1000) (745)	24.2	—0.013 mg/cm^2-hr		

(a) All tests of 100-hour duration.

(b) Chemical form of U not determined (could have been UO_2 in suspension).

Tests were run at 1000°F (537°C), 1200°F (649°C), and 1500°F (815°C). The 815°C tests resulted in capsule failure, presumably because of formation of the eutectics U_6Fe plus UFe_2 (m.p. 725°C) or U_6Ni plus Ni(m.p. 737°C). There were no capsule failures at lower temperatures. Results of the latter tests, all of which were of 100 hour duration, are summarized in Table 5.

All specimens were found to be covered by a surface layer of thickness varying from 2×10^{-3} to 5×10^{-3} inch (5×10^{-3} to 12.5×10^{-3} cm). Both UO_2 and a phase tentatively labeled as UO were identified in the corrosion products by X-ray diffraction. Microhardness measurements were made on the layers, and the uranium content of the sodium was determined after test. Also, microdrillings were taken from the hot and cold zones of the Type 347 stainless-steel containers and were analyzed for uranium content, and the uranium specimens were analyzed for the presence of constituents of stainless steel. The weight loss from the 538°C run (SS 190) is reflected in the high uranium pickup by the stainless-steel container. The container wall generally showed no evidence of attack. However, from analysis of successive layers, 10×10^{-3} inch thick, that were cut from the specimens, there is evidence of deposition of stainless steel. For example, in Specimen SS-189 (see Table 5), the Fe found in the first and second layers, respectively, was 0.045 and 0.011 weight percent. In SS-190, the corresponding values were 0.049 and 0.014 weight percent.

Figure 4 is a representative photomicrograph of the uranium before test. After electropolishing and prior to test, all the specimens were found to contain carbide inclusions and a few oxide stringers, but no uniform oxide surface layer. Figure 5 shows the uranium surface condition after exposure at 1200°F (648°C). Only a single corrosion product is apparent

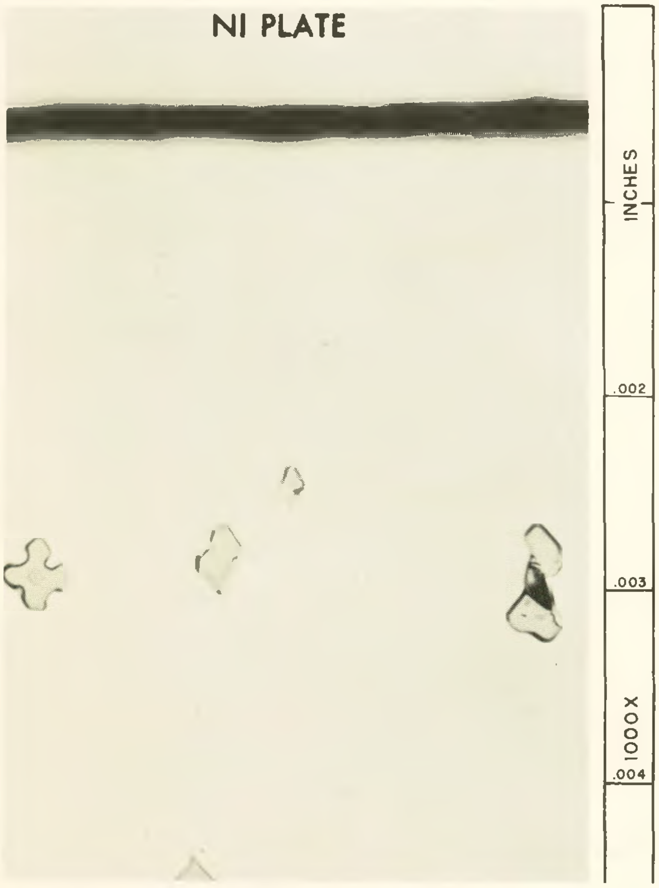

Figure 4. Uranium Surface Before Test

(Specimen nickel-plated to preserve edge during metallographic polishing. Particles are UC_2 Electrolytic etch. Magnification-100x)

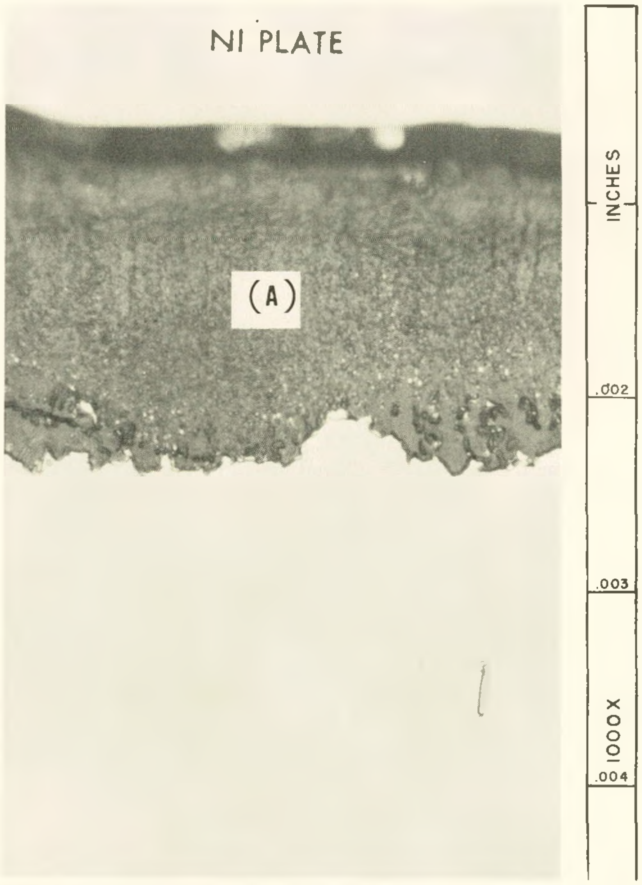

Figure 5. Uranium Surface After Test in Sodium at 1200°F.

(Specimen nickel-plated to preserve edge during metallographic polishing. Electrolytic etch. Magnification-100x. Diamond pyramid hardness at (A): 720 ± 15 DPH)

(UO_2). Figure 6 shows the multi-layer structure observed on the 1000°F (538°C) specimen surface. Despite the three hardness values found, X-ray diffraction revealed only two phases, UO_2 and UO. Multi-layer structure like that in Figure 6 has been previously reported.(12)

The oxide formation in these tests must be attributed principally to the reaction with oxygen initially present in the sodium. The mechanism of material transfer between the specimens and the stainless-steel surface is not known.

2.4.2 Loop Tests, Unclad Specimens

The corrosion rate in loop-type experiments where unclad uranium is exposed to a relatively large volume of flowing sodium has been investigated at Argonne National Laboratory.[13, 14] The loop capacity was 30 gallons (114 liters). Maximum temperature at the sample was 500°C (932°F), but the loop was not isothermal, so that there was opportunity for thermal mass-transfer. The test loop is shown schematically in Fig. 7. It was made of Type 347 stainless steel, in 2-inch and 6-inch sizes.

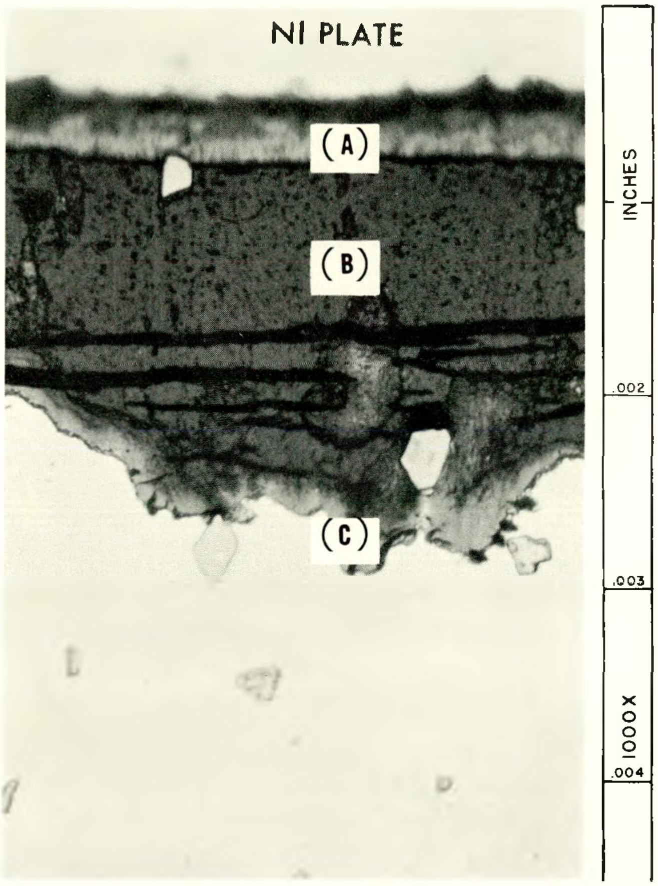

Figure 6. Uranium Surface After Test at 1000°F

(Specimen nickel-plated to preserve edge during metallographic polishing. Electrolytic etch. Magnification-1000x. Diamond pyramid hardness at (A): 405 ± 50; (B) 610 ± 20; (C) 770 ± 15 DPH)

Filtered sodium was charged to the loop. Sodium flowed from the electromagnetic pump, the coldest point in the loop, past the electric immersion heaters and over the specimens. For a specimen temperature of 500°C, the highest sodium temperature in the loop was about 600°C, and the lowest was about 400°C. Samples for oxygen determination were withdrawn from an outlet that permitted removal of a well-mixed sample. Determination of oxygen was made by a distillation technique. In tests with unirradiated uranium, corrosion was monitored by weight loss. Tests were also made with irradiated specimens, and corrosion was qualitatively followed by monitoring the buildup of radioactivity at several points on the loop.

The unirradiated specimens were of normal uranium cast and rolled to final size, 1/8 inch diameter by 1¼ inch long (0.32 by 3.2 cm). The irradiated specimens were identical to these, except that they had been irradiated to burnups of the order of 0.006 to 0.02 percent of total uranium atoms. Results are

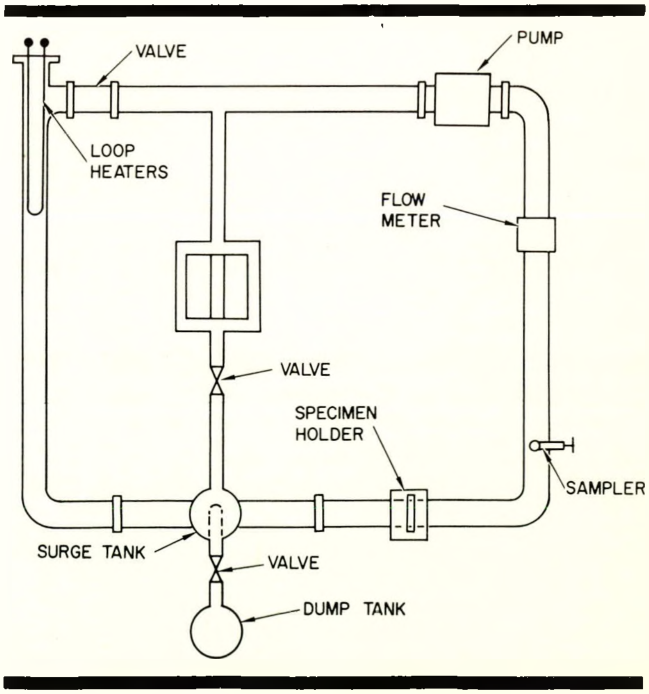

Figure 7. Schematic Diagram of Sodium Corrosion Loop

summarized in Table 6 and are shown graphically in Fig. 8.

An average corrosion rate of —616 mg/cm²-mo was observed for the unirradiated specimens. All specimens appeared rough and pitted following exposure. From the trends shown in Fig. 8, it may be concluded that the products of uranium corrosion by sodium are transported, perhaps as a suspension in the flowing sodium, and settle out in low velocity sections of a circulating system (flanges, surge tank, etc.). The radioactivity growth rate—and inferentially the uranium corrosion rate—shows an increase with increasing temperature, and also with increasing sodium flow rate. The corrosion product that accumulated on the inside of the loop piping was identified as UO_2. No uranium was found in the sodium. It appears therefore that the oxide sloughs off as it forms on the uranium specimens, so that the curves of Fig. 8 reflect a combined corrosion-erosion phenomenon. Several other points are noteworthy. If the total weight loss of 6.7 grams of uranium in the 781-hour unirradiated test appears as UO_2, this corresponds roughly to a reduction of loop oxygen content at a rate of just less than 0.001 weight percent/mo (10 ppm/mo). Also, the ratio of sodium volume to uranium surface in this test was about 12 liters/cm², which greatly exceeds the ratio in small capsule-type static corrosion experiments.

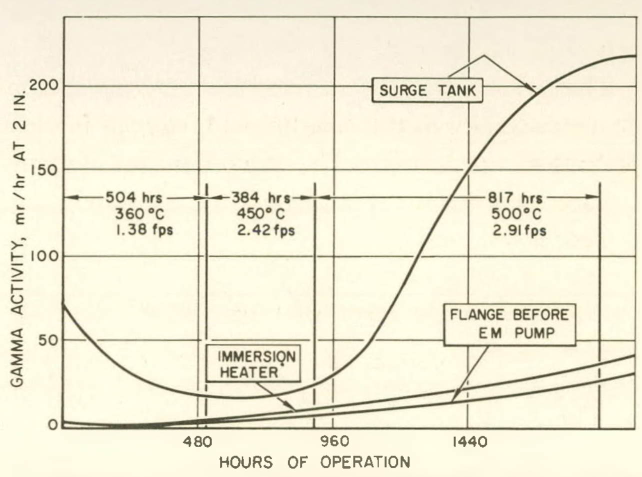

Figure 8. Activity Buildup; Dynamic Loop Test with Pre-Irradiated Uranium Specimens

2.4.3 Loop Tests, Defected-Clad Specimens

Additional experiments have been conducted at Argonne National Laboratory in which a prototype fuel pin for the second Experimental Breeder Reactor (EBR II) was exposed to flowing

TABLE 6

LOOP CORROSION TESTS ON UNIRRADIATED
AND IRRADIATED URANIUM

Specimen Dimensions	Irradiation History	Test History	Oxygen Content	Observations
1/8″ diam. by 1 1/4″ long	None	781 hrs total, in 8-hr increments; 400°-500°C; flow 8 ft/sec	0.061 to 0.001 wt. % (610 to 10 ppm); mostly between 0.008 & 0.001 wt. %	Average corrosion rate; —616 mg/cm²-mo; specimens lost a total of 6.7 gm or 18.9% of initial weight.
1/8″ diam. by 1 1/4″ long	0.006 to 0.02% burnup	1705 hrs, continuous: 504 hrs at 360°C; then 384 hrs at 450°C; then 817 hrs at 500° C; flow varied from 1.4 to 2.9 ft/sec	0.008 to 0.001 wt. % (80 to 10 ppm); usually near 0.004 wt. %	Gamma radiation level near surge tank rose from 20 mr/hr at 500 hrs to 200 mr/hr at 1705 hrs, increasing with temperature and with flow rate.

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sodium through a small hole drilled in the pin cladding.[15] The results of a 3500-hour run at about 540°C, made with an irradiated uranium slug, and with sodium flowing past the defected cladding at 35-40ft/sec in a closed loop, indicated that corrosion was undetectably low.

The slug used was normal uranium, 0.164 inch in diameter by 12.2 inches long (0.416 cm by 36.1 cm). The cladding was Type 304 stainless-steel tubing, 0.172 inch ID by 0.188 inch OD by 18 inches long (0.437 cm by 0.477 cm by 45.7 cm). The radial annulus, 0.004 inch (0.01 cm) thick, became filled with sodium in the course of operating the test. The tubing was closed at top and bottom by welded plugs, except that the top plug contained a drilled hole 0.04 inch (0.1 cm) in diameter. The assembled fuel pin was mounted, in a loop constructed of stainless steel, so that the hole was at the downstream end. The loop contained about 10 liters of sodium.

Oxygen concentration in the loop was reduced by cold-trapping to 0.002 weight percent (20 ppm) before operation of the test section began, and was subsequently maintained at that value. Temperature at the test section was maintained usually at 540°C, except that at weekly intervals the temperature was briefly lowered to 250°C in order to promote the "breathing" of sodium through the drilled hole into and out of the annular space. In all, fourteen temperature cycles were made during the test. No radioactivity was detected at any time, either in sodium samples withdrawn at weekly intervals or in surveys of the loop exterior.

The lower corrosion rate inferred from this defected-cladding experiment, compared with that observed in the previous loop corrosion test, may be explained by differences in the uranium environment. These include the facts that no part of the uranium was directly exposed to flowing sodium and that the oxygen content of the sodium was at all times very low (0.002 wt. %).

2.5 *Effects of Radiation on Corrosion*

Radiation has no apparent effect on the corrosion rate of uranium by sodium or by NaK at temperatures up to about 600°C. Evidence for this conclusion is available from four different experimental sources.

2.5.1 *Foil Experiments (Knolls Atomic Power Laboratory)*

Early experiments with highly enriched uranium foils irradiated to burnup of 0.42 to 10.8 atomic percent, in sodium at 450°C, resulted in disintegration of the foils.[16] That this was a fission effect in the enriched uranium, and not a radiation-corrosion effect, was demonstrated by the following check experiments. Foils identical in dimensions to the enriched ones, but made of natural and of highly depleted uranium, were exposed in sodium contained in the same capsule material (iron). Duration of run, temperature, and irradiation conditions were the same as in the enriched foil runs. The normal and depleted foils were found after test to show only relatively minor surface effects. No disintegration occurred. Oxygen content was probably no more than 0.01 weight percent in all experiments.

2.5.2 *Cyclotron Irradiation (Atomics International)*

A specimen of alpha-rolled uranium was irradiated, while immersed in sodium at bulk temperatures near 475°C, with protons whose energy at the sodium-uranium interface was 5 Mev.[17] This is below the energy at which protons can cause fission in uranium. The uranium and sodium were contained in a Type 347 stainless-steel capsule, provided with a thin window to admit protons, obtained from the 60-inch cyclotron at the University of California at Berkeley.

After 64 hours at temperature, under an irradiation of 121 microampere-hours, the capsule was opened for examination. No weight change was detected in the uranium specimen. No alpha activity was detected in the sodium. It is concluded that no corrosion occurred, even though post-run metallographic examination of the uranium showed that the irradiated surface had been heated briefly at least to the alpha-beta transition temperature, about 660°C, at some interval during the run.

2.5.3 Slug Irradiation (Argonne National Laboratory)

A uranium slug 0.364 inch in diameter by 1 inch long (0.92 cm by 2.5 cm), immersed in NaK in a Type 347 stainless-steel capsule, was irradiated for a period of 30 days in the central thimble of the CP-3 reactor.[18] The temperature was approximately 375°C. A weight loss of 0.7 mg was observed, corresponding to a corrosion rate of the order of —0.1 mg/cm²-mo. This rate is less than that observed in the absence of radiation (see Table 4). (In light of the difficulty of making accurate weighings of irradiated uranium in a hot cell, perhaps the safer conclusion is that the corrosion rate is not greater than in unirradiated tests.)

2.5.4 EBR-I Post-Meltdown Observations

Observations have been made on the core of EBR-I, which was removed from the reactor following an experimental power excursion that resulted in partial melting of the core. Temperature at the fuel-NaK bond interface was in the range 500-600°C in experimental operation just prior to the excursion. The fuel was in the form of cast slugs of U-2 wt. % Zr alloy, 0.364 inch diameter by 1.9 inch long (0.92 by 4.8 cm), bonded by a layer of NaK to the thin-walled stainless-steel cladding. Post-removal examination indicated no evidence of corrosive attack on the fuel alloy in elements where no cladding failure occurred.[19] Extensive formation of eutectics between uranium and the constituents of the stainless-steel

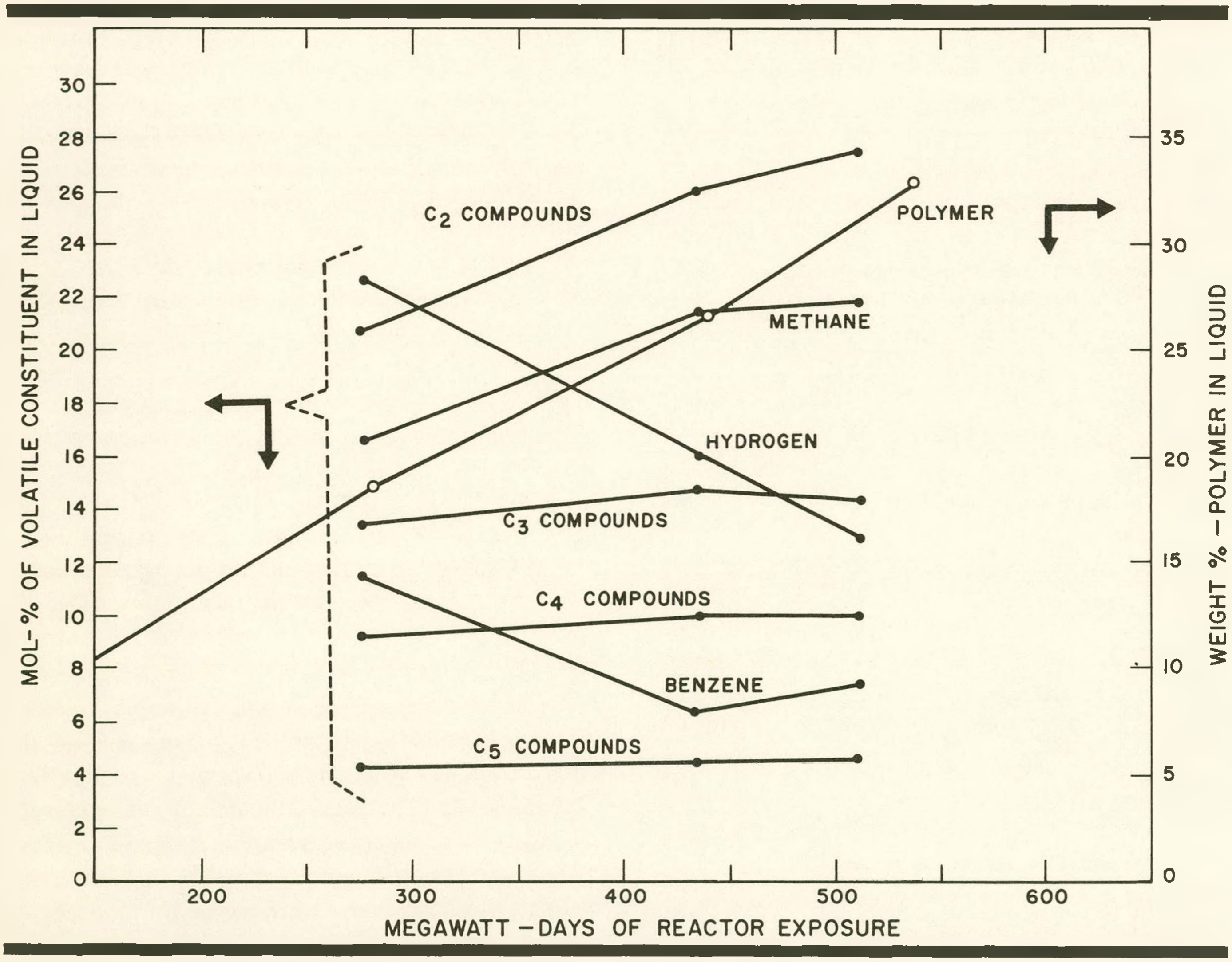


Figure 9. Principal Solutes in Santowax OM Exposed in MTR

cladding indicates that the temperature attained during the excursion exceeded 750°C.

3. CORROSION IN ORGANICS

The poor heat-transfer characteristics of the polyphenyls—for example, thermal conductivity of about 0.07 Btu/hr-ft-°F (2.9×10^{-4} cal/sec-cm-°C)—as well as radiation decomposition rule out the use of these organics as more or less static liquid bonds in direct contact with the fuel metal. Fuel elements for organic moderated reactors are metal-clad. The Organic Moderated Reactor Experiment (OMRE) operates with Type 304 stainless-steel-clad plates;[9] and the use of aluminum cladding is under consideration in other organic moderated reactors.[20]

Contact between fuel metal and the organic coolant can occur, therefore, only as a result of cladding failure. There have been rather few experimental investigations that have been aimed at determining corrosion rates. None is known that duplicates exactly the conditions surrounding an actual cladding failure in a reactor.

3.1 Radiolysis and Pyrolysis of Polyphenyls

An organic coolant in an operating power reactor presents a somewhat complex chemical environment. From studies of the radiation chemistry of polyphenyls at elevated temperatures, it has been established that the liquid reacts to form (1) gaseous products (principally hydrogen), (2) solid polymeric materials, which remain dissolved in the liquid up to certain concentration levels, and (3) some elemental carbon. Listed in Table 7 are a few properties of some organic coolants that either have received consideration or are actually being used in reactor experiments. Recent reactor experiments in the United States have been principally concerned with biphenyl, isopropyl biphenyl, and the eutectic between ortho- and meta-terphenyl.

The changes in composition of an organic, induced during exposure in an operating reactor, are illustrated in Fig. 9.[21] The curves show the changes in percentages of some of the principal radiolytic and pyrolytic products dissolved in Santowax OM, as a function of exposure in the Materials Testing Reactor (MTR) at Idaho Falls. Also shown is the increase in concentration of polymeric material (defined as having a boiling point above that of the starting material). In this experiment, the Santowax OM was pumped through a loop built of mild steel piping, past a heater section located near the core of the MTR. The heater section consisted of a stainless-steel-clad enriched-uranium fuel element. The system was initially pressurized with nitrogen at 200 psi, and maintained near that pressure. The temperature range was 550 to 600°F (288 to 315°C). Neutron flux at the hot zone was near 10^{13}/cm^2-sec.

All the products listed as well as the parent material show at least a thermodynamic possibility of reacting with uranium. Hydrogen, however, is probably the most important constituent in such reactions.

3.2 Corrosion in Static Systems

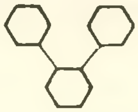
Impurities dissolved in polyphenyls, principally air and water, account for the corrosion observed on uranium at relatively low temperatures. Figure 10 shows macrophotographs of metal specimens after exposure in several different fluids for periods up to two months, over the temperature range from about 70 to 350°F (about 20 to 177°C),[22] taken from studies at Atomics International. The flaky deposit, which was only loosely adherent, was identified by X-ray diffraction as UO_2. Also shown in Fig. 10 is a photomicrograph of the surface structure, taken after a one-week exposure in Santowax-R at 350°F (177°C). The weight gain rate for this specimen was 0.006 mg/cm^2-hr (equivalent to 4.5 mg/cm^2-mo), but there was evidence that the rate accelerated with time. Use of nitrogen ~~of~~ or CO_2 instead of air as cover gas, reduced the rate by a factor of ~~10~~.[23] TEN.

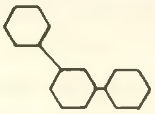
In the above tests, specimens were cut from as-cast depleted uranium rods into disks ¾ inch diameter by ⅛ inch (1.9 by 0.32 cm; surface area = 7.6 cm^2). The disks were electrolytically etched, cleaned, and dried, and immediately immersed in the liquid organic contained in a heated vessel that was open to air. The liquid was agitated by a stirrer, which provided circulation over the entire surface of the specimens mounted in a rack. The organic layer over the specimens was about 10 cm thick.

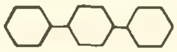
TABLE 7

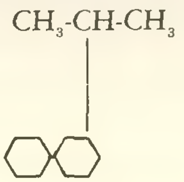
SOME PROPERTIES OF ORGANIC MODERATOR-COOLANTS

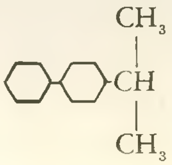

Biphenyl
$C_{12}H_{10}$


Ortho-Terphenyl
$C_{18}H_{14}$


Meta-Terphenyl


Para-Terphenyl


Meta-Isopropyl
Biphenyl
$C_{15}H_{16}$


Para-Isopropyl
Biphenyl

	Biphenyl	Santowax-R[a]	Santowax-OM[b]	Mono-Isipropyl[c] Biphenyl	Water
Melting point (°C)	70	60 to 145	38	—40	0
Boiling point (°C)	255	371	343	290	100
Vapor pressure (psia) at 620°F/327°C	54	6	11	35	1794
Vapor pressure (psia) at 800°F/427°C	220	38	57	190	(supercritical)
Hydrogen density (10^{22} atoms H/cm^3) at 620°F/327°C	3.04	3.18	3.18	3.74	2.16

[a] Commercial mixture of isomeric terphenyls

[b] Commercial mixture of orth- and meta-terphenyls (approx 2:1) plus some para-terphenyl

[c] Commercial mixture of 62% meta- and 38% ortho-terphenyl

3.2.1 Corrosion in Chlorinated Biphenyl

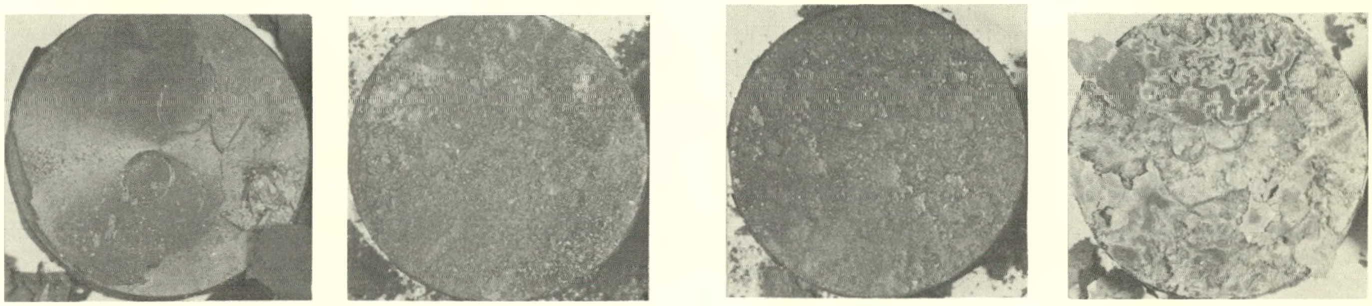
Static corrosion of uranium in "Arochlor 1248," a commercially available mixture of chlorinated biphenyls, was investivated over the temperature range 60 to 310°C while exposed to air and inert atmospheres.[24] Results are given in Table 8. Uranium specimens were exposed in 200 cm^3 of organic in glass vessels, open to the air (except that tank helium was passed over the liquid surface in the last two runs). Corrosion rates listed are for stripped specimens.

The product was identified by qualitative chemical tests as a mixture of UO_2 and a soluble chloride, probably UO_2Cl_2.

There is no interest in using chlorinated biphenyl as a reactor coolant for reasons other than corrosion of fuel metal. The data in Table 8 do point up

Mono-isopropyl biphenyl
Room temperature (~20°C)
Not stirred
Exposure—2 months

Portion of surface (500x)
Santowax R, 350°F (177°C)
Stirred
Exposure—1 week



Biphenyl, 200°F (93°c)
Stirred
Exposure 1 month

Same

Exposure—2 months

Santowax R, 350°F (177°c)
Stirred
Exposure 1 month

Same

Exposure—2 months

Figure 10. Uranium Immersed in Organics, in Vessel Open to Air.

the desirability of eliminating chloride impurity from polyphenyls for coolant use.

3.2.2 *Corrosion in Biphenyl*

An extensive series of experiments was performed at Argonne National Laboratory on corrosion of uranium and several of its alloys in biphenyl under static conditions over a temperature range from 500 to 750°F (260 to 400°C).[25] Tests were performed in 100 cm^3 capacity, stainless-steel (Type 304 or 347) autoclaves. Specimens were held in stainless-steel racks that permitted free access of liquid to all but a very small part of the specimen area, as shown in Fig. 11. Specimens were cut from stock to a size approximately 1½ by ¾ inch (3.9 by 1.9 cm), with thickness from 0.059 to 0.071 inch (0.15 to 0.18 cm).

TABLE 8

CORROSION OF URANIUM BY "AROCHLOR"

Temperature (°C)	Atmosphere	Exposure (hrs)	Corrosion Rate (mg/cm^2-mo)
60	Air	742	5.3
100	Air	598	33.4
200	Air	286	277
200	Helium	191	131
310	Helium	48	655

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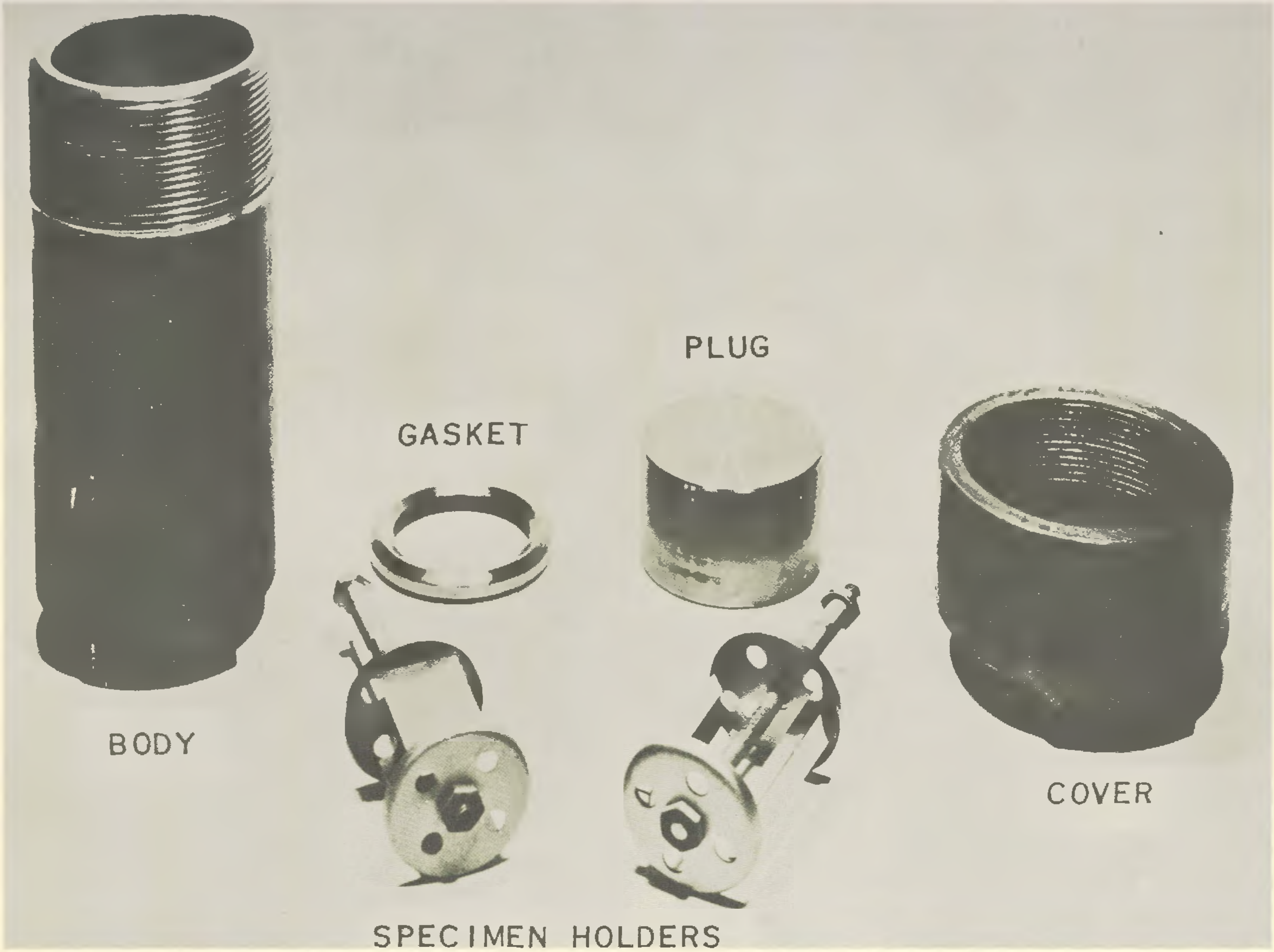

Figure 11. Autoclave Components

Wherever possible, the original stock was used for specimens at all temperatures. After scrubbing, careful drying, and degreasing, the specimens were loaded into the autoclaves.

In all tests, the biphenyl was de-aired by heating it to boiling (or near boiling) in the autoclave, which was then closed as soon as possible. Some tests were performed under a blanket of nitrogen gas initially at 515 psia (35 atm). Autoclaves used in the latter tests were provided with a pressure gage and vent line to permit maintenance of pressure by bleeding off gas. The biphenyl was commercial grade, and the same charge, without addition, was used throughout the test, wherever possible.

At intervals through the runs (some of which lasted over 6900 hours), the autoclaves were opened to permit removal of specimens, and then quickly closed. Specimens were degreased, dried, weighed, and then returned to the autoclaves, using the same de-airing procedure as on initial loading. The observed corrosion rates for fuel and for several structural materials are summarized in Table 9 for runs made without added cover gas.

The data listed in Table 9 are average rates, calculated from measured weight changes over the entire test interval. Where duplicate specimens were run, results check within 10 to 35 percent. The observed decreased corrosion rates at higher temperatures may reflect different metallurgical history (as well as composition), which was not known for all

TABLE 9

STATIC CORROSION IN BIPHENYL(a)

Material	Weight Change Rate(b) (mg/cm^2-mo)		
	500°F (260°C)(c)	680°F (360°C)(d)	750°F (400°C)(e)
Uranium	−4.06	(f)	−2.73
U-2 wt. % Mo	−3.12	(g)	−2.29(h)
U-2 wt. % Zr	−4.82(h)	−5.14(h)(i)	
U-5 wt. % Zr	−3.58	−1.87(i)	
U-5 wt. % Zr-1.5 wt % Nb	−0.369	−1.55(i)	
Zr-2.5 wt. % Sn-9 wt. % U	+0.016	−1.84(i)	
Al-8.2 wt. % U	−0.003	−0.004(j)	
Al, Type 2S	−0.001	−0.007	
Stainless steel, Type 347	−0.003	−0.003	
Zircaloy-2	+0.017	+0.224	+0.252

(a) No added cover gas.

(b) Average rates for entire test period.

(c) First four materials in this column were exposed for 4508 hrs; last six, 4463 hrs.

(d) Temperature during all these runs was also maintained at 750°F over an appreciable fraction of the total exposure.

(e) Total exposure 3825 hrs: 3562 hrs at 750°F, 263 hrs at 680°F.

(f) Cracking noted after 1163 hrs; partial disintegration after 2310 hrs.

(g) Blistering and cracking noted after 2310 hrs; partial disintegration after 3094 hrs.

(h) Average of two determinations.

(i) Total exposure 6919 hrs: more than half of this at 750°F.

(j) Total exposure 4718 hrs: 3094 hrs at 680°F, 1624 hrs at 750°F.

stock; or it may reflect the effects of removing specimens for weighings during the runs. Rates determined from the intermediate weighings showed some scatter, even on the same specimen.

The uranium corrosion rate at 500°F, −4.06 mg/cm^2-mo after 4508 hr, is to be compared with an earlier Argonne observation[26] after 692 hr in de-aired commercial biphenyl, −8.3 mg/cm^2-mo.

On all specimens where significant corrosion occurred, rather loose, powdery deposits were found. Generally, these were not identified. Under the test conditions, some carbon and tar from pyrolysis of the biphenyl is to be expected. The corrosion products on both the U and U-Mo alloy that partly disintegrated in the 680°F run were found by X-ray diffraction to contain UC. This was verified by chemical analysis. Cause of the failure of these two specimens was not established.

A few corrosion tests were made in biphenyl under an initial pressure of 515 psia (35 atm) of nitrogen gas. After 2029 hours at 500°F, the average weight change rate for the Al-8.2 wt. % U alloy was +0.006 mg/cm^2-mo. However, duplicate specimens of U-2 wt. % Zr alloy disintegrated after 337 hours. X-ray diffraction and chemical analyses established the corrosion product of the latter alloy as UN_2.

3.2.3 *Corrosion in Ortho-Terphenyl*

The terphenyls have higher boiling points than biphenyl (see Table 7). They are also more resistant to pyrolysis, and (particularly the para-isomer) more stable under irradiation. The greater chemical inertness implied by the last two properties should permit exposure to uranium at higher temperatures than in biphenyl, without increase in corrosion rate.

Preliminary survey tests over the temperature range 700 to 900°F (371 to 482°C) were made with uranium and thorium immersed in o-terphenyl contained in stainless-steel capsules sealed with an argon gas atmosphere.[27] Each capsule contained one specimen each of uranium, thorium, and also aluminum. Capsules were opened after 2, 4, 6, and 8 weeks at temperature. Observations are summarized in Table 10.

3.2.4 *Corrosion in Mono-Isopropyl Biphenyl*

The greater liquid range and hydrogen density of mono-isopropyl biphenyl (MIPB), compared to biphenyl, are advantages in reactor application, although the presence of the alkyl side-chain makes this compound less stable than biphenyl toward both pyrolysis and radiolysis.

At Hanford Atomic Products Operation, screening experiments were made with unclad and defected-clad uranium specimens, exposed to MIPB in stainless-steel containers at temperatures up to 400°C.[28] In these experiments, uranium specimens $\frac{3}{4}$ by $\frac{1}{2}$ by $\frac{1}{8}$ inch (1.9 by 1.3 by 0.32 cm; surface area $= 7$ cm^2) cut from beta heat-treated bar, were immersed in about 50 cm^3 of MIPB in a container of about 100 cm^3 volume. Both normal and pre-irradiated uranium specimens were used; they exhibited no differences in behavior in these tests.

3.2.4.1 *Results with Unclad Uranium*

The results of the experiments with unclad uranium indicate that hydrogen pressure determines the extent of the reaction. Attack on the uranium was limited to relatively light surface corrosion, provided the pressure did not exceed a threshold

TABLE 10

STATIC CORROSION IN O-TERPHENYL

Material[a]	2 Weeks	4 Weeks	6 Weeks	8 Weeks
700°F (371°C)				
Uranium	−0.5[b]	−0.1	0.0	0.0
Thorium	−4.6	−1.5	−0.8	−0.6
800°F (427°C)				
Uranium	−0.4	−0.7	−4.5	[c]
Thorium	−3.3	[d]	−15.5	[c]
900°F (482°C)				
Uranium	+1.0	[e]		
Thorium	+75.0	[e]		

[a] The aluminum specimens were essentially unchanged in all tests.

[b] Weight change rate, mg/cm^2-mo, for specimen removed after indicated exposure.

[c] Specimen disintegrated.

[d] Partial disintegration.

[e] Tests discontinued because of pyrolysis of organic.

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value, which increased with temperature. The data are summarized in Table 11. The threshold for reaction at 300°C appears to be below 1 atm. At 350°C, it is between 55 and 65 psia; at 375°C near 165 psia; and at 400°C, near 225 psia. In all cases, the only corrosion product found was uranium monocarbide; this was identified by X-ray diffraction and verified by chemical analysis.

Hydrogen, methane, ethane, and ethylene are among the principal pyrolysis products of MIPB that remain in solution. The role of pressure in the corrosion reaction has been taken[28] to indicate that uranium hydride, UH_3, is an intermediary in the corrosion process. No hydride was found in these tests; but the formation of UH_3 by reaction of uranium metal with a hydrogenated aromatic (tetralin) has been reported

TABLE 11

REACTION OF UNCLAD URANIUM WITH MIPB

Temperature (°C)	Maximum Pressure (psia)	(atm)	Exposure (days)	Observations
300	14.7	(1)	106	Surface Attack
350	55	(3.7)	28	Surface Attack
	65	(4.4)	39	¼ Destroyed
375	125	(8.5)	6	Surface Attack
	175	(11.9)	9	½ Destroyed
	185	(12.6)	13	Surface Attack
	175	(9.9)	14	¼ Destroyed
	295	(20.0)	14	Destroyed
	185	(12.6)	20	½ Destroyed
400	115	(7.8)	1	Surface Attack
	145	(9.9)	2	Surface Attack
	205	(13.9)	3	Surface Attack
	215	(14.6)	7	Surface Attack
	215	(14.6)	11	Surface Attack
	215	(14.6)	14	Surface Attack
	215	(14.6)	21	½ Destroyed
	195	(13.3)	25	Surface Attack
	225	(15.3)	37	Surface Attack
	225	(15.3)	44	Surface Attack
	225	(15.3)	59	Surface Attack
	285	(19.4)	5	¼ Destroyed
	440	(30)	5	½ Destroyed
	515	(35)	5	¾ Destroyed
	735	(50)	7	Destroyed
	900	(60)	7	Destroyed
	1000	(70)	19	Destroyed

elsewhere.[29] Also, UH_3 has been found to react with C_2H_4 (ethylene) to form a carbide, possibly UC.[30]

It may be seen from Table 9 that the uranium specimens in biphenyl showed a weight loss of less than 15 mg/cm^2 after 160 days at 400°C. The pressure in the capsules used in these experiments was close to, if not greater than 225 psia. Comparison with the results in Table 11 leads to the conclusion that biphenyl is less corrosive than MIPB.

3.2.4.2 *Experiments with Defected-Clad Uranium*

To assess the consequences of defective cladding on a fuel element, tests were made with uranium slugs clad with Type 2S aluminum. Slugs were machined from beta heat-treated rod to the following dimensions: 0.5 inch diameter by 2 inches long (1.3 by 5 cm). The cladding was closed at both ends, except that a 1/16 inch diameter (0.16 cm) hole was drilled through to the uranium at one end. Each slug was immersed in MIPB in a stainless-steel pressure vessel. Table 12 contains a summary of the experimental results. It appears that the reaction rate through a relatively small opening in fuel element cladding would be slow enough, in practical reactor operation, so as not to require immediate shutdown for replacement.

3.2.5 *Corrosion in Dynamic Systems*

Specimens of Zr-7 wt. % U alloy, along with other materials, were exposed in a large loop to biphenyl at 800°F (427°C), at flow rates up to 27 ft/sec (8.2 m/sec) for a total of 60 days.[31] The loop, which was constructed of carbon steel, is shown schematically in Fig. 12. This work was performed at the Mine Safety Appliances Company.

The loop was charged with about 1000 lb (465 kg) of commercially pure biphenyl. Water content of the biphenyl was between 0.005 and 0.015 weight percent during the first 30-day run. Oxygen impurity was not measured. The loop was initially pressurized to 315 psia with nitrogen gas. As the operation progressed, pressure was maintained at this value by venting, so that the nitrogen was diluted somewhat by gas formed by pyrolysis.

The Zr-7 wt. % U specimens were pickled, washed, dried, and weighed prior to insertion in the loop. Specimen dimensions are shown in Fig. 13, which shows schematically the arrangement of 18 specimens (two of each material) in a holder, and also identifies the other materials tested. Six holders were located in each of the five velocity sections of the loop. Specimen surface area was 21.1 cm^2.

After exposure, specimens were cleaned with solvents, but not stripped to bare metal, and reweighed. Results of the first 30-day run are summarized in Table 13. Data for structural materials are included for comparison.

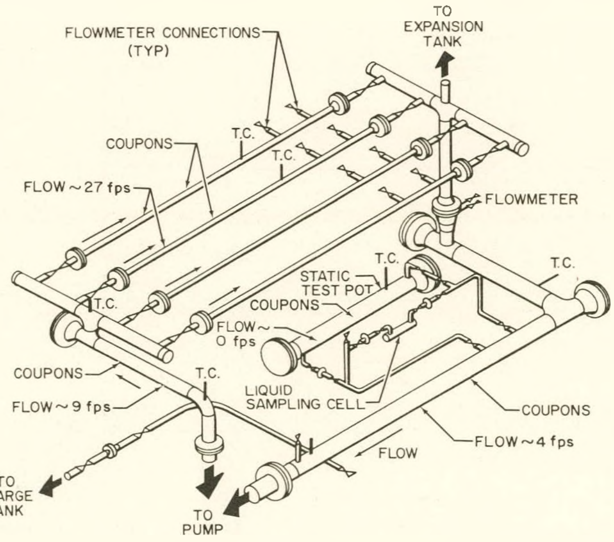

Figure 12. Biphenyl Dynamic Corrosion Loop

The surface of the Zr-7 wt. % U specimens was pitted and blistered. This was different from the result reported for the Zr-2.5 wt. % Sn-9 wt. % U alloy in the static tests (Table 9), where a fine, powdery deposit was observed. Accurate comparison obviously can not be made where alloy compositions differ; however, it should be noted that the static rate for the uranium alloy in Table 13 (at 800°F) is less than that reported for the ternary alloy at 680°-750°F in Table 9.

TABLE 12

REACTION OF DEFECTED-CLAD URANIUM WITH MIPB

Temperature (°C)	Pressure (psia)	Pressure (atm)	Time (days)	Observations
350	55	(3.7)	12	No attack
	95	(6.5)	19	No attack
	115	(7.8)	34	Starting to swell at hole
400	135	(9.2)	2	No attack
	<215	(<14.6)	11	No attack
	<215	(<14.6)	21	No attack
	<215	(<14.6)	37	No attack
	<215	(<14.6)	56	No attack
	245	(16.7)	4	No attack
	425	(28.9)	7	No attack
	575	(39.1)	12	Swelling at hole
	595	(40.5)	17	Badly swollen
	617	(42.0)	19	Badly swollen
	695	(47.2)	7	Swelling at hole

TABLE 13

DYNAMIC CORROSION IN BIPHENYL AT 800°F (427°C)

Material	Weight Change Rate (mg/cm^2-mo)[a]				
	27 ft/sec		9 ft/sec	4 ft/sec	Static
	Position 1	Position 2			
Zr-7 wt. % U	+3.10	+2.28	+2.28	+2.52	+1.41
Carbon Steel (A 212)	+0.08	+0.05	+0.38	+0.22	+0.18
Zircaloy II	+2.59	+2.70	+2.88	+1.88	+2.62

[a] 30-day run.

During the operation of the loop for a second 30-day period under essentially the same conditions as for the first, the temperature accidentally was permitted to exceed 1012°F (535°C) for an undetermined interval, probably short. On post-run examination, the U-Zr alloy specimens were found to be dimensionally distorted and heavily coated by a layer of brown, loosely-adherent material. The coating probably consisted of a mixture of zirconium hydride and oxides of uranium and zirconium. In general, all the zirconium metal and alloy specimens were found to be in comparably poor condition.

3.2.6 Effects of Radiation on Corrosion

No experimental data are available on systems under irradiation; only a few tests have been

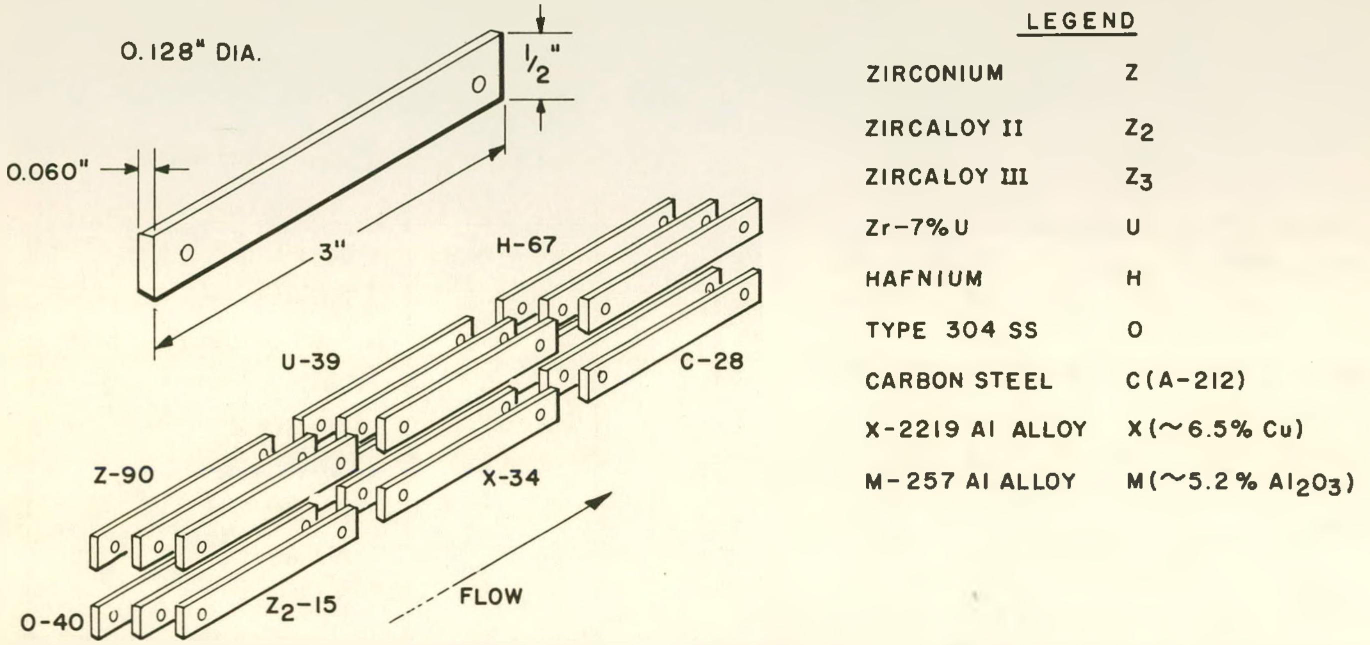

Figure 13. Specimens for Biphenyl Dynamic Corrosion Loop

made with pre-irradiated fuel.[28] These indicate no detectable difference from unirradiated material.

4. CONCLUSIONS

Metal Fuels in Sodium and NaK

Data obtained from experiments under widely varying laboratory conditions suggested an acceptably low corrosion rate, which has been verified in reactor experiments (EBR-I, SRE). Corrosion products UO_2 and UO have been identified, arising from chemical reaction with impurity oxygen in the liquid metal. Available data indicate a corrosion rate from 1 to 10 mg/cm^2-mo in static liquid metal, of oxygen content 0.01 weight percent. Older data give the higher values. Tests at temperatures up to 750°C are included in the above rate range.

The corrosion rate in dynamic systems depends on local conditions: fluid velocity, the degree of contact between the metal and liquid metal, temperature and temperature differences in the loop, and—most important—the oxygen content of the liquid metal. Corrosion rates near ~600 mg/cm^2-mo have been obtained for uranium at 500°C in loop experiments.

Data are too slight to determine the most corrosion-resistant among uranium, high uranium alloys, and thorium. Thorium appears to be more resistant than uranium at 750°C in a static system. Low uranium alloys, such as Al-U, follow the corrosion pattern of the major constituent.

As-cast, heat-treated, and rolled metal exhibit no difference in corrosion rate in liquid metal.

There is no effect of radiation on the corrosion rate, at temperatures to 600°C.

Use of sodium or NaK as a liquid bond inside a metal clad fuel element appears satisfactory from a corrosion standpoint, at least to 750°C.

Metal Fuels in Organics

Relatively few investigations have been made on these systems.

Uranium is corroded by dissolved air and water when immersed in organics (biphenyl or derivatives) at temperatures as low as 200°F (93°C). Uranium dioxide (UO_2) has been identified as a corrosion product. Chlorinated biphenyl corrodes uranium even in the absence of oxygen or water.

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In static biphenyl, the corrosion rate of uranium is about 3 mg/cm^2-mo at 400°C. Uranium monocarbide (UC) has been identified as a corrosion product in these systems. When nitrogen is used as a cover gas, UN_2 may be formed.

Among the high U alloys, U-2wt. %Mo is slightly more resistant to static 750°F (400°C) biphenyl than pure uranium; and U-Zr alloys are slightly less resistant. Under these same conditions, the corrosion rate of Al-8.2wt. %U is 0.004 mg/cm^2-mo (less than that observed for 2S aluminum). Exploratory static tests at 700°F (371°C) indicate that uranium is more resistant than thorium to corrosion in ortho-terphenyl.

Flow velocity increases the corrosion rate of a Zr-7wt. %U alloy in biphenyl at 800°F (427°C) from 1.4 mg/cm^2-mo (static) to 3 mg/cm^2-mo (27 ft/sec).

From a corrosion standpoint, and on the basis of available data, no fuel alloy can be recommended for use without cladding in an organic-cooled reactor. Corrosion rates are low enough to ensure that no operating problem would result if there were a cladding failure, with almost any metal fuel alloy.

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ERRATA

Page 13, paragraph 3.2, line 16:

"nitrogen of CO_2" *should read* "nitrogen or CO_2"

Page 13, paragraph 3.2, line 17:

"factor of 10" *should read* "factor of ten"

Page 20, paragraph 3.2.5, line 1:

"U–7wt.% Zr" *should read* "Zr–7wt.%U"

Page 23, third paragraph, line 2:

"Zr–8wt.%U" *should read* "Zr–7wt.% U"

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