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 II AUTOCLAVE 2-19.

TO: E. G. Bohlmann

FROM: K. S. Warren, R. J. Davis and G. H. Jenks

 Work done by: H. A. Fisch, G. H. Jenks, D. T. Jones, A. R. Olsen, F. J. Walter,
 K. S. Warren, R. J. Davis, L. F. Woo, and H. C. Savage
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ABSTRACT

In order to test the effect of the molybdate ion on the corrosion of Zircaloy-2, a 0.16 M uranyl sulfate solution (enriched) containing copper sulfate and 487 ppm of Mo as K_2MoO_4 was autoclaved (bomb Z-19) with rocking at 280° and 300°C for a total of 72 hours in the HB-5 facility of the LITR. The average corrosion rate established by the rate of consumption of oxygen was:

24 mpy at 280°C; power density of 19.0 w/ml

33 mpy at 300°C; power density of 18.2 w/ml.

Virtually all of the molybdenum originally in solution was found in the ZrO_2 film upon opening the bomb: any efficacy of Mo as a corrosion inhibitor was not demonstrated. No further work with molybdates is contemplated.

The penetration by corrosion of two niobium alloys, (85% Zr, 15% Nb and 83.5% Zr, 15% Nb, 1.5% Sn) present in bomb Z-19 as special test specimens, was observed to be about one-half that of the Zircaloy-2.

I. Purpose:

Various materials have been considered as potential inhibitors of radiation corrosion of Zircaloy-2 by aqueous uranyl sulfate solutions in the presence of oxygen. For example, the introduction of chromium as the chromate ion (bombs Z-8 and Z-18), technetium as pertechnetate (Z-11), Li_2SO_4 (Z-21), MgSO_4 (Z-26), CuSO_4 and H_2SO_4 in several experiments as well as varying concentrations of UO_2SO_4 .

Some of the above sulfate additions have shown a marked inhibitory effect on the radiation corrosion of Zircaloy-2. Excess H_2SO_4 is one of these, and the inhibition by this reagent is accompanied by the finding of a smaller amount of uranium in the film than in films from experiments without the excess acid. It is reasonable to expect that the lower pH is responsible for retarding absorption of uranium by the oxide film. The retardation of corrosion by acid may be a result of the smaller amount of uranium in the film and hence the smaller amount of localized fission power density. At the present time it is also considered possible that the effect of H_2SO_4 on corrosion is due to a degree of protection afforded by adsorbed sulfate ion.

Experiments employing 300 g U/l UO_2SO_4 solutions have shown a much lower corrosion rate than 40 g U/l solutions, at similar fission power densities. Again protection of the corroding surface by an adsorbed layer of ions is a possible explanation.

One experiment indicated that the addition of Li_2SO_4 also retarded corrosion.

Kraus, et al.,⁶ have observed anion exchange properties of hydrous zirconium oxide. In particular, strong absorption of sulfate ion was

observed.

It is considered reasonable to expect that a tenaciously absorbed ion might effect the desired inhibition of corrosion. To this end, Z-19, an experiment with added molybdic acid was performed.

II. Experimental:

A. Pre-irradiation Work.

1. Fabrication.--The bomb, specimens and related metal components were fabricated according to Drawing D-19052, bomb type 2² from Zircaloy-2 of the following analysis:

Table I

Composition of Bomb Specimens

	Sample No.	Analysis Wt. %				
		Zr	Sn	Nb	Fe	Cr
Bomb	20	--	1.32	--	0.24	0.045
Pin Rack	42	97.7	1.39	--	0.215	--
Pins (2)	43	97.7	1.39	--	0.215	0.045
Pins (2)	56	83.5*	1.5	15.0	--	--
Pins (2)	57	85.0*	--	15.0	--	--

	Sample No.	Analysis Wt. %					
		Ni	Al	C	H ₂	O ₂	N ₂
Bomb	20	0.01	0.084	0.022	0.0066	0.18	0.003
Pin Rack	42	0.01	0.16	0.043	0.0038	0.035	0.0003
Pins (2)	43	0.01	0.16	0.043	0.0038	0.035	0.0003
Pins (2)	56	---	--	--	--	--	--
Pins (2)	57	---	--	--	--	--	--

* Zirconium Sponge

It should be noted that of the six pins, two were Zircaloy-2, two were of a zirconium-niobium alloy, and two were of a zirconium-niobium-tin alloy.

2. Assembly.-- Component inspection, assembly, pressure testing and loading with fuel solution were conducted in accordance with the standard procedure described in a separate report². Oxygen pressure was supplied by the thermal decomposition of hydrogen peroxide.

3. Solution.-- Pure molybdic acid or molybdenum oxide was not immediately available. As a consequence a method of synthesis was developed which started with ammonium molybdate of adequate purity. The ammonium salt was dissolved in water and passed through a cation exchanger which replaced NH_4^+ with H^+ . A stock molybdic acid solution with a concentration of 1200 ppm was obtained free of ammonium and fluoride ions.

It was found that a precipitate formed when the stock molybdic acid was added to uranyl sulfate solution, dissolving only partially at 110°C . However, heating the slurry to 250°C in a quartz tube resulted in a clear, apparently stable solution. The question of compatibility with hydrogen peroxide was answered by adding H_2O_2 to a sample of the slurry and also to a sample of the 1200 ppm H_2MoO_4 , with the observation that no oxygen was released.

For bomb Z-19, then, 3.868 ml (25°C) of a solution, density 1.0548 g/ml, of the following composition was employed:

0.160 m UO_2SO_4 (93.2% enriched)

0.010 m CuSO_4

487 ppm Mo as H_2MoO_4

in which allowance has been made for the dilution effect of 0.442 ml of 33.68% H_2O_2 .

4. Other Bomb Statistics.-- Bomb geometry and loading conditions determined the following constants for Bomb Z-19 and its solution at 280°C:

Total internal area of bomb, pins and rack	50.34 cm ²
Total capacity of bomb with pins in place	6.48 ml
Volume of solution added (at 280°C)	5.06 ml
Percent of fill (at 280°C)	78%
Ratio of bomb area to solution volume at (280°)	9.96

5. Pretreatment.-- The hydrostatic pressure test² affiliated with the assembly subjected the as-machined interior surfaces of this experiment to 310°C, air saturated water for 6 hours. Extrapolation of available data³ on the corrosion of Zircaloy-2 by high temperature water indicated that about 0.006 mil of metal would be oxidized by this treatment. After the bomb was filled with the above described solution the experiment was operated at 250°C for 17 hr. Very little corrosion during the 17 hr operation was indicated by no significant loss of oxygen pressure. The corrosion penetration from pretreatment is then estimated to be 0.008 mil.

B. Irradiation:

1. Installation.-- Bomb Z-19 and its associated system were placed in the EB-5 experimental access hole of the LTR on May 29, 1956, without noted irregularity.

2. Temperature and Time of Exposure.-- The in-reactor temperature of bomb Z-19 was maintained at 280°C for 53 hr of irradiation and then at 300°C for 19 hr. Readings were taken at the prevailing temperatures only, so that no thermal cycling occurred.

3. Oxygen Pressure.-- During the course of the 72.6 hr radiation the oxygen pressure dropped from 832 psi to 172 psi (measured at 280°C), or

from 343 psi to 97 psi at 25°C. The oxygen pressures measured at various times during the experiment are tabulated in Table II (section III).

4. Radiolytic Gas Pressure.-- The behavior of the radiolytic gas pressure during the run is outlined in the following table:

Cumulative Radiation Time (3 Mw/hr)	Radiolytic Gas Pressure During Reactor Operation (psi)	Temperature (°C)
31	360	280
53	500	280
54	235	300
72	320	300

No anomalous radiolytic gas pressure decrease⁵ was observed. This is typical of experiments which are started at 280°C.

Although there were only a few observations and these are admittedly not very accurate² it is quite apparent that the radiolytic gas pressure was continually increasing during the experiment. If one assumes that the pressure increase during the 280°C portion of the experiment was linear with time, then an initial radiolytic pressure of about 160 psi can be calculated. It appears, then, that the radiolytic gas pressure increased by about a factor of three during the 53 hr at 280°C and another factor of about 1.3 during the 19 hr at 300°C or a total increase of a factor of four.

It should also be noted that the pressure increase occurred both during the 280°C and 300°C portions of the experiment and at about the same rate, i.e., about 35% of the total radiolytic gas pressure per twenty hours. The correlation of copper concentration and radiolytic pressure is discussed later.

5. LTR Operation During Experiment.-- The reactor was operated at the 3 Mw total power level during the entire experiment except for the usual periods of zero power operation. During the 91 hr in which the experiment was in the reactor, the reactor was at full power (3 Mw) for 72 hr. Total time and exposure time at the points when pressure measurements were made are tabulated in Table II (section III).

6. Removal from Reactor.-- The removal was made on June 2, 1956, according to procedure² without noteworthy incident.

C. Post Irradiation Work:

1. Disassembly.-- The bomb was opened according to prescribed procedure² without difficulty, except for loosening the pin rack.

2. Examination of Solution.-- The solution as removed from the bomb (about 5 days after removal from the reactor) was a light-green in color and contained an appreciable amount of precipitate. The rinse solution was cloudy in appearance presumably because of unsettled precipitate. The results of the analysis of the solution and rinse are listed in Table III. The analytical methods used are listed and described in separate reports². The volume of the rinse tabulated is the volume of the rinse solution removed from the bomb and is not necessarily the total volume of rinse solution.

3. Corrosion Specimens.-- The six pins as removed from the bomb were covered with a uniform brass-colored film. The pins were subjected to the standard treatment² i.e., they were rinsed with water and acetone, dried, weighed, defilmed cathodically and reweighed. The pin weights (original and defilmed) are tabulated in section III (Table IV).

It is of interest to note that the niobium alloy samples appeared

similar to the Zr-2 samples as removed from the bomb, i.e., they were uniformly covered with a brass colored scale. After treatment with acetone and drying most of the scale from all specimens popped off. The Zr-2 specimens, as usual, then appeared uniform and dull grey in color. The alloy pins were also uniform but appeared greasy and black. The cathodic defilming operation appeared to work equally well with all pins. Nearly twice as much pickling of the niobium containing pins, compared to the Zr-2 pins, was required to reduce the gross activity to a value not further changed by more pickling. This may indicate only that the niobium containing alloys are less soluble in the pickling solutions².

III. Results:

A. Corrosion Penetration from Oxygen Consumption:

The corrosion penetration as determined incrementally from oxygen pressure measurements is tabulated in Table II. These data are plotted (penetration vs. exposure time) in the attached graph. The slope of the 280°C portion of the curve is 24.2 mpy (at a power density of 19.0 w/ml); that of the 300°C segment is 32.8 mpy (PD = 18.2 w/ml) although it is defined by only two sets of readings.

Since irradiation of bomb Z-19 was conducted at two temperatures, a graph of the depth of surface penetration (calculated from oxygen consumption data) plotted against cumulative radiation time shows a break in the curve where the operating temperature was changed from 280° to 300°C (see graph attached). Corrosion data as given are adjusted so as to represent Zircaloy-2 corrosion only² and to exclude the effect of the niobium alloy present.

Table II

Oxygen Consumption Data

Exposure Time (hr)	Total Time in Reactor (hr)	O ₂ Pressure (psi)	Corrosion* Penetration (mils)
Data taken at the operating Temperature of 300°C			
0	0	878.4	0
53	67.1	397.0	.140
72	90.1	181.0	.215
Data taken at the operating Temperature of 280°C			
0	0	832.0	0
19	24.8	693.0	.044
31	43.4	563.0	.087
53	67.1	389.0	.148
72	90.1	172.0	.229
Data taken at the operating Temperature of 100°C			
0	0	441.0	0
72	90.1	119.0	.212
Data taken at the operating Temperature of 25°C			
0	0	343.0	0
72	90.1	96.5	.206

* This penetration does not include the 0.006 mil estimated as the corrosion during pretreatment.

Table III

Original and Final Chemical Analysis for In-Pile Bomb Z-19

	Original Solution	Irradiated Solution	Rinse	Combined ¹ Precipitates	Film
Volume	3.87 cc	3.2 cc	9.35 cc	---	22.2 mg
U	37.60 mg/ml	35.30 mg/ml	1.94 mg/ml	0.80 mg/total	1.06%
SO ₄	16.32 "	14.45 "	0.65 "	0 "	0
pH	2.3 ²	2.4	---	---	---
Cu	0.630 "	0.285 "	0.011 "	0 "	0.15%
Cr	---	0.029 "	0.030 "	0.08 "	0.35%
Ni	---	0.023 "	0.011 "	0.015 "	0
Fe	---	0.233 "	0.032 "	0.44 "	0.31%
Zr	---	0.072 "	0.009 "	7.10 "	54.1%
Mo	0.487 mg/ml	0	0	0.30 "	1.46%
Pu	---	0			

- (1) Combined Precipitates - All solids from both the solution and rinse are combined, dissolved and analyzed collectively.
- (2) The original solution contained considerable precipitate at room temperature, which dissolved on heating, (see text). The room temperature pH, therefore, is not completely comparable to the final pH or pH's measured for other experiments.

B. Corrosion Penetrations from Pin Weight Changes:

Pin weights, weight losses, and corresponding corrosion penetrations are compared in Table IV with the penetrations calculated from oxygen consumption. Note that the penetrations observed with the 85-15 Zr-Nb and 83-5-15-1.5 Zr-Nb-Sn alloys were respectively 52% and 50% of that observed with Zircaloy-2.

Table IV

Pin Weight Data

Pin	Pin Weight g	Pin Area, cm ²	Weight Loss g	Penetration, mils	Special Material
L	0.5682	2.16	0.0045	0.115	Zr-Nb (85-15)
L'	0.5218	2.16	0.0045	0.116	"
M	0.5068	2.00	0.0039	0.108	Zr-Nb-Sn (83.5-15-1.5)
M'	0.5185	2.03	0.0040	0.110	"
S	0.4850	1.96	0.0077	0.236	Zr-2
S'	0.4824	1.96	0.0068	0.208	"

Average for Zr-Nb Alloy (85-15) 0.116

Average for Zr-Nb-Sn alloy (83.5/15/1.5) 0.109

Average for Zircaloy-2 0.222

Penetration from O₂ data including 0.006 mil estimated penetration during pre-treatment

300°C data	0.221
280°C data	0.235
100°C data	0.218
25°C data	0.212

CORROSION DATA FROM OXYGEN MEASUREMENTS
EXPERIMENT (Z-19) (Zr-2)

C. Power Density

The standard techniques for estimating Zr^{95} activation by slow neutrons⁴ and back calculating slow neutron flux was applied to the six metal pins from bomb Z-19. The average power density in the solution during the periods when the reactor was operating was, in turn, calculated from the slow neutron flux values, assuming a value of 200 Mev of energy dissipated per fission. These results, along with similar values from an estimation of total fissions via analysis for the Cs fission product are tabulated below.

Table V
Slow Neutron Flux and Power Density

Pin No.	Slow Flux, (n/cm ² /sec)	Fission Power Density (280°C), (w/ml)
<u>From Zr⁹⁵ activation:</u>		
L	1.50×10^{13}	19.84
L'	1.55×10^{13}	20.50
M	1.42×10^{13}	18.78
M'	1.48×10^{13}	19.58
S	1.40×10^{13}	18.52
S'	1.27×10^{13}	16.80
Average of pins	1.44×10^{13}	19.0
<u>From Cs fission product analysis:</u>		
Solution	0.68×10^{13}	9.0

The power density at 300°C, similarly calculated from Zr^{95} activation was 18.2 w/ml. The lower power density at the higher temperature is due only to the solution density change with temperature.

D. Material Balance

Material balances, to add confidence to the chemical analysis of solution and film removed from the bombs, have been attempted from time to time but not often successfully. The following treatment may also require revision at some future time. The calculations are explained below and the results are tabulated in Table VI.

1. Material in Irradiated Solution.

$$\text{mg ion in soln.} = (\text{original soln. vol.}) \times (\text{analytical concentration in irradiated soln.})$$

$$\text{mg U} = 3.87 \text{ ml} \times 35.30 \text{ mg/ml} = 136.6 \text{ mg U in soln.}$$

2. Material in Film.-- Two methods, using independent numbers are illustrated here.

Method A: $\text{mg ion in film} = (\text{wt. film collected from pins}) + (\text{pin wt. change on defilming cathodically}) \times \frac{\text{total bomb area}}{\text{pin area}} \times (\% \text{ of constituent})$

$$\text{mg U} = (22.2 + 4.2) \text{ mg} \times \frac{50.34}{12.27} (0.0106) = 1.15 \text{ mg U in film.}$$

Method B: $\text{mg ion in film} = (\text{mils penetration from O}_2 \text{ data} \times \frac{\text{cm}}{\text{mil}} \times (\text{bomb area}) \times$

$$\frac{1000 \text{ mg}}{\text{g}} (\text{density of Zircaloy-2}) \times \frac{\text{ZrO}_2}{\text{Zr}} \times \frac{\% \text{ Zr in ZrO}_2}{\% \text{ Zr in film}} \times$$

(% constituent in film from analysis)

$$\text{mg U} = 0.224 (0.00254)(50.34)(6.55)(\frac{123.22}{91.22}) \times 1000 \times \frac{0.740}{0.540}$$

$$(0.0106) = 3.67 \text{ mg U in film.}$$

Table VI
Material Balance

Material	mg added	mg found							mg found
									mg added
		Soln.	Method A		Method B		Total		
Film	Ppt		Film & Ppt	A	B	Avg.			
U	145.5	136.6	1.15	0.80	3.67	138.6	140.3	139.4	0.96
Cu	2.5	1.1	0.16	0.0	0.52	1.3	1.6	1.5	0.60
SO ₄ ²⁻	63.2	55.9	0.0	0.0	0.0	55.9	55.9	55.9	0.89
Mo	1.88	0	1.58	0.30	5.00	1.88	5.00	3.4	1.81

The reader should be cautioned that the film analyzed was a sample collected from all six pins, including four 15% niobium alloy pins (see section on Assembly). The possibility of varying film compositions is very real, and the assumption that the film over the entire interior area of the bomb had the composition indicated by the analysis may be in error. Furthermore, the temperature of the pins was probably somewhat higher than that of the bomb walls, since 2-3 w/cm² of heat was passing through the wall surfaces.

The material balance for uranium shown in Table VI seems to be satisfactory. The sulfate recovery is also reasonable. It should be noted that 89% of the initial sulfate was found in the irradiated solution as compared to 93% of the uranium. This may indicate that at least as much of the sulfate as uranium is adsorbed on the film.

The low recovery of copper is not particularly extraordinary but the reason for it is not known. The 56% loss of copper in solution is qualitatively in agreement with the approximately four-fold increase in radiolytic gas pressure. The indicated material balance of molybdenum is very bad, but it

should be noted that if one accepts Method A for determining the amount of molybdenum in the film, then the balance is perfect.

The method A calculation is based on the observed film weights and will include only film retained on the surface at the end of the experiment. By comparison, Method B uses oxygen consumption to determine the weight of the film and all of the film, including any which flakes off is included.

IV. Discussion:

This experiment was quite clear-cut in many respects. The oxygen consumption data are very interconsistent and the penetration from oxygen and pin weight loss data agree very well.

The Z-19 bomb operated at about twice the power density of others which contained similar solution but without molybdenum. Direct comparison to judge the effect of molybdenum is therefore not possible. Extrapolation of the data available according to the formula due to Jenks¹, with the most recent values of the constants:

$$CR = 2.45 PD(1 - e^{-95/CR^{1.5}})$$

very strongly indicates that the corrosion rate observed at 280°C was that which one would have expected without molybdenum present. As mentioned previously, the extrapolation was made to twice the power density for which data are available but the success of the Jenks formula for other solutions and temperatures, (using appropriately different constants) makes the extrapolation referred to here¹ reasonable.

It is probable that very little or no molybdenum was left in the solution at the termination of the experiment. The molybdenum found in the

precipitate, i.e., 16% of the total, possibly was in solution until the experiment was cooled, since as described earlier in this paper, the solution used formed a precipitate at room temperature, but became clear on heating to 250°C. It is more likely that much less molybdenum remained in solution. The large amount of zirconium in the precipitate attests to much of the precipitate having been formed from flaked off film. The molybdenum to zirconium ratio in the precipitate (0.041) is somewhat higher than that in the film (0.028). If it is assumed that the flaked off film had the same molybdenum to zirconium ratio as that remaining on the metal, then the observed difference in the ratio between film and precipitate would indicate that only 5% of the original molybdenum was not included in the film. This means that probably no more than 5% of the molybdenum was available in solution at the end of the run.

The small amount of material in solution may have been responsible for the lack of inhibiting effect. However, this seems very unlikely since the corrosion rate observed at 280°C was quite constant, i.e., no inhibition even for a short time was observed. It seems quite clear that molybdenum was adsorbed but did not inhibit corrosion.

It was noted earlier that the radiolytic gas pressure increased nearly linearly with time of exposure and at the end of the experiment was about four times the initial radiolytic pressure. This is only roughly in agreement with the ratio of dissolved copper initially to that in solution finally, i.e., 2.2. It is interesting to note that no particular change in the increase in radiolytic pressure occurred on raising the temperature to 300°C.

About 2.2% of the uranium was found in the film and precipitate combined. This is 50-60% of typical values of the fraction of uranium found in the film at the end of 0.17 m UO_2SO_4 experiments. It appears that the molybdenum retarded the amount of uranium absorbed in the film. It should be noted that this experiment operated at about twice the power density of comparable experiments and at 300°C for 19 hr. One of these two conditions may have contributed to uranium absorption.

Very little data are presently available for corrosion at 300°C and it seems that the 300°C data reported here will have to await new information for comparison. At the present time it is clear that the temperature and power density effects on radiation corrosion are interdependent¹. The general topic of the temperature variable will be treated in a separate report.

Z-19 contained two 85% Zr, 15% Nb pins, two 83.5% Zr, 15% Nb, 1.5% Sn pins as well as two Zr-2 pins. The data presented show very simply that the two niobium alloys corroded about half as much as the Zircaloy-2. More work with the niobium alloys is planned.

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