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IN-PILE-AUTOCLAVE TEST OF ZIRCALOY-2
CORROSION IN $UO_2(NO_3)_2$ SOLUTION AND
OF SOLUTION STABILITY

R. J. Davis
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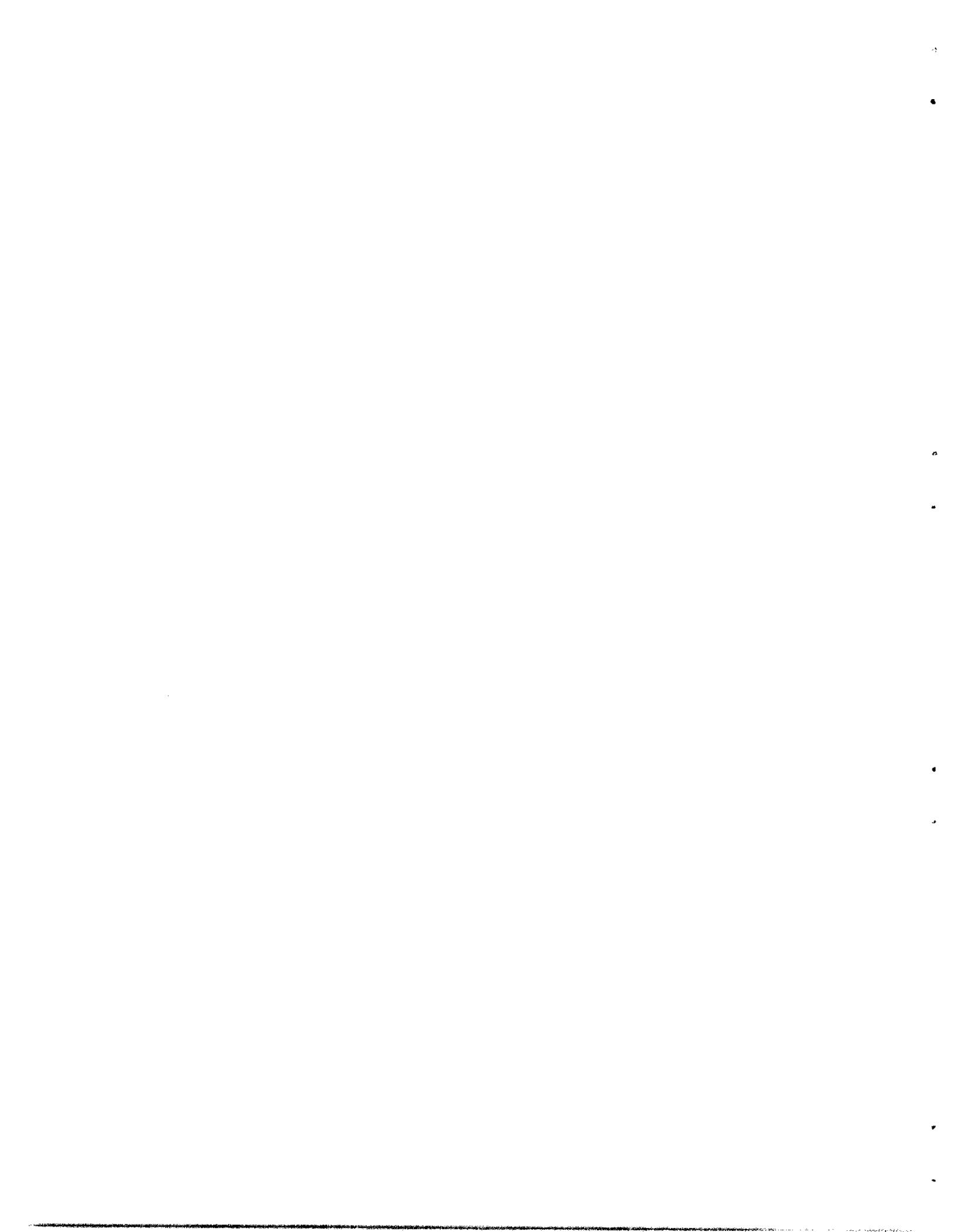
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ABSTRACT

A rocking-autoclave experiment was performed in which a D₂O solution of uranyl nitrate (0.032 m) with Cu(NO₃)₂ and excess DNO₃ was exposed in Zircaloy-2. Low-power low-temperature exposures of short duration were made in order to obtain pressure data from which G_{D₂} and K_{Cu} (225°C) values could be estimated. Exposure at 280°C to the full reactor power was made in five periods, the total irradiation time being 134 hr. Pressure and temperature were followed closely both during and between irradiation periods. Analyses were made of the irradiated solution, the autoclave rinse solution, a large amount of precipitate, and the specimen surfaces.

The value for K_{Cu} (225°C) was estimated to be 1600 to 1700 liters mole⁻¹ hr⁻¹, about three times as large as out-of-pile values found by others. The G_{D₂} value was estimated to be 1.3 to 1.4. The various pertinent pressure and analytical data were not completely consistent but allow estimates of the Zircaloy-2 corrosion rate of 6 to 12 mils/yr for most of the exposure. The corrosion rate appeared to increase during the last 30 hr of exposure, and the final rate was probably 30 mils/yr or more. From various features of the pressure data, estimates of G_{N₂} of 2 × 10⁻³ to 2.5 × 10⁻² were made, which are 7 to 70 times larger than reported values from fission-fragment irradiations of Ca(NO₃)₂ solution. Recombination of nitrogen and oxygen was indicated. If it is assumed that the recombination occurred in the vapor phase, the estimated G_{NO₃} - value was in the range 1 to 3, which is comparable with values for vapor-phase fixation previously reported by others.

* * * * *

1. INTRODUCTION

The possibility of using $\text{UO}_2(\text{NO}_3)_2$ fuel solutions in aqueous homogeneous reactors has recently been reviewed by Marshall.¹ He points out that the nitrate system shows some advantage over the sulfate with respect to high-temperature stability toward two-liquid-phase formation and solubility of fission and corrosion products. Direct experimental information regarding the radiation decomposition of the nitrate ion in $\text{UO}_2(\text{NO}_3)_2$ fuel solutions was not available, but from considerations of the data of Boyle and Mahlman² for radiation decomposition of $\text{Th}(\text{NO}_3)_4$ solutions, Marshall suggests that the radiolytic generation of nitrogen gas may be negligible in the dilute $\text{UO}_2(\text{NO}_3)_2$ solutions which could be employed in reactors.

In an effort to obtain experimental information about the nitrate stability and about other factors of importance in the evaluation of a fuel solution, an in-pile-autoclave experiment with a $\text{UO}_2(\text{NO}_3)_2$ solution was carried out. The other factors investigated were: radiolytic-gas formation and copper-catalyzed recombination, and radiation-induced corrosion of Zircaloy-2 in the nitrate solution.

2. REVIEW OF LITERATURE

No information has been reported previously on the radiation corrosion of Zircaloy-2 in $\text{UO}_2(\text{NO}_3)_2$ solutions.

Recombination of H_2 and O_2 (ref 3) and D_2 and O_2 (ref 4) catalyzed by copper has been investigated out-of-pile by Kelly et al. They found that (1) the activation energy was similar to that in sulfate systems, (2) the K_{Cu} values for light-water nitrate solutions were about half those for

¹W. L. Marshall, Consideration of $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}(\text{D}_2\text{O})$ as a High Temperature Reactor Fuel, ORNL CF-59-5-100 (May 26, 1959).

²J. W. Boyle and H. A. Mahlman, Nuclear Sci. and Eng. 2, 492-500 (1957).

³M. J. Kelly et al., The Effectiveness of Cupric Ion as a Homogeneous Catalyst in the $\text{UO}_3\text{-HNO}_3\text{-H}_2\text{O}$ System for the Recombination of Hydrogen and Oxygen Produced by Radiolytic Decomposition, ORNL CF-59-9-15 (Sept. 3, 1959).

⁴M. J. Kelly, Reactor Chemistry Division, ORNL, private communication.

similar sulfate solutions, and (3) D₂O as solvent reduced the K_{Cu} by another factor of ~2.

As mentioned above, Boyle and Mahlman² report values of G_{N_2} in rather concentrated Th(NO₃)₄ solutions [~ 0.3 to $3 \text{ M Th(NO}_3)_4$]. For fission fragments, G_{N_2} was considerably higher than for fast neutrons or gamma rays, and it decreased rapidly with decreasing concentration of Th(NO₃)₄. Some N₂O was found - as much as about 10% of the amount of N₂. Sowden and Lynde⁵ subjected Ca(NO₃)₂ solutions (0.21 to 4 M NO_3^-) to fission recoils and reported $G_{N_2} = 0.004 (\text{NO}_3^-)^{1.5}$ for the entire concentration range. The G_{N_2} values of Boyle and Mahlman for nitrate concentration within the indicated limits are expressed fairly well by this equation, as are the G_{N_2} values reported⁶ for UO₂(NO₃)₂ ($\sim 1 \text{ M}$) in Los Alamos water boilers. Gas-phase recombination of nitrogen with oxygen has been studied.^{7,8} The G_{NO_2} values increase with increases in the ratio of oxygen to nitrogen and with the addition of water vapor, and are considerably higher at elevated temperatures than at room temperature. Values of G_{NO_2} from 0.3 to 5 were reported. Varying amounts of N₂O were also formed, the average being about half the amount of NO₂. Values of G_{H_2} were also measured by Sowden and Lynde, and these results were expressed by $G_{H_2} = 2.0 - [0.8(\text{NO}_3^-)^{1/3}]$.

3. EQUIPMENT AND MATERIALS

The autoclave and specimens were of the type IV design shown in Fig. 1. The materials, solution composition, and other data pertinent to the autoclave loading are listed in Table 1.

4. PROCEDURE

Information concerning the decomposition of nitrate and the corrosion of Zircaloy-2 during irradiation was sought in the usual type of pressure

⁵R. G. Sowden and Elizabeth M. Lynde, The Effect of Fission Recoil Energy on Calcium Nitrate Solutions, A.E.R.E. C/R 2480 (February 1958).

⁶R. M. Bidwell, L. D. P. King, and W. R. Wykoff, *Nuclear Sci. and Eng.* 1, 452 (1956).

⁷C. G. Edwards and F. Moseley, The Production of Chemicals from Reactors, Part 1. The Fixation of Atmospheric Nitrogen by Fission Fragments, A.E.R.E. C/R 2710 (October 1958).

⁸P. Harteck and S. Dondes, *Nucleonics* 14(7), 22-25 (1956).

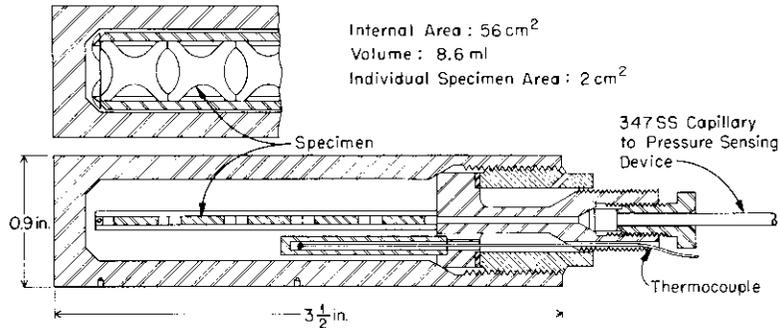


Fig. 1. Autoclave Assembly.

Table 1. Experiment L5Z-140; Autoclave, Specimens, and Loading

Autoclave	
Material	Zircaloy-2, Item 1244C
Design	Type IV, Dwg. D-34757
Internal area	56.1 cm ²
Volume	8.64 ml
Specimen	
Material	Zircaloy-2, Item 60
Design	Five scalloped coupons in rack
Surface	As-machined
Area	2 cm ² per coupon
Solution	
Volume at 25°C	5.87 ml
Density at 25°C	1.119
Composition	0.031 \bar{m} (0.035 \bar{M}) UO ₂ (NO ₃) ₂ , 93.2% U ²³⁵ 0.008 \bar{m} (0.009 \bar{M}) CuSO ₄ 0.090 \bar{m} (0.101 \bar{M}) DNO ₃ Solvent, D ₂ O
Stability in quartz tube	White crystals at 327°C
Overpressure	
Oxygen	Added as O ₂ gas
Nitrogen	Purged from system
Initial pressure, at 25°C	335 psi
Final pressure, at 25°C	252 psi
(110 to 250 psi of final pressure estimated to have been due to nitrate decomposition products)	
Oxygen consumed, estimated	34 to 60 cc (STP)

obtained by short exposures at 225°C and with the reactor at 20% full power. The initial exposure of this type was at 235°C.

After completion of the exposure, the autoclave was immediately cooled and vented, and about three weeks later was opened for examination. The solution, the autoclave rinse water, and the large amount of suspended solid material were chemically analyzed. The specimens were visually examined and then weighed. Some were defilmed and others were pickled to remove a surface sample for analyses. After further pickling, two samples were used for Zr^{95} activity determination and estimation of thermal-neutron flux.

5. RESULTS

5.1 Description and General Interpretation of Pressure Results

(a) Low-Power Low-Temperature Measurements. - The series of short-time low-power 225°C exposures provided smooth pressure-buildup curves, as shown in Fig. 3, from which K_{Cu} and G_{D_2} values could be estimated.

During the initial series of these exposures, small but significant increases in pressure persisted following retraction and after sufficient time had passed for the radiolytic gas to recombine. These increases amounted to 42 psi after the first exposure, which was at 235°C, and 5 and 7 psi in the two following exposures at 225°C. The exposure period for most of the measurements was less than 1 hr, and the pressure during exposure appeared to be leveling off. One exposure was continued for about 4 hr, however, and during this time a continuing increase in pressure was apparent.

As judged from past experience with uranyl sulfate solutions, these pressure increases are not fully explained by fluctuations and/or uncertainties in pressure measurements, and thus at least part of the increase is ascribed to the formation of nitrate decomposition products during irradiation.

(b) High-Reactor-Power 280°C Measurements. - The pressure data are summarized in Fig. 4. During each of the five full-power exposure periods, the pressure underwent changes qualitatively similar to those shown schematically in Fig. 5, although differences in detail were observed. Also,

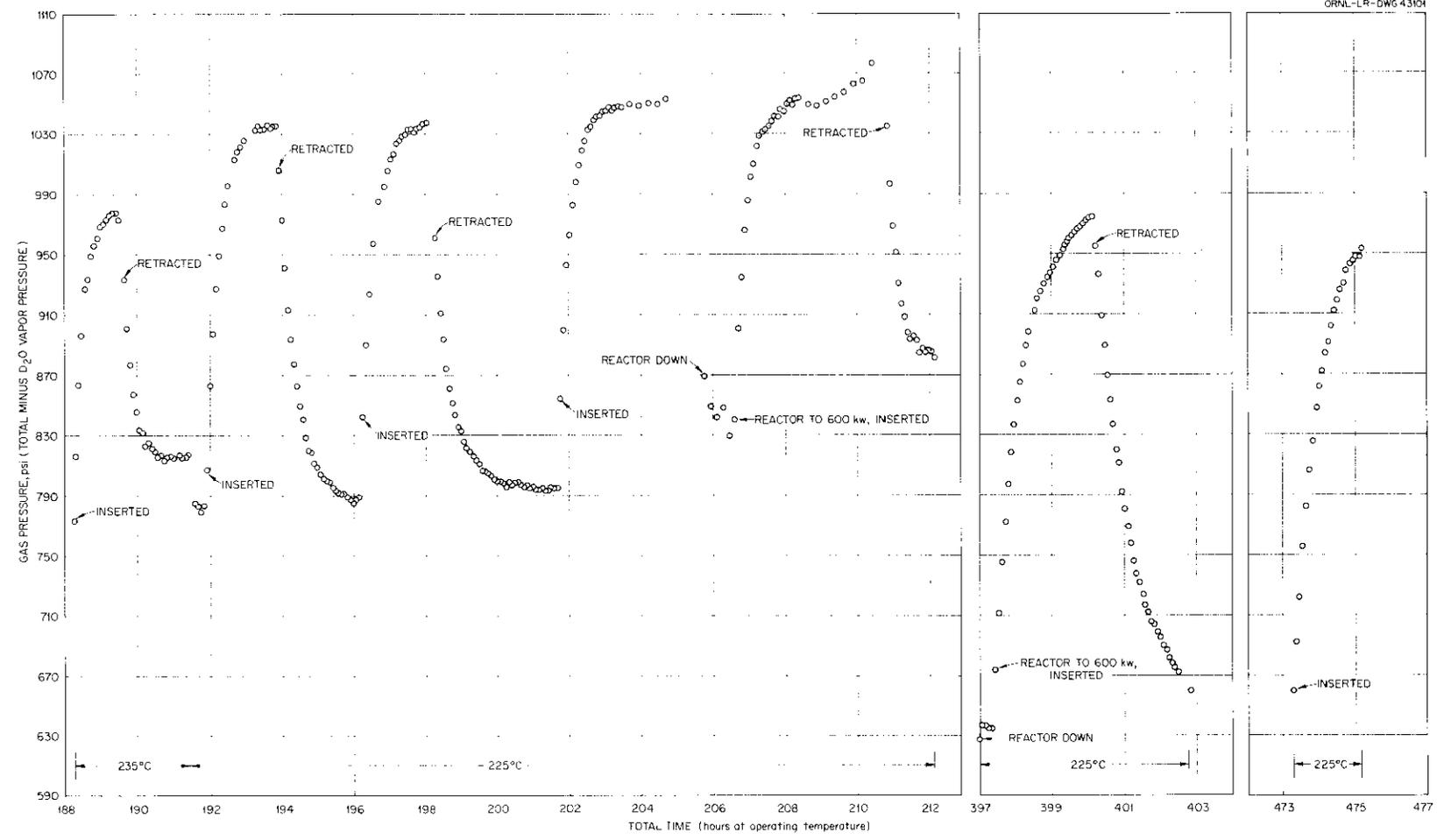


Fig. 3. Autoclave L5Z-140, Gas Pressure vs Total Time During 600-kw Radiolytic-Gas Runs.

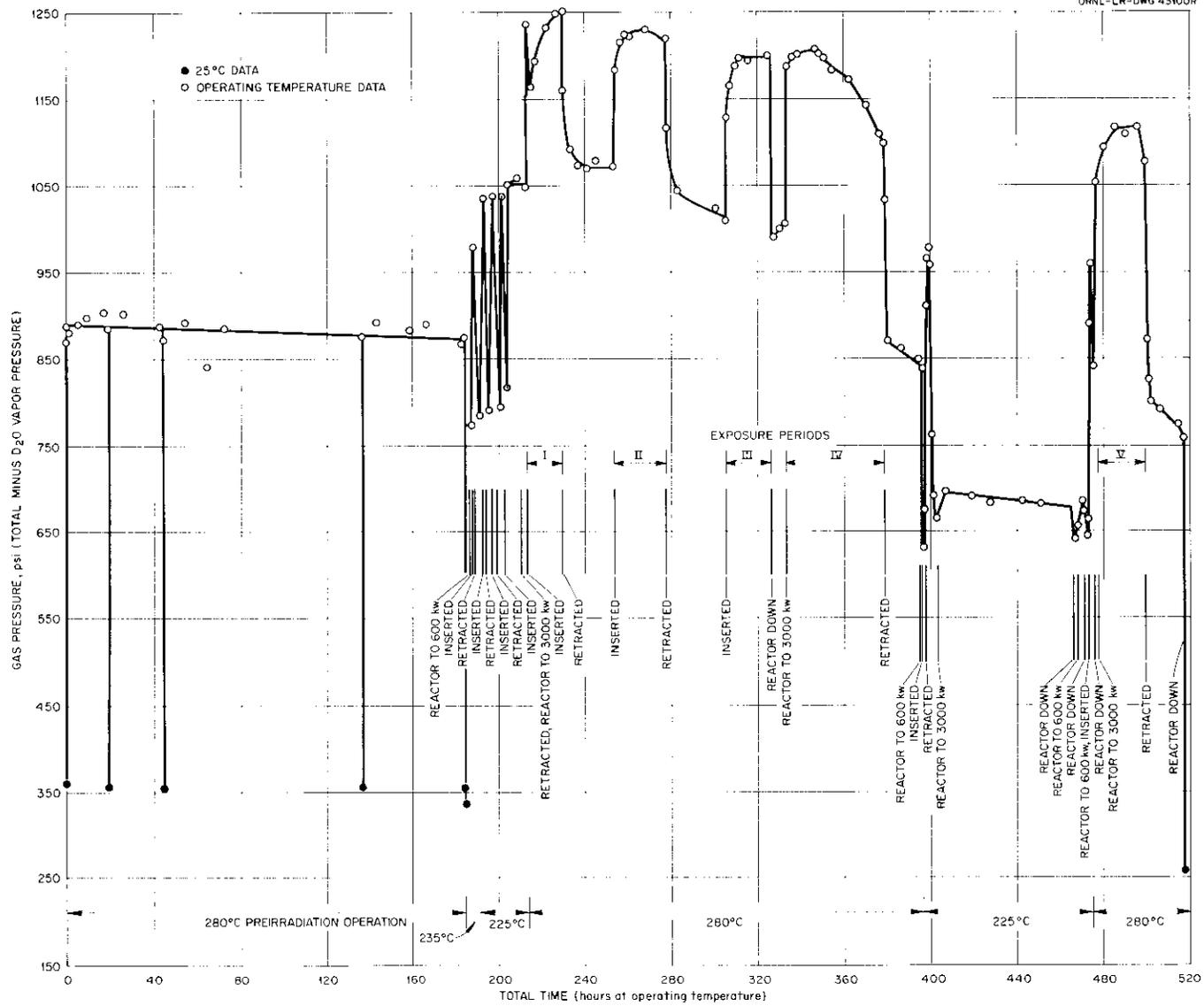


Fig. 4. Autoclave L5Z-140, Gas Pressure vs Total Time.

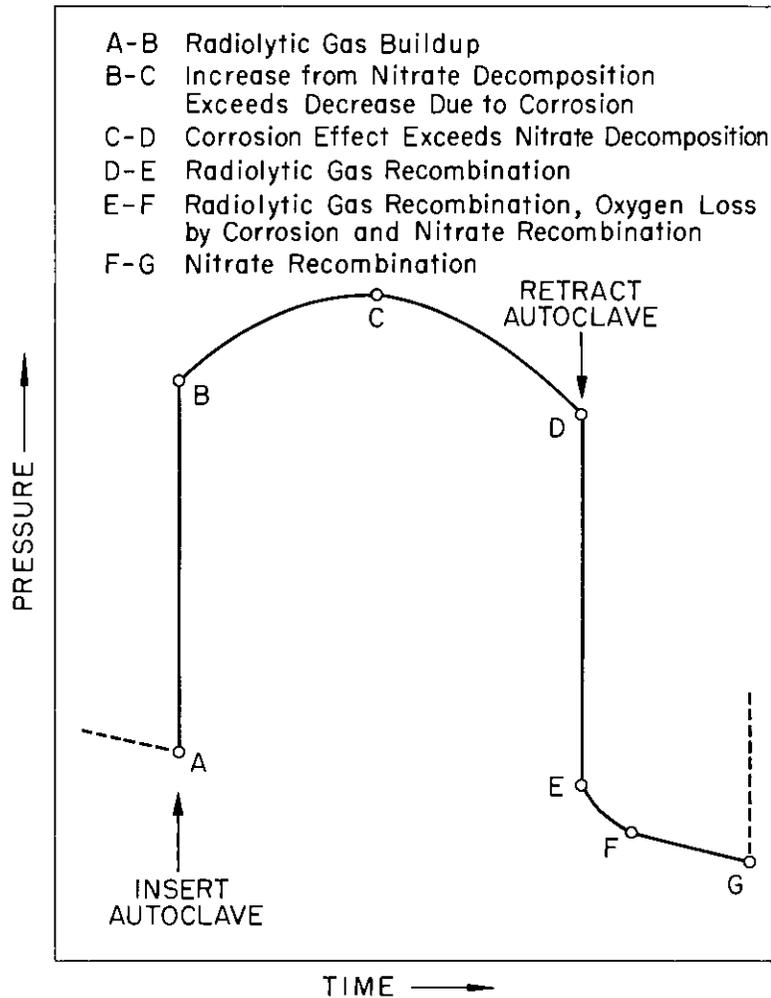


Fig. 5. Schematic Diagram of Progress of Pressure During Each Irradiation Period.

during the hour after the start of the first of these exposures and after the radiolytic pressure had leveled off to some extent, a rapid pressure excursion occurred in which the pressure rose appreciably and then decreased to about that existing before the excursion. The difference between the peak pressure of the excursion and that immediately following was 184 psi. Following the excursion, the pressure behaved as illustrated in Fig. 5. Pressures measured at the different points during each of the five exposures are listed in Table 2. Point B for exposure No. 1 was taken as the lowest pressure reached after the initial pressure excursion.

Table 2. Gas Pressures Observed at Various Times During High-Power Exposures

Exposure Time (3-Mwhr LITR Energy)	Pressure (psi at 280°C) at Points Labeled on Fig. 5							Radiolytic-Gas Pressure	
	Before Insertion (A)	After Insertion (B)	Pressure Maximum (C)	Before Retraction (D)	After Retraction (E)	1 to 8 hr After Retraction (F)	15 to 20 hr After Retraction (G)	A to B	D to E
2-20	1048	1146 ^a	1227 ^a	1227 ^a	1088 ^a	1088 ^a	1047 ^a	e	139
20-45	1047 ^a	1192 ^a	1201 ^a	1193 ^a	1051 ^a	1026 ^a	993 ^a	145	142
45-63	993 ^a	1133 ^a	1155 ^b	1155 ^b	(1010) ^d		938 ^c	140	(145) ^d
63-109	938 ^c	1111 ^c	1133 ^c	1018 ^c	823 ^c	800 ^c	769 ^c	173	195
109-134	769 ^c	998 ^c	1050 ^c	995 ^c	748 ^c	718 ^c	683 ^c	229	247
Pressure before any irradiation (prior to the low-power low-temperature irradiation):								975 ^f	

^{a,b,c}Data corrected for effect of valve turns so that each value is on the same basis:

- (a) correction, 24 psi;
- (b) correction, 40 psi;
- (c) correction, 72 psi.

^dEstimated.

^eApparent value, 117 psi; but it may be confused with the initial pressure-peak phenomenon.

^fThis value calculated from a 25°C measurement.

The magnitudes of the rapid changes in pressure following insertion (A-B) and retraction (D-E) increased gradually with increasing irradiation time. The slow pressure increase B-C during the first exposure was greater than that in subsequent exposures. Pressure decreases C-D were not observed during the first and third exposures, probably because of the short irradiation periods. Those observed in the other exposures increased in amount with increasing time of irradiation. The pressure loss rate F-G starting a few hours after retraction was negligible for the first exposure but was appreciable for subsequent exposures. The total drop in pressure E-G during the 15- to 20-hr period of retraction was roughly the same in each exposure. In the first two exposures, the pressure shortly after retraction, E, was greater than the initial pressure, A. In the last two exposures, the pressure at E was less than that at A. For the other exposure, the pressure at E was uncertain.

Based on prior experience with UO_2SO_4 solutions, G_{D_2} and K_{Cu} values determined from the low-power low-temperature results, and the general consistency of the results, the general interpretations of these pressure results are the following: The detailed explanation for the pressure excursion immediately following the first insertion is unknown. However, it appears likely that the effect is related to somewhat similar effects observed in autoclave experiments with UO_2SO_4 solutions. Some of these previous effects have been interpreted in terms of a loss of copper from solution during the initial exposure, followed by a re-solution of the copper.¹⁰ The pressure changes A to B and D to E represented the formation and recombination of radiolytic gas upon insertion and retraction, respectively. The pressure buildup following point B was due to the formation of gaseous nitrate decomposition products. The occurrence of a maximum in the pressure was a result of a back reaction of the decomposition products, a loss of oxygen pressure due to corrosion, and probably a decrease in the rate of nitrate decomposition as the solution became

¹⁰G. H. Jenks et al., HRP Quart. Progr. Rept. July 31, 1958, ORNL-2561, pp 234-36.

more dilute in nitrate upon decomposition. The decrease in pressure after the maximum C was due primarily to oxygen loss as a result of corrosion. The pressure at point E includes the pressures of excess oxygen and that of the nitrate decomposition products. The latter pressures were probably near those which prevailed at the end of each flux exposure, although a small amount of recombination may have occurred. The nearly constant rate of pressure loss from F to G may have been due either to corrosion which continued after retraction or to a recombination of nitrate decomposition products under the influence of the gamma-ray field in the retracted position, or possibly to both factors. The rapid pressure changes E-F after retraction and the recombination of radiolytic gas were probably also a result of oxygen loss due to corrosion which continued after retraction and of recombination of nitrate decomposition products. No evaluation can be made of the relative contribution of the two possible processes.

5.2 Results of Examination and Analyses of Autoclave Contents

The solution and rinse water were muddy, with tan-colored suspended material, when removed from the autoclave. The solution was observed after settling for 24 hr and the supernatant liquid was clear and nearly colorless. The specimens were observed and photographed (PIE photograph Nos. 88 through 94) with a stereomicroscope. The appearance of the surfaces under water was similar to the appearance after drying. The surfaces were green-brown or olive drab and were smooth and without evidence of preferential attack.

Postirradiation analyses of the solution, rinse, the part of the suspended material soluble in dilute H_2SO_4 , the part insoluble or difficultly soluble in dilute H_2SO_4 , and the specimen surface analyses are listed in Table 3.

Analytical results show that the irradiated solution contained 39, 27, and 50%, respectively, of the original uranium, nitrogen, and copper, if it is assumed, as usual, that the solution was not diluted or concentrated and that the unrecovered volume was lost in venting or handling. The pH and ion balance indicate that the acid concentration was about 0.01 m.

Table 3. Summary of Postirradiation Analyses

	Original Solution	Irradiated Solution	Autoclave Rinse	Suspended Material		Material on Surface of Dried Specimens (Average of 12 Values) (mg/cm ²)
				Part Soluble in 25 ml of 0.1 M H ₂ SO ₄ (mg)	Difficultly Soluble Part (mg)	
Sample size	5.9 ml ^a	3.9 ml ^c	4.0 ml ^c			
pH	0.95 ^b	2.35 ^b				
Uranium	8.3 mg/ml	3.2 mg/ml	0.7 mg/ml	6.8	9.4	0.16
Peroxide				5.8 U ^d		
Total N	2.6 mg/ml	0.7 mg/ml	1.1 mg/ml	0.03		
N as NH ₃		0.01 mg/ml	0	0.03		
Free acid	0.08 N					
Copper	0.6 mg/ml	0.2 mg/ml	0.02 mg/ml	0.18	0.44	0.04
Chromium		0.002 mg/ml	0.004 mg/ml	0.01	0.34	0
Nickel		0.13 mg/ml	0.07 mg/ml	0.25	0.20	0.07
Iron		0	0.01 mg/ml	0.06	0.73	0.64

^aVolume of solution originally loaded into autoclave.

^bpH values reported are glass-electrode values, using buffers of H₂O solutions plus a correction of 0.25 pH unit for D₂O solutions.

^cThese values are the volumes of samples collected.

^dExpressed as milligrams of uranium, assuming that the peroxide titrated was UO₄.

The amount of nitrogen found in the rinse was greater than that found in the recovered solution, but no pH or free-acid data which are required for validating this result were obtained.

Appreciable amounts of uranium were found in the suspended material. The 6.8 mg found in the soluble part was probably mostly peroxide, which may have formed after the irradiation and prior to separation of solution from the suspended material. The 9.4 mg in the insoluble part, however, amounts to about 20% of the total uranium in the autoclave.

The analyses of specimen surfaces showed appreciable amounts of iron, nickel, and uranium, and consideration of these data and of those for weight losses upon defilming indicates that these oxides remained on the defilmed surfaces to the extent of 1.3 mg/cm². The iron and nickel presumably came from corrosion of the steel capillary.

Weight losses of two defilmed Zircaloy-2 specimens (Table 4) average 2.3 mg/cm², corresponding to 0.14 mil of penetration and an average corrosion rate of 9.1 mils/yr during exposure. However, if the analytical results are assumed correct for the amounts of iron, nickel, and uranium

Table 4. Coupon Weight Data

Coupon No.	Coupon Area (cm ²)	As-Dried Weight Loss (mg/cm ²)	Defilmed Weight Loss (mg/cm ²)	Penetration from Defilmed Weight Losses (mils)	Penetration* from As-Dried Weight Loss Corrected by Surface Analysis Data (mils)
ZB-93	2.05	2.39			
ZB-102	2.06	2.14	2.23	0.135	
ZB-104	2.07	2.08			
ZB-164	2.05	2.10	2.39	0.144	
ZB-165	2.05	2.20			
Av value		2.18	2.31	0.140	0.207

*Surface analysis data indicated a 1.26-mg/cm² average weight loss in addition to the average as-dried weight loss of 2.18 mg/cm², or a total of 3.4 mg/cm².

on the dried specimens (Table 3), an additional Zircaloy-2 weight loss of 1.26 mg/cm² occurred. This would correspond to an average total penetration of 0.21 mil and a rate of 13.5 mils/yr.

The neutron flux during insertion at full reactor power corresponded to a calculated solution power density of 2.6 w/ml, based on the composition of the original solution.

6. DERIVED VALUES FOR K_{Cu} , G_{D_2} , G_{N_2} , AND G_{NO_3} ; ZIRCALOY-2 CORROSION RATES; NITRATE DECOMPOSITION DURING RADIATION EXPOSURE

In using the pressure data to calculate the various factors of interest, it was assumed that the nitrate decomposition products were comprised entirely of N₂ and O₂ in a molar ratio of 2:5. As mentioned previously, the work of other investigators shows that N₂ is the major product of the decomposition, although small amounts of nitrogen oxides also have been found. It was also assumed that the solubilities of nitrogen and oxygen in the UO₂(NO₃)₂ solution are the same as that of oxygen in UO₂SO₄ solutions of similar concentrations. Comparisons of pressure data obtained at 25°C and at the elevated temperatures in this experiment indicate that this is a reasonable assumption. It was also assumed that deuterium solubilities are the same in the UO₂(NO₃)₂ solution and in UO₂SO₄ solutions. No estimate of the validity of this assumption for D₂ is available.

(a) K_{Cu} and G_{D_2} . - Values for K_{Cu} and G_{D_2} calculated from the results of 225°C measurements are shown in Table 5. The results of the measurements made during insertion are considered more correct than those obtained during retraction because of the possibility that the rates of the recombination during retraction are partly controlled by diffusion processes. The apparently low values for K_{Cu} and G_{D_2} after 109 hr exposure presumably resulted from copper and uranium losses from solution during the 109 hr. The results of the high-temperature exposures are not suitable for accurate evaluation of G_{D_2} and K_{Cu} , but the pressures observed during the initial exposures are in rough agreement with those predicted from the results obtained at low temperature.

(b) G_{N_2} . - Values for G_{N_2} estimated from various pressure data are listed in Table 6. It should be noted that the value calculated from

Table 5. Values for G_{D_2} and K_{Cu} Based on Low-Power Exposures at 225°C

Basis	K_{Cu} [liters (STP) mole ⁻¹ hr ⁻¹]	G_{D_2} (molecules/100 ev)
Values from Data Obtained at Beginning of Irradiation		
Pressure-buildup data	1600	1.3
	1600	1.3
	1700	1.4
	1700	1.4
Recombination data	1200	0.9
	1100	0.9
Values from Data Obtained after 109 hr of Irradiation		
Pressure-buildup data	800	0.9
	800	0.9
Recombination data	500	0.6

the rate of pressure rise (B-C, Fig. 5) during the initial high-temperature exposure should be regarded as a minimum value. Some loss of pressure due to corrosion and to recombination of nitrate decomposition products may have been taking place during the rise in pressure. Also, during the low-temperature exposure, some recombination may have occurred. No corrections for these possible pressure losses were attempted. Rates of pressure increase following insertions during the exposures subsequent to the first at high temperature were less than that for the first. No attempt was made to evaluate G_{N_2} values from these subsequent exposure data.

(c) G_{NO_3} - - Rough values for the rate of recombination of N_2 and O_2 can be estimated if it is assumed that the formation of a steady-state pressure during the first high-temperature exposure resulted primarily from the recombination of nitrate decomposition products. For this exposure, in which the G_{N_2} was 3×10^{-3} , estimated from the initial pressure rise, the gas-phase recombination required to form a steady state

Table 6. Estimates of G_{N_2}

G_{N_2} (molecules/100 ev)	Exposure Time (3-Mwhr LITR Energy)
Low-power 225 and 235°C data (incremental increases in apparent equilibrium retracted pressures)	
2.5×10^{-2}	0-0.3
2×10^{-3}	0.3-0.7
3×10^{-3}	0.7-1
Low-power 225°C data (approximate linear pressure increase after apparent radiolytic H ₂ -O ₂ equilibrium)	
1×10^{-2}	2
High-power 280°C inserted data (rate of pressure buildup after apparent radiolytic H ₂ -O ₂ equilibrium)	
3×10^{-3}	5

at the estimated gamma-ray and fast-neutron fluxes prevailing in the inserted position can be estimated to be that which corresponds to a G_{NO_3} of 1 to 3. The true G_{NO_3} values are probably somewhat lower than the value thus obtained, since some decrease in nitrate decomposition rate would be expected as the nitrate concentration in solution decreased due to decomposition. Also, the rate of loss of oxygen as a result of corrosion may have increased as the time of irradiation exposure increased.

(d) Zircaloy-2 Corrosion Rates and Nitrate Decomposition as a Function of Time During Radiation Exposure. - Limits for the rates of Zircaloy-2 corrosion at different times during the radiation exposure can be estimated from the rates of pressure decrease observed during different exposures, the total Zircaloy-2 corrosion indicated by the weight losses of defilmed specimens, the possible presence of Fe₂O₃ and other oxides on

the defilmed specimens and other surfaces, and the total amount of nitrate decomposition as shown by the analyses of the final solution.

The probable minimum rates of oxygen consumption as a function of time during radiation exposure are those represented by line A of Fig. 6. The points are those calculated from the rates of pressure loss measured during the final portions of the high-temperature exposures.

The estimated maximum oxygen consumption rates, illustrated by line B of Fig. 6, were selected such that the area under the curve corresponds to the total Zircaloy-2 corrosion which occurred if the analytical results for the amounts of Fe_2O_3 and other oxides on the coupon surfaces are considered correct and if those specimen surfaces were representative of other surfaces in the autoclave. The area under this curve includes the amount of oxygen consumed in corroding 0.21 mil of Zircaloy-2, as indicated by weight loss data corrected for possible retained oxides, plus stainless steel (capillary) in sufficient amount to account for the nickel found in solution and on the Zircaloy-2 surfaces.

It was arbitrarily assumed that the high rates of pressure loss measured during the final 40 hr of exposure were the actual oxygen consumption rates. Therefore all the rate adjustments were applied to the first 100 hr of irradiation.

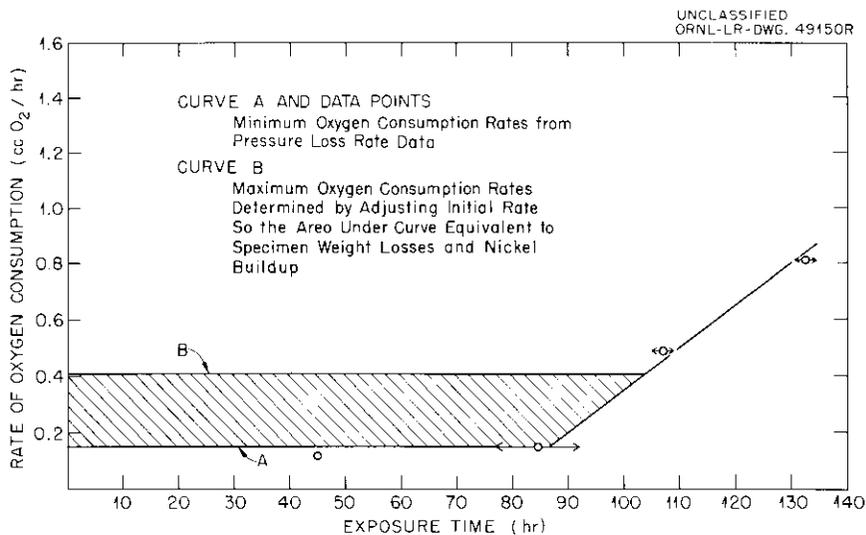


Fig. 6. Estimated Rates of Oxygen Consumption as a Function of Exposure Time.

By graphical integration of the curves in Fig. 6, maximum and minimum values for the volumes of excess oxygen in the autoclave can be estimated to give those illustrated by curves A and B in Fig. 7. The difference between the values illustrated by a given one of these curves and the measured values (pressure data) for the total volumes of excess oxygen plus nitrate decomposition products in the system, shown by curve C in Fig. 7, yields the maximum and minimum values for the volumes of the gaseous decomposition products, which are illustrated by curves B' and A' respectively.

If it is assumed that the minimum oxygen consumption rate (line A in Fig. 6) represents rates of oxygen consumption in Zircaloy-2 corrosion, the rate for this material during the first 90 hr of radiation was about 6 mils/yr. The rate at the end of the final exposure was about 30 mils/yr. The average corrosion rate was about 10 mils/yr, a value in near agreement with that estimated from the weight loss of defilmed specimens.

The corresponding curve A' in Fig. 7 for the minimum volumes of gaseous nitrate decomposition products shows that the volumes increased rapidly to about 10 to 12 cc (23 to 25% decomposition) during the initial

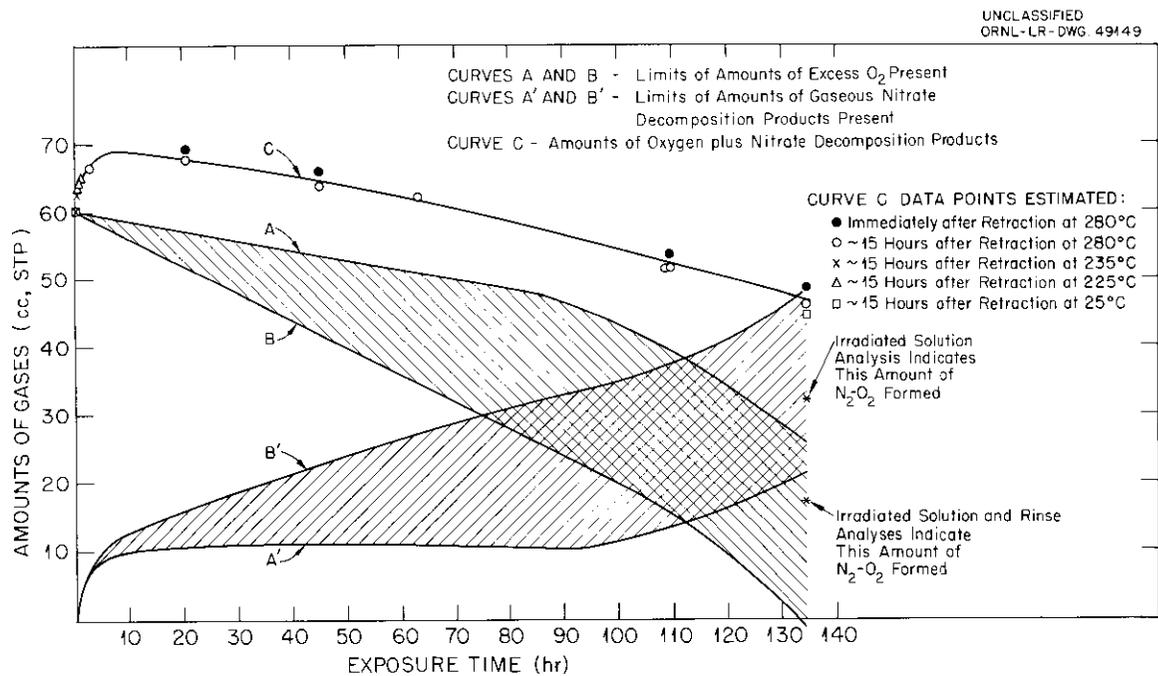


Fig. 7. Estimated Amounts of Excess Oxygen and Gaseous Nitrate Decomposition Products vs Exposure Time.

exposures and then remained nearly constant until the final exposure, during which they increased to about 20 cc (47% decomposition). It may be noted that the indicated amount of gaseous decomposition products at the end of the experiment is in fair agreement with that indicated by the analytical results for the total amount of nitrogen in the solution and rinse. These results showed about 27% of the original nitrogen to be in the solution and 28% in the rinse. A discrepancy in the interpretation of the final two rate values in Fig. 6 is apparent in this treatment of the data. The treatment indicates that the pressure of nitrate decomposition products was increasing at the time the total pressure in the system during exposure was decreasing; therefore the rates of oxygen consumption may have been greater than those calculated from the rate of pressure decrease. The proper correlation of these facts is not apparent. It is possible that the oxygen consumption rates were greater than those employed. It is also possible that the rates did not increase regularly with exposure time in this region and that the high rates occurred only during the time that the observed pressures were decreasing rapidly. Other treatments of the data to include these possibilities do not appear worth while in view of other appreciable uncertainties in the results.

The estimated maximum rates of oxygen consumption due to corrosion, illustrated in line B, Fig. 6, correspond to a Zircaloy-2 corrosion rate of about 12 mils/yr during the 100 hr of radiation when it is assumed that the steel corrosion rate remained constant throughout the 134 hr of exposure. Curve B' in Fig. 7, illustrating the estimated maximum amounts of gaseous nitrate decomposition products, shows a rapid rise to about 12 cc during the initial exposures and then a slower but steady increase during subsequent exposures to a value of about 48 cc. This volume is slightly more than that which would be produced by 100% decomposition of the nitrate in solution. Again the interpretation of the final two rate points in Fig. 6 is in question because the indicated pressures of nitrate decomposition products were increasing at the times the pressures were decreasing and, again, attempts to resolve these discrepancies by other treatments do not appear worth while because of over-all uncertainties in the results.

The true amounts of corrosion and of gaseous decomposition products probably fall between the limits indicated in Figs. 6 and 7, with the exception that during the final 30 hr of exposure, oxygen consumption rates greater than those indicated in Fig. 6 may have occurred.

7. DISCUSSION

Although appreciable uncertainty exists in the interpretation of some of the results, the factors comprising the objectives of the experiment were evaluated, but with limited accuracy.

All the results are consistent with the occurrence of nitrate decomposition during radiation exposure. The results of pressure measurements during the initial 225 to 235°C exposures and during the initial 280°C exposure provide evidence that the initial nitrate decomposition rate was greater than that predicted by the reported results of Sowden and Lynde, by factors of from about 7 to 70. Comparisons with the Sowden and Lynde data and with other data are given in Fig. 8.

A back reaction of the nitrate decomposition products is indicated by the results of the first 280°C radiation exposure. The $G_{NO_3^-}$ value of about 1 to 3 for gas-phase recombination, estimated from these results by assuming that NO_3^- is the sole product of recombination, is within the range of values reported by others. It should be noted, however, that

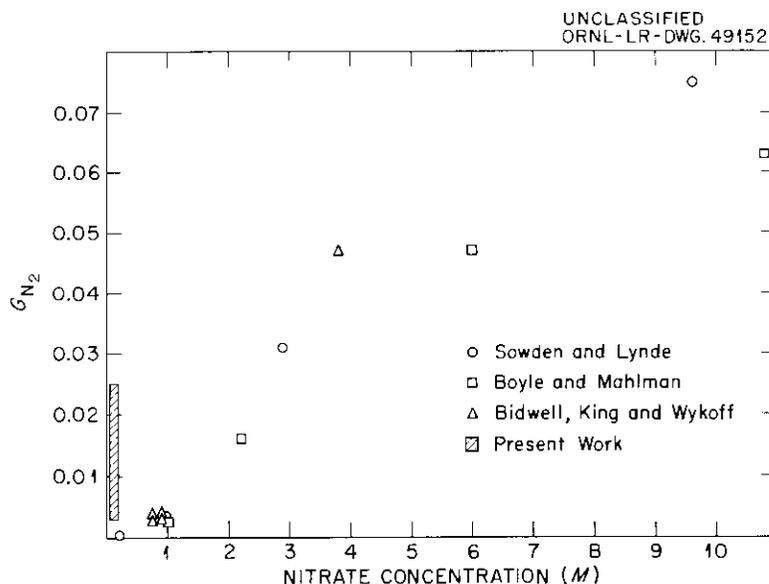


Fig. 8. G_{N_2} vs NO_3^- Concentration.

the conditions of pressure, temperature, and gas-phase composition in this experiment differ from those employed in the other reported studies, and that the $G_{\text{NO}_3^-}$ value for the present experiment cannot be accurately predicted from the other studies.

The initial K_{Cu} values (225°C) are about three times as large as those found out-of-pile by Kelly *et al.*¹¹ The initial G_{D_2} value of 1.3 is in near agreement with the value of about 1.5 found for nitrate solutions by other workers, as shown in Fig. 9. The apparent decreases in K_{Cu} and G_{D_2} throughout the exposure can be ascribed to a loss of uranium and copper from solution.

The Zircaloy-2 corrosion rates during the initial 100 hr of radiation at 280°C were probably in the range 6 to 12 mils/yr. A corrosion rate in the same range would be expected for uranyl sulfate solutions of similar concentrations. During the final 34 hr, the rate was greater than 12 mils/yr and probably as high as 30 or more. The large amount of sorbed uranium (0.16 mg/cm²) indicates that a high effective power density prevailed at the metal surface and probably accounts for the high rate near the end of exposure.

¹¹M. J. Kelly, Reactor Chemistry Division, ORNL, private communication.

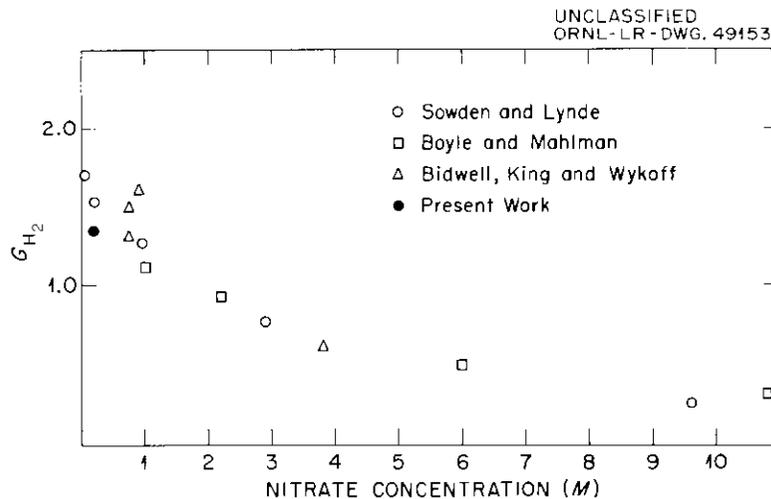


Fig. 9. G_{H_2} vs NO_3^- Concentration.

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