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SUBJECT: IN-REACTOR AUTOCLAVE CORROSION STUDIES, LITR
I OUTLINE OF METHODS AND PROCEDURES

TO: E. G. Bohlmann

FROM: K. S. Warren and R. J. Davis

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ABSTRACT

During the development of in-reactor corrosion experiments three types of bomb designs have been developed for following quantitatively the consumption of oxygen in a bomb which is fabricated from the particular metal under test. The bombs are designed so as to be rocked continuously during their in-reactor exposure, consequently agitating the uranium salt solution contained in the bomb and permitting gentle movement of the solution past metal specimens and other corroding surfaces. The oxygen pressure is produced within the bomb at the beginning of the run either by the withdrawal of gas from an oxygen tank or by the decomposition of hydrogen peroxide added just prior to closure. Temperature measurements are obtained by means of thermocouples placed in a well within the bomb body or, in the latest design, there will also be thermocouples staked at several points on the outer wall of the bomb. The assembly is inserted in an experimental access hole in the reactor, brought up to a predetermined operating temperature by means of an electric furnace in close contact with the bomb, and allowed to remain for the desired amount of exposure to reactor radiation. Periodic measurements of temperature and pressure are made and the bomb assembly is finally removed from the reactor before the oxygen supply is depleted. The bomb and associated components are dismantled, and the solution, the film from the metal specimens, and the precipitate, if any, are subjected to chemical analysis. The metal specimens are further decontaminated and utilized to obtain an estimate of the in-reactor flux from activation analysis data. Corrosion data is generally available from two independent sources:

- 1) The consumption of oxygen is calculated from the periodic temperature and pressure measurements along with known bomb volumes, available solubility data for oxygen and the knowledge of the composition of the alloys involved.
- 2) Loss in weight of the metal specimens in the bomb.

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The cumulative radiation time, (in P Mw-hr, when exposure is made with reactor at P Mw), is used together with penetration data (from oxygen consumption) to plot curves, the slope of which represents the corrosion rate for the given set of conditions. Frequently a bomb may be operated at 2 or more different temperatures during an in-reactor exposure and treatment of these data consequently furnishes corrosion rates for each of the temperatures.

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A. Introduction

The purpose of this report is to present in limited detail the procedures which have been followed in forty-seven rocking bomb corrosion experiments already made in the LITR and which presumably will be followed in many experiments yet to be made. It is important that the reader realize that the various techniques and equipment involved have been developed over a period of time. Essentially all equipment and methods which have been used are described. The exact procedure used in any particular experiment is clarified in the more detailed reports on individual experiments.

Even as there has been an evolution of design and technique in the in-reactor rocking autoclave experiment, there have also been several people engaged in the work from time to time. J. W. Boyle and others exposed autoclaves containing aqueous solutions at elevated temperature and pressure in the graphite reactor. D. M. Richardson, F. H. Sweeton, H. F. McDuffie, C. H. Secoy, and others^{3,4} made in-pile autoclave exposures in the LITR; some of these experiments were devoted to corrosion studies. F. H. Sweeton⁴ instigated the use of pressure measurements on in-pile autoclaves to follow corrosion, F. H. Sweeton, W. C. Yee, et al., later started the rocking of in-pile autoclaves devoted to corrosion measurements. The conception of the type II experiment, installed in HB-5 in the fall of 1954, was largely that of B. O. Heston. Design and development was carried out by D. T. Jones, H. A. Fisch, and the Engineering and Mechanical Division. H. H. Stone and L. F. Woo developed the defilming method used very successfully on Zircaloy-2. H. O. Day, Jr., is responsible for much of the refinement in data treatment, primarily in regard to oxygen consumption calculations.

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Others who have directly contributed to the program, but have not been mentioned include: A. L. Bacarella, S. F. Clark, W. E. Clark, R. J. Davis, V. A. DeCarlo, H. A. Fisch, D. N. Hess, G. H. Jenks, Q. V. Larson, A. R. Olsen, R. M. Pierce, H. C. Savage, M. D. Silverman, F. J. Walter, and K. S. Warren.

Since July of 1954, the rocking bomb experiments have been a part of the Radiation Group of the HRP Reactor Materials Research Section. At the present time the responsibility is broken down more or less as follows:

Solution preparation, necessary laboratory tests, etc.: L. F. Woo.

Fabrication, assembly and pretreatment of the experiment: V. A. DeCarlo.

Installation, irradiation, removal from the LITR and partial dismantling:

F. J. Walter and J. W. Brown.

Remote evaluation: A. R. Olsen

Data handling: K. S. Warren

B. Procedure for Solution Make-up for In-Reactor Studies

Uranyl sulfate enriched with U^{235} is kept on hand in concentrations of approximately 80 g U/l. This stock solution is checked for compliance with HRT specifications¹, as follows (earlier bomb solutions were not tested to this extent):

(Analyses based upon a solution containing 430 g U/kilogram of water or 500 g U/l of solution)

Uranium/sulfate ratio 1.00 ± 0.02

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Cations, total, exclusive of U	500 ppm, max.
Nitrogen	75 ppm, max. ^a
Halides, total, exclusive of F	10 ppm, max.
Fluoride ion	10 ppm, max. ^b

- a Originally this was stated as "nitrogen as nitrate - 75 ppm, max." but later changed to the form given above.
- b Maximum fluoride ion concentration in the final solution (prepared for a bomb) is currently taken as 5 ppm.

The stock sulfuric acid is a 0.5 molar solution and likewise known to be essentially halogen-free. Copper sulfate pentahydrate, obtained from a freshly opened bottle, is made up into a 0.5 molar solution and maintained as a stock solution free of possible contamination. A communication from the commercial supplier states that the particular reagent grade hydrogen peroxide currently in use as a source of oxygen contains no additives for preservative purposes. The material is supplied to the following specifications which meet ACS requirements:

Assay (H_2O_2)	30.0-32.0%
Residue after evaporation	0.005 %
Free acid (as H_2SO_4)	0.003 "
Chloride (Cl)	0.001 "
Nitrate (NO_3)	0.0003 "
Phosphate (PO_4)	0.0005 "
Sulfate (SO_4)	0.0005 "
Ammonium (NH_4)	0.0003 "
Heavy metals (as Pb)	0.0001 "
Iron (Fe)	0.00005 "

Other materials and additives are obtained in as pure a form as possible and recrystallized when deemed necessary. When a given composition for a programmed bomb test has been selected, 50 ml of the proposed fuel solution is prepared volumetrically using stock solutions. In cases where the use of hydrogen peroxide as a source of gaseous oxygen is anticipated, allowance is made in the concentration of the fuel solution for the resultant dilution by water from the peroxide addition. The prepared fuel solution is (with the exception of the tests de-

scribed in the next paragraph) reserved for use in one or more programmed in-reactor experiments.

A 2 ml aliquot is taken from the flask for a density determination, and a 7 ml aliquot is reserved for confirmation of pH and absence of halogen. The density of the uranium solution is determined with a pycnometer in the usual manner, making necessary bouyancy corrections. A portion of this sample is also utilized in a high temperature stability test by the semimicro quartz tube technique developed by Marshall². The apparatus used in such semimicro phase studies consists simply of an electrically heated aluminum block with a slot in the side which serves as a window. The solution sample, sealed in a small quartz tube, is inserted in a central hole in the block so as to be easily visible through the window. Violent agitation of the liquid during heating of the block is obtained by fastening the outer end of the extended quartz tube to a vibrating tool. The temperature of the unit is raised gradually with frequent observations of the sample. Cognizance is taken of the appearance of a second phase at any temperature up to the planned operating temperature (of the bomb) and at least 10 degrees beyond the latter. Limitations of the data obtained from such phase transitions may be tabulated as follows:

- (a) Such data for earlier bomb solutions are not available; only recently has this technique come to be employed as a routine stability check for all solutions before loading into bombs.
- (b) A measured quantity of water is used to dilute the small sample of bomb solution, thus simulating the dilution by 30% hydrogen peroxide in the actual bomb loading procedure. The estimated dilution of course does not exactly reproduce the bomb condition, nor is an oxygen over-pressure provided in the quartz ampule, such as obtains in the bomb.

(c) The transition temperature for the appearance of two liquid phases is reproducible within $\pm 2^{\circ}\text{C}$.

(d) For uranium concentrations of 0.17 m, in which other additive(s) are present in excess of 0.01 m, the appearance of a solid phase at a given elevated temperature generally appears sharp and seems to be reproducible within $\pm 2^{\circ}\text{C}$.

(e) For uranium concentrations of 10 g/l the temperature of formation of a solid phase is quite difficult to observe; the solid precipitate is small in quantity and size. Repeated tests aid in narrowing the temperature range reported.

C. Bomb Design and Fabrication

1. Description

Bombs to date have been made up in three designs: type I (and IA), type II and type III (see Dwgs. ORNL-LR-16662, 16663, 17439, and 18328). Sketches of the assembled experiment and equipment are appended. The four types of bombs may be considered as a gradual evolution of design. Type IA, the earliest in-reactor bomb in the present series, contained four loose metal specimen pins and a thermocouple well which required a difficult weld in the fabrication of the bomb body. Because of the orientation of the bomb during its in-reactor exposure, it was necessary to bend the capillary tubing (leading from the bomb to the pressure transducer) in a small radius of curvature for insertion into its protective sheath. This disadvantage was eliminated by the design of type I, in which a right angle fitting to the mouth of the bomb, was incorporated. In type IA and type I, however, the freedom of the four loose pins in the bomb may have permitted sufficient attrition during the continual rocking of the experiment to reduce the accuracy of subsequent physical and chemical analysis

of the surface film on the pins. This led to the design of type II, incorporating a solidly-mounted pin rack in which six pins were locked in place by recessed washers and a nut. In addition, openings on both ends of the type II bomb eliminated the necessity of a weld with its attendant focal points for corrosion.

In response to the exigent need for corrosion data requisite for the homogeneous reactor program, one test facility was redesigned so that the test bomb was in effect reoriented in the experimental access hole in the reactor to allow the simultaneous operation of three experiments instead of only one. This latest bomb is designated as type III. The type III bomb uses a thermocouple well which is seal welded in place. The long axis of the type III bomb is expected to acquire a significant flux gradient from the new orientation in the reactor. As corrosion specimens, the 1.5 in. 0.062 in. diameter pins (common to types IA, I, and II) were replaced with rectangular metal coupons, (0.4 x 0.25 x 0.062 in). The 0.25 in. dimension is parallel to the axis of the experimental access hole of the reactor. A cobalt flux monitor (a cobalt-aluminum wire sealed into a tube made of the bomb material) has also been incorporated. The mechanical design work has been done by the Engineering and Mechanical Division.

Adequate bomb design should of course secure ample agitation of the solution so as to wet all internal surfaces of the bomb and preclude the possibility of any portion of the metal surface drying appreciably. The two arrangements employed for in-reactor corrosion studies may be described briefly as follows:

- (a) In the case of bomb types IA, I, and II, gentle agitation is secured by rocking the bomb about 12 times a minute about an axis perpendicular to the long axis of the bomb and passing through its center. The amplitude

of the oscillation is about 60 degrees, permitting angular movement approximately 30 degrees above and below the horizontal.

(b) In the case of the type III bomb, gentle agitation of the solution is obtained by causing the bomb to be oscillated about its longitudinal axis, turning about seventy degrees in both directions at approximately nine cycles per minute.

For recent experiments, all bomb materials have been ordered to comply with HRP specifications for: Zircaloy-2, titanium and type 347 stainless steel. Occasionally, however, pins or coupons are machined from other alloy stock for special corrosion testing.

After machining a desired bomb under its applicable specifications, the bomb and associated metal components are cleaned with benzene, petroleum ether, acetone, and water, and dried at 110°C. This cleaning technique applies likewise to capillary tubing, connector, and pin or coupon specimens.

The dimensions of pin or coupon specimens are measured with a micrometer; the specimens are then identified with file scratches or numbers and photographed. The bomb assembly is subjected to a hydraulic pressure test of 4800 psia, at room temperature, followed by a second test at 310°C. Changes in bomb diameters at 1/2 in. intervals along the length are determined. Increments in diameter of 0.5 mil are considered acceptable. The volume of the bomb is next calibrated by weighing it empty and filled with water at a known temperature. This filling and weighing is repeated until three calibration values check within ± 0.02 g.

The metal test pins or coupons are carefully weighed and all external dimensions, as measured with a micrometer, are recorded.

The depth of penetration of metal by the corrosion process as computed at the end of a run for a given consumption of oxygen is a function of the surface area within the bomb which is exposed to the corroding solution. Such

computation normally assumes ideally smooth surfaces, a condition not realized in actual practice. The surface roughness left by the last machining operation is therefore controlled as closely as is feasible. The maximum average height deviation from the mean surface is specified on each drawing for the following bomb designs:

<u>Bomb type</u>	<u>Part</u>	<u>Max. Deviation (microinches)</u>
I and IA	wall	6
II and III	wall	32
III	coupon	16

It may be remarked that the 6 microinches originally specified for the earlier bomb designs (types I and IA, which are no longer in use) represents a surface smoothness which was probably not attained by the machining operations in use.

2. Partial Drawing List

a. Type I Rocking Bomb Experiment

E-12860 Assembly of Corrosion Study Facility
 E-15743 Assembly of Drive Mechanism
 D-19031 Sub-assembly and Details of Bomb Model I (this bomb is described as type I in this report)
 D-19647 Sub-assembly and Details of Bomb Model III (this bomb is described as type IA in this report)

b. Type II Rocking Bomb Experiment

E-18933 Assembly of Corrosion Test Facility
 E-18934 A Sub-assembly of In-Pile Equipment
 D-19052 Sub-assembly and Details of Bomb Model II (Type II in report).
 Q-1235-1 Alarm panel for Expts. in HB-5 of LITR

c. Type III Rocking Bomb Experiment

E-24550 Layout of Equipment
 D-24551 Schematic Flow Sheet
 E-24552 Assembly of In-Pile Equipment
 D-24555 Sub-assembly of Rocking Plug Sheet #1
 D-24556 Sub-assembly of Rocking Plug Sheet #2
 D-24559 Sub-assembly and Details of Test Bomb Model II (this is described as type III bomb in this report)
 TD-D-4661 Instrument Flow Sheet
 TD-E-4662 Control Circuit Schematic
 TD-D-4699 Pressure and Thermocouple Connections

d. Bomb Dismantling Equipment

E-19625 Bomb Dismantling - Equipment - Assembly - Plan Views

D. Calibration and Assembly of Baldwin Cell

The Baldwin fluid pressure cell (Baldwin-Lima-Hamilton Corp., Phila., 42, Pa.) is a pressure-sensitive transducer in which variations of fluid pressure produce corresponding variations in electrical output. A Wheatstone bridge made of fine wires is bonded to a 410 stainless steel tube; internal pressure within the tube affects the relative resistance of the four bridge arms. For the present work a type "A" 5,000 psia SR-4 cell is employed, together with a transducer calibration adapter circuit (Dwg. Q-902-1); however plans are being made to simplify the present adapter circuit considerably.

To prepare a Baldwin cell for assembly to a bomb, the cell (at atmospheric pressure) is first connected to the adapter circuit at the facility where its use is contemplated, zeroed and calibrated. The Baldwin cell is then removed from the electrical circuit, and its inner tube is filled with a two percent solution of potassium dichromate and a number of stainless steel balls. (Before June 1955, cells were filled with distilled water without metal balls). The potassium dichromate is added to reduce corrosion, and the presence of the steel balls reduces undesirable side effects resulting from the compressibility of water simply by reducing the volume of water. The valve and the capillary tubing are filled with distilled water, care being taken to avoid air bubbles in the system. The Baldwin cell and attached capillary with valve are next subjected to a pressure check by slowly turning down a valve. A plot of the number of valve turns against pressure developed should be a straight line. A curve indicates the presence of air bubbles or a leak in the system. In addition, the maximum pressure developed in this test, about 1600 psi, is observed for at least 10 hours as a leak test. The capillary and Baldwin cell are then ready for assembly to the bomb.

E. Bomb Loading and Assembly

Specimen assembly and bomb are weighed dry. The required amount of uranium

fuel solution is added to the bomb and the total weight is obtained. If hydrogen peroxide is to be used it is added from a weighed micro-pipette. The connector fitting is immediately screwed into the bomb to avoid evaporation of water.

Using the calibrated Baldwin cell, the pressure is followed during decomposition of the hydrogen peroxide in the bomb in the course of a furnace treatment for 1-1/2 hr at 150°C. After cooling to room temperature, the bomb pressure is observed during a period of about 12 hours. After checking for leaks the bomb assembly is ready to be installed in the furnace-cooler assembly.

In the type I or II assemblies the bomb is inserted in the furnace which in turn fits into an air- or water-cooled aluminum receptacle. The type III bomb fits into a heater-cooler assembly (see attached sketches). Iron-constantin thermocouples are inserted into holes in the furnace provided for that purpose (type I and II only). Two thermocouples are introduced into the bomb well in all assembly types. In the type III bomb, provision has been made for securing three thermocouple junctions to the outer surface of the bomb. One pair of junctions is located so as to provide temperature information at the ends of the bomb. The third is secured at the center. The capillary which transmits the pressure to be measured, the thermocouple wires, the two furnace lead wires, etc. are properly placed (see sketches attached or detailed drawings). Upon completing the assembly, thermocouples are checked for continuity, and the system is ready for the "pretreatment."

F. Bomb Pretreatment

The complete assembly is connected to a test panel board similar to the panel board used at the irradiation facility. The assembly is agitated for 30 minutes in the same manner as that specified for its in-reactor operation to

attain thermal and pressure equilibrium. Measurements of temperature and pressure are then conducted without rocking and with the bomb outlet as high as possible. Next the bomb is heated to 100°C for 30 minutes, and the temperature and pressure measurements are repeated. The temperature is next raised to 250°C (or 280°C). The experiment is agitated for 30 minutes, the agitation is stopped and the pressure and temperature are measured. Then agitation at 250°C (or 280°C) is started and continued for 24 hours. A small drop in the oxygen pressure during this period is interpreted as an initial corrosion attack of the metal surfaces by the uranium solution and the formation of a potentially significant film or scale. The hydrostatic test of the bomb containing air-saturated water at 310°C, prior to assembly, will have produced a film and should not be overlooked.

Following the pretreatment at 250°C (or 280°C) the temperature is reduced stepwise, so as to permit temperature and pressure measurements at 100°C and 25°C, as before. Proper furnace control, uniformity of thermocouple output, and freedom from leaks in the system are judged from the pretreatment procedure.

G. Procedure for Irradiating Bombs

The procedure for insertion of bombs will vary somewhat according to the type of bomb and the particular experimental hole in the facility being utilized. In all cases, the equipment design includes a continual venting of the sealed assembly to the reactor off-gas system. Having inserted an experiment and special shielding plugs in the experimental access hole, connections are made to the cooling fluid supply and discharge lines, and suitable electrical connectors are utilized for thermocouple leads, Baldwin cell transducer leads, and heater leads. The rocking mechanism is connected to the experimental unit. The instrumentation and safety interlock system is thoroughly checked out before installation of the experiment, and attention is given to all instrumentation, particularly

during reactor start-up periods. Reactor shutdown periods are required at suitable intervals in order to take accurate readings of temperature and pressure. These readings are taken on precision potentiometers connected to suitable thermocouples and pressure transducers. A measurement of the pressure is always made at the operating temperature of the bomb. ~~Other measurements may be made~~ during reactor shutdown at lower temperatures if desired.

Provision has been made in the design of the type III bomb and its associated equipment to take temperature and pressure readings with the reactor at full power. It is hoped that this will be possible through the use of a cadmium sleeve into which the bomb will be withdrawn during measurements. More detailed description of insertion and withdrawal techniques for this bomb design has been reported by R. J. Davis, D. T. Jones and F. J. Walter⁵. It should be pointed out that the orientation of the type III bomb in the experimental access hole may cause a temperature gradient in the solution from one end of the bomb to the other. In order to estimate this gradient, three thermocouples are employed in contact with the external surface of the bomb. In addition, a temperature gradient through the wall of the bomb exists, regardless of design, depending upon the rate of heat generation within the bomb. In general, temperature gradients are minimized when the reactor is down so that the precision measurements, which yield oxygen consumption data, are least affected.

Termination of an in-reactor experiment is always accomplished before the oxygen supply in the bomb is exhausted. Before the experiment is removed from the reactor the bomb is cooled and the excess oxygen pressure and fission product gases are vented and flushed from the bomb into the reactor off-gas system. Using specially designed shielding, the experimental unit is withdrawn from the reactor with the usual precautions in connection with handling radioactive sources. After a short decay period the bomb is removed from the furnace-cooler assembly and

transferred to a hot cell for dismantling.

Greater detail of instrumentation and the safety interlock system is available for type III bomb experiments in a report by R. J. Davis, D. T. Jones, and F. J. Walter⁵.

H. Radiolytic Pressure Measurements

The steady-state pressure of the radiolytic hydrogen and oxygen in a bomb during irradiation is determined by subtracting -

- (1) the combined pressure of steam and residual oxygen at the operating temperature during a reactor shutdown period, from
- (2) the corresponding total pressure in the bomb, measured after the reactor has been operating at the desired power level for an hour, or sufficient time in which to establish a radiolysis-recombination equilibrium.

For bomb types IA, I, and II, continuously recording potentiometers are usually employed. The completed record consists of a strip-chart with inked temperature and pressure curves from which values for (1) and (2), above, may be subsequently obtained. The accuracy of such data from the strip-charts is not better than ± 25 psi and $\pm 1^\circ\text{C}$. The absolute accuracy of the radiolytic gas pressure measurements can be seriously affected by bias in the temperature readings due to gamma radiation heating in the thermocouple junctions.

Although in-reactor experiments have not yet been conducted with the type III bomb, better precision in the pressure and temperature measurements can be expected, perhaps ± 5 psi and 0.5°C , in the determination of pile-up and pile-down conditions from which the "radiolytic pressure" is to be calculated. In addition to the continuous recording potentiometer readings of temperature or pressure, precision potentiometers can also be used while the reactor is operating.

I. Examination of Irradiated Bomb and Contents

1. Dismantling of Bomb

The bomb and associated components are dismantled by standard procedures which vary only with the variety of difficulties encountered. Generally the capillary is removed and a dummy plug is inserted in its place. The plug behind the pin assembly is then removed and the pin rack withdrawn from the bomb.

The solution is drawn from the bomb with a remote pipette and transferred to a centrifuge cone. The same pipette is then used to rinse the bomb one or more times with approximately 10 ml of distilled water for each rinse. Each rinse is collected in a separate centrifuge cone.

The pin assembly is rinsed with distilled water and disassembled. The pins are placed in a tared weighing bottle and rinsed with acetone. This bottle, with pins is then dried in an oven at 110°C . After drying, the pins are removed, and the bottle reweighed to determine the amount of film removed by the drying operation. The pins are then weighed, defilmed cathodically in a rhodine inhibited 5% sulfuric acid solution, dried and reweighed for the determination of the metal weight loss. Since an estimate of the neutron flux which prevailed in the bomb is obtained from a γ -ray spectrometer measurement of the induced activity in the metal specimens, they must be completely freed of all adhering surface contamination. This is accomplished by a two-stage pickling procedure. The pins are individually immersed in two successive baths containing a fresh solution of the following composition:

<u>Component</u>	<u>Amount (parts by volume)</u>
Distilled H_2O	50
Concentrated HNO_3	40
Concentrated HCl	20
Concentrated HF	5

followed by immersion in a single bath containing a fresh solution of the

following composition:

<u>Component</u>	<u>Amount (parts by volume)</u>
Distilled H ₂ O	86
Concentrated HNO ₃	10
Concentrated HF	4

Each pin is dried with acetone between each bath, and the gross activity of the pin is measured with a paper chamber cutie-pie. This pickling procedure is repeated until the gross activity essentially ceases to decrease. The pins are then weighed and mounted for comparative activation analysis. This analysis is made by comparing a specific isotopic activity in a pin with that in a standard of the same material which has been exposed in a flux the magnitude of which in turn has been determined by means of a cobalt-aluminum alloy monitor.

The solution, rinse, and film recovered from the drying of the pins are subjected to chemical analysis for uranium, sulfate, copper, chromium, iron, nickel, zirconium, cesium and plutonium. Other elements and compounds are determined by chemical analysis as required by specific experiments. If solid material is removed with the solution and/or rinse, the solid phase is separated with a centrifuge, combined, dissolved and analyzed separately. This is reported as a precipitate.

2. Chemical Analysis Procedures

Analytical work with highly radioactive solids and solutions in many cases use scaled-down versions of standard procedures, but occasionally a special method must be developed for determining certain ions. Preliminary processing of the solutions frequently includes ion exchange; Dowex-1 resin is accepted for all such work except for the sulfate ion, where Dowex-50 is preferred.

The more common ions and determinations encountered in recent bomb solution analyses are listed below. For each there is given a reference in a detailed description of the method and apparatus used.

Chemical analyses of hot and cold materials are conducted by Urpo Koskela and his group and by Paul Thomason and his group, of the Analytical Division.

Activation analyses and cesium analyses are conducted by Henry W. Wright, J. S. Eldridge, and H. A. Parker, of the Analytical Division.

Radioactive standards are prepared and counted by G. W. Leddicotte of the Analytical Division.

Chromium	W. D. Shults, II, "Chromium in Homogeneous Reactor Solutions, Coulometric Titration Method," Method 9 082212 (Tentative), (2-17-55) ORNL Master Analytical Manual.
Copper	A. D. Horton, "Copper in Homogeneous Reactor Fuel, Polarographic Versenate Method," Method No. 9 082210 (R. 3-28-56) ORNL Master Analytical Manual.
Iron	J. J. McCowan, "Iron in Homogeneous Reactor Fuel Solutions, Spectrographic 1, 10-Phenanthroline Method," Method No. 9 082213 (5-25-56) ORNL Master Analytical Manual.
Lithium	W. R. Laing, "Lithium, Flame Photometric Method," Method Nos. 1 214530 and 9 00714530 (In Press) ORNL Master Analytical Manual.
Nickel	J. J. Lingane and H. Kerlinger, "Polarographic Determination of Nickel and Cobalt," Ind. Eng. Chem., Anal. Ed. <u>13</u> , 77 (1941).
Plutonium	R. L. Walker, "Plutonium, Lanthanum Fluoride Method," Method Nos. 2 31620 and 9 008620 (5-19-53), ORNL Master Analytical Manual and R. L. Walker, "Total Plutonium, Thenoyltrifluoroacetone Extraction Method," Method Nos. 2 31621 and 9 008621 (5-18-53) ORNL Master Analytical Manual.
Uranium	L. T. Corbin and J. H. Cooper, "Uranium Potentiometric Ceric Sulfate Method," Method Nos. 1 219221 and 9 00719221 (3-25-54) ORNL Master Analytical Manual.
Zirconium	A. D. Horton, "Zirconium in Homogeneous Reactor Fuel, Spectrophotometric Thoron Method," Method No. 9 082209 (R. 4-4-56) ORNL Master Analytical Manual.
pH	H. L. Hemphill, "Disposable Microelectrode Assembly for pH Determinations," Method Nos. 1 001003 and 9 001003 (12-16-54) ORNL Master Analytical Manual.
Chloride Ion	W. D. Shults, II, "Chloride in Homogeneous Reactor Type Solutions, Coulometric Titration Method," Method No. 9 082211 (Tentative) (2-8-55) ORNL Master Analytical Manual.
Sulfate Ion	F. J. Miller and P. F. Thomason, "Automatic Photometric Titration of Sulfate," ORNL-2040 (Feb. 29, 1956).

J. Typical Example of Corrosion Calculations from Oxygen Consumption Data.

For an example of corrosion calculations, data from the bomb run L6Z-101 will be used as an illustration. From the in-reactor pressure and temperature data, known bomb dimensions, steam pressure tables, quantitative information con-

cerning the solution and its composition, etc., the corrosion penetration for a given length of exposure is computed in detail.

1. Bomb Fill Data

a. Solution - The solution as prepared for bomb 16Z-101 had the following composition:

46.06 g U/l as UO_2SO_4

0.046 m CuSO_4

0.046 m H_2SO_4

and a density of 1.070 g/ml, as measured with a pycnometer. To this solution was added hydrogen peroxide, resulting in a reduction of the concentrations given above. This is dealt with later.

b. Bomb and Pins - A type II bomb, pin rack and four pins were fabricated from Zircaloy-2 having the composition, in percent by weight; zirconium 97.7, tin 1.4, iron 0.2, and nickel 0.05. In addition, two pins were turned out of stock alloy with the analysis: zirconium 80%, niobium 20%. These were slightly longer than the four Zircaloy-2 pins and were readily identifiable by this feature.

The pins were measured with a micrometer and weighed on an analytical balance, which furnished the following values:

Pin	Marks	Av. Diam. (in.)	Length (in.)	Weight (g)	From Which Could Be Calculated	
					Area (cm^2)	Theor. area (cm^2)
Long	One	0.601	1.7516	0.5671	2.1337	1.8272
Long	Two	0.611	1.7502	0.5788	2.1674	1.8576
Medium	One	0.614	1.6799	0.5311	2.0906	1.8667
Medium	Two	0.612	1.6738	0.5335	2.0762	1.8606
Short	One	0.610	1.5960	0.4941	1.9732	1.8546
Short	Two	0.631	1.5960	0.5279	2.0412	1.9184
Totals				3.2325	12.4823	11.1851

In this table the "theoretical area" equals the total area of a given pin less the combined area of the ends of the pin which are recessed in the washers which hold it in position in the bomb. This "recessed area" is included in the theoretical area of the bomb design for type II, as will be mentioned again below.

The diameters of the bomb parallel and perpendicular to an alignment slot were measured both before and after the 310° -4800 psi test. The following data show that the diameter of the bomb was not significantly changed by this pressure test.

Results of Ten Measurements	Bomb Diameters as Measured With A Micrometer			
	Parallel to Slot		Perpendicular to Slot	
	Before Press. Test	After Press. Test	Before Press. Test	After Press. Test
High Value	0.8113	0.8113	0.8114	0.8114
Low Value	0.8112	0.8111	0.8112	0.8111
Average of Ten	0.8112 ₄	0.8112 ₁	0.8113 ₃	0.8112 ₃

c. Bomb Fill

(1) Fuel Solution - Before loading the bomb with solution the volume of the bomb was calibrated as follows:

Weight of bomb filled with water at 25°C , (avg. of five weighings)	167.247 g
Weight of bomb filled with air	<u>160.697</u>

Average apparent weight of water at 25°C	6.550
--	-------

Error in weighing due to buoyancy effect of air on water (against brass weights) taken as 0.0069 g

Pycnometric volume of bomb	=	$\frac{\text{Apparent wt water} + 0.0069}{\text{Density of water at } 25^{\circ}\text{C}}$	=	$\frac{6.557}{0.99707}$
				6.576 ml

After adding about 3.3 cc of the uranyl sulfate solution prepared for bomb L6Z-101, the exact mass of solution was given by:

Weight of bomb + 3.3 cc solution	164.285
Weight of bomb empty	<u>160.697</u>
Apparent mass of solution	3.588
Buoyancy correction against brass weights	<u>0.004</u>
True mass of solution	3.592

(2) Hydrogen Peroxide - Micropipettes delivering a total of 0.500 ml were recalibrated with water and used to introduce a determined weight of hydrogen peroxide:

Average weight of pipettes filled with water (5 determinations) at avg. of 30.1°C	8.3649 g
Weight of pipettes empty	<u>7.8730</u>

Average weight of water contained in pipettes = 0.4919

Volume of pipettes as calibrated above = $\frac{\text{weight of water at } 30.1^{\circ}\text{C}}{\text{density of water at } 30.1^{\circ}\text{C}}$ =

(introducing buoyancy of air
effect of 0.0005 g) $\frac{0.4919 \text{ g} + 0.0005}{0.99564 \text{ g/ml}}$ = 0.4946 ml

To find the actual mass of hydrogen peroxide introduced into the bomb:

Weight of pipettes + H ₂ O ₂ residue (after delivery)	7.8737 g
Weight of pipettes empty	<u>7.8730</u>
Weight of H ₂ O ₂ residue	0.0007 g

$$\begin{aligned} \text{Mass of H}_2\text{O}_2 &= (\text{Volume of H}_2\text{O}_2 \times \text{Density of H}_2\text{O}_2) - 0.0007 \\ &= (0.4946 \text{ ml} \times 1.109 \text{ g/ml}) - 0.0007 = 0.548 \text{ g} \end{aligned}$$

After the addition of 0.548 g of 33.68% hydrogen peroxide, the bomb was capped and heated to decompose the H₂O₂ into (1) water, which diluted the uranyl sulfate solution, and (2) oxygen, which developed 300 psi in the gaseous phase in the bomb at 25°C, apart from dissolving in the liquid to a slight extent. A new liquid volume is thus established which in turn fixes the volume of the gaseous phase in the sealed bomb. To find this volume at 25°, 100°, 250°, and

280°C, the 33.68% hydrogen peroxide must be considered as:

66.32% liquid water = 66.32% of 0.548 g = 0.363 g H₂O

33.68% x 0.548 g = 0.184 g H₂O₂ forming 0.098 g H₂O by decomposition.

Total H₂O residual from H₂O₂ decomposition: 0.461 g. This liquid is assumed to be additive in mass and volume to the uranyl sulfate solution in the bomb.

	Weight (g)	Volume (ml)	Density (g/ml)	Source
Original uranyl sulfate solution in bomb	3.592	3.356	1.070	(measured)
Increment supplied by hydrogen peroxide	<u>0.461</u>	<u>0.462</u>	0.99707	(literature)
New total liquid characteristic at 25°C	4.053	3.818	1.062	(calculated)

2. Solution Density vs. Temperature Relation

Having obtained the density of the final bomb solution (in readiness for irradiation), density-temperature relationships as derived by Marshall⁶ are employed to compute the density at several elevated temperatures:

The weight percent UO₂SO₄, S, is given by $S = 115.7 - \frac{115.3}{\text{Density}}$

Substituting the newly calculated density at 25°C: $S = 115.7 - \frac{115.3}{1.06} = 7.1\%$ UO₂SO₄. The solution density of water-uranyl sulfate solutions between 120° and 280°C has been expressed in terms of the concentration up to 51 percent UO₂SO₄:

$$\text{Density at temperature, } t, = \frac{1}{\frac{120.9}{S} - 1.046} + \text{Density of H}_2\text{O at } t.$$

Substituting the value 7.1% for S, and known water density values, there is obtained:

Temperature, degrees Centigrade (t)	<u>25°</u>	<u>100°</u>	<u>250°</u>	<u>280°</u>
Density of water (from handbook tables), g/ml	0.997	0.958	0.799	0.751
Final density of bomb solution, g/ml	1.062	1.021	0.862	0.813
Solution volume, ml	3.818	3.970	4.703	4.984
Available volume of bomb, ml	6.578	6.588	6.607	6.611
Total gas space in bomb, ml	2.760	2.618	1.904	1.627

- Notes: (1) Marshall's⁶ equations were assumed to hold between 100° and 280°C, inclusive.
- (2) The amount of water lost from the solution to the gas space at temperatures up to and including 280°C has been assumed to be too small to significantly affect the solution volume and thence the volume of the gas space.
- (3) No correction was made for the slight increase of gas space resulting from the slight compressibility of water in the bomb and also in the Baldwin cell. At higher steam pressures (above 300°C a correction for this volume change is made¹⁴.
- (4) The side effects mentioned in (2) and (3) above affect the mass of the solution remaining in the bomb. This reduction in magnitude of the liquid phase in turn affects subsequent calculations dealing with the amount of oxygen dissolved in the solution.
- (5) The "available volume" of the bomb is based on the volume (already calculated) at 25°C, together with the known cubical coefficient of thermal expansion. Values of the coefficient for three common reactor metals are:

Stainless steel 347	51×10^{-6}	1/°C
Titanium	25.6×10^{-6}	
Zircaloy-2	19.5×10^{-6}	

- (6) The total gas space in the bomb is obtained by subtracting the "solution volume" from the "available volume," at a given temperature.

3. Solubility of Oxygen

Measurements of the temperature and pressure in bomb L6Z-101 before and after a given period of irradiation permitted a calculation of the quantity of oxygen consumed during that period. One such calculation will suffice for purposes of illustration here, although while the bomb was in the reactor (LITR), 3 sets of T-P measurements and calculations served to establish a corrosion rate at 250°C, and 4 additional sets of similar data were treated to obtain the 280°C rate. The simple gas laws enable one to compute the oxygen remaining in the gas space above the liquid phase. At the elevated temperatures an appreciable fraction of unreacted oxygen dissolves in the uranyl sulfate solution, and so resort must be had to solubility data⁷⁻¹⁰, for oxygen in water, sulfuric acid,

and uranyl sulfate. For example, quantitative information on the solubility of oxygen in the L6Z-101 solution at 280°C was needed. Dilution of the original stock solution resulted from addition and subsequent decomposition of hydrogen peroxide (as already discussed) necessitating a recalculation of the new concentrations:

UO ₂ SO ₄	46.06 g U/l	became 40.0 g U/l
CuSO ₄	0.046 <u>m</u>	became 0.040 <u>m</u>
H ₂ SO ₄	0.046 <u>m</u>	became 0.040 <u>m</u>

It is customary to handle the H₂SO₄ and CuSO₄ by assuming that their combined effect is the same as H₂SO₄ along with regard to the lowering of solubility of oxygen in the uranyl sulfate solution. From reference (10) the following two values are used to form a straight-line plot of the "solubility lowering" of oxygen in aqueous sulfuric acid:

H ₂ SO ₄ Concentration (M)	Solubility (cc O ₂ /cc-psi 25°C)	Density of liquid (g/cc)	Solubility (cc O ₂ /g - psi)	Solubility Ratio (H ₂ O/acid)
0.00	0.02831	0.99707	0.02839	
0.25	0.0264	1.0131	0.02606	0.9179

Points along the solubility ratio-molarity curve (drawn from the above data) represent "solubility lowering" fractions which are assumed to be valid when applied to acid concentrations in uranyl sulfate solutions, even at elevated temperatures. Assuming linearity of the curve just mentioned between zero and 0.25 molar sulfate, the solubility lowering fraction, F_s is given by the following relation:

$$F_s = 1.000 - 0.3284 M$$

where M is the sum of the molarities of H₂SO₄ and CuSO₄.

Data on the solubility of oxygen in aqueous uranyl salt solutions at elevated temperatures and pressures are available⁸. These data are used in conjunction with the above described "solubility lowering fraction," F_s , in an effort to arrive at the "best" approximation of dissolved oxygen in the various bomb solutions. Continuing with the present example, L6Z-101 (0.04 $\underline{m}$ H_2SO_4 and 0.04 $\underline{m}$ $CuSO_4$):

$$\begin{aligned}
 \text{Solubility of } O_2 \text{ at } 280^\circ C \text{ for} &= \text{Solubility of } O_2 && \text{Solubility} \\
 \text{L6Z-101 solution} &= \text{in } UO_2SO_4 \text{ at the} && \text{X lowering by "total} \\
 &\text{desired concentration} && \text{sulfates" added} \\
 &(\text{from tables}) && (\text{combining } H_2SO_4 \text{ and} \\
 & && CuSO_4 \text{ molarities}) \\
 &= 0.00445 \frac{\text{cc } O_2(\text{STP})}{\text{g soln. x psi } O_2} && \text{X } 0.972 \\
 & && = 0.00433 \text{ cc } O_2/\text{g X psi of L6Z-101 solution.}
 \end{aligned}$$

The value 0.00445 ml/g is valid (according to the tables⁸) only in the range near 150 psi partial pressure of oxygen. If the partial pressure is found to lie in a different range, a slightly different value will be found in the tables.

4. Oxygen Consumed

As previously stated in the discussion, the total unreacted oxygen in the bomb is calculated from pressure and temperature measurements by the following equation:

$$\text{Vol. of } O_2 \text{ in cc at S.T.P.} = P \frac{18.587}{T} \times \frac{\text{Gas space}}{(\text{cc})} + \frac{\text{Wt. soln.}}{(\text{g})} \times \frac{\text{Solubility of } O_2}{(\text{cc/g-psi})}$$

After 211.3 hours of exposure to radiation in HB-6 of the LITR, the reactor power was reduced to zero and the following was recorded:

E.M.F. of iron-constantin thermocouples in the bomb well: For ten readings

High 15.206 mv
 Low 15.199
 Avg. 15.201 equiv. to
 280.00°C.

E.M.F. of output of Baldwin cell: For ten readings

High 1087.5 microvolts
 Low 1085.3
 Avg. 1086.4 equiv. to 1086.4 psi

At 280.00°C the steam pressure is given as 931.0 psi. Subtracting 931.0 from

the total combined oxygen and steam pressure: Total pressure 1086.4 psi
 Steam pressure 931.0

Oxygen pressure 155.4 psi

After 211.3 hours of irradiation, the remaining oxygen amounted to:

Vol. of oxygen at S.T.P. = 155.4 psi $\frac{18.587}{280^\circ \div 273.16^\circ} \times 1.627 \text{ cc} \div$

$(4.053 \text{ g} \times 0.00433 \text{ cc/g} \cdot \text{psi}) =$

155.4 $\left[0.05466 \div 0.01755 \right] = 11.22 \text{ cc of oxygen total in bomb.}$

Similar treatment of the T-P data at the start of the 280°C portion of the in-reactor exposure showed that the initial oxygen S.T.P. volume was 30.33 cc, at which time the L6Z-101 experiment had just completed a 128.3 hour exposure at 250°C.

By difference:	<u>Hours exposure</u>	<u>Volume of O₂, cc</u>
	211.3 hr total	11.22
	- 128.3 at 250°	- 30.33
	<u>83.0 hr at 280°C</u>	<u>19.11 cc of oxygen consumed during this period of operation.</u>

5. Corrosion Penetration from Oxygen Consumed

a. Corrosion Constant k - It now remains to convert "oxygen consumed" into "mils of penetration" of the metal which presumably underwent corrosion at the expense of the oxygen in the bomb. For this final computation two additional "constants" must be obtained: the corrosion constant "k" for Zircaloy-2, i.e. the volume of metal (mil-cm²) consumed per cm³ (STP) of oxygen and the area of the corroding Zircaloy-2 surface (cm²).

The procedure used in calculating a value of k for a particular alloy will be cited in the case of Zircaloy-2, having the composition given in the table below.

Element	Oxide	% of Constituent	A Combining wt. (g/ccO ₂ STP) X 10 ³	B g Constituent in 1 mil-cm ² , X 10 ²	B/A = ccO ₂ /mil- cm ² of metal
Zr	ZrO ₂	98.29	4.070	1.635	4.017
Sn	SnO ₂	1.45	5.295	.0241	.046
Fe	Fe ₂ O ₃	0.115	3.322	.00191	.006
Cr	Cr ₂ O ₃	0.09	3.094	.00150	.005
Ni	NiO	0.05	5.236	.00083	.002

4.076 cc O₂/
mil-cm²

$$k = \frac{1}{4.076} = 0.2453 \frac{\text{mil-cm}^2}{\text{cc O}_2(\text{STP})}$$

The value of the corrosion constant "k" for various materials is listed below:

Metal	Density, g/ml	Corrosion Constant "k", mil-cm ² /cc O ₂ S.T.P.
Zircaloy-2	6.55	0.2453
Stainless Steel 347	8.027	0.1397 ^a
Stainless Steel 347	8.027	0.1675 ^b
Titanium	4.534	0.1851
80/20 Zr/Nb alloy	7.07	0.2182
83.5/15/1.5 Zr/Nb/Sn alloy	7.00 ^c	0.2236

Notes:
a assuming complete oxidation of chromium to Cr VI.
b assuming complete oxidation of chromium to Cr III.
c estimated from the known densities of the elements.

b. Area

The second "constant" which is peculiar to the L6Z-101 bomb is the surface area of metal susceptible to corrosion. For this the following formula is employed:

For the type II bomb, the surface area = area of pin ends and recesses + area of swage + (calculated area X $\frac{\text{Pycnometric volume}}{\text{calculated volume}}$)

$$\text{Area of L6Z-101} = \left[2.59 \text{ cm}^2 + 0.20 \text{ cm}^2 + \left(6.5764 \times \frac{46.95}{6.37} \right) \right] \text{ cm}^2 = 51.30 \text{ cm}^2.$$

In the above formula the "area of the swage," the "calculated area," and the "calculated volume" are values computed from the original drawing utilized by the machinist during fabrication.

c. Penetration

The quantity of oxygen consumed during 83 hours of irradiation at 280°C, the surface area of metal in contact with the uranyl sulfate solution, and the corrosion constant for Zircaloy-2 are related to the depth of penetration in the following way:

$$\text{Corrosion penetration in mils} = \frac{19.11 \text{ ml O}_2}{51.30 \text{ cm}^2} \times 0.2454 \text{ mil cm}^2/\text{cc of O}_2 = 0.0914 \text{ mils in 83 hours.}$$

This may be simplified to a corrosion rate of 0.0011 mil/hour or 9.6 mil/yr. at 280°C. As explained previously, the rate data to be reported as final will not be obtained from two points but from a least squares treatment¹¹ of several points, thereby reducing the possibility for error.

6. Correction to Be Applied When "Foreign" Alloys are Present

a. Penetration from Pin Weight Losses - In the case of bomb L6Z-101 an adjustment of the corrosion rate (as just calculated) should be made. This adjustment stems from the observed difference in depth of corrosion penetration of the Zircaloy-2 pins and the 80/20 Zr/Nb alloy pins present in the bomb; such

observation being based on the relative loss in weight of the defilmed specimens which are of course available for examination only at the end of an in-reactor exposure when the bomb is disassembled. Cathodic defilming of the six L6Z-101 bomb pins resulted in an actual loss in weight (when compared with the before-exposure weight) which may be summarized thus:

Four Zircaloy-2 pins lost 0.0347 g (original surface area = 8.181 cm²)

Two Zr/Nb (80/20 alloy) pins lost 0.0152 g (original surface area = 4.301 cm²)

In order to convert this information to depth of penetration values the following formulas are derived:

$$\begin{aligned} \text{Penetration of Zircaloy-2 (mils)} &= \frac{\text{Loss in wt. g}}{\text{Area of pins, cm}^2} \times \frac{1}{6.55 \text{ g/cm}^3} \times \frac{1000 \text{ mils}}{2.54 \text{ cm}} \\ &= 60.106 \frac{\text{Loss in wt. g}}{\text{Area of pins, cm}^2} \end{aligned}$$

$$\begin{aligned} \text{Penetration of Zr/Nb alloy (mils)} &= \frac{\text{Loss in wt. g}}{\text{Area of pins, cm}^2} \times \frac{1}{7.07 \text{ g/cm}^3} \times \frac{1000 \text{ mils}}{2.54 \text{ cm}} \\ &= 55.685 \frac{\text{Loss in wt. g}}{\text{Area of pins, cm}^2} \end{aligned}$$

Substituting the known quantities in the above equations results in the values for surface penetration:

Zircaloy-2 0.255 mil

Zr/Nb alloy 0.197 mil

b. Adjustment in Oxygen Consumed for "Foreign Alloy" Present

By comparing these two quantities it may be seen that the zirconium-niobium alloy apparently corroded at 77 percent of the rate of the Zircaloy-2 pins. Therefore the rate previously calculated from oxygen consumption data, in order to apply exclusively to the Zircaloy-2 present (representing about 91.6 percent of the entire area), must be adjusted to a slightly higher value. To accomplish this adjustment, the following relationships and assumptions may be utilized:

$$\frac{\text{Volume of O}_2 \text{ consumed by Zircaloy-2}}{\text{Volume of O}_2 \text{ consumed by Zr/Nb alloy}} = \frac{\text{Volume of Zircaloy-2 oxidized}}{\text{Volume of Zr/Nb alloy oxidized}} \times$$

$$\frac{\text{Corrosion constant for Zr/Nb alloy}}{\text{Corrosion constant for Zircaloy-2}}$$

$$\text{For L6Z-101, this oxygen ratio becomes: } \frac{0.255 \text{ ml} \times 47.00 \text{ cm}^2}{0.197 \text{ ml} \times 4.30 \text{ cm}^2} \times \frac{0.2182}{0.2454} = 12.58$$

Realistically, the ratio 12.58 may not necessarily be valid for either 250° or 280°C; the in-reactor experiment was conducted for a period of time at each of the two temperatures, and the ratio of the depths of penetration of the two metals would probably vary with change in temperature. However, in order to determine the more probable value for the corrosion rate of Zircaloy-2 for the conditions of experiment L6Z-101, the ratio 12.58 must be employed as a first approximation.

It has already been determined that 19.11 ml of oxygen was consumed during the first 83.0 hours of irradiation at 280°C. Then

$$\frac{19.11 \text{ ml} - (\text{Vol. O}_2 \text{ removed by Zr/Nb})}{(\text{Vol. O}_2 \text{ removed by Zr/Nb})} = 12.58$$

Solving, it is found that the Zr/Nb alloy must have reacted with 1.41 ml of O₂; the remainder, then, reacted with the Zircaloy-2, namely, 17.70 ml. Converting the latter figure to penetration, and thence to a corrosion rate:

$$\frac{17.70 \text{ ml} \times k}{47.00 \text{ cm}^2} = 0.092 \text{ mil penetration, or } 9.7 \text{ mil/year.}$$

K. Corrosion Penetration from Pin Weight Changes

The penetration calculation from pin weight losses simply involved re-stating the quantity of metal loss as a volume, i.e. weight/density and dividing by the corroding area to get a depth of penetration. The accuracy of the results are limited by the ability to defilm the pins. Zr-2 and 347 SS can presently be defilmed very satisfactorily as described previously. Titanium

results have been variable.

Pin weight gains require a knowledge of the stoichiometry of the oxidation. The assumptions usually made are outlined in connection with the oxygen consumption data. The calculation assumes that all the oxide is retained on the specimen and it involves deriving an expression for the thickness of film in terms of weight of oxygen consumed. In general, all of the oxide is not retained on the metal surfaces, making weight gains useless. On occasion, the weight gain idea has been used in connection with titanium experiments.

For reference some corrosion penetration-weight loss formulas are given:

$$\begin{aligned} \text{Zr-2 mils penetration} &= \frac{\text{loss in wt. (g)}}{\text{area of pins, (cm}^2\text{)}} \times \frac{1}{\text{density, (g/cc)}} \times \frac{1000 \text{ (mils)}}{2.54 \text{ (cm)}} \\ &= 60.107 \times \frac{\text{Wt. loss (g)}}{\text{Area, (cm}^2\text{)}} \end{aligned}$$

$$\text{Stainless Steel} = 49.047 \times \frac{\text{Wt. loss, (g)}}{\text{Area, (cm}^2\text{)}}$$

$$\text{Titanium} = 86.833 \times \frac{\text{Wt. loss, (g)}}{\text{Area, (cm}^2\text{)}}$$

$$\text{80/20 Zr/Nb} = 55.686 \times \frac{\text{Wt. loss, (g)}}{\text{Area, (cm}^2\text{)}}$$

Corrosion penetration from weight gains:

$$\begin{aligned} \text{Titanium, mils penetration} &= \frac{\text{Wt. gain, (g)}}{\text{Area, (cm}^2\text{)}} \times \frac{\text{Ti}}{2(0)} \times \frac{1}{\text{density, (g/cc)}} \times \frac{1000 \text{ (mils)}}{2.54 \text{ (cm)}} \\ &= 130.512 \times \frac{\text{Wt. gain, (g)}}{\text{Area, (cm}^2\text{)}} \end{aligned}$$

L. Power Density Calculated from Cs¹³⁷ Fission Product Analysis

In addition to estimates of flux from count data on metal specimens, as described by Baker¹², estimates have also been obtained from count data on the U²³⁵ fission product, Cs¹³⁷, present in the irradiated solution. An aliquot of the latter is diluted, a known weight of dead cesium added, and total cesium is

finally precipitated from solution as the chlorostannate. The weighed precipitate is counted against a standard sample of radioactive cesium which has been calibrated in terms of fissions. A second count is made three months later when short-lived Cs^{136} will have suffered considerable decay. The reported count, in fissions/ml for the in-reactor period of time, provides a quick means of obtaining a value for the power density which is referable to the temperature of the solution at the time of count.

$$\text{Watts/ml} = \frac{\text{fissions/ml}}{\text{irrad. time in hr}} \times \frac{8.93 \times 10^{-15} \text{ watt/hr/fission}}{1}$$

As an example of this type of calculation bomb Z-24 will be taken.

$$\text{Power density at } 25^{\circ}\text{C} = \frac{9.67 \times 10^{16} \text{ fissions/ml}}{81.137 \text{ hr irrad. time}} \times \frac{8.93 \times 10^{-15}}{1} = 10.6 \text{ w/ml}$$

This value may be translated into the corresponding power density at any other temperature for which the density of the solution is available or may be computed by making use of the density ratio: Power density at 280°C =

$$10.6 \text{ w/ml} \times \frac{0.805}{1.053} = 8.13 \text{ w/ml.}$$

It may be remarked that the power density value which was derived from pin activation data for bomb Z-24 was 14.0 w/ml. In general, it has been observed that cesium analyses furnish lower values than those calculated from the pin activation data. Possible reasons for lack of agreement are:

- (1) A slight trace of fission products still adhering to the surface of "defilmed" pins at the time of activation analysis will give rise to an abnormally high calculated power density. However, when ambiguity from this source is suspected, i.e. when the neutron flux from Zr^{95} activation analysis is abnormally high or when agreement between pins is poor, the pins can be pickled again and reanalyzed.

(2) The accuracy of the radio-cesium analysis depends on no adsorption of cesium on the film. It is believed at the present time that a considerable and varying degree of adsorption does occur.

M. Power Density From Pin Activation Analysis

The pins or coupons which had been exposed to the corrosive environment of the uranyl salt solution are also characterized by induced radioactivity through exposure to in-pile neutrons. After thorough removal of all interfering surface contamination from the pins or coupons a comparative activation analysis is conducted on the clean metal specimens. The resulting values, relative to metal "standards" (which have been previously irradiated in a flux of pre-determined magnitude), are employed in a calculation of the flux which prevailed at each pin or coupon site. The equations employed are in general similar to those given by Baker¹². Having arrived at a value of the flux at a given location, the fission power density is readily calculated from the relationship:

$$\text{Power density (watts/ml)} = \frac{\phi (\text{U conc.})(\text{U enrichment}) \times 4.7618 \times 10^{-14}}{\frac{\text{Density of soln. at } 25^{\circ}}{\text{Density of soln. at operating temp.}}}$$

where ϕ is the flux in neutrons/cm²·sec.

(U conc.) is expressed in g uranium per liter

and (U enrichment) is the concentration of the U²³⁵ isotope expressed as a decimal fraction and

the factor 4.7618×10^{-14} is derived as a product of the following factors:

$$\frac{1 \text{ fission}}{1 \text{ neutron}} \times \frac{2 \times 10^8 \text{ ev}}{1 \text{ fission}} \times \frac{1.602 \times 10^{12} \text{ ergs}}{1 \text{ ev}} \times \frac{1 \text{ kilowatt}}{10^{10} \text{ ergs/sec}} \times \frac{6.023 \times 10^{23} \text{ atoms U}^{235}}{235.05 \text{ g U}^{235}} \times \frac{5.80 \times 10^{-22} \text{ cm}^2}{1 \text{ atom U}^{235}}$$

Note that the value of the fission cross section of U²³⁵ is taken as 580 barns, and the energy of fission is regarded as 200 Mev.

FIGURES

1. LIIR Rocking Autoclave Corrosion Test Facilities
2. Schematic Diagram of In-Reactor Rocking Autoclave Experiment Type I
3. Bomb Assembly for Radiation Corrosion Studies Type I
4. Bomb Assembly for Radiation Corrosion Studies Type IA
5. Schematic Diagram of In-Reactor Rocking Autoclave Experiment Type II
6. Bomb Assembly for Radiation Corrosion Studies Type II
7. In-Reactor Rocking Autoclave Experiment Type III
8. Bomb Assembly for Radiation Corrosion Studies Type III

LITR ROCKING AUTOCLAVE CORROSION TEST FACILITIES

FIGURE 1

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UNCLASSIFIED
ORNL-LR-DWG. 21737

SCHEMATIC DIAGRAM OF IN-REACTOR ROCKING AUTOCLAVE EXPERIMENT TYPE I (HB-6 Feb. 1954 - Oct. 1956)

FIGURE 2

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UNCLASSIFIED
ORNL-LR-DWG. 17439A
(Taken from D-19,647)

TYPICAL VALUES AT 250°C

TOTAL INTERNAL AREA
INCLUDING 4 PINS

43. sq. cm.

VOLUME OF BOMB

8.8 ml.

VOLUME OF SOLUTION

6.2 ml.

PERCENT OF FILL

71 %

BOMB AREA
SOLN. VOL.

7.0

Single Specimen Pin Area = 2.4 sq. cm.

TO
PRESSURE
MEASURING
DEVICE

BOMB ASSEMBLY
FOR
RADIATION CORROSION STUDIES
TYPE I

FIGURE 3

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TYPICAL VALUES AT 250°C

TOTAL INTERNAL AREA INCLUDING 4 PINS	43. sq.cm.
VOLUME OF BOMB	8.8 ml.
VOLUME OF SOLUTION	6.2 ml.
PERCENT OF FILL	71 %
<u>BOMB AREA</u> SOLN. VOL.	7.0

BOMB ASSEMBLY
FOR
RADIATION CORROSION STUDIES
TYPE IA

FIGURE 4

SCHEMATIC DIAGRAM OF IN-REACTOR ROCKING AUTOCLAVE EXPERIMENT TYPE II (HB-5 Jan.1955-Mar.'57, HB-6 Oct.1956-date)

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UNCLASSIFIED
ORNL-LR-DWG. 16662A
(Taken from D-19052)

TYPICAL VALUES AT 250°C

TOTAL INTERNAL AREA INCLUDING 6 PINS	50. sq. cm.
VOLUME OF BOMB	6.5 ml.
VOLUME OF SOLUTION	4.8 ml.
PERCENT OF FILL	74 %
<u>BOMB AREA</u> <u>SOLN. VOL.</u>	10.6

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BOMB ASSEMBLY
FOR
RADIATION CORROSION STUDIES
TYPE II

FIGURE 6

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UNCLASSIFIED
ORNL-LR-DWG. 21739

IN-REACTOR ROCKING AUTOCLAVE EXPERIMENT TYPE III (HB-5 June 1957 to Date)

FIGURE 7

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UNCLASSIFIED
ORNL-LR-DWG. 18328A
(Taken from D-24559)

TYPICAL VALUES AT 250°C

TOTAL INTERNAL AREA, INCLUDING COUPONS	70 sq.cm.
VOLUME OF BOMB	9.9 ml.
VOLUME OF SOLUTION	7.4 ml.
PERCENT OF FILL	75%
<u>BOMB AREA</u> <u>SOLN. VOL.</u>	9.4

COUPON
Specimen Coupon Area = 1.81 sq.cm.

FIGURE 8

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