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DECOMPOSITION AND RECOMBINATION IN
IRRADIATED STATIC WATER SYSTEM AT HIGH TEMPERATURES

by

J. R. Humphreys, E. K. Abers, and Y. Solomon

March 1953

REACTOR ENGINEERING DIVISION

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DECOMPOSITION AND RECOMBINATION IN IRRADIATED
STATIC WATER SYSTEMS AT HIGH TEMPERATURES

by

J. R. Humphreys, E. K. Abers, and Y. Solomon

ABSTRACT

Static water samples were exposed to pile radiation in the graphite reflector blanket of the Heavy Water Reactor at Chalk River, Ontario. These water samples were contained in an AISI type 347 stainless steel autoclave.

The data indicate that between 300 and 500F the hydrogen concentration was primarily a function of stainless steel corrosion and organic impurity oxidation reactions. The oxygen concentration, being repressed by the resulting hydrogen excess, approached trace concentrations.

The decomposition product concentrations at 140F were influenced by variations in the ionic impurity concentrations, while the higher temperature operations (300 - 500F) were much less sensitive both to the presence of inorganic impurities and to variations in their concentrations.

Small amounts of organic impurities in the water appear to be completely oxidized upon exposure to reactor radiation. In the experiments described, the quantities of CO₂ generated by organic oxidation were independent of temperature in the range of 300 - 500F.

With presence of a vapor space in the autoclave, the total autoclave gas content was lower than in the all-liquid-phase runs. The difference between the theoretical stoichiometric oxygen content (calculated from the measured quantities of hydrogen, carbon dioxide, and nitrogen) and the measured oxygen content was greater in the case of all-liquid-phase runs than in runs containing a vapor phase.

A small excess of hydrogen in the two-phase experiments between 300 and 500F greatly suppressed the amount of oxygen in the system. A small excess of oxygen, under the same conditions, correspondingly repressed the hydrogen concentration.

Initial combination rates of hydrogen and oxygen added to two-phase, steady-state irradiated water systems between 327 and 500F were essentially constant and independent of temperature. The initial combination rate at 295F was lower than rates observed in the higher temperature range.

A general evaluation of the experimental data indicates that the vapor phase combination reaction of hydrogen and oxygen is appreciable. In runs with addition of hydrogen and oxygen the major portion of the total combination reaction occurred in the vapor phase.

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I. INTRODUCTION

The previous knowledge and experimental data on the effects of radiation on various high-temperature water systems were inadequate for detailed design application to several high-temperature water-cooled and moderated reactors under consideration or development. The investigation reported here is a continuation of the static autoclave experimental program, started in the Oak Ridge Static Autoclave Water Decomposition Test.¹

Previous investigators² have shown that the concentrations of the decomposition products produced by the irradiation of pure water will rise to steady-state values. At this point, the recombination reaction of the decomposition products is equal in rate to the breakdown of the water by radiation. The variation in the decomposition product concentrations at this steady-state condition with such variables as temperature, radiation intensity, and ionic impurities has been studied extensively at the lower temperatures, but very little work has been done in the 300 to 500F temperature range.

The first work including the effect of temperature on the steady-state condition of water under reactor irradiation is reported by A. O. Allen.² While this investigation was confined to quartz ampoule experiments in the X-10 reactor over a limited temperature range, the results indicated a lowering of steady-state decomposition product concentrations with increasing temperatures in the range of 100 to 340F. L. W. Fromm³ worked at a higher temperature and reported lowering of steady-state decomposition product pressures with increasing temperature in the range 350 to 450F.

It has been predicted by Allen⁴ and Toulis⁵ that the steady-state decomposition product concentrations in the liquid phase vary as the square root of the radiation intensity.

Allen's work² indicated that the steady-state concentrations of decomposition products are very sensitive to the presence of ionic impurities in the water at the lower temperatures. Some dissolved substances, such as the halogens, raised the steady-state level considerably, while other solutes such as H_3PO_4 and KOH resulted in no significant change from the pure water conditions. Allen also reported that the container material very greatly affected the steady-state level. Experiments with Pyrex glass, gold, tin, zirconium, and aluminum containers showed that all these materials raised the steady-state level when compared with results obtained in quartz containers. Material balances were poor in containers made from materials other than quartz.

In previous work with the Oak Ridge autoclave,¹ decomposition product steady-state partial pressures of 0.4 to 0.65 psi were obtained for 235F water exposed to an epithermal neutron flux of about 2×10^{11} . There was a small vapor phase present in all runs under the conditions of this test, so that these results are not necessarily applicable to an all-liquid-phase system. Direct measurements of the decomposition product partial pressures at higher temperatures were indeterminate owing to the methods of measurement used in this test.

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Recombination studies in the Oak Ridge Test were made by adding hydrogen and oxygen gases to a two-phase water system at different temperature and flux levels. The data showed a significant effect of temperature on the rate of pressure drop in the partial pressures of the added hydrogen and oxygen from 200F to 485F. In operating at two epithermal neutron flux levels, 1.2×10^{11} and 2.0×10^{11} , no difference in the rate of pressure decrease with flux could be detected with the instrumentation on the test apparatus.

The operational experience and techniques developed in this test were very useful in the Chalk River experimental program, and while the information gained in the Oak Ridge Static Autoclave Test was principally qualitative, the results more clearly defined the experimental direction of the Chalk River high-temperature water irradiation study. Thus the objectives of the Chalk River water decomposition program were:

1. To determine steady-state concentrations of gaseous decomposition products of pure water under irradiation in the Chalk River reactor at temperatures from 300 to 500F.
2. To determine the effects of temperature and radiation intensity upon the steady-state condition of water systems from 300 to 500F.
3. To determine the effects of the various systemic impurities present in the water under the different operating conditions.
4. To determine the effects of temperature and radiation intensity on the combination of added hydrogen and oxygen in two-phase water systems.

By agreement between the United States Atomic Energy Commission, the National Research Council of Canada (later the Atomic Energy of Canada, Limited), and Argonne National Laboratory, the experimental program in the NRX reactor at Chalk River was conducted on a cooperative basis. By this agreement, Argonne supplied the experimental equipment and operating personnel, while the National Research Council supplied the reactor facility and radiation plugs, as well as the necessary shop work and analytical chemistry services. Experimental data were mutually shared by both groups. It was agreed also that the experimental apparatus and flux converter facility would be made available to the National Research Council of Canada for an extension of the program upon completion of the experimental operations by Argonne personnel.

The authors would like to express their appreciation for the courtesy and cooperation extended to them in the course of this experimental program by the staff of the National Research Council of Canada.

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II. TEST FACILITY AND APPARATUS

A. Irradiation Facility

1. General

The irradiation of the water samples contained in a stainless steel autoclave was conducted in the NRX reactor at the Chalk River, Ontario, Canada plant of Atomic Energy of Canada, Limited.

Two 4-inch experimental side holes were used. Hole E-6 was used in the first phase of the experimental program, in which the first autoclave was placed in the graphite reflector blanket surrounding the callandria. Hole E-3 was used in the final phase of the experimental program, in which the autoclave positions relative to the callandria were the same except for the addition of the natural uranium neutron flux converter.

Holes E-6 and E-3 are at the same height on the callandria wall and have approximately the same symmetry with respect to the reactor structure. Thus, the two facilities were both exposed to about the same reactor flux level except for possible flux distortions by adjacent experimental equipment within the reflector blanket. This condition should not cause appreciable change, as these absorbers are all external to the reactor proper and are fairly evenly distributed about each of the holes.

2. Flux Converter Facility

In the second phase of the experiment, the second autoclave was placed inside a cylindrical natural uranium neutron converter. The function of this converter was to transform part of the thermal neutron flux to fast neutron flux by undergoing thermal neutron capture and fission. In this way, the fast neutron flux realized was higher than that otherwise available (at the facility). A cutaway drawing of the Chalk River converter is shown in Figure 1.

Neutron monitoring foils were mounted in the annular space between the autoclave and the converter to measure the total dosage of both fast and thermal neutron flux.

The fast neutron foil consisted of about 15 micrograms of neptunium in a nickel-cadmium alloy sandwich. The thermal neutron foil contained approximately 15 micrograms of cobalt in an aluminum sandwich.

Analysis of these foils indicated that the average fast neutron flux was $2.05 \pm 0.4 \times 10^{12}$ neutrons/cm²/sec at full pile power with a thermal neutron flux of $2.7 \pm 0.5 \times 10^{12}$ neutrons/cm²/sec.

An estimation of the neutron flux zone into which the first autoclave was placed without a converter is $1.2 \pm 0.5 \times 10^{12}$ fast neutrons/cm²/sec and $5 \pm 2 \times 10^{12}$ thermal neutrons/cm²/sec. No foils were used in this phase of the experiment.

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DETAIL B-COOLING CHANNELS
TWICE SIZE

FIG. 1
CUTAWAY OF CHALK RIVER CONVERTOR

B. Apparatus

1. Pressure System

The reaction vessel consisted of a horizontal AISI type 347 stainless steel autoclave with a 120 cc capacity, as shown in Figure 2. Thermocouple wells were positioned in the autoclave for two thermocouples and one platinum resistance temperature control element. Two 1/16 inch ID capillary lines entered the autoclave at the top and at the bottom. These were used for filling, sampling, cleaning, and purging the autoclave. A Nichrome heating element and a water coolant line were externally wound around the autoclave for temperature control and cooling.

At the reactor face, the top (or vapor-phase) sampling line terminated at the sampling valve. The bottom (or liquid-phase) sampling line was connected to the liquid-phase header. A sample valve, pressure gauge, rupture disc, and the system pressurizer joined the system at the liquid-phase header.

The system pressurizer consisted of a second high pressure autoclave of approximately twice the capacity of the in-pile autoclave. The power supply to an external heater around the pressurizer was regulated by the pressure recorder and controller.

The entire pressure system was fabricated of AISI type 347 stainless steel with the exception of the Teflon valve packing. Figure 3 represents a schematic layout of the pressure system. The autoclave and converter are illustrated in Figures 4 and 5 respectively.

2. Instrumentation and Control

A schematic drawing of the instrumentation and control units is shown in Figure 6.

Two platinum - platinum 10 per cent rhodium thermocouples were used to indicate the temperature in the autoclave. A Rubicon Type B Potentiometer was used to determine, precisely, the thermocouple emf, while a Leeds and Northrup strip chart recorder was used to provide a continuous record of the autoclave temperature. A series of switches made it possible to connect either of the thermocouples to the Rubicon Type B Potentiometer while connecting the remaining thermocouple to the recorder.

A saturable reactor in the heater power supply was used to control the autoclave temperature. A platinum thermal resistance element, located inside the autoclave, operated as one leg in an a-c bridge. The unbalanced potential in this bridge was determined by the relative resistance values of the preset control resistor in the bridge circuit and the platinum resistance element in the autoclave. The unbalanced bridge potential was then amplified and rectified through a thyatron circuit to provide a direct current control signal to the saturable reactor.

System pressure was indicated by a Heise 15-inch Bourdon tube type precision pressure gage connected to the pressure system at the liquid-phase header. Its range was -15 to +800 psi; the minor scale divisions were 1 psi.

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FIG. 2
CUTAWAY OF CHALK RIVER AUTOCLAVE

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FIG. 3
PRESSURE SYSTEM

NR-G-3050-A

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AUTOCLAVE PLUG ATTACHMENT

FIG. 4
AUTOCLAVE AND PILE PLUG ASSEMBLY

AUTOCLAVE PILE PLUG

CONVERTER PLUG ATTACHMENT

FIG. 5
CONVERTER AND PLUG ATTACHMENT

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A pressure recorder and controller was connected to the vapor phase of the system pressurizer. This instrument actuated a relay which acted as an on-off control of power to the external heater of the system pressurizer.

In the second series of tests, using the flux converter, it was necessary to monitor the temperature of the converter to assure that adequate cooling was being maintained. Four 22-gage iron-constantan thermocouples, connected to a Brown Strip Chart Recorder, were used for this purpose. Two of these thermocouples were located in wells in the aluminum can on the converter, and the other two were attached to the inlet and outlet water coolant lines at their juncture with the converter body.

3. Autoclave Sampling System

A schematic diagram of the gas sample removal and transfer system is shown in Figure 7. The system consisted of a stainless steel extension to the vapor-phase capillary line attached to valve (V) by a high pressure tube fitting. A U-shaped section of the extension was immersed in an ice bath to permit cooling of the sample before it reached the sample container connected through the greased ball joint (B). The connection between (B) and the stainless steel line was made by means of a compression fitting followed by a Kovar seal to the glass.

The transfer apparatus, shown in Figure 7, consisted of a Welch Duo-Seal mechanical vacuum pump, a liquid nitrogen-cooled fore trap, a Toeppler pump to transfer gas from the sample container to the buret, a gas buret, and a Pirani gage. The sample container was connected to the transfer apparatus through tapered joint (A).

The gas analyses were performed with a commercially available Blacet-Leighton micro gas analytical apparatus, also shown schematically in Figure 7.

III. EXPERIMENTAL PROCEDURES

A. Water Treatment

1. General Purification

Two steps were used in purification of the charge water used in these tests. Plant water was first distilled and then passed through an ion exchange column which contained a Rohm and Haas (MB-1) mixed bed of IRA-140 strong acid anion and IR-400 strong base cation resins.

2. Degassing Method

After most of the impurities had been removed by the distillation and ion exchange treatment, the water was boiled to remove dissolved atmospheric gases before being charged into the autoclave.

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FIG. 7
GAS SAMPLING, TRANSFER AND ANALYSIS APPARATUS

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In the experiments made with the first autoclave, the water was boiled in a 500-cc Pyrex Erlenmeyer flask at atmospheric pressure until 10 to 15 per cent of the water volume had evaporated.⁶ In the later experiment, with the converter, Vycor instead of Pyrex ware was employed in the degassing treatment.

Upon completion of the boiling period, the water was charged immediately into the autoclave.

B. Operational Procedures

Three basic types of experiments were conducted in the Chalk River Program. They are designated as Type A, Type B, and Type C runs.

The Type A runs are those in which the autoclave was completely filled with water and in which the autoclave was externally pressurized to insure a complete liquid phase system.

The Type B runs are those in which both liquid and vapor phases are present, usually in equal volume.

In the Type C runs both a liquid and a vapor phase were present with gaseous hydrogen and oxygen added to the autoclave.

An outline of operational procedures used in these three types of runs follows, with reference to Figure 3.

1. Type A Runs

(a) The pressurizer was first evacuated through the condenser valve, and 200 cc (75% capacity) of degassed water was added through the funnel valve.

(b) With all pressurizer valves closed, the pressure in the vessel was brought up to 100 - 150 psig by raising the pressurizer temperature with the external heater. Then about 65 cc of condensate was blown through the condenser as a second step in degassing the water in the pressurizer.

(c) The pressure controller connected to the pressurizer was then set about 200 psi higher than the proposed autoclave test saturation pressure.

(d) With both liquid phase (L.P.) valves closed, the autoclave system was evacuated through the vapor phase (V.P.) sampling line.

(e) After system evacuation, the hot degassed charge water was placed under the L.P. sample valve in an open 500-ml Pyrex Erlenmeyer flask so that a downcomer line from that valve extended to the bottom of the flask.

(f) With the V.P. sampling valve still open to the vacuum system, the L.P. sampling valve was opened, allowing the autoclave system to fill. After permitting 25 - 50 cc of water to overflow into a trap in the

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vacuum line, the V.P. sampling valve was closed. One minute later, the L.P. sampling valve was closed. In this manner the autoclave system was completely filled with water.

(g) The two valves connecting the pressurizer to the L.P. header were opened to impose the preset pressure upon the autoclave system.

(h) The autoclave contents were then heated to the operating temperature, which was maintained by the autoclave temperature controller for the duration of the run. The expansion of the water in the autoclave, upon heating, was accommodated in the pressurizer.

(i) At the conclusion of the run, after closing the pressurizer connector valve, the total gas content of the autoclave was blown through the V.P. sampling line into the evacuated gas sample carrier.

2. Type B Runs

(a) The autoclave system was completely filled, as described under Type A Runs, paragraphs (d) - (f).

(b) The autoclave heaters were turned on. As the temperature increased, the all-liquid-phase system pressures in the autoclave increased rapidly, because of thermal expansion of the water.

(c) When the all-liquid-phase system pressure reached a point about 200 - 300 psi above the saturation pressure for the proposed operating temperature, water was bled slowly through the V.P. sampling valve at a rate just sufficient to maintain a constant system pressure. When the desired operating temperature was reached and the heaters cut back, the V.P. sampling valve was closed, leaving an all-liquid-phase system in the autoclave at the selected operating temperature.

(d) Water was then bled from the autoclave to permit the formation of a vapor phase. Usually, 35 cc of water was drawn from the V.P. line, which served as a second degassing treatment. This point in the procedure was considered to represent zero time for the run. The remainder of the bleed-off water required to yield the desired vapor-phase volume was then drawn from the L.P. sampling valve.

(e) At the conclusion of the run, the total gas content of the autoclave was blown through the V.P. sampling line into the evacuated gas sample carrier.

3. Type C Runs

(a) Steps (a) through (d) were duplicated as outlined in the operational procedures for Type B runs with the exception of providing for a vapor space 18 cc greater than that at which the experiment was conducted.

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(b) Hydrogen gas was then added through the liquid-phase sampling line. The gas was added from a pressure container of known volume from which the quantity of gas delivered to the autoclave was determined from the pressures in the pressure container before and after the gas charging operation.

(c) The hydraulic piston water charger was then used to introduce 6 cc of water, through the liquid-phase sample valve, to form a plug between the hydrogen and oxygen gas additions. Figure 8 is a sketch of the high pressure water charger.

(d) An approximately stoichiometric quantity of oxygen gas was charged through the liquid-phase sampling valve in the same manner as was the hydrogen.

(e) The injection of 12 cc of water through the L.P. sample valve moved all of the oxygen into the autoclave.

(f) System pressures and temperatures were then noted on a time scale until they became constant.

(g) At this point, the total gas content of the autoclave was blown through the V.P. sampling line into the evacuated gas sample carrier.

C. Gas Sampling and Analysis

This section contains an outline of the procedures for autoclave sampling, gas transfer, and analysis. In the ensuing discussion, reference is made to Figure 7.

1. Autoclave Sampling

While connected to the transfer system, the sample container was evacuated through the standard taper joint (A) and stopcock (S_1). After evacuation (S_1) was closed and the sample container was removed from the transfer system at (A) and was connected to the V.P. sampling line extension at ball joint (B). The sampling line was then evacuated through (C) and (S_2). To sample, it was necessary only to open the valve (V) and the stopcock (S_2) and to permit the existing pressure differential to affect the transfer of the sample from the autoclave to the sample container.

2. Gas Transfer

The sample container was connected to the transfer system at the standard taper joint (A). This joint was mercury-sealed to prevent the entry of air into the system. The gas buret, Toeppler pump, and connecting tubing were filled completely with mercury. The transfer system was evacuated through stopcocks (S_3) and (S_4), with stopcocks (S_1), (S_5), and (S_6) closed. The traps (T_1) and (T_2) were filled with a Dry Ice-trichloroethylene coolant mixture. When the Pirani gage indicated that a pressure less than 1 micron had been attained, stopcock (S_3) was closed,

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FIG. 8
HIGH-PRESSURE WATER CHARGER

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and the gas was permitted to expand into the transfer system through stopcock (S_1).

Ten strokes of the Toeppler pump usually sufficed to transfer the gas sample to the gas buret. For each sample, however, Toeppler pump operation was continued until no gas bubble was detected in the capillary tubing at the end of a stroke.

The total volume of the autoclave gas sample was then measured directly in the gas buret, and then all, or a portion, of the gas was transferred, through stopcock (S_7), to a glass thimble in the analytical apparatus.

3. Gas Analysis

Aliquot portions of the gas were withdrawn for analysis from the thimble containing the gas sample. These aliquots consisted of 90 - 100 cu mm of sample. The gas was drawn into the Blacet-Leighton buret, the volume was measured, and the aliquot transferred to another thimble. An absorbent for one of the components of the sample was introduced into the thimble, and, after 15 minutes, the volume of the unabsorbed gas was measured in the Blacet-Leighton buret. From the volume decrease, the percentage of that component in the mixture was calculated. The reagents used were as follows:

- (a) For CO_2 - A bead of KOH, fused to a platinum loop.
- (b) For O_2 - A bead of yellow phosphorus, fused to a platinum loop.
- (c) For H_2 - Powdered CuO , fused to a platinum loop, and KOH melted on the CuO bead. A temperature of about 250°C was required for the combustion of the H_2 . The heat for this reaction was supplied by an electrically heated furnace, provided with the apparatus, which fitted the thimble.

IV. RESULTS

The test results are divided into two main categories. In the steady-state runs, designated Type A and Type B, direct measurement of the amounts of the gaseous decomposition products, H_2 and O_2 , were made for steady-state conditions in the autoclave at temperatures in the range of 145°F to 500°F .

The second category, designated Type C runs, included the runs in which H_2 and O_2 were added to the autoclave contents and the rate of combination of these gases was studied as a means of determining the variation in the rate of back reaction as a function of temperature.

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A. Steady-State Results

An important objective of this program was to obtain data on the steady-state concentrations of decomposition products. The most direct experimental method of obtaining this information is by sampling and measuring the steady-state gas concentrations in the autoclave as in the Type A runs.

The Type A runs were those in which the autoclave was completely filled with water, and in which the autoclave was pressurized with an external boiler to a pressure at least 200 psi higher than the saturation pressure for the autoclave temperature. This external pressurizing insured an all-liquid-phase in the autoclave and guarded against excessively high system pressures resulting from possible temperature variation in a closed system completely filled with water. Type A runs were made only with the first autoclave, without the neutron converter. Time limitations and autoclave failure, in the second series of tests, precluded repetition of this type of run with the second autoclave, which was equipped with the neutron converter.

The Type B runs were those in which both a liquid and a vapor phase were present, usually of equal volume. In this series of tests runs were made with the original autoclave and with the duplicate autoclave provided with a neutron converter.

1. Data Presentation

The data for all Type A and Type B runs are presented in Tables I and II. The designation used for individual runs consists of type of run (A or B), general temperature level, and series number. For example, run B3-2 indicates a Type B, or two-phase, run at approximately 300F, the second run in that series, without converter. Following the series number, a C represents the use of the duplicate autoclave with the neutron converter. The notation P.D. indicates a pile down run.

In Tables I and II hydrogen, oxygen, carbon dioxide, and inert gas analyses are reported as the total cc (STP) of each gas found in the autoclave, and as concentrations, cc (STP)/liter volume. In the case of the Type B runs, the concentration of each gas is divided into liquid-phase and vapor-phase concentration, based on the known solubility factors⁷ with the exception of CO₂, for which solubility factors are not known for the higher temperatures. The inert gas is assumed to be nitrogen introduced by atmospheric contamination of the charge water or to atmospheric leakage during sampling.

Oxygen deficiencies in the gas samples are listed in both cc (STP) and cc (STP)/day as a measure of material balance. The oxygen deficiency figure is corrected for CO₂ generation and for atmospheric leakage using N₂ or inert as an index.

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Table I

ALL-LIQUID-PHASE IRRADIATIONS -
ANALYTICAL RESULTS

Run No.	Temp, F	Time at Flux, hr	Time at Temp, hr	Gas Content								Total Gas Content,		O ₂ Deficiency		Water Resistivity, megohm-cm	
				H ₂		O ₂		CO ₂		Inert							
				cc	cc/l	cc	cc/l	cc	cc/l	cc	cc/l	cc	cc/l	cc	cc/day	Charge	Drain
A1-1	140	39.3	42.8	0.18 ± 0.01	1.4	0.062 ± 0.002	0.50	0.090 ± 0.002	0.72	0.27	2.1	0.6	4.8	.03	.02	0.60	0.32
A1-2	140	65.2	68.1	0.29 ± 0.01	2.32	0.145 ± 0.002	1.12	0.080 ± 0.001	0.64	0.34	2.7	0.85	6.8	.03	.01	0.20	0.12
A3-1	300	21.3	21.3	0.60 ± 0.03	4.8	0.060 ± 0.000	0.48	0.060 ± 0.002	0.48	0.48	3.8	1.2	9.6	.27	.30	0.21	0.14
A3-2	300	22.3	22.3	0.43 ± 0.04	3.4	0.050 ± 0.001	0.40	0.090 ± 0.002	0.72	0.93	7.5	1.5	12.0	.26	.28	0.36	0.18
A4-1	400	19.0	26.0	0.585 ± 0.04	4.7	0.088 ± 0.003	0.70	0.052 ± 0.002	0.40	0.63	5.0	1.35	10.8	.28	.26	0.61	0.20
A4-2	400	19.9	21.3	0.592 ± 0.005	4.7	0.071 ± 0.001	0.57	0.031 ± 0.002	0.25	0.28	2.2	0.97	7.8	.25	.28	0.58	0.29
A4-3	400	41.4	41.4	0.675 ± --	5.4	0.058 ± 0.001	0.46	0.060 ± 0.002	0.48	0.31	2.5	1.1	8.8	.27	.16	0.61	0.28
A5-1	500	20.5	20.6	0.60 ± 0.01	4.8	0.089 ± 0.003	0.72	0.045 ± 0.012	0.4	0.35	2.7	1.1	8.6	.24	.28	0.70	0.16
A5-2	500	21.1	21.1	0.80 ± 0.02	6.4	0.105 ± 0.000	0.84	0.050 ± 0.002	0.40	0.28	2.3	1.24	9.9	.30	.34	0.76	0.20
A5-3	500	21.8	21.8	0.675 ± 0.02	5.4	0.076 ± 0.003	0.61	0.118 ± 0.003	0.94	0.25	2.1	1.1	9.0	.15	.16	0.57	0.20
A1-1PD	140	0.0	0.9	0.062 ± 0.001	0.50	0.059 ± 0.002	0.47	0.035 ± 0.001	0.26	0.34	2.8	0.5	4.0	.01	.26	0.12	--

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Table II

IRRADIATIONS WITH VAPOR PHASE -
ANALYTICAL RESULTS

Run No.	Temp, F	Time at Flux, hr	Time at Temp, hr	Vap/ Liq. Vol.	H ₂			O ₂			CO ₂	Inert			Total Gas, cc	O ₂ Defic- iency		Resistivity, megohm-cm	
					cc in Autoclave	L.P. cc/1	V.P. cc/1	cc in Autoclave	L.P. cc/1	V.P. cc/1	cc in Autoclave	cc in Auto- clave	L.P. cc/1	V.P. cc/1		cc	cc/day	Charge	Drain
B1-1	145	30.8	30.8	1:1	0.270 ± 0.005	0.10	4.33	0.030 ± 0.001	0.015	0.48	0.034 ± 0.001	0.32	0.07	5.17	0.65	.13	.10	0.80	0.31
B3-1	300	21.1	21.1	1:1	0.175 ± 0.003	0.08	2.79	0.067 ± 0.001	0.03	1.07	0	0.32	0.09	5.15	0.56	.19	.22	0.32	0.32
B3-2	300	25.4	25.6	1:1	0.196 ± 0.001	0.09	3.13	0.003 ± 0.001	--	0.05	0.010 ± 0.002	0.02	0.006	0.32	0.23	.086	.08	0.58	0.50
B3-3	300	42.5	42.5	3:1	0.200 ± 0.001	0.06	2.16	0.045 ± 0.001	0.015	0.50	0.009 ± 0.001	0.025	0.005	0.27	0.28	.05	.03	--	0.16
B5-1	500	5.3	5.3	1:1	0.230 ± 0.001	0.33	3.44	0.003 ± 0.000	0.005	0.05	0.012 ± 0.001	0.02	0.02	0.31	0.265	.09	.41	0.33	0.32
B5-2	500	14.7	14.7	1:1	0.240 ± --	0.35	3.59	0.087 ± 0.001	0.13	1.29	0.003 ± 0.000	0.33	0.34	5.07	0.66	.11	.18	0.41	0.25
B5-3	500	20.5	20.5	1:1	0.311 ± 0.004	0.45	4.65	0.088 ± 0.005	0.13	1.31	0	0.75	0.76	11.53	1.15	.26	.30	0.20	0.10
B5-4	500	31.8	31.8	1:1	0.557 ± 0.004	0.80	8.33	0.052 ± 0.001	0.08	0.77	0.032 ± 0.003	0.05	0.05	0.77	0.69	.20	.15	0.26	0.32
B5-5	500	21.9	21.9	3:1	0.333 ± 0.003	0.345	3.58	0	0	0	0.014 ± 0.001	0.02	0.015	0.22	0.37	.15	.16	0.90	--
B5-6	500	23.1	23.1	∞	0.11 ± --	--	0.88	0	0	0	0	0.025	--	0.14	0.135	.06	.06	0.77	--
B3-1C	300	16.0	16.0	1:1	0.84 ± 0.02	0.37	13.4	0.02 ± 0.01	0.01	0.32	0.29 ± 0.02	0.07	0.07	1.13	1.22	.015	.02	0.60	0.12
B3-2C	300	42.0	42.0	1:1	1.02 ± 0.01	0.45	16.3	0.05 ± 0.01	0.02	0.79	0.225 ± 0.005	0.08	0.03	1.29	1.35	.14	.08	0.77	0.08
B3-3C	300	5.6	5.6	1:1	0.359 ± 0.002	0.16	5.73	0.016 ± 0.002	0.08	0.25	0.033 ± 0.002	0.04	0.012	0.65	0.45	.12	.51	0.91	0.39
B5-1C	500	20.6	20.6	1:1	2.310 ± 0.006	3.33	34.5	0.152 ± 0.005	0.23	2.26	0.15 ± 0.01	0.07	0.07	1.08	2.68	.80	.93	0.54	--
B5-2C	500	16.7	16.7	1:1	1.59 ± 0.02	2.29	23.8	0.14 ± 0.01	0.21	2.08	0.032 ± 0.003	0.02	0.02	0.31	1.78	.62	.39	0.65	0.19
B3-1PD	325	0	15.6	1:1	0.116 ± 0.002	0.08	2.64	0.004 ± 0.001	0.002	0.06	0.001 ± 0.001	0.10	0.03	1.61	0.27	.10	.15	--	--
B3-1aPD	325	0	1.1	2:1											0.045				
B3-2PD	300	0	16.0	1:1	0.052 ± 0.001	0.023	0.83	0.052 ± 0.008	0.023	0.83	0.005 ± 0.002	0.16	0.05	2.57	0.27	.01	.015	0.97	--
B3-2aPD	300	0	.8	2:1	0.025 ± --	0.01	0.31	0	0	0	0.005 ± --	0.015	0.003	0.19	0.04	.014	.42	--	--

Water purity is listed in terms of the specific resistance for the original charge water and for the liquid-phase blow-off following sampling. In Table V are listed some representative spectrographic analyses for impurities present in the water.

2. Outline of Variables

There are a number of variables which could affect the kind and quantity of steady-state decomposition products present in irradiated water. Flux density and temperature variation are two basic factors which should be considered in the case of pure water. However, in practice, it is unlikely that the water used as the coolant or moderator in an operating reactor would not contain impurities peculiar to the water treatment and to the reactor system. Therefore, it is also important to investigate the effects of systemic impurities, CO_2 generation, and the possible reactions of all substances present, with each other and with structural materials.

a. Temperature

The liquid-phase, or Type A, runs provide the best index as to the effect of temperature on the steady-state concentrations of decomposition products. It is only for this series of runs that variables other than temperature remain sufficiently constant to permit the identification of a reproducible temperature effect.

Table III

VARIATION OF HYDROGEN WITH TEMPERATURE

Run No.	Temp, F	Run Time, hr	Gas Sample, cc(STP)			Drain Water Resistivity, megohm-cm
			H ₂	O ₂	CO ₂	
A1-1	140	39.3	0.18	0.06	0.09	0.32
A1-2	140	65.2	0.29	0.14	0.08	0.12
A3-1	300	21.3	0.60	0.06	0.06	0.14
A3-2	300	22.3	0.43	0.05	0.09	0.18
A4-1	400	19.0	0.58	0.09	0.05	0.29
A4-2	400	19.9	0.59	0.07	0.03	0.29
A5-1	500	20.5	0.60	0.09	0.04	0.16
A5-2	500	21.1	0.80	0.10	0.05	0.20
A5-3	500	21.8	0.68	0.08	0.12	0.20
B3-1	300	21.1	0.18	0.07	0	0.32
B3-2	300	25.4	0.20	0.003	0.01	0.50
B5-3	500	20.5	0.31	0.09	0	0.10
B3-3C	300	5.6	0.36	0.02	0.03	0.39
B5-1C	500	20.6	2.31	0.15	0.15	----
B5-2C	500	16.7	1.59	0.14	0.03	0.19

In Table III are listed runs of comparable duration and water purity, but characterized by different operational temperatures. Despite the difference in run duration, runs A1-1 and A1-2 are included, since these are the only runs of Type A made at temperatures below 300F.

It may be seen in Table III that of the three gases, H_2 , O_2 , and CO_2 , only the yield of hydrogen appears to vary in a determinate manner with change of temperature. The greatest change in hydrogen yield occurs between 140F and 300F. At 140F the hydrogen content of the autoclave is about 0.2 cc (STP), and for 300F the yield is about 0.5 cc (STP), so that the difference is 0.3 cc (STP). An average H_2 content of 0.6 and 0.7 cc (STP) is observed for 400F and 500F, respectively, or a difference of 0.1 cc (STP) from 300F to 400F and from 400F to 500F. Three Type B runs are listed, for which the ratio of the yield of hydrogen at 300F to that at 500F is about 2:3.

Three Type BC runs (with converter) are included in Table III for qualitative comparison with the Type B runs with the first autoclave and without the converter. However, wide variation between the B and BC runs in duration and water purity precludes quantitative comparison of these results.

b. Radiation Intensity

Operations with and without the thermal neutron converter provided the only means of determining the effect of a flux variation on the steady-state yields of the decomposition products. Unfortunately from the viewpoint of keeping variables unchanged, it was necessary to use two different autoclaves for the two conditions of operation. The two autoclaves were of the same design and material, but this provision would not assure identical corrosion rates in the two autoclaves at the higher temperatures of operation.

As the second series of tests with the converter and duplicate autoclave included only Type BC and CC runs, only the Type BC runs may be considered for steady-state flux variation evaluation. Runs B3-1C and B3-2C are not comparable with the other Type B runs since the organic content of the charge water was known to be excessively high for these two runs.

It is apparent, however, from Table II, that the hydrogen yields are considerably higher for the Type BC experiments with the converter than for comparable Type B experiments without the converter. The oxygen deficiency also increased in the BC series of experiments. The higher hydrogen yield could be attributed to the following factors:

- (1) The higher fast flux in the second autoclave.
- (2) Higher corrosion rate in the second, or BC, autoclave.

On the basis of an over-all evaluation, it appears that a higher corrosion rate in the second autoclave is primarily responsible for greater yield of hydrogen in the BC series of experiments. This topic will be discussed in greater detail later in this report.

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c. Test Duration

In the preceding sections describing the effects of temperature and flux on the steady-state decomposition product concentrations, equal duration of experiments being compared was stressed, particularly at the higher temperatures, since the hydrogen yield was observed to increase with longer run times.

Table IV
DECOMPOSITION PRODUCT YIELD - TIME VARIATION

Run No.	Temp, F	Time, hr	Sampled Gas, cc (STP)		
			H ₂	O ₂	CO ₂
B3-1	300	21.1	0.18	0.07	0.00
B3-2	300	25.4	.20	.00	.01
B3-3	300	42.5	.20	.04	.01
A4-1	400	19.0	0.58	0.09	0.05
A4-2	400	19.0	.59	.07	.03
A4-3	400	41.4	.68	.06	.06
B5-1	500	5.3	0.23	0.00	0.01
B5-2	500	14.7	.24	.09	.00
B5-3	500	20.5	.31	.09	.00
B5-4	500	31.8	.56	.05	.03
B5-2C	500	16.7	1.59	.14	.03
B5-1C	500	20.6	2.31	0.15	0.15

In Table IV are listed data for four different sets of experiments in which the principle variable within each group is run duration. The 300F runs, which involve a time factor of two, show essentially no change in hydrogen yield with time. The 400F series indicates a slight rise in hydrogen yield with time. At 500F, there appears to be a marked increase in hydrogen yield with increasing time.

Oxygen and carbon dioxide again show no correlation with time, being quite random within each group.

d. Water Purity

Specific resistivity measurements were used throughout the experimental program as an indication of water purity. For each run, specific resistivity measurements were made with aliquots of the charge water and with the autoclave discharge water. These values are reported in megohm-centimeters at room temperature and are tabulated in Tables I and II.

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Pyrex vessels were used for water handling, degassing, and sample storage in the series of runs in which the autoclave without the neutron converter was employed. In these runs, the samples were stored in Pyrex containers for periods of from one week to four weeks before resistivity measurements could be taken. As may be seen in Table V, the water specimens from the autoclave without the converter contain much more boron, sodium, and silicon than do the samples from runs B3-3C, C3-2C, and C5-1C.

The converter series of runs was made using Vycor water handling and degassing vessels, and the samples were contained in polyethylene sample bottles. The specific resistivity measurements were taken immediately after sampling. Replacing the Pyrexware with Vycor eliminated most of the impurities introduced by the dissolution of contaminants from the water containers.

Table V

SOME REPRESENTATIVE SPECTROGRAPHIC ANALYTICAL RESULTS

Results in parts per million

	Al	B	Ba	Ca	Cr	Cu	Fe	Mg	Mn	Na	Bi	Sr	NO ₃
A1-1 (Drain)	0.3	>>2	<0.01	0.07	--	0.01	--	0.006	--	>>2	>2	<0.01	0.06
A3-2 (Drain)	0.3	>>2	--	0.2	--	0.01	--	0.006	--	>>2	>2	<0.01	0.09
B3-3C (Drain)	--	<0.03	0.01	0.2	--	--	--	0.01	--	<0.2	0.01	--	--
C3-2 (Charge)	0.02	0.06	<0.01	0.06	--	0.06	--	0.03	--	--	0.08	--	--
C3-2 (Drain)	0.02	2	<0.01	0.1	0.06	0.02	0.03	0.03	0.02	--	2	<0.01	--
C3-2C } (Charge)	--	<0.03	0.01	0.2	--	--	--	0.01	--	<0.2	0.01	--	--
C5-1C }													

e. Decomposition Product Material Balance

The material balances for the analytical results listed in Tables I and II are characterized by an oxygen deficiency in almost every case. Therefore, the values for material balance are listed as the oxygen deficiency, expressed as cc (STP) of oxygen, and as the rate, cc (STP) O₂/day. The oxygen deficiency values were calculated by the following formula in which the first two terms represent the sources of oxygen and the last two terms represent the oxygen accounted for. Gas volumes are those at (STP).

$$\text{Oxygen Deficiency (cc O}_2\text{)} = \frac{(\text{cc H}_2) - (\text{cc CO}_2)}{2} + \frac{(\text{cc N}_2)}{4} - (\text{cc O}_2) - (\text{cc CO}_2)$$

In correcting the material balance for the presence of carbon dioxide, it was assumed that the organic impurity was of the C_nH_{2n} type. Therefore, for each molecule of CO₂ formed, one molecule of H₂ was released from the organic compound in addition to the two molecules of H₂ released from water, by the fixation of the oxygen contained in the CO₂ molecule. It is also assumed, in this calculation, that atmospheric oxygen was introduced with the nitrogen owing either to incomplete degassing of the charge water

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or to leakage of air during charging or sampling. Thus, 25 per cent of the measured quantity of nitrogen found was taken as the amount of oxygen simultaneously added with the nitrogen (inert gas), to correct the material balance for oxygen introduced in these ways.

It may be seen in Table VI that material balance is most closely approached in the two 140F runs. In the rest of the A series of experiments at 300, 400, and 500F, for run times of about 20 hours, there is little variation in the oxygen deficiency. Discounting the oxygen deficiency in run A5-3, which is inconsistent with those in the rest of the Type A runs, the other six runs from 300 to 500F show an oxygen deficiency of 0.27 ± 0.03 cc (STP). In no other series of experiments was there a sufficient number of runs of similar duration to permit further analysis of the variation of the oxygen deficiency with temperature.

Table VI

OXYGEN DEFICIENCY VARIATION WITH TEMPERATURE

Run No.	Temp, F	Oxygen Deficiency, cc (STP)	Run Time, hr
A1-1	140	-0.03	39.3
A1-2	140	-0.03	65.3
A3-1	300	0.27	21.3
A3-2	300	0.26	22.3
A4-1	400	0.28	19.0
A4-2	400	0.25	19.9
A5-1	500	0.24	20.5
A5-2	500	0.30	21.1
A5-3	500	0.15	21.8

Five groups of runs are listed in Table VII, in which the principal variable is time.

The data for Group 1 in Table VII, at 300F, appear to be too inconsistent to yield valid interpretation. The difference in oxygen deficiency between runs B3-1 and B3-2 is much greater than could be explained by the small difference in the duration of the runs.

The Group 2 results are more consistent than those of Group 1. Runs A4-1 and A4-2 yield approximately the same oxygen deficiency for similar run times. However, run A4-3, of 40 hr duration, yielded the same oxygen deficiency as runs A4-1 and A4-2, each of which was 20 hours in duration.

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Table VII

OXYGEN DEFICIENCY VARIATION WITH TIME

Run No.	Temp, F	Run Time, hr	Oxygen Deficiency, cc (STP)	Oxygen Deficiency, cc (STP)/day
<u>Group 1</u>				
B3-1	300	21.1	0.19	0.22
B3-2	300	25.4	0.09	0.08
B3-3	300	42.5	0.05	0.03
<u>Group 2</u>				
A4-1	400	19.0	0.28	0.26
A4-2	400	19.9	0.25	0.28
A4-3	400	41.4	0.27	0.16
<u>Group 3</u>				
B5-1	500	5.3	0.09	0.41
B5-2	500	14.7	0.11	0.18
B5-3	500	20.5	0.26	0.30
B5-4	500	31.8	0.20	0.15
<u>Group 4</u>				
B5-2C	500	16.7	0.62	0.89
B5-1C	500	20.6	0.80	0.93
<u>Group 5</u>				
B3-1C	300	16.0	-0.01	-0.02
B3-2C	300	42.0	0.14	0.08

The Group 3 runs at 500F represent the widest variation in run time and show two distinct groupings of oxygen deficiencies with respect to run times. Runs B5-1 and B5-2, which are 5.3 and 14.7 hr in length, show significantly lower oxygen deficiencies than runs B5-3 and B5-4 of 20.5 and 31.8 hours duration.

Group 4 runs are included in Table VII as the only comparable runs in the second series of experiments for which the second autoclave, with converter, was used. There are insufficient data available for the determination of definite trends within this group.

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Group 5 includes the two experiments performed at 300F with resin-saturated charge water. For the 16-hour run B3-1C, the sample gases were essentially stoichiometric mixtures, and in B3-2C of 42 hours duration, the existence of a small oxygen deficiency indicates a definite influence on the material balance by the presence of organic matter in the sample water.

In Table VIII are listed comparable runs in the two autoclaves at temperatures of 300F and 500F. A comparison of 500F runs in the two reaction vessels shows that the oxygen deficiencies for the second autoclave appear to be greater, by at least a factor of three, than those of comparable run times in the first autoclave.

At 300F, only one run with the second autoclave is available for comparison with runs in the original autoclave. However, run B3-3C presents an oxygen deficiency, in 5.6 hr, comparable with those obtained in 20 to 40 hr in the original autoclave.

Table VIII

OXYGEN DEFICIENCY DIFFERENCE WITH REACTION VESSELS

Run No.	Temp, F	Run Time, hr	Oxygen Deficiency, cc (STP)
B5-1	500	5.3	0.09
B5-2	500	14.7	0.11
B5-3	500	20.5	0.26
B5-4	500	31.8	0.20
B5-2C	500	16.7	0.62
B5-1C	500	20.6	0.80
B3-1	300	21.1	0.19
B3-2	300	25.4	0.09
B3-3	300	42.5	0.05
B3-3C	300	5.6	0.12

f. Effect of Vapor Phase on Gas Formation

The over-all effect of operating with a vapor phase present in the autoclave is to reduce both the total quantity of gas produced and the concentration of gas in the liquid phase.

Table IX tabulates total product variation with vapor-liquid volume ratio at different temperature levels for a number of comparative Type A and Type B experiments. Runs having an all-liquid fill, a half-liquid fill, a quarter-liquid fill, and an all-vapor-phase fill are

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included. In the half-filled autoclave runs, the hydrogen yield is about half that obtained in the Type A runs: the quantities of oxygen and carbon dioxide for the half-filled runs are also lower. An exception appears in group 1 of Table IX, in which the quantity of hydrogen remains essentially the same. However, it is believed that this apparent difference from the higher temperature trend is due to the operational differences between the Type A and Type B runs at the lower temperatures. In the Type B runs, it was necessary to raise the temperature of the completely filled autoclave to about 375F to blow-off the amount of water required to provide for a 50 per cent vapor space. The Type A runs, however, were charged and operated with low temperature water. Therefore, hydrogen generated by corrosion processes would necessarily be higher in the low temperature Type B runs owing to this higher initial start-up temperature.

Table IX

TOTAL PRODUCT GAS VARIATION WITH VAPOR-LIQUID VOLUME RATIO

Run No.	Vap./Liq. Vol. Ratio	Temp, F	Time at Temp, hr	Total Product Gas, cc (STP)				
				H ₂	O ₂	CO ₂	N ₂	O ₂ Def.
Group 1								
A1-1	0	140	42.8	0.18	0.06	0.09	0.27	-0.03
A1-2	0	140	68.1	.29	.14	.08	.34	-0.03
B1-1	1:1	145	30.8	0.27	0.03	0.03	0.32	0.13
Group 2								
A3-1	0	300	21.3	0.60	0.06	0.06	0.48	0.27
A3-2	0	300	22.3	.43	.05	.09	.93	.26
B3-1	1:1	300	21.1	0.18	0.07	0	0.32	0.19
B3-2	1:1	300	25.6	.20	.00	0.01	.02	.08
B3-3	3:1	300	42.5	0.20	0.04	0.01	0.02	0.05
Group 3								
A5-1	0	500	20.6	0.60	0.09	0.04	0.35	0.24
A5-2	0	500	21.1	.80	.10	.05	.28	.30
A5-3	0	500	21.8	.68	.08	.12	.25	.15
B5-3	1:1	500	20.5	0.31	0.09	0.00	0.75	0.26
B5-4	1:1	500	31.8	.56	.05	.03	.05	.20
B5-5	3:1	500	21.9	0.33	0	0.01	0.02	0.15
B5-6	∞	500	23.1	0.11	0	0	0.02	0.06

There appears to be little difference in the hydrogen yield between the half-filled and quarter-filled Type B runs, at 300F and 500F, although the oxygen and carbon dioxide yields are lower in both of the quarter-filled runs. The smallest quantity of gas was generated during the all-vapor-phase run, B5-6.

Groups 2 and 3 in Table IX show a definite variation in the material balance of the product gases with changes in the ratio of the vapor phase - liquid phase volume. It appears that a larger vapor space in a high-temperature water system inside a reactor will result in a reduction of both total gas and oxygen deficiency. The group 1 results show an exception in which the oxygen deficiency is greater in the Type B run. However, this again is attributed to the differences in operation between the Type A and Type B runs at the low temperatures.

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The quantities of product gases listed in Table IX represent total autoclave contents at the conclusion of a run without respect to the distribution of these gases between the liquid and vapor phases present in the autoclave.

Table X lists the same experiments presented in Table IX but includes the calculated concentration of each gas dissolved in each phase. Henry's Law, with the solubility factors reported by Battelle Memorial Institute,⁷ was used for the calculation of gas distribution. The calculations are not corrected for deviations from ideality.

Table X

DISSOLVED GAS CONCENTRATION VARIATION WITH VAPOR-LIQUID VOLUME RATIO

Run No.	Vap./Liq. Vol. Ratio	Temp., F	Liquid Phase, cc(STP)/liter		Vapor Phase, cc(STP)/liter	
			H ₂	O ₂	H ₂	O ₂
<u>Group 1</u>						
A1-1	0	140	1.4	0.5	-	-
A1-2	0	140	2.31	1.1	-	-
B1-1	1:1	145	0.1	0.02	4.3	0.5
<u>Group 2</u>						
A3-1	0	300	4.8	0.5	-	-
A3-2	0	300	3.4	0.4	-	-
B3-1	1:1	300	0.08	0.03	2.8	1.1
B3-2	1:1	300	0.09	0	3.1	0.05
B3-3	3:1	300	0.06	0.02	2.2	0.5
<u>Group 3</u>						
A5-1	0	500	4.8	0.7	-	-
A5-2	0	500	6.4	0.8	-	-
A5-3	0	500	5.4	0.6	-	-
B5-3	1:1	500	0.4	0.1	4.6	1.3
B5-4	1:1	500	0.8	0.1	8.3	0.8
B5-5	3:1	500	0.3	0	3.6	0
B5-6	0	500	-	-	0.9	0

The vapor phase product gas concentrations in Table X vary with vapor-liquid volume ratio in the same manner as the Type B total gas variation presented in Table IX. However, the concentrations of the gas dissolved in the liquid phase decrease precipitously with the introduction of a vapor phase and continue to decrease as the vapor space volume is increased.

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B. Recombination Results

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A series of experiments was included in the test program in which hydrogen and oxygen gases were added to two-phase static water systems at various temperatures. The purpose of these experiments was to provide direct measurement of the effect of temperature and radiation intensity on the back reaction of the decomposition products of water. As the decomposition product concentrations resulting from the irradiation of water represent a balance between the rate of decomposition of the water molecules and the rate of recombination of the decomposition products, a measure of the changes in the rate of combination of excess hydrogen and oxygen would provide an index for the dependence of the steady-state concentrations upon temperature and flux conditions.

The experiments in which excess hydrogen and oxygen were added are designated Type C runs. In these Type C runs, the gases were added to half-liquid and half-vapor phase systems at the desired experimental temperature. The rate of combination of the excess hydrogen and oxygen was then calculated from periodic systemic pressure and temperature measurements.

1. Data Presentation

The Type C results appear as combination rate curves in Figures 9 and 10. In order to obtain the datum points for these curves, systemic pressure and temperature were observed simultaneously and recorded as a function of time, in which zero time was designated as the instant of the second gas addition. Using the observed temperature, the difference (ΔP) between the observed pressure and saturation pressure for that temperature was calculated. The ΔP readings were then converted to total cc of gas (at STP) in the autoclave by using the known vapor space volume, system temperature, and solubility coefficients. This reduced the runs at various temperatures to a common basis for comparison.

2. Outline of Variables

The two major variables which affect the rate of recombination are temperature and radiation intensity. Water purity appears to have little effect on the initial combination rate in a two-phase, high-temperature, water system.

a. Temperature

The combination rates for the hydrogen and oxygen addition runs are listed in Table XI as total gas ($2H_2 + O_2$) expressed in cc (STP) combining per unit time.

Group 1 in Table XI shows very little difference in recombination rates between 327F and 501F. Group 2 contains the experiments in the second autoclave with converter and covers a wider temperature range than Group 1. The three runs in Group 2 between 345F and 495F again indicate little difference in combination rates. However, C3-1C at 293F has a combination rate significantly lower.

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Table XI

HYDROGEN AND OXYGEN COMBINATION RATES

Run No.	Temp, F	Recombination Rate, cc(STP)(2H ₂ + O ₂)/min	Fast Neutron Flux
		<u>Group 1</u>	
C3-1	327	1.58 ± 0.06	1.2 x 10 ¹² ± 50%
C3-2	327	1.55 ± 0.06	1.2 x 10 ¹² ± 50%
C5-1	501	1.65 ± 0.06	1.2 x 10 ¹² ± 50%
		<u>Group 2</u>	
C3-1C	293	1.13 ± 0.04	2.05 x 10 ¹² ± 20%
C3-2C	345	1.86 ± 0.07	2.05 x 10 ¹² ± 20%
C5-1C	496	1.95 ± 0.09	2.05 x 10 ¹² ± 20%
C5-2C	495	1.89 ± 0.06	2.05 x 10 ¹² ± 20%

b. Radiation Intensity

In Table XI Group 1 includes those experiments made in the original autoclave with a calculated fast neutron flux of $1.2 \times 10^{12} \pm 50$ per cent. Group 2 includes those experiments conducted in the second autoclave with a measured fast neutron flux of $2.05 \times 10^{12} \pm 20$ per cent. For these differences in flux intensity, the recombination rate in the second autoclave with converter was increased from approximately 1.6 cc(STP)(2H₂ + O₂)/min to 1.9 cc(STP)(2H₂ + O₂)/min.

C. Sources of Errors1. Sampling

White and co-workers⁶ have found that dissolved oxygen is completely removed from an aqueous solution when one-tenth of the solution is removed by distillation. This technique was used in the sampling procedure to remove the entire gas content of the autoclave, even though the entire water content could not be removed in this manner. The quantity of water which could be removed by the sampling procedure adopted in this experiment was limited by the fact that, during sampling, the vapor phase was removed, resulting in a chilling of the autoclave with a corresponding pressure decrease. Since a positive pressure and water flow from autoclave to sample container was required to prevent the back diffusion of gas, it was necessary to stop the sampling process while there was still a positive pressure in the autoclave. This limitation required either that the sample be withdrawn very slowly to allow the heaters to compensate for the temperature drop due to evaporation, or that the sample be removed quickly, so that some water remained in the autoclave. Since the first procedure involved prolonged exposure of the evacuated sampling system to leakage of air through a high pressure valve not specifically designed for vacuum application, the latter method of sampling was adopted. Obviously, more water could be boiled from

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the autoclave if the temperature, at the start of sampling, was 500F rather than 300F. Setting an arbitrary limit, of 15 per cent, for the minimum amount of water to be removed limited the lowest temperature at which a sample could be taken to about 300F.

In order to test the effectiveness of the sampling procedure, two successive samples were taken, with the pile not in operation, and at the poorest sampling conditions, i.e. with a half-filled autoclave at 300F. This was done twice. In both cases, the total quantity of gas contained in the second sample was 0.04 cc (STP). However, there was a lapse of approximately one hour between the two sampling operations because of the time required to re-establish temperature and to evacuate the sampling line. Since the 0.04 cc of gas was predominantly hydrogen, it is likely that this amount of gas was generated during the one-hour interval between sampling.

The buret used to measure the total volume of gas could be read with an accuracy of ± 0.01 cc, and the errors in the estimation of room temperature and barometric pressure could result in another 0.01 cc error in the value for the total gas volume. Therefore, all values of total gas listed in Tables I and II are subject to systemic errors of ± 0.02 cc.

2. Analytical

a. Gas Transfer

The volume of water delivered to the sample container was between 20 and 40 cc. The volume of the vapor space of the transfer system (Figure 7) was about 1500 cc. Considering the solubility of the gases in water at about room temperature, approximately 1/300 of the gas would be dissolved in the liquid phase. However, in the transfer process, water vapor was removed from the sample by two Dry Ice - trichlorethylene refrigerant baths arranged in series. These refrigerant baths maintained a very low water vapor pressure, so that the water was quickly cooled below its freezing point by continuous evaporation. To investigate the possibility of gas entrapment in the ice, all of the gas was pumped from the container. The ice was allowed to melt, and the gas transfer process was repeated. No additional gas was detected.

b. Analysis

The Blacet-Leighton buret used in the analysis had a capacity of 100 cu mm. In repeated measurements of the same sample, it was found that the volume could be reproduced to ± 0.3 cu mm. The reproducibility of analytical results by the Blacet-Leighton method is not limited by this factor, however. The limitations on reproducibility are the indeterminate errors inherent in the operational procedures, and can best be attributed to human errors. Therefore, in all cases in which a sufficient amount of sample was available, duplicate analyses were performed. In the event that reproducibility was poor, a third, and on a few occasions a fourth, analysis was performed. Hence, in the listing of the analytical results in Tables I and II, the average of the analyses is given, and the error shown corresponds

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to the arithmetic mean of the deviations for that set of analyses. The percentage error in the analysis for a minor component of a gas sample will be greater than that for a major component, because the precision of measurement (0.3 cu mm) is increasingly significant as the volume of gas measured decreases. Since the quantity of inert gas was obtained by the difference (total gas $-(H_2 + O_2 + CO_2)$), the error in this value is an indeterminate cumulation of the errors in the determinations of the other components and, hence, is not listed. To investigate the effectiveness of water vapor removal by the two refrigerant baths, several analyses for water vapor were made, using P_2O_5 as the absorbent. No water vapor was detected in any of these tests; in subsequent analyses this step was eliminated.

3. Temperature Measurement

The temperature of the autoclave contents was measured with two platinum-platinum - 10 per cent rhodium thermocouples which were calibrated at four temperatures by comparison with a platinum resistance thermometer.

One thermocouple was positioned in the upper and the other in the lower half of the autoclave. In the case of Type B and Type C runs, this arrangement made it possible to measure both the liquid and vapor phase temperatures.

These thermocouples were, however, subject to gamma heating while the reactor was in operation. Special contact blocks were used to give good thermal contact between the thermocouple junctions and the walls of the thermocouple wells. These aluminum contact blocks are shown in Figure 11.

This method of obtaining thermal bonding served to minimize the temperature gradient between the thermocouple junction and the water surrounding the thermowell but could not eliminate it completely. The water and steam films offered the greatest resistance to the removal of the gamma-induced heat from the platinum thermocouple elements.

While neither vapor phase nor liquid phase temperatures could be determined directly from the corresponding thermocouple readings in view of this temperature gradient established by gamma heating of the thermocouple junction, slight variations in temperature were easily measureable to within 0.1F.

The magnitude of the temperature difference between the thermocouple junctions and the surrounding autoclave contents was estimated by a comparison of the steam saturation values with the observed system pressures and thermocouple readings. In the Type B half-filled runs the difference between the equivalent saturation temperature for the observed system pressure and liquid phase thermocouple reading varied from 0.3F to about 1.5F for ambient temperature levels of 300F to 500F. The difference for the vapor phase thermocouple at 300F was 15 to 25F, and at 500F it was 8 to 11F. It will be noted that the temperature difference between the vapor phase element and the equivalent saturation temperature for the system pressure was much greater than the corresponding difference for the liquid phase

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FIG. II
SPECIAL THERMOCOUPLE JUNCTION
CONTACT BLOCKS

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thermocouple. This discrepancy is attributed to better heat transfer characteristics in the liquid phase and probably to a small degree of superheating of the vapor phase.

The ability to distinguish small temperature variations was essential in calculating the rate and extent of reaction of added hydrogen and oxygen gases. While absolute temperatures of the autoclave contents could not be determined accurately, small variations in temperature with time were easily measured with precision. The stability of temperature control was quite satisfactory. Temperature oscillation was well below 0.1F in amplitude, and the maximum drift in temperature for any autoclave loading condition never exceeded 0.2F per hr or 2F per day. The drift was caused mainly by the effect of variation in gamma-radiation intensity on the gamma heating of the temperature control resistance element.

These conditions of thermal stability greatly aided in the determination of the partial pressures of hydrogen and oxygen and in correcting these values for small temperature variations. Thus the uncertainty in the partial pressure measurements of the hydrogen and oxygen cannot be more than the equivalent water pressure variation for a 0.1F temperature change.

V. DISCUSSION AND CONCLUSIONS

A. Corrosion Characteristics of Reaction Vessel

There is sufficient evidence to indicate that corrosion of the reaction vessel played an important part in generating some of the gas found at the conclusion of these experiments. As the corrosion of stainless steel is primarily a metal oxidation process, the effect of this process is to increase the amount of hydrogen and to decrease the amount of oxygen present in the autoclave at the conclusion of a run. Two possible mechanisms for the corrosion process are:

Some evidence for both of these reactions is found in the experimental results. In out-of-pile and pile-down experiments with the first Chalk River autoclave, hydrogen was detected in approximately the same quantities as in corresponding irradiation experiments. This finding indicates that water supplies the oxygen for oxidation of the autoclave walls, producing free hydrogen by the first mechanism.

Also, in these out-of-pile tests and pile-down runs, the final oxygen content was well below the 25 per cent of the inert content which must necessarily have been added with the inert (N_2) as either air leakage or as incomplete gas removal of atmospheric solution in the charge water. Since this condition is also characteristic of the irradiation experiments, in which high concentrations of inert gas existed, oxygen consumption by the second mechanism is indicated.

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A study of gas product material balances for the in-pile experiments provides further evidence for the existence of a corrosion process and may also be used to estimate its approximate magnitude. Tables VI, VII, and VIII contain material balance information for different types of runs. These results are marked by an oxygen deficiency in almost every case, indicating corrosion the extent of which is a function of the magnitude of the oxygen deficiency and of the duration of the run. Using these factors the corrosion rate of the autoclave is calculated by the equation.

$$\text{Corrosion Rate (mg Fe/cm}^2\text{/mo)} \cong 10.5 \left(\frac{\text{O}_2 \text{ Deficiency, cc(STP)}}{\text{Run Time (hours)}} \right)$$

The constant, 10.5 includes the necessary conversion factors and the surface area of the Chalk River Autoclave. The oxygen deficiency is calculated as shown earlier, including correction for the oxidation of organic contaminants. In making this correction it was assumed that the organic material from the resin column is a compound of the type, C_nH_{2n} . Such an assumption was necessary because very little is known about the exact nature of the organic materials introduced into the system by contact with the charge water. Neither the anion exchange resin (quaternary amino groups) nor the cation exchange resin (sulfonated polystyrene) was chemically pure. Organic reagents and washes were undoubtedly occluded in the active resins and contributed to the organic-impurity content of the water. Any errors in the oxygen deficiency calculations caused by deviation from the C_nH_{2n} assumption will therefore be greatest for the runs with the large concentrations of CO_2 in the product gases.

The calculated corrosion rates for the first stainless steel AISI type 347 autoclave are presented in Table XII.

Table XII

AUTOCLAVE CORROSION RATE CALCULATIONS - TYPE A RUNS

Run No.	Run Time, hr	Corrosion Rate, mg Fe/cm ² /mo
A1-1	39.3	0.00
A1-2	65.3	0.00
A3-1	21.3	0.13
A3-2	22.3	0.12
A4-1	19.0	0.15
A4-2	19.9	0.13
A5-1	20.5	0.12
A5-2	21.1	0.15

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Runs A1-1 and A1-2 in Table XII show essentially no corrosion at 140F. All other runs from 300F to 500F indicate corrosion rates of 0.12 to 0.15 mg Fe/cm²/mo. This range of values agrees very well with other values for the corrosion rate of AISI type 347 stainless steel, at 500F, determined by the standard weight change methods.

Since the duration of the Type A runs was varied in only two cases, it is not possible to draw a conclusion concerning the variation of corrosion rate with time.

The results of corrosion calculations for the Type B runs are listed in Table XIII.

Table XIII

AUTOCCLAVE CORROSION RATE CALCULATIONS - TYPE B RUNS

Run No.	Run Time, hr	Corrosion Rate, mg Fe/cm ² /mo
B5-1	5.3	0.18
B5-2	14.7	0.08
B5-3	20.5	0.13
B5-4	31.8	0.07
B5-1C	20.6	0.41
B5-2C	16.7	0.39
B3-1	21.1	0.09
B3-2	25.4	0.04
B3-3C	5.6	0.22

The corrosion rate calculations for the Type B results are associated with a much wider variation in run time. In addition, it must be emphasized that the corrosion rates listed in Table XIII pertain to corrosion in a two-phase system. The corrosion mechanism for the autoclave surfaces exposed to the vapor phase might differ from that in the liquid phase, so that the over-all corrosion rate for a Type B run is not necessarily directly comparable to that for a Type A run.

The data in Table XIII may be employed for a comparison of the corrosion rates in the first autoclave with those in the second autoclave (with converter). Both at 300F and 500F the second autoclave corrosion rates are between 2 and 3 times those for the first autoclave. The higher corrosion rate in the second autoclave was undoubtedly a contributing factor to its eventual failure.

The variation of corrosion rate with time is another relationship illustrated in Table XIII for the B5 series of runs. It has already been demonstrated that the oxygen deficiency, which is directly proportional to total autoclave corrosion, is a function of time. This correlation was

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established in the earlier discussion of Table VII. The data in Group 3 of Table VII indicate an increase of oxygen deficiency at 500F for increasing run time, the only exception being run B5-3 of 20.5 hr duration, the oxygen deficiency for which is larger than that for run B5-4, of 31.8 hr duration. The presence of a large quantity of inert gas (N_2) in run B5-3 is evidence that much more dissolved oxygen was present in the charge water for this run than for the other runs in this group. This relatively large amount of oxygen would accelerate the oxygen-iron reaction while the water-iron reaction would continue at a rate comparable to those in the other 500F runs. Therefore, due to this circumstance, the oxygen deficiency and the corrosion rate based on this value are not directly comparable to those for the other runs in the B5 series.

In Table XIII, there is evidence that the corrosion rate may decrease initially with time (run B5-1) and eventually approach a constant value (runs B5-2 and B5-4). At present there is insufficient variation in run time at other temperatures for a similar rate analysis.

B. Steady-State Concentrations of Decomposition Products

Steady-state concentrations of decomposition products established in the presence of radiation tend to be obscured by corrosion of the autoclave and by oxidation of organic contaminant. The steady-state concentrations of H_2 and O_2 are not in the stoichiometric proportion because both corrosion and organic material oxidation increase the total amount of hydrogen and reduce the total amount of oxygen present. The resultant excessive hydrogen concentration then tends further to depress the oxygen concentration by promoting the back-reaction. It is extremely difficult to separate the effects of the three gas-producing processes. It is believed, however, that corrosion plays the major role in gas generation in most of the experiments, particularly in those at the higher temperature levels.

1. Temperature

The Type A runs in the original autoclave are the only runs in which an attempt was made directly to measure the steady-state concentrations of decomposition products in the liquid phase. Of these cases only runs A1-1 and A1-2, at 140F, were not characterized by an oxygen deficiency. The results of these two runs are listed in Table XIV.

By comparing the inert gas contents in Table XIV, it may be seen that about the same degree of degasification was achieved for the charge water in both runs. There was small variation in run time and a more significant change in the resistivity of the drain water for these two runs. The amount of oxygen removed by organic oxidation was almost compensated by the dissolved oxygen added with the inert gas (N_2), leaving H_2 and O_2 in almost stoichiometric proportion. Therefore, these two experiments indicate that for 140F water of not less than 0.12 megohm purity the total of the steady-state concentrations of hydrogen and oxygen will be less than 4 cc/l.

Very few differences can be detected in the gas contents of the remaining Type A runs from 300F to 500F. The run times vary only slightly from 20.5 hr to 26 hr. Hydrogen concentrations vary from 3.4 to 6.4 cc/l.

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Table XIV

DECOMPOSITION PRODUCT CONCENTRATIONS FOR RUNS A1-1 AND A1-2

Run No.	Temp, F	Run Time, hr	H ₂ , cc/l	O ₂ , cc/l	N ₂ , cc/l	Total, cc/l	Resistivity of Drain Water, megohm-cm
A1-1	140	39.3	1.4	0.5	2.1	4.8	0.32
A1-2	140	65.2	2.3	1.1	2.7	6.8	0.12

Oxygen concentrations vary from 0.50 to 0.90 cc/l. Inert gas concentrations are in the range of 2.0 to 5.0 cc/l. The resistivity of the irradiated water varies from 0.14 to 0.30 megohm-cm. These are the runs in the temperature range 300F to 500F that were previously reported as having autoclave corrosion rates of 0.12 - 0.15 mg Fe/cm²/mo. Considering the relative magnitudes of the oxygen deficiencies (corrosion reactions) and of carbon dioxide production, it is quite likely that most of the product hydrogen is generated by these two processes and not by processes involving only radiation and pure water.

The dependence of hydrogen concentration on temperature (Table III) and run time (Table IV), coupled with the relative independence of oxygen concentration with respect to these variables, suggests the predominance of the corrosion reaction in the production of gas. This interpretation is substantiated by the magnitudes of the oxygen deficiencies, which are such that hydrogen generation in the 300F to 500F Type A runs (Table VI) is primarily a function of corrosion. As corrosion is a rate process, the hydrogen evolution by corrosion mechanisms must also be a rate process. The resulting excess hydrogen progressively depresses the oxygen concentration as the non-stoichiometric steady-state condition resulting from the greater hydrogen concentration is established in the system. This oxygen repression progresses until a very low level of oxygen is present in the system, after which the amount of hydrogen quantitatively approaches that resulting from the integrated corrosion process from the system zero time.

This effectively means that in any irradiated high-temperature pure water system, the hydrogen concentration will be determined by the total corrosion of the container material, while the oxygen concentration will be depressed to a very low value. These resulting hydrogen and oxygen concentrations will be affected by the radiation-decomposition-recombination reactions only as the sustained presence of a very low concentration of oxygen and as the presence of free radicals affect the corrosion characteristic of the container materials.

The oxygen concentrations cannot successfully be used in analyzing the data for decomposition product steady-state conditions since oxygen is present in such small amounts that any leakage or extraneous additions of air during charging or sampling operations mask the true steady-state condition.

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2. Effects of Excess Hydrogen or Oxygen

The operational methods for the Type C experiments were developed so that the hydrogen and oxygen gases would be added in approximately stoichiometric mixtures to the autoclave. While in most cases deviation from stoichiometry was slight, there were several Type C runs in which either a hydrogen excess or an oxygen excess resulted. Since each Type C experiment was continued until a final steady-state condition was established following the gas introduction operations, the necessary conditions were present for a study of the effects of excess hydrogen or oxygen on the steady-state conditions.

Those Type C experiments in which excess oxygen or hydrogen existed in the final steady-state condition are listed in Table XV.

Table XV

EFFECTS OF EXCESS OXYGEN OR HYDROGEN

Run No.	Temp., F	Final Gas Analysis, cc (STP)	
		H ₂	O ₂
		<u>Oxygen Excess</u>	
C3-1	327	0.14	3.9
C3-2	327	0.20	5.8
C5-1	501	0.00	16.8
		<u>Hydrogen Excess</u>	
C3-2C	345	30.1	0.4

The results listed in Table XV indicate that, in the presence of a slight excess of oxygen, the formation of hydrogen is suppressed. The suppression of hydrogen is apparently sufficiently effective so that the total amount of hydrogen from all contributing sources - gas addition, corrosion, CO₂ formation, and water decomposition - is considerably lower than that found in the corresponding series of Type B steady-state runs. In the case of run C5-1, at 501F, no hydrogen was found. It was in this run that the largest excess of oxygen was present.

There was only one Type C run in which an excess of hydrogen existed. In run C3-2C, at 345F, the oxygen concentration in the autoclave was probably lower than the 0.4 cc (STP) reported in Table XV. In the gas additions for this run, oxygen was added last, and it is likely that incomplete flushing permitted some oxygen to remain in the sampling valve and sampling line. The trapped oxygen would thus be included in the autoclave gas sample with the result that the 0.4 cc (STP) oxygen reported for run C3-2C is high and represents more than the amount of oxygen completely within the autoclave at the time of sampling. Thus, it appears on the basis of this run that excess hydrogen in a two-phase system will suppress the formation of free oxygen.

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3. Effect of Inorganic Impurities

Impurities present in the test water were of two general types: (1) foreign material added by the water handling and degasifying vessels, and (2) corrosion products occurring in a high temperature water - stainless steel system.

As may be seen by the tabulated analytical results in Table V, the series of runs in the second autoclave with the converter contains considerably less sodium, silicon, boron, and aluminum than were present in the runs with the first autoclave. This difference is attributed to the fact that, in the series of experiments with the original autoclave, Pyrex vessels were used during all pre-test water handling operations, while for the experiments with the second autoclave impurities dissolved from Pyrex glass were eliminated by the use of Vycor water containers and polyethylene containers for sample storage. Therefore, it is believed that the analyses reported for runs B3-3C, C3-2C, and C5-1C more closely represent the conditions existing within the autoclave at the time of sampling.

To investigate the possibility that nitrogen in the autoclave was being oxidized to nitric acid, the water remaining in the autoclave at the completion of runs A1-1 and A3-2 was analyzed for nitrate ion. However, the determined concentrations of 0.06 and 0.09 ppm, shown in Table V, are negligible.

The specific resistance of every sample was determined. This method of analysis is more sensitive than the spectrographic method for the detection of small variations in the trace amounts of inorganic impurities present in water. Therefore, in determining the effect of inorganic impurities on the steady-state total gas concentrations, the specific resistance values were used as the index of water purity.

As indicated in Table I, the residual water in the autoclave ranged in specific resistance from 0.08 to 0.50 megohm-cm. Within this range no relationship between specific resistance and gas yield was noted from 300F to 500F. Thus it appears that, in this temperature range, the total gas content of the autoclave is rather insensitive to a variation of impurity concentration within the range 0.08 to 0.50 megohm-cm.

However, run A1-2 at 140F shows a rise in both hydrogen and oxygen concentrations over those for run A1-1, also at 140F. The resistivity determinations on the autoclave drain water for the two runs are 0.32 and 0.12 megohm-cm for runs A1-1 and A1-2 respectively. The duration of run A1-2 is longer than run A1-1, but hydrogen produced by corrosion at 140F must be negligible since the material balance of oxygen and hydrogen shows the same very slight excess of oxygen in both runs. It seems, therefore, that the factor determining the difference in decomposition product concentrations for these two runs must be primarily an effect of ionic impurity.

Therefore, while the 140F runs exhibit a marked influence of water purity in agreement with previously published low temperature data, the higher temperature operation appears to be much less sensitive both to the presence of systemic inorganic impurities and to variations in their concentrations.

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C. Oxidation of Organic Material

Carbon dioxide was detected in almost all of the experiments with both autoclaves. The amount of this gas present bore no relationship to temperature or duration of run, resistivity of the charge water, or to the amount of any other gas in the autoclave.

This suggests that carbon dioxide, or an organic compound which could be oxidized to carbon dioxide, was added in varying amounts to the charge water used in each run. Since, in most of the experiments, the quantities of carbon dioxide present were much greater than the amount of carbon dioxide present in water saturated with air (at room temperature), the carbon dioxide found in these experiments must have resulted from the oxidation of an organic contaminant in the charge water. One step in the purification of charge water consisted of passing the water through an ion exchange resin column. It seems quite likely that this was the source of the organic contaminant.

To investigate this possibility, five gallons of charge water were recirculated for one week through a two-inch ion exchange column containing Rohm and Haas mixed bed resin MB-1. This water, saturated with the organic compound, was then used as charge water in runs B3-1C and B3-2C. As is shown in Tables I and II, the carbon dioxide yields for these runs are considerably higher than those for any of the other runs. Since the amount of carbon dioxide formed in 42 hours (run B3-2C) was not greater than that formed in 16 hours (run B3-1C), it may be assumed that the organic impurity was oxidized completely within 16 hours.

The water used as charge in all other runs was passed through the ion exchange column only once. The amount of resin contaminant in the effluent water was known to be determined by the length of time the column had contained stagnant water and by the amount of water flushed through the column before the effluent was retained for use as charge water. In the first phase of the program, during which the flux converter was not used, the volume of water purged through the column was usually less than the capacity of the column so that the water used to charge the autoclave contained varying amounts of water which had been stagnant in the resin column. In the second series of runs, with the flux converter, greater attention was given to the operation of the column; the column was always purged with the same large volume of water. However, it will be noted, in Table II, that a significantly greater amount of carbon dioxide was found in runs B3-3C, B5-1C, and B5-2C than in the Type B runs without converter. This observation may be traced to the fact that the resin in the ion exchange column had been changed just prior to the time that work was begun on the Type BC runs. The fresh resin used for this later series of experiments very probably still contained a greater portion of the more soluble organic compounds than did the original resin which had been in use for some time. The oxidation of the organic impurities in the water from the fresh resin would then account for the relatively large quantities of carbon dioxide found in the autoclave in the series of experiments with the converter.

In a Type A run, the autoclave contained twice as much water and hence twice as much organic impurity as was present in a corresponding Type B run. During the initial phase of a Type B run, the autoclave was filled completely with water and irradiated for a period of from 30 minutes to 2 hours

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before the selected operating temperature was established and before a vapor phase was formed in the autoclave. As water was removed from the autoclave to form the vapor space, the gases stripped from solution and swept from the autoclave included some carbon dioxide formed during the preliminary irradiation period. The data listed in Tables I and II are consonant with the foregoing postulation in that the values for the amounts of carbon dioxide found in runs of Type A are larger and more consistent than those reported for runs of Type B.

A comparison of oxygen deficiencies for runs B3-1C and B3-2C, for which resin-saturated charge water was used, reveals an interesting condition with respect to run duration. Run B3-1C, after 16 hours at 300F, had evidenced an oxygen deficiency of zero, while run B3-2C, with the same charge water, showed an appreciable oxygen deficiency after 42 hours at 300F (Table II), indicating significant autoclave corrosion in the latter case and none in the former. This difference suggests the possibility that the organic oxidation reaction not only proceeds much faster than the corrosion reactions but also that the corrosion reactions may actually be inhibited by the organic oxidation process until the latter has proceeded to completion.

D. Effect of Vapor Phase

1. Steady-State Concentrations

It was believed, at the start of this experimental program, that both the radiation-induced decomposition and recombination of water occurred primarily in the liquid phase. This behavior was expected because the greater density of the liquid phase led to greater absorption of radiant energy per unit of volume with resulting larger concentrations of free radicals available to promote and sustain the back-reactions. It was reasoned that any vapor phase present would act as a reservoir for the gas generated in the liquid phase, and that this gas would accumulate in the vapor phase until the partial pressures were such as to be in equilibrium with the steady-state concentrations of the water decomposition products in the liquid phase. For example, at 300F, with equal liquid and vapor phase volumes, the total gas within the autoclave by this reasoning should be greater by a factor of about 30 than the quantity which would be present in an all-liquid system. Actually, less gas was obtained in the two-phase steady-state runs than was found in the single-phase runs, as may be seen in Tables I and II.

Comparisons of single phase and two-phase runs with respect to product gas contents and concentrations are presented in Tables IX and X.

These tables show the hydrogen yields for the half-filled autoclave (Type B) runs to be half those obtained in corresponding all-liquid (Type A) runs. The quantities of oxygen and carbon dioxide are also lower in the half-filled runs.

The total amount of gas formed is slightly smaller for the quarter-filled runs than for comparable half-filled runs, the greatest reduction being in the amounts of oxygen and carbon dioxide. Of all runs, the smallest quantity of gas was generated in run B5-6, the all-vapor-phase run.

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The oxygen deficiency, as an index of corrosion, varied in approximately the same manner with the ratio of vapor-liquid phase volume as did the gas generation data. The oxygen deficiencies for the half-filled runs are about half those for the completely filled autoclave runs, the smallest oxygen deficiencies in this series of runs being those for runs B3-3 (quarter-filled) and B5-6 (all-vapor phase).

Thus, it appears that the presence of a vapor phase will decrease the oxygen deficiency and the total gas content of the autoclave, and that the amount of this decrease is dependent upon the vapor-liquid volume ratio.

As may be seen in Table X, the liquid-phase gas concentrations drop sharply with the introduction of a vapor phase and decrease further as the vapor space volume is increased. This reduction in product gas concentration is most evident at 300F (minimum gas solubility), with hydrogen concentrations dropping by a factor of about 50 in the presence of a 50 per cent vapor phase, while at 140F reduction by a factor of 15 to 20 is detected. At 500F, the reduction factor is about 10. In the 75 per cent vapor phase runs, the product gas concentration is reduced to about half that of the 50 per cent vapor phase experiments.

There are two processes which could contribute to reductions in both total gas content and liquid-phase gas concentration in the presence of a vapor phase.

- (1) The recombination process in the vapor phase is not insignificant; or
- (2) Radiation-induced decomposition of water is so negligible at these elevated temperatures that increasing the steady-state decomposition product concentrations by a factor of 10 to 50 yields an amount of gas which is still insignificant with respect to the quantity of gas generated by corrosion.

If the reduction in the total amount of gas produced is the result of a back-reaction occurring in the vapor phase, then the vapor-phase back-reaction must be considerably more efficient than liquid-phase back-reactions in order to cause a net reduction in the total quantity of product gas. Support for this theory may be adduced by noting that smaller quantities of total gas were formed in the quarter-filled runs than were produced in comparable half-filled runs.

It is more difficult to present experimental evidence in support of the hypothesis that the steady-state gas concentrations due only to radiation are insignificantly small with respect to the quantities of gas produced by corrosion. Such evidence as is available has been presented in the preceding sections of this report dealing with corrosion and the variation of steady-state gas concentration with temperature.

The lowering of both the total amount of gas and liquid-phase gas concentrations probably results from a combination of back-reactions in both phases with the vigorous vapor-phase back-reaction being the more important factor.

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2. Combination Rates

Excess hydrogen and oxygen gases were added to two-phase static water systems in the presence of pile radiation in order to investigate the effects of temperature and radiation intensity on the back-reaction. As the back-reaction is the radiation-induced combination of hydrogen and oxygen, a study of the combination of an added excess of these gases at different operating temperatures and flux conditions should yield direct information concerning the effect of these variables on the back-reaction in a two-phase water system. Moreover, as the radiation-induced decomposition of water is a function of the density of energy absorption and is relatively independent of temperature, the steady-state decomposition product concentrations at a given flux depend primarily on the rate of back-reaction. Therefore, information pertaining to the variation with temperature and flux of hydrogen and oxygen combination rate characteristics would indicate a similar variation in the steady-state decomposition product concentrations.

a. Temperature Effects

The rate characteristics of the hydrogen and oxygen combination reactions may be seen in Figure 9 for operation without the neutron flux converter and in Figure 10 for operation with the flux converter. In all experiments, the rate of combination is constant throughout the initial stage of the reaction. This phase of reaction is characteristically followed by a gradual reduction in the measured combination rate as a steady-state condition is established in the autoclave.

In Figure 9, the three combination experiments conducted without the neutron converter show essentially the same initial combination rates for two runs at 327F and one run at 501F, indicating very little effect of temperature in this range.

In Figure 10, three of the combination experiments with the neutron converter show essentially the same initial combination rates for run C3-2C at 345F and for runs C5-1C and C5-2C at 495F. However, for run C3-1C at 293F, the initial combination rate suggests a definite effect of temperature on the combination rate at this lower temperature level.

Therefore, it appears that there is little change in combination rates between 327F and 501F and consequently little change in the steady-state decomposition product concentrations in this temperature range. However, between 293F and 327F there is a temperature below which variation in temperature will have significant effect on the combination rates.

b. Radiation Intensity Effects

Operation without the neutron converter and with the neutron converter offered two levels of fast neutron flux with which to study the effects of reactor flux variation on hydrogen and oxygen combination rates. The fast neutron flux with the converter as measured with a neptunium foil was $2.05 (\pm 0.4) \times 10^{12}$ neutrons/cm²/sec. The fast neutron flux without the neutron converter is estimated to be $1.2 (\pm 0.5) \times 10^{12}$ neutrons/cm²/sec.

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From Figure 9 the hydrogen and oxygen combination rate is found to be 1.6 cc (STP) ($2\text{H}_2 + \text{O}_2$)/min for 327F to 501F in a fast neutron flux of about 1.2×10^{12} . From Figure 10, the combination rate is calculated to be 1.9 cc (STP) ($2\text{H}_2 + \text{O}_2$)/min for 345F to 496F in a fast neutron flux of 2.05×10^{12} . Therefore, for an estimated two-fold increase in fast neutron flux, the combination rate rises from 1.6 to 1.9 cc ($2\text{H}_2 + \text{O}_2$)/min. The values differ so little in magnitude and are known with such poor precision that a quantitative estimate cannot be made of the effect of neutron flux variation.

c. General

An interesting feature of Figures 9 and 10 is the initially constant combination rate which is exhibited in all Type C experiments. This condition shows that the rate-determining variable is radiation intensity and that the combination process is independent of hydrogen and oxygen concentrations above a minimum concentration level. The points of deviation from constant reaction rate in the hydrogen and oxygen combination curves are listed in Table XVI.

Table XVI

POINTS OF DEVIATION FROM CONSTANT REACTION RATE IN COMBINATION CURVES

Run No.	Temp, F	Point of Deviation from Constant Rate, Total Gas, cc (STP)	Final Steady-State Autoclave Gas, Total, cc (STP)	Autoclave Gas Combined after Deviation Point, cc ($2\text{H}_2 + \text{O}_2$) (STP)
C3-1	325	65 ± 5	10	55 ± 5
C3-2	325	85 ± 5	10	75 ± 5
C5-1	500	75 ± 5	20	55 ± 5
C3-1C	295	105 ± 5	40	65 ± 5
C3-2C	345	100 ± 5	40	60 ± 5
C5-1C	500	95 ± 5	30	65 ± 5
C5-2C	500	110 ± 5	30	80 ± 5

The quantities of hydrogen and oxygen which combined to form water after the autoclave contents reached the point of deviation from constant reaction rate ranged from about 55 to 80 cc (STP) and showed little variation with temperature or with varying excess of either added gas. Thus, the point at which flux is no longer the sole rate-determining factor and diminishing reactant concentration becomes significant in the combination process is about 1 cc (STP) ($2\text{H}_2 + \text{O}_2$)/cc in the vapor phase with a corresponding 25 to 50 cc/l in the liquid phase for the temperature range of 300 to 500F.

The constant initial combination rate and the independence of the reaction to reactant concentrations above a definite point indicate that the initial phase of the combination reaction is zero order. Thus, the possibility that back-reaction occurring in the vapor phase by a chain mechanism

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significantly contributes to the initial combination reaction is eliminated. As combination in the liquid phase is generally believed to proceed by a chain mechanism, it appears that the predominant combination reaction in a two-phase static water system occurs in the vapor phase.

This predominance of the vapor phase combination reaction over that in the liquid phase effectively nullifies the usefulness of two-phase systems, such as the Type B and C experiments, for investigating steady-state conditions in the liquid phase at these higher temperatures.

Additional work will be necessary for a more complete understanding of the vapor-phase reaction. The flux dependence of the hydrogen and oxygen combination reaction in the vapor phase should be studied over a wide range of radiation intensities where error contributed by absolute flux level determinations will be minimized. Also, the effects of varying the ratios of water vapor with stoichiometric mixtures of hydrogen and oxygen gases above 300F in all-vapor systems should be investigated. More work should be done with systems in which both hydrogen and oxygen are in varying excess.

The results from such extensions of the present knowledge should lend themselves to a rather detailed kinetics study of the vapor-phase hydrogen and oxygen reaction in the presence of pile radiation.

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