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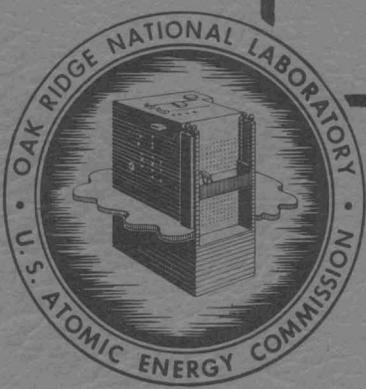
HOMOGENEOUS REACTOR PROJECT

QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING NOVEMBER 15, 1951

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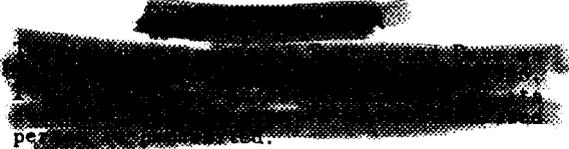
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Reports previously issued in this series are as follows:

- ORNL-527 Date Issued, December 28, 1949
- ORNL-630 Period Ending February 28, 1950
- ORNL-730 Feasibility Report - Date Issued, July 6, 1950
- ORNL-826 Period Ending August 31, 1950
- ORNL-925 Period Ending November 30, 1950
- ORNL-990 Period Ending February 28, 1951
- ORNL-1057 Period Ending May 15, 1951
- ORNL-1121 Period Ending August 15, 1951



Room-temperature exposure to oxygen permitted later exposure of pretreated stainless steel specimens to air for periods up to 14 days without loss of passive characteristics when subsequently immersed in 0.17 M uranyl sulfate at 250°C; without the prior exposure to oxygen gas, pretreated stainless steel samples lose their passivity after exposure in air for three days. An untreated type-347 stainless steel system containing 0.17 M uranyl sulfate and pressurized with 500 psig of oxygen at room temperature was operated successfully at 250°C for 268 hours. The calculated corrosion rate on the stainless steel was 0.3 mil per year.

The corrosion of SAE-1030 carbon steel as observed in static tests with heavy water was greater than corrosion observed in similar tests with natural water. The addition of 300 ppm of trisodium phosphate to the heavy water reduced the corrosion rate for uncoupled SAE-1030 carbon steel from 13.5 to 0.4 mil/yr at 200°C and reduced the corrosion of SAE-1030 carbon steel coupled to type-347 stainless steel from 11.3 to 3.1 mils per year. Initial studies of the effect of different partial pressures of oxygen on the corrosion of SAE-1030 carbon steel in natural water at 200°C have disclosed a marked inhibition by the higher concentrations (2500 ppm) of oxygen.

Dynamic-Corrosion Studies. The work of this quarter has further

established the stability of oxygenated uranyl sulfate solution containing 40 g of uranium per liter in contact with type-347 stainless steel at 250°C. It appears that an oxygen concentration of approximately 50 to 100 ppm may be adequate to assure stability, but refinements in the means of adding oxygen and controlling its concentration are required to provide more quantitative information.

A study at 150°C has shown that the generalized corrosion rate calculated from the rate of nickel build-up in the fuel solution can vary substantially under supposedly constant conditions. Such results can be rationalized but it is apparent that long-term experiments with careful control of variables are necessary to the attainment of meaningful data.

Radiation Stability. Long-time irradiation experiments in the X-10 graphite pile have confirmed previous reports of solution stability; after 2900 hrs solutions in chromate-pretreated type-347 stainless steel containers appear as yet to be unaffected, whereas solutions in oxygen-pretreated type-347 stainless steel containers appeared to decompose at around 1400 hours.

Copper ions have been found extremely effective in causing homogeneous recombination of hydrogen and oxygen in solutions of uranyl sulfate. Uranyl sulfate solutions (93% enrichment, 40 g of uranium per liter) that were

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0.009 M in CuSO_4 demonstrated equilibrium pressures (gas and steam) of 700 psi at 250°C when irradiated in a bomb at a flux of 5 to 8×10^{11} in hole 12 of the X-10 graphite pile.

A promising method has been developed through cooperation with the Chemical Technology Division for decontaminating type-347 stainless steel after irradiation in contact with enriched uranyl sulfate solution.

Irradiation in the X-10 graphite pile of D_2O in contact with SAE-1030 carbon steel showed no difference in corrosion from results obtained in the absence of radiation.

Plans for radiation experiments at flux levels up to 2×10^{13} are complete and the experiments are to be initiated at once.

Engineering Studies of Components

Fuel Test Loops and Pumps. One of the 100-gpm pump loops was dismantled and cut up for inspection after 1700 hr of operation. No serious corrosion effects were noted except at reduced sections (impeller discharge opening and a flow-limiting orifice) where some pitting was found. From an engineering standpoint, operation of all three circulating loops has been satisfactory to date. A fourth loop has been placed in operation to test the operating characteristics of a new type of shaft seal that has a Stellite

No. 6 face running against No. 14 Graphitar. Some leakage is occurring through the seal. It is expected that two additional test loops will be placed in operation during the next quarter. Operation of the Westinghouse 100-A pumps in the loops has shown the Stellite No. 98M2 journal, No. 14 Graphitar bearing combination to be very satisfactory.

Operation of the HRE Mockup. In an effort to keep the mockup as nearly a replica of the HRE fuel system as possible, it has been rebuilt with the addition of several new components. The system has been cleaned, treated, and put in operation with natural uranium fuel solution.

Homogeneous Reactor Cores. A complete analysis of data obtained with a full-size lucite model of the HRE core under the variable density conditions prevalent in actual operation shows that safe performance is to be expected at 250°C outlet temperature and full power. A program of testing leading toward the selection of an optimum core flow pattern for future homogeneous reactors has been started. Studies of means of effecting gas removal from reactor fuel systems at points outside the core have been started. Final tests of the HRE recombiner with hydrogen and oxygen gas introduced from cylinders into the mockup indicate that successful operation under all conditions of flow, up to the maximum design value of 15 cfm, is to be expected.

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Chemical Control

Electromagnetic Densitometer. An instrument for continuously monitoring uranium concentration in the HRE fuel by density measurement has been developed. The instrument operates best at a solution temperature of 50°C; at this temperature the analytical error is $\pm 0.5\%$ in the determination of uranium in solutions containing about 30 g of uranium per liter. An additional instrument for use at 250°C has been ordered.

Q Measurement. The major problem in the measurement of the Q of a high-frequency coil as affected by changes in uranium concentration is in developing a suitably corrosion- and radiation-resistant electrical insulator for the coil, which will be immersed in fuel solution at 250°C and 1000 psi pressure. Glazed ceramic insulators have given encouraging results.

Physics. Work has been done on (1) nonlinear reactor kinetics, (2) reactor stability, and (3) criticality calculations.

Nonlinear Reactor Kinetics. A moderately ambitious calculation was performed on the SEAC to explore the effect of changing excess reactivity, pressurizer friction, and delayed-neutron fraction. In general, nothing strikingly different from expectations was found. The principal object of

this work was to obtain a reasonable body of numerical information against which to check various useful approximate formulas for peak power, pressure, etc.

Reactor Stability. Arguments are reported for the pressurizer modification that has been adopted to suppress the mechanical instability reported in ORNL-1121.⁽¹⁾ It now seems probable that this instability has been removed for all possible operating conditions. A preliminary calculation has been made of the stability of the complete HRE reactor system. Although a great deal of idealization has been made in the calculation, it is very probable that the control of the HRE by power demand will actually lead to stable operation.

Criticality Calculations. Some general work has been done to check the accuracy of the methods reported in ORNL-1121.⁽¹⁾ These methods seem to be quite acceptable and they are very simple. Best values and estimates of error are given for the essential reactor constants. The effectiveness of the HRE safety plates has been recalculated, and it seems likely that they will control less than 3% reactivity. No serious results seem

⁽¹⁾T. A. Welton, H. T. Williams, L. H. Thacker, and P. M. Wood, "Criticality Calculations," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 84.

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possible. Finally, the modification of the delayed-neutron law by the flow has been considered as an aid in the experimental program.

Controls. Major emphasis has been on the installation and testing of HRE controls. An integrating unit for registering total reactor energy has been built and found to operate satisfactorily. A study of thermocouples for use in the HRE indicates the best type to be a special bayonet in a deep well that is welded to the pipe in such a way as to project into the center of the pipe; however, the objection to such a well on a corrosion basis may dictate the use of an alternate with a slower response. An improved control and regulating system for the HRE oxygen supply has been developed, and other refinements in the control system have been made.

PART II

ALTERNATE SYSTEMS

Solution Chemistry. Solubility studies indicate that at 100°C over 90% of the plutonium ion originally present in 1.26 M uranyl sulfate is precipitated. Solubilities of various fission products have also been measured over a wide temperature range. In connection with the use of the copper ion as a homogeneous solution catalyst for the recombination of hydrogen and oxygen, the solubility of CuF_2 in UO_2F_2 solutions was measured. It was found that adequate amounts for

complete recombination are soluble at 250°C in 0.126 and 1.26 M UO_2F_2 solutions.

The conductivity of UO_2SO_4 solutions at 25°C and vapor pressures at temperatures from 200 to 350°C have also been measured.

An analytical method has been developed for the determination of $\text{SO}_4^{=}$ in production-grade UO_2SO_4 .

Corrosion. The corrosion of welded and annealed commercial-grade titanium metal was less than 0.01 mil/yr after 2000 hr in 0.17 M uranyl sulfate at 250°C. Hot-rolled titanium exhibited weight gains of 0.01 mg/cm² after 225 hr and 0.09 mg/cm² after 800 hr in 1.71 M uranyl sulfate at 250°C. In the presence of high oxygen concentrations in 0.17 M uranyl sulfate at 250°C, hot-rolled titanium gained 0.05 mg/cm² after 100 hours. A slight galvanic couple effect was found between titanium and type-347 stainless steel exposed to oxygen-pressurized uranyl sulfate systems at 250°C. After 173 hours, the corrosion rate on titanium was 0.9 mil/yr as compared to 0.2 mil/yr for the stainless steel.

A difference in behavior was observed between Bureau of Mines resistance-melted zirconium containing 3% and 5% tin additions after 5000 hr in 0.17 M uranyl sulfate at 250°C. The 3% tin alloy showed a cumulative weight gain of 0.37 mg/cm²; the 5%

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alloy lost weight at a rate of 0.04 mil per year. Induction-melted zirconium containing 5% tin gained 0.06 to 0.08 mg/cm² after exposure up to 5000 hours. A weight gain of 0.12 mg/cm² was found for arc-melted crystal-bar zirconium with 5% tin addition after 4200 hr in 0.17 M uranyl sulfate at 250°C. Unalloyed, consumable-arc-melted zirconium from the Bureau of Mines showed considerably greater weight gain than zirconium with the tin alloys; gains of 2.3 to 3.6 mg/cm² were reported after 1700 hr in 0.17 M uranyl sulfate at 250°C.

Uranyl fluoride solutions (1.26 M) exposed at 250°C in CrO₃-pretreated type-347 stainless steel bombs were partially reduced after periods of 5 to 17 weeks. Corrosion rates for the type-316 ELC and type-347 stainless steel samples exposed in these tests for four weeks were 0.95 and 0.73 mil/yr, respectively. Corrosion rates for types-309 and -321 stainless steel samples after 9 and 16 weeks of exposure were 0.73 and 0.45 mil/yr, respectively. In another 12-week test, a corrosion rate of 0.13 mil/yr was obtained for HNO₃-pretreated type-347 stainless steel exposed to 1.26 M UO₂F₂ at 250°C.

A series of tests were run at 150°C to determine the effect of UO₂F₂ concentration on the corrosion resistance of HNO₃-pretreated type-347 stainless steel. No reduction of 0.42 M UO₂F₂ was observed for a period of eight

weeks; the corrosion rate was 0.82 mil per year. The stability of 0.84 M UO₂F₂ was erratic. Partial reduction occurred in one test after a period of one week, whereas in another test no precipitation occurred for a period of eight weeks. A corrosion rate of 2.53 mil/yr was obtained for the latter test. The HNO₃-pretreatment was ineffective in inhibiting the reduction of 1.26 M UO₂F₂ after a period of one week.

Radiation Stability. Gas production from uranyl solutions under pile irradiation has been studied over a range of enrichments, concentrations, and temperatures. The G values obtained have been interpreted in terms of the probable mechanisms involved.

Homogeneous recombination of hydrogen and oxygen in solution has been demonstrated to take place in the presence of a variety of substances. A common characteristic appears to be the existence of multiple valence states for metallic ions. Among the ions showing some activity are uranyl, copper, iron, chromium, tin, and thallium. Of these, the activity of copper is much the highest, being roughly 100,000 times that of uranyl ion. Studies are under way to establish details of the kinetics of this reaction.

Catalytic Recombination. Recombination of hydrogen and oxygen on a platinum catalyst has been shown to take

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place at a rate sufficiently high to handle maximum gas production of the HRE, and thus an alternate primary recombiner is available should the flame recombiner fail.

Slurry Studies. Studies of the chemistry of uranium trioxide are directed toward selecting the most suitable allotropic form for reactor slurry fuel use. Slurry stabilizing and antipacking agents have been investigated without finding any particularly helpful additive.

Slurry Pumping Studies. Studies of the viscosities of UO_3 slurries have been started. Abrasion and slurry pumping tests indicate that abrasion is not a severe problem unless the clearance between moving parts is small.

Preliminary investigations of the behavior of slurries during boiling have been started.

Boiling Reactor Studies. Operation of the Los Alamos "Supo" water boiler under boiling conditions at near atmospheric pressure was encouraging, and as a result design of a small, boiling homogeneous reactor, "critical" experiment has been started to determine operating and control characteristics at higher power densities and pressures.

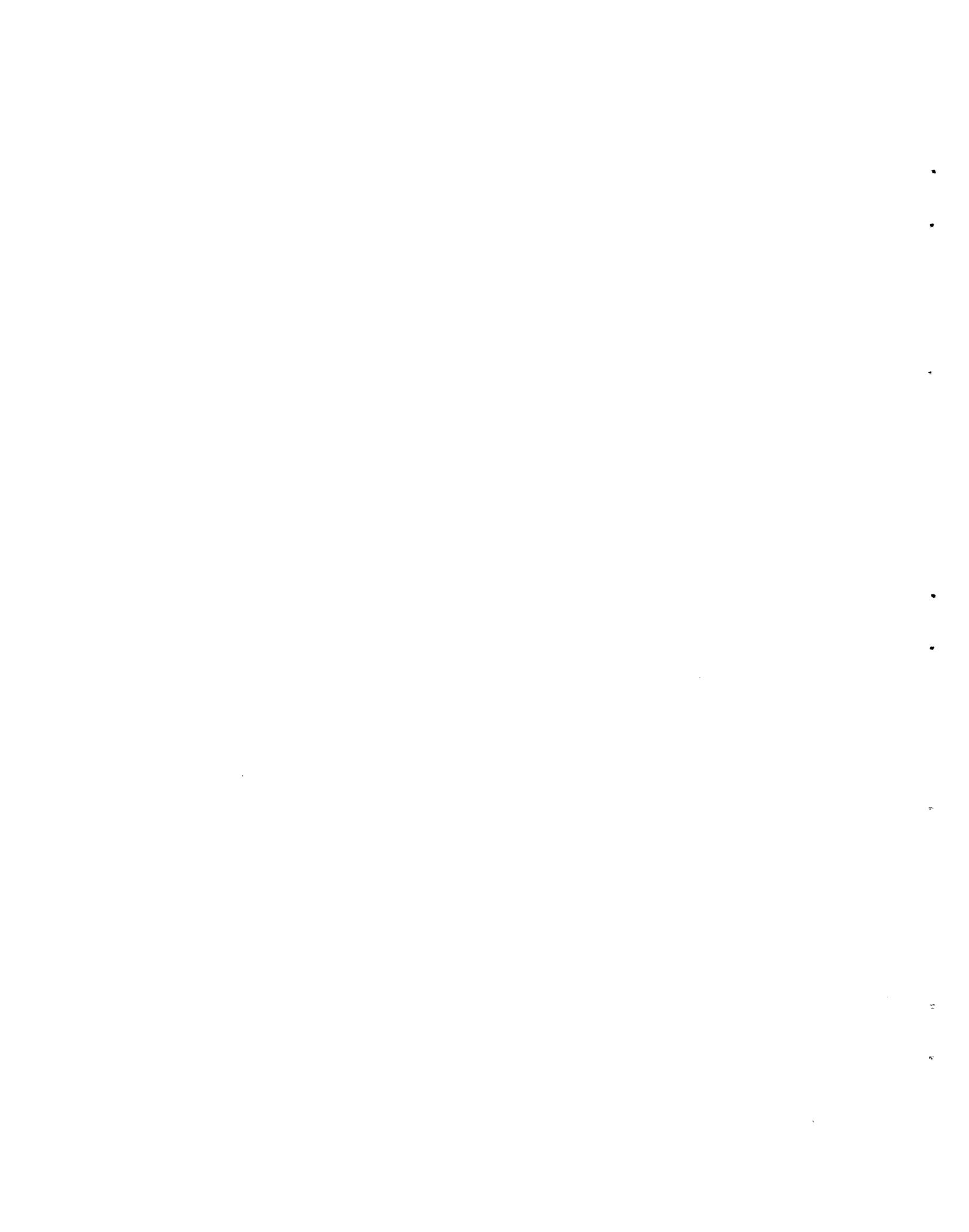
Homogeneous Reactor Chemical Processing. Study of possible processing methods indicates that the fewest unknowns would be encountered in using the following steps to process the fuel from a uranyl sulfate-heavy water plutonium producer: removal of the fuel from the reactor in one batch; evaporation to dryness for heavy-water recovery; conversion to a natural water system; 18-day decay period for plutonium build-up from neptunium; separation of plutonium, uranium, and fission products by tributyl phosphate solvent extraction.

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SECRET

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SECURITY INFORMATION

TABLE OF CONTENTS

	PAGE
SUMMARY	v
PART I - HOMOGENEOUS REACTOR EXPERIMENT	
CONSTRUCTION OF HRE	3
Experimental Program	3
DESIGN PROGRESS	11
Design Status	11
Revisions to the core tank	12
Fuel cooler	12
Pressurizer	13
Regulating plate and drive assembly	13
Low-pressure catalytic recombiner for fuel off-gas	13
Steamer	14
Oxygen metering system	14
Deuterium-oxygen recombiner loop for the reflector off-gas	14
D ₂ O sampler with provision for filling and emptying system	14
Sampler for the high-pressure helium loop	15
One-gallon-per-hour pulsafeeder purge-pump installation	15
Main-heat-exchanger leak-detection system	15
Alternate feed pumps	15
Alternate tube-bundle for main heat exchanger	16
Test of turbine-generator set	16
Dumping, purging, and concentrating in the fuel system	17
Rupture disk locations	17
Corrosion sampler	17
HRE flowsheets	17
Pump Loop Design	17
Westinghouse Model 100-A pump loops	17
Westinghouse Model 30-A pump loop	18
Westinghouse Model 150-B pump loop	18
Canned-rotor 4000-gpm pump test loop	18

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SECURITY INFORMATION

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	PAGE
CORROSION	21
Scouting Studies	21
Study of fundamental HRE corrosion problems	21
Studies with organic inhibitors in uranyl sulfate systems	23
Fundamental corrosion study	24
Static Tests	25
Uranyl sulfate corrosion studies	25
Corrosion behavior of 150°C nitric-acid-pretreated type-347-stain- less steel in 0.17 M uranyl sulfate at 150°C	25
Corrosion behavior of untreated metals in 0.17 M uranyl sulfate at 150°C	26
Effect of continuous exposure on chromic-acid-pretreated type-347 stainless steel in 0.42 M uranyl sulfate at 250°C	26
Vapor phase corrosion of type-347 stainless steel above 0.17 M uranyl sulfate solutions at 250°C	27
Effect of oxygen treatment on pretreated type-347 stainless steel	27
Effect of oxygen on uranyl sulfate stability in untreated type-347 stainless steel at 250°C	28
Reflector corrosion studies	28
Heavy-water studies	29
Effect of partial pressure of oxygen	31
Dynamic-Corrosion Studies	32
Fuel stability	32
Start-up conditions	33
Operation at reduced temperature	34
Additives	34
RADIATION STABILITY	35
Irradiation Experiments in the X-10 Graphite Pile	35
Effect of Copper Ions on Equilibrium Pressures Over HRE Solution Under X-10 Graphite Pile Irradiation	36
Decontamination of Irradiated Type-347 Stainless Steel	38
Radiation Effects on the HRE Reflector System	39
Experiments at Higher Fluxes	40
Plans for Next Quarter	41

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~~SECURITY INFORMATION~~

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SECURITY INFORMATION

	PAGE
ENGINEERING STUDIES OF COMPONENTS	42
Fuel Test Loops and Pumps	42
Fuel-recirculating test loops	42
Water-recirculating test loop	44
Westinghouse Model 100-A pump	45
Westinghouse pump bearings	46
One-gpm pulsafeeder pump	46
Operation of the HRE Mockup	47
Stability of the letdown system	47
Revisions of the mockup for operation with fuel	47
Operation of the rebuilt mockup	49
Homogeneous Reactor Cores	49
Flow in the HRE core	49
Intermediate core development	50
Gas separators	50
Recombiners	51
CHEMICAL CONTROL	53
Electromagnetic Densitometer	53
Development of a Densitrol for use at an average operating temperature of 50°C	54
Development of a Densitrol for use at an average operating temperature of 250°C	55
Q Measurement	57
Radiation-resistant Glasses	60
PHYSICS	62
Nonlinear HRE Kinetics with Gas Production	62
Over-all Stability of the HRE	65
Kinetic Calculations for Homogeneous Reactors	68
Modification of the Pressurizer Design to Eliminate Mechanical Instability	79
Criticality Calculations for Homogeneous Reactors	81

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SECRET

SECURITY INFORMATION

SECRET

SECURITY INFORMATION

	PAGE
Effect of Circulation on the Inhour Relation for the HRE	82
Nuclear Constants for the HRE	88
Effectiveness of HRE Control Plates	90
CONTROLS	91
PART II - ALTERNATE SYSTEMS	
SOLUTION CHEMISTRY	97
Stability of Plutonium Sulfate in Uranyl Sulfate Solution	97
Preparation of plutonium sulfate stock solution	97
Apparatus and procedure	97
Results	98
Fission-Product Solubilities in Uranyl Sulfate Solutions at High Temperatures	99
Lanthanum sulfate and yttrium sulfate	99
Cesium sulfate	102
Ceric sulfate	102
Molybdenum oxide	102
Zirconium sulfate	102
Cadmium sulfate	103
Solubility of Cupric Fluoride in Uranyl Fluoride Solution	103
Conductivity of Uranyl Sulfate Solution	103
Vapor-Pressure Studies of Uranyl Salt Solutions	105
Sulfate Analysis of Production-grade Uranyl Sulfate	107
CORROSION	110
Uranyl Sulfate Corrosion Studies	110
Titanium metal	110
Welded titanium tubing	110
Titanium in concentrated uranyl sulfate	110
Effect of oxygen	111
Galvanic corrosion effects	111

RESTRICTED DATA

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SECRET

SECURITY INFORMATION

SECRET

SECURITY INFORMATION

	PAGE
Zirconium	111
Resistance-melted zirconium-tin alloy	112
Induction-melted zirconium-tin alloy	112
Arc-melted crystal-bar zirconium-tin alloy	113
Consumable-arc-melted zirconium	114
Uranyl Fluoride Stability and Corrosion Studies	114
Corrosion resistance of pretreated stainless steels	114
Effect of dissolved oxygen on the solution stability of uranyl fluoride	116
RADIATION STABILITY	117
Radiation Decomposition of Homogeneous Reactor Fuel Solutions	117
Initial yields of gas from pile-irradiated uranyl solutions	117
Measurement of rate of energy absorption in water and in uranium solutions irradiated in the X-10 graphite pile	119
Homogeneous Recombination of Hydrogen and Oxygen	122
CATALYTIC RECOMBINATION	124
Full-Scale Catalytic Recombiner	124
Removal of Heat from the Catalyst	124
Comparison of Platinum with Palladium	126
SLURRY STUDIES	128
Uranium Trioxide Chemistry	128
Magnesium Uranate Studies	130
SLURRY PUMPING STUDIES	133
Circulating Slurry Experiments	133
Apparent viscosity of UO_3 slurries	133
Abrasion tests	133
Temperature cycle loop	133
Boiling Experiments	133

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SECRET

SECURITY INFORMATION

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	PAGE
Stability and uniformity of boiling slurry	134
Foaming	134
BOILING REACTOR STUDIES	135
HOMOGENEOUS REACTOR CHEMICAL PROCESSING	137
Heavy-water Recovery	137
Plutonium Chemistry	137
Solvent Extraction	138
APPENDIX	
BEARING OPERATION AT LOW VALUES OF THE SOMMERFELD NUMBER	143
Schedule of Experimental Studies	144
Experimental Facilities	144
Estimated Schedule of Activities	145

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~~SECRET~~

~~SECURITY INFORMATION~~

SECRET

SECURITY INFORMATION

LIST OF FIGURES

FIGURE	TITLE	PAGE
1	HRE Core and Top Flange Assembly	4
2	Heat-exchanger Cell, Fuel-circulating Pump, and Steam Generator	5
3	HRE Reflector Cell	6
4	HRE Control Room, Console and Instrument Panels	7
5	Top of HRE Shield	8
6	North Face of HRE Shield	9
7	HRE Turbine-generator Installation	10
8	Flow Sheet for 4000-gpm Pump Loop	19
9	Effect of Temperature and Copper on Equilibrium Gas Pressure	37
10	Effect of Temperature on Pressure for the System Aqueous Uranyl Sulfate plus Copper Sulfate	38
11	Piping Layout of HRE Mockup	48
12	Proposal Densitrol-installation Flow Diagram	53
13	Component Parts of Titanium Plummets Before Welding	56
14	Component Parts of Titanium Plummets Before Welding	56
15	Revised Q-coil Test Bomb	58
16	Power as a Function of Time for a δ Step Function of 0.01	70
17	Power as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients	73
18	Temperature as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients	73

RESTRICTED DATA

This document contains Restricted Data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to any unauthorized person is prohibited.

SECRET

SECURITY INFORMATION

SECRET

SECURITY INFORMATION

FIGURE	TITLE	PAGE
19	Density as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients	74
20	Velocity as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients	74
21	Pressure as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients	75
22	Power as a Function of Time with δ Step Functions of 0.005 and 0.007	75
23	Power vs. δ Step Functions	76
24	Pressure vs. δ Step Functions	76
25	Uranium Concentrations Required for Criticality as a Function of Core Radius	83
26	Ratio of Decay Rate in Core to Total Decay Without Circulation	85
27	Percentage of Total Contribution of Delayed Neutrons as a Function of Flow Rate	86
28	Excess Reactivity	87
29	Excess Reactivity	87
30	Rate of Change of Reactivity at Criticality	88
31	Thermocouple Transient Response	92
32	Oxygen-supply Flow Diagram	93
33	Solubility of Lanthanum Sulfate in Aqueous Uranyl Sulfate	100
34	Solubility of Yttrium Sulfate in Aqueous Uranyl Sulfate	101
35	Solubility of Cesium Sulfate in 1.26 M Uranyl Sulfate	102
36	Conductivity of Uranyl Sulfate	106

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FIGURE	TITLE	PAGE
37	Hydrogen-Oxygen Unbalance in Irradiated Uranyl Sulfate Solutions as a Function of Energy Input	119
38	Hydrogen Yield per Unit Energy Input as a Function of Concentration for UO_2SO_4 Solutions	120
39	Gas Production From Pile-irradiated UO_2SO_4 Solutions Containing 44.6 g Natural Uranium per Liter	121
40	Gas Production From Pile-irradiated UO_2SO_4 Solutions Containing 297.0 g Natural Uranium per Liter	122
41	Formation of Gamma and Delta Uranium Trioxide Monohydrates	129

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SECRET

SECURITY INFORMATION



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LIST OF TABLES

TABLE	TITLE	PAGE
1	Analysis of Uranyl Sulfate Solution Samples from Test at 250°C	29
2	Comparison of the Corrosion Rates for SAE-1030 Carbon Steel Exposed in Normal Water and Heavy Water at 200°C	31
3	Experimental Data on Recombination Test Runs	37
4	Decontamination of Irradiated Type-347 Stainless Steel Bomb	39
5	Radiation Effects on the HRE Reflector	40
6	Corrosion Studies in Boiling 0.17 M Uranyl Sulfate	59
7	Chemical Composition of Neutron-absorbing Glasses	60
8	Corrosion Tests in Boiling 0.17 M Uranyl Sulfate	61
9	Dimensions of Pressurizer Tube Sections	80
10	Residence Time in the Reactor vs. Rate of Flow	85
11	Total Reactivity Contribution of Delayed-neutron Groups at a Flow Rate of 100 gpm	85
12	Delayed-neutron Contributions at Various Flow Rates	86
13	Excess Reactivity as a Function of the Reciprocal of the Reactor Period	87
14	Rate of Change of Reactivity at Criticality as a Function of Flow Rate	87
15	Stability of Plutonium Sulfate in 1.26 M Uranyl Sulfate Solution	98
16	Solubility of Lanthanum Sulfate in 1.26 M Uranyl Sulfate	99
17	Solubility of Yttrium Sulfate in 1.08 and 1.26 M Uranyl Sulfate Solutions	99

~~RESTRICTED DATA~~

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~~SECRET~~

~~SECURITY INFORMATION~~

SECRET

SECURITY INFORMATION

TABLE	TITLE	PAGE
18	Comparative Solubilities of Yttrium Sulfate and Lanthanum Sulfate at 250°C	99
19	Solubility of Cesium Sulfate	102
20	Solubility of Cupric Fluoride in Uranyl Fluoride Solutions	104
21	Equivalent Conductivity of Uranyl Sulfate	105
22	Equivalent Conductivity of Uranyl Sulfate and Nickel Sulfate	105
23	Vapor Pressure of Uranyl Sulfate and Uranyl Nitrate Solutions	107
24	Comparative Sulfate Analyses of a Uranyl Sulfate Solution	108
25	Titration Analysis for Sulfate after Ion-exchange Removal of Uranium	109
26	Corrosion of Resistance-melted Zirconium-Tin Alloy	112
27	Corrosion of Induction-melted Zirconium-Tin Alloy	113
28	Corrosion of Arc-melted Crystal-bar Zirconium-Tin Alloy	113
29	Corrosion of Consumable-arc-melted Zirconium	114
30	Corrosion Data for CrO ₃ -Pretreated Stainless Steels Exposed to 1.26 M UO ₂ F ₂ at 250°C	115
31	Corrosion of HNO ₃ -Pretreated Type-347 Stainless Steel by 1.26 M UO ₂ F ₂ at 250°C	115
32	Corrosion Data for HNO ₃ -Pretreated Stainless Steel Exposed to 0.42 and 0.84 M UO ₂ F ₂ at 150°C	116
33	Initial Yields of H ₂ from Pile-irradiated Uranyl Solutions	118
34	Energy Absorption in Uranyl Solutions Irradiated in the Maximum Flux in Hole 12 in the X-10 Graphite Pile	122
35	Operational Data for Experimental Recombiners	125
36	Comparison of Platinum and Palladium as Recombination Catalysts	126

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SECRET

SECURITY INFORMATION

SECRET

SECURITY INFORMATION

TABLE	TITLE	PAGE
37	Summary of Uranium Oxides	130
38	Stability of UO_3 Slurries Containing Additives	131
39	Effect of Heating and Kaolin Addition on Slurry Particle Size	131
40	Solubility of Plutonium in 1 M $UO_2SO_4-H_2SO_4$ on Heating at 250°C	138

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Part I

HOMOGENEOUS REACTOR EXPERIMENT

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HRP QUARTERLY PROGRESS REPORT

CONSTRUCTION OF HRE

S. E. Beall, Section Chief
J. J. Hairston V. K. Pare'
J. W. Hill L. H. Thacker
D. T. Jones T. H. Thomas
T. H. Mauney S. Visner
P. M. Wood

The status of the construction work on the various phases of the Homogeneous Reactor Experiment is given below. Photographs of several installations are shown in Figs. 1 through 7.

Fuel System. Construction of the fuel system was completed on November 15. Component testing and chemical pretreatment will begin immediately.

D₂O System. The D₂O system has been finished, as originally designed, for several weeks. Revisions requiring approximately two weeks of work were begun on November 15.

Instrumentation. The control and process instrumentation is installed but must be checked out. Approximately one week of work will be required for 100% completion.

Shielding. The mortered block walls on three faces of the shield and the removal plugs for the top are complete. Work on the inner shield and the one remaining outer wall will continue for several weeks.

Steam System. The steam system is 100% complete and ready for operation.

Turbine-generator Installation. Final connections are being made on the turbine and generator. Testing with building steam is scheduled for December. Installation was 90% complete on November 15.

EXPERIMENTAL PROGRAM

The HRE experimental program has been outlined in three memorandums covering both nuclear and engineering tests on the reflector and fuel systems:

J. W. Hill, *Testing of the HRE Reflector System*, November 14, 1951.

T. H. Thomas, *Testing to be Performed on Fuel System Components of the HRE*, November 14, 1951.

S. Visner, *Experimental Physics Program for the HRE*, ORNL CF-51-11-149, November 14, 1951.

HRP QUARTERLY PROGRESS REPORT

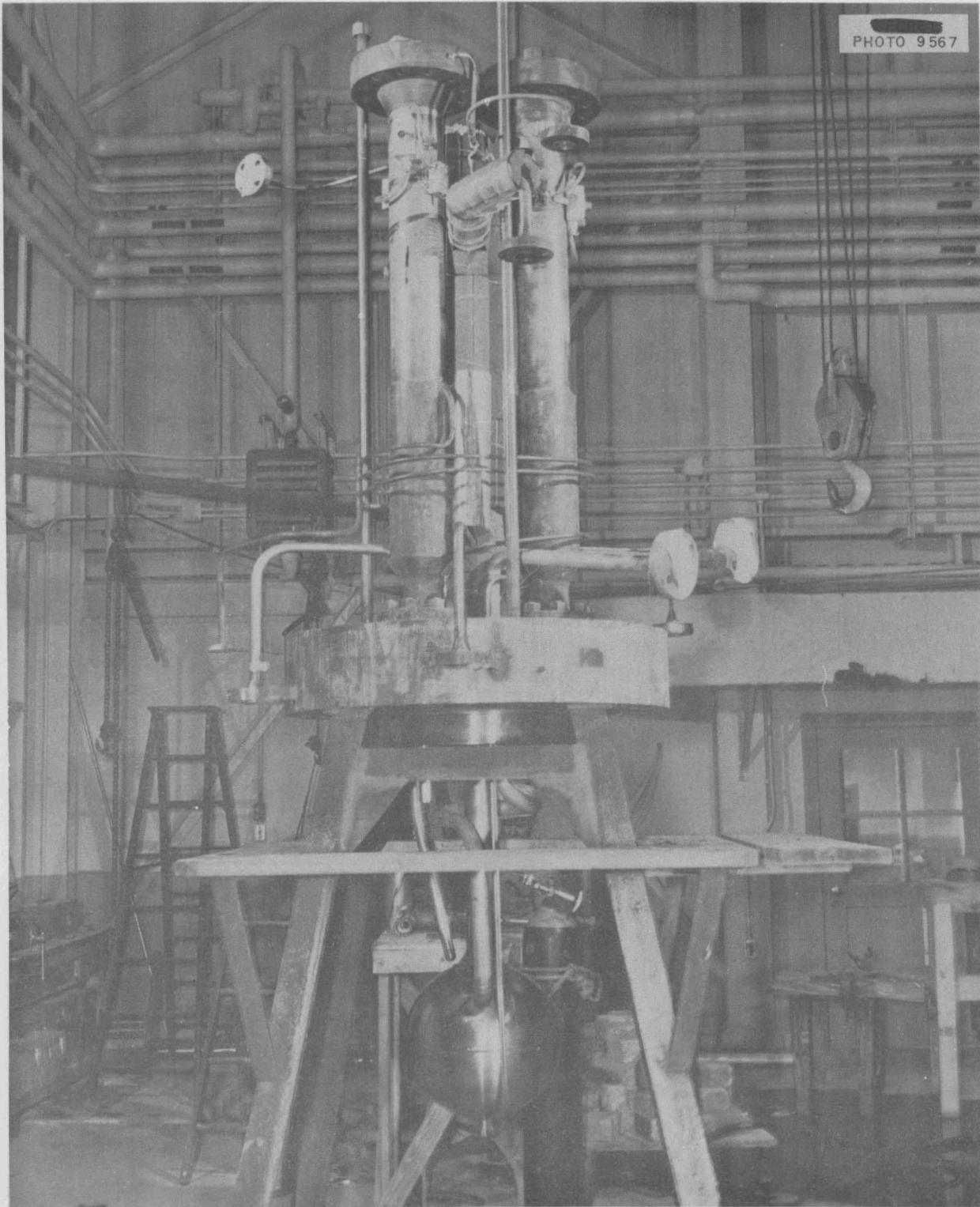


Fig. 1. HRE Core and Top Flange Assembly. Fuel inlet and exit lines and control-rod housings are shown.

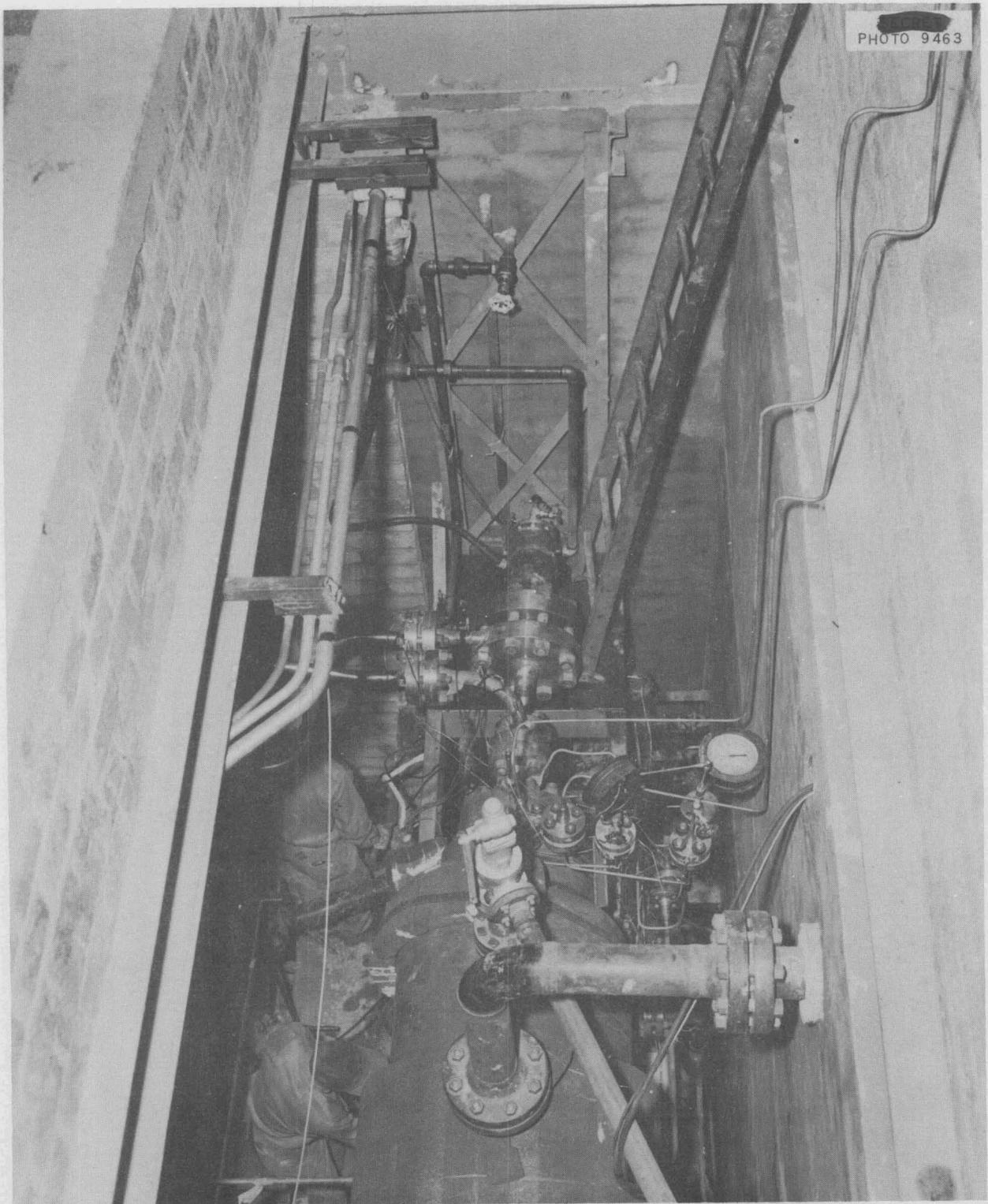


Fig. 2. Heat-Exchanger Cell, Fuel-Circulating Pump, and Steam Generator.

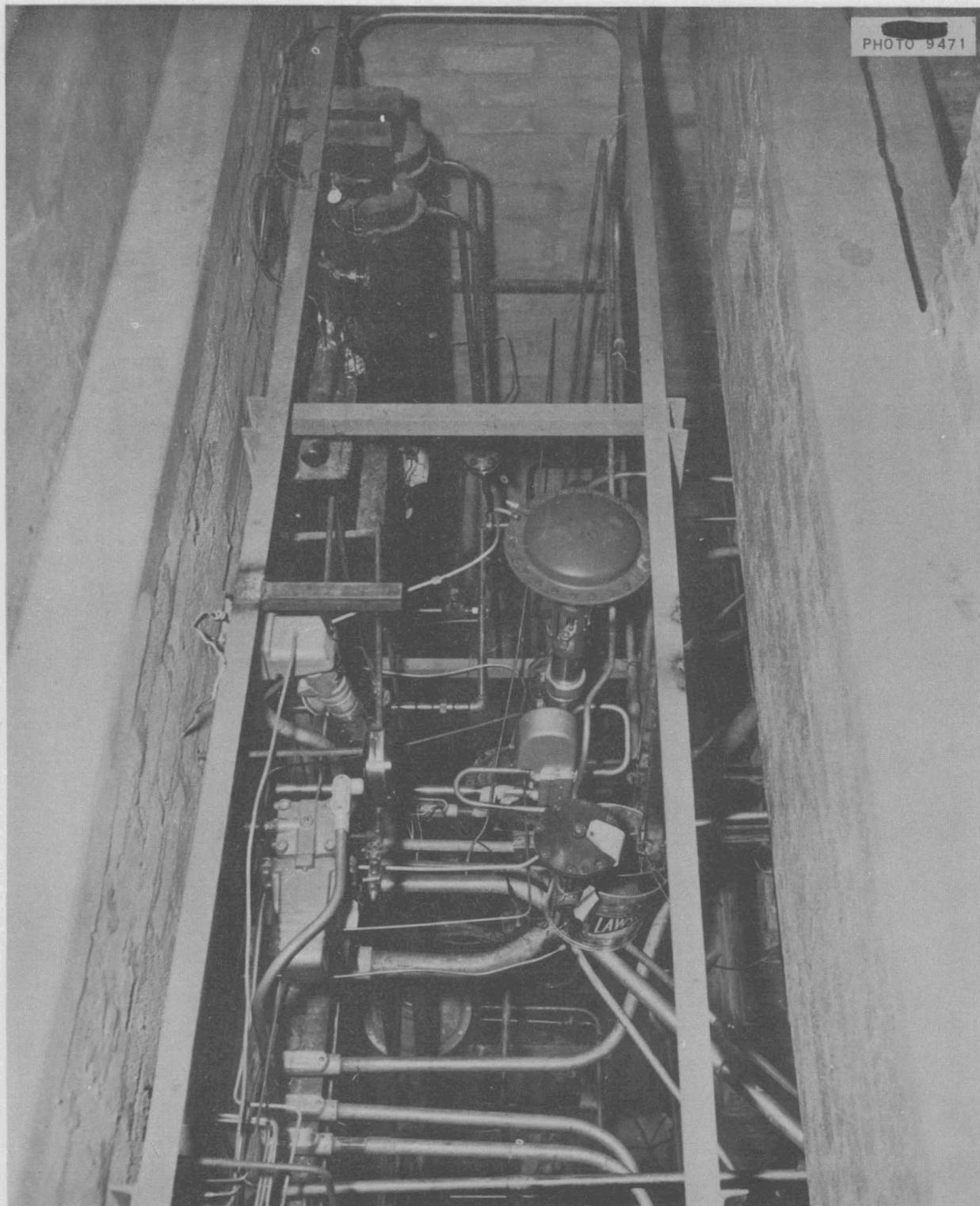


Fig. 3. HRE Reflector Cell. Photograph taken from above.



Fig. 4. HRE Control Room, Console and Instrument Panels.

FOR PERIOD ENDING NOVEMBER 15, 1951

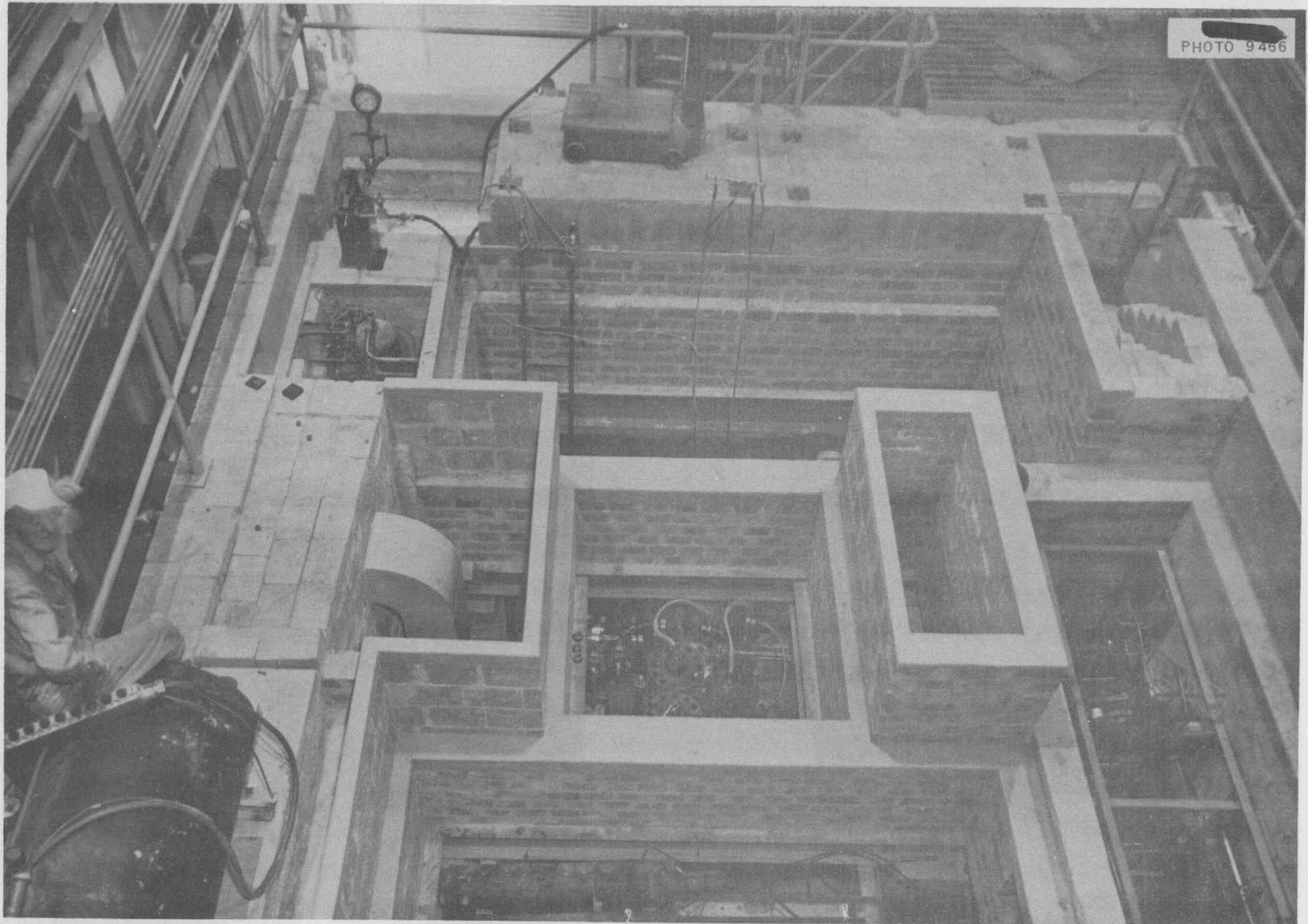


Fig. 5. Top of HRE Shield. This photograph, taken looking west, shows the main reactor cell in the center with the top shielding blocks removed.

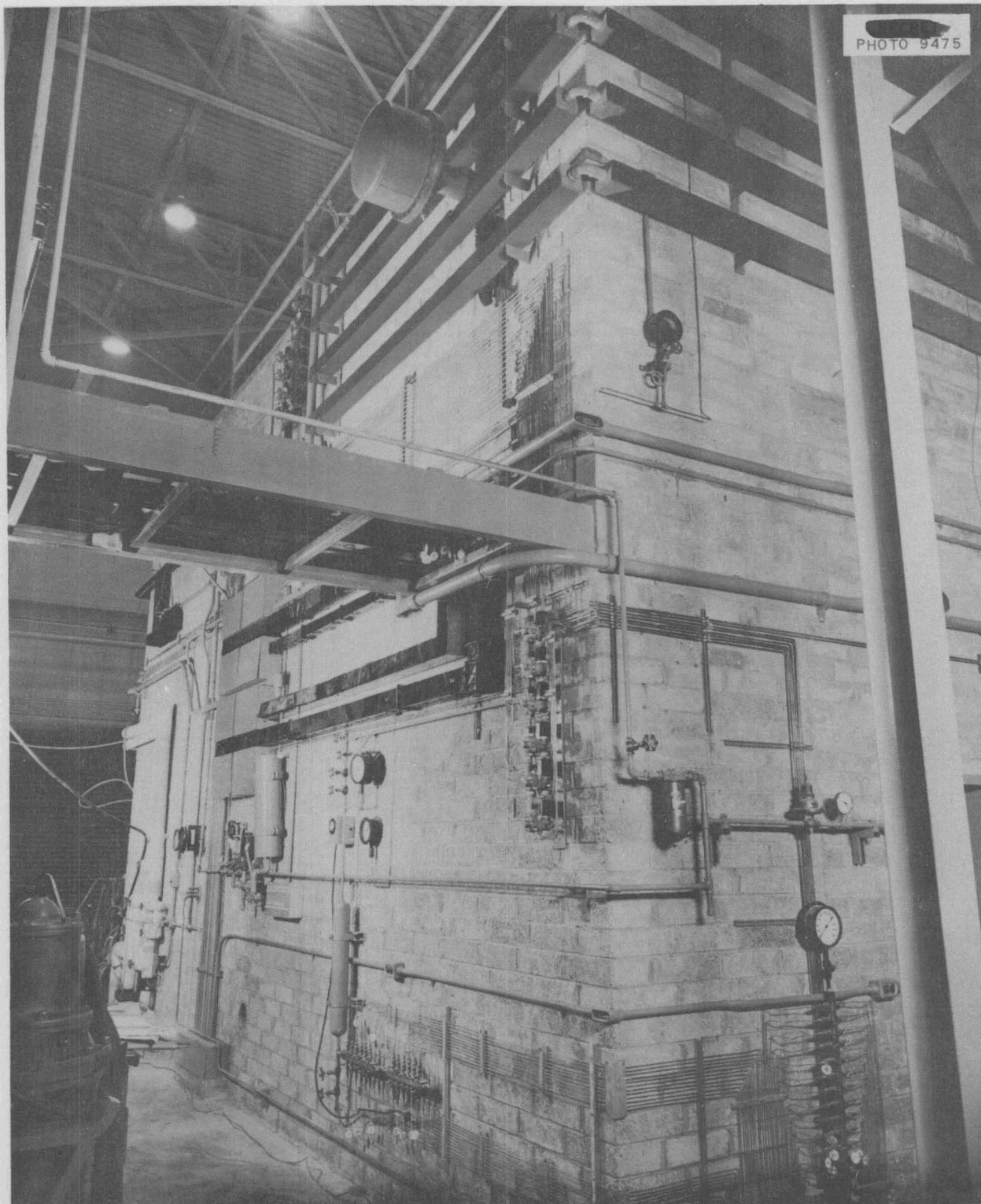


Fig. 6. North Face of HRE Shield. Photograph taken from northwest corner.

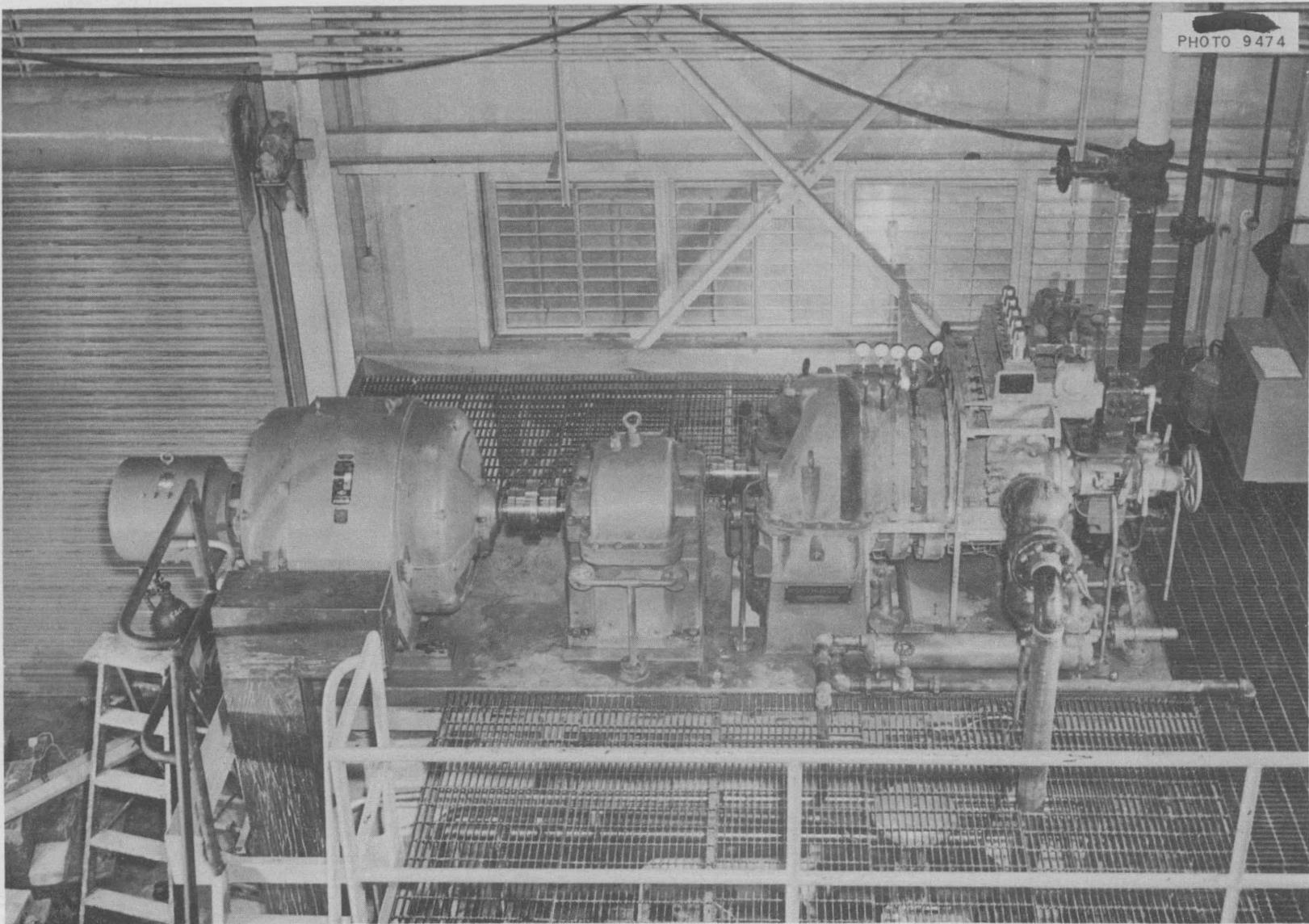


Fig. 7. HRE Turbine-Generator Installation.

DESIGN PROGRESS

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 W. Terry

DESIGN STATUS

Almost all the items required for the initial cleanup procedure and mechanical testing of the HRE have been designed, and the necessary working drawings have been issued for fabrication. The major items remaining to be designed are samplers for the fuel, gas, and reflector systems. A temporary sampling device for the fuel system and tentative designs for the reflector and gas system samplers have been issued. It is anticipated that these will be adequate during the initial phases of HRE operation. The efforts of the entire design group will be devoted to these problems during the forthcoming quarter, if necessary, to have approved sampling devices designed and constructed before the critical experiments are started.

During the past quarter designs have been completed and approved drawings have been issued for construction of the following units.

1	Revised core-tank assembly	D-10113
	Core-tank details	D-10114
95	Accumulator tank and details	D-10121
	Oxygen-metering station	D-10120
47	Revised assembly of regulating-rod	F-10123
	Regulating-rod and plate assembly	D-10124
	Regulating-rod guide tube and switch assembly	D-10125
	Regulating-rod limit switch details	D-10126
18	Reflector-vessel flange piping and elevations	E-8627

Design information for the installation of the following systems was issued during the past quarter.

ITEM NO.	DESCRIPTION	ORNL DRAWING NO.	METHOD OF CONVEYING INFORMATION
			SYSTEM DESCRIPTION
			D ₂ O sampler with provision for filling and emptying system
			Memo to HRE file dated 11/7/51, with sketches
			Deuterium-oxygen re-combiner loop for the reflector off-gas
			Memo to HRE file dated 11/14/51, with sketches
			Sampler for the high-pressure helium loop
			Memo to HRE file dated 10/31/51, with sketches
98	Surge tank	D-10119	
2	Pressurizer	D-10103	One-gallon-per-hour pulsafeeder purge-pump installation
	Pressurizer details	D-10104	Memo to HRE file dated 10/24/51, with ORNL drawing D-8645
	Liquid-level controller	D-10117	
93	Steamer	D-10105	Main-heat-exchanger leak-detector system
(a & b)			Memo to HRE file dated 10/25/51, with sketches
7	Fuel cooler	D-10107	
88	Low-pressure catalytic re-combiner for fuel gas	D-10108	Steam-turbine and generator installation
			ORNL drawings D-8646, D-8647, and D-8648

HRP QUARTERLY PROGRESS REPORT

(continued)

SYSTEM DESCRIPTION	METHOD OF CONVEYING INFORMATION
Fuel pulsafeeder and filter assembly	ORNL drawings D-9590, D-9598, and D-9591
Revised HRE flowsheet	ORNL drawing E-8623
HRE flowsheet line schedule	Memorandum to HRE file

Revisions to the Core Tank. The core-tank outlet-pipe arrangement was altered at the request of the Theoretical Physics Section to reduce the pressure drop between the core tank and the pressurizer when sudden increases in reactivity cause some of the fuel in the core to be ejected into the pressurizer. Originally the design consisted of two concentric pipes. The inner pipe had an outside diameter of 1.900 in. and a 0.200-in.-thick wall, and the outer pipe had an inside diameter of 2.900 inches. Both pipes were flared into the core tank to streamline the flow where fuel leaves the core. At the bottom of the pressurizer an elbow in the inner pipe passed through the outer-pipe wall and connected to the piping in the fuel-circulating system.

In the original arrangement all the fuel exited from the core through the inner pipe, and the annulus provided the relief connection to the pressurizer. The physicists requested either that the elbow in the inner pipe be removed and the circulating pipe be teed directly into the outer pipe or that holes be cut in the inner pipe communicating to the annulus so that essentially the entire cross section was available for flow to the pressurizer. The inner pipe was to be retained in either case to provide additional surface for frictional damping of small oscillations that might be set up between the core and the pressurizer.

The original request of the physicists was not acceptable to the Experimental Engineering Section because their design increased greatly the diameter of the opening at which the bulk of the fluid is removed from the core. This increase in the diameter reduced the angular velocity of the forced-liquid vortex in the center of the core and was expected to affect adversely the stability of the gas vortex.

The final compromise is shown in ORNL drawing D-10113. It contains a 1 3/4-in.-OD by 13-ga concentric tube in the 3-in. schedule-80 pipe connection to the pressurizer. The inner tube is perforated to provide communication with the annulus. The diameter was selected so that the hydraulic radii of the inner channel and annulus are equal. Where the fluid leaves the core, the diameter of the 3-in. outer pipe was reduced by 1/4 inch. On one hand this reduces the total cross section of the exit for a short distance; on the other it increases the cross section through which the bulk of the fuel passes and may decrease the stability of the vortex. In general, it was the best compromise considered that proved acceptable to both the physicists and the engineers.

The 1/4-in. pipe outlet at the bottom of the core tank was also altered at the request of the Theoretical Physics Section. The change converted a long sweeping bend into a bend of the shortest possible radius. The purpose of the alteration was to reduce to a minimum the amount of liquid remaining in the pipe when the bulk of the line fills with gas formed by radiation decomposition of the moderator. Minimizing the liquid volume minimizes the effect of this line on pressure oscillations in the core.

Fuel Cooler. The fuel cooler, Item 7, was redesigned to provide greater

cooling area with consequent lower exit temperature of the fuel. The lower this temperature, the greater will be the amount of gas retained in solution and there will be less tendency to gas-bind the fuel pulsafeeder pump. Adding 9 ft to the length of the previous exchanger results in reducing the fuel exit temperature from the cooler by approximately 35°F, with 1 liter more holdup of fuel.

Pressurizer. A new design of the pressurizer, Item 2, was issued with the inner steam-heated wall thickened in order to comply with requirements of the 1950 ASME Code for Unfired Pressure Vessels for tubes or pipes subject to external pressure. In general, the entire pressurizer design was reviewed from this point of view and the vessel was subsequently designed to comply throughout, as nearly as possible, with the ASME code.

A water-cooled by-pass line from the liquid-level indicator to the bottom drain connection of the pressurizer was added to induce circulation of fluid through the pressurizer. The type of liquid-level indicator to use with the pressurizer was decided upon and drawings were prepared and issued for construction. The design of this liquid-level indicator is approved on ORNL drawing D-10117.

Regulating Plate and Drive Assembly. At the request of the Operating Section, design studies were made to determine the feasibility of adding more surface area to the proposed regulating plate. Based on these studies, the regulating plate area was increased to approximately eight times the previous area. Increasing the plate area necessitated a redesign of the drive mechanism to allow access for maintenance. With the previous design the width of the regulating plate was small enough to permit withdrawal through the hole in the top

pressure-vessel flange when the regulating plate mechanism housing is removed. This procedure is no longer possible with the widened plate, hence it is necessary to be able to disconnect the plate screw from the mechanism internally so that only the mechanism itself is removable. Working drawings showing the revised design were subsequently prepared and issued to the field, and on November 15, 1951 fabrication was complete and the plate was partially assembled. It is reported that the new design is satisfactory.

Low-pressure Catalytic Recombiner for Fuel Off-Gas. Final design for the low-pressure catalytic recombimer for the fuel off-gas system was issued as ORNL drawing D-10108. The specifications for this recombimer were based on data furnished by the Experimental Engineering Section modified to comply with the 1950 ASME Code for Unfired Pressure Vessels. The 5-in.-deep catalyst bed consists of approximately 1.1 lb of platinized alumina contained in a 3-in. schedule-40 stainless steel pipe. Thermocouple wells are inserted in both ends of the bed for measurement and control of the catalyst temperature. Welded to the recombimer body adjacent to the catalyst bed is a jacket through which steam may be circulated for preheating the catalyst material or which may be used as a coolant jacket, if necessary. This jacket is made from a section of 5-in. schedule-40 pipe split circumferentially in the middle with the halves joined by a corrugated expansion joint. Calculations indicate that without this expansion joint the shell stresses may become excessively high because of differential thermal expansion of the inner and outer pipes. The recombimer was installed essentially parallel to the off-gas condenser to minimize the possibility of the catalyst bed becoming filled with condensate.

HRP QUARTERLY PROGRESS REPORT

Steamer. Two steam generators were designed for installation in the fuel off-gas system to provide a diluent for the hydrogen and oxygen entering the recombiners. The steamers were designed to have a vapor rate of approximately 5 lb/hr at 15 psia. The heat of vaporization is supplied by 40-psi steam circulated through a jacket surrounding the vapor space. The steamers are designed so that there will be a constant flow rate of 5 to 10 lb/hr of feed water supplied from the fuel-gas condenser to minimize sludge accumulation. Design of the steamer was approved on ORNL drawing D-10105.

Oxygen Metering System. To inhibit corrosion in the piping system, it is desirable to admit from 10 to 1000 ppm of oxygen to the high-pressure fuel-circulating system. The system was designed to admit oxygen in these proportions to the vapor space of a surge tank (Item 98, ORNL drawing D-10119) inserted in the high-pressure fuel-return line from the dump tanks at a position just before the existing letdown heat exchanger. The surge tank was designed to damp pressure oscillations from the fuel pulsafeeder pump and to present adequate surface area for the absorption of the required oxygen into the system.

Oxygen is metered through a calibrated capillary tube inserted between two isolation valves, which are interlocked so that it is impossible to open both simultaneously. This interlocking of the valves is necessary for safety, since it is essential that no direct path be established for the escape of radioactive solution from the shielding. Also, between the two valves is an accumulator tank of approximately 0.670 ft³, which is operable between pressure limits slightly above the fuel pressure. A Mercoid Pressure Controller, with the necessary instrumentation, determines which of

the two valves is open at a particular time. The valves are located in the biological shielding, whereas the accumulator tank is in the fuel cell. Oxygen is initially supplied from a manifold located external to the biological shielding. This system was approved on ORNL drawings D-9595, D-9051, D-10119, D-10120, and D-10121.

Deuterium-Oxygen Recombiner Loop for the Reflector Off-Gas. A type-347 stainless steel jet exhaustor was installed from the D₂O-circulating-pump outlet to the D₂O-return line, so that it was in parallel with the D₂O cooler and came before the first flange to the pressure-vessel inlet nozzle. With 20% of the total D₂O flow as the driving medium, this jet is reported to be capable of exhausting the required 0.5 cfm of gas-vapor mixture through the D₂O off-gas recombiner, provided the back pressure on the jet discharge is kept as low as possible. Therefore, to minimize this back pressure, the exhaustor is mounted 14.5 ft above the cell floor and next to the south wall of the D₂O shielding compartment. The 20% D₂O flow through the exhaustor may be cooled by jacketing the by-pass line to maintain the desired reflector temperature and obtain maximum jet efficiency. This system is described in detail in the memorandum to HRE file entitled *Deuterium-Oxygen Recombiner Loop*, dated November 15, 1951.

D₂O Sampler with Provision for Filling and Emptying System. A system has been devised for obtaining samples of the reflector fluid that may also be used as a means of filling or emptying the reflector system. With this method, a 10-ml sample of D₂O may be obtained from either the low pressure or suction side of the reflector pulsafeeder pump or from the high pressure or discharge side of the pump by proper sequential manipulation of valves. The sampling

system is shielded with lead because it has been assumed that impurities present in the D_2O will become radioactive under reactor irradiation. This system is described in detail by the memorandum to HRE file entitled *D₂O Sampler with Provision for Filling or Emptying System*, dated November 7, 1951.

Sampler for the High-pressure Helium Loop. A design has been submitted for a device for obtaining a sample of the helium-gas-vapor mixture from the reflector-vessel vapor space. Two types of gas sample containers capable of containing gas at 1000-psi pressure are shown. The gas sample is obtained from the reflector-vessel vapor line before the catalytic recombiner by running a 1/8-in. stainless steel pipe from this line to a pit in the top of the shield. To obtain a sample, the sample holder is purged by allowing approximately 500 cc of gas to flow through the system to the dump tanks. The downstream side of the sample carrier is then valved off and the sample brought up to the required pressure. All valves are then closed and the carrier removed. This system is described in detail by a memorandum to HRE file, dated October 31, 1951.

One-Gallon-per-Hour Pulsafeeder Purge-Pump Installation. The proposed location for the 1-gph pulsafeeder purge-pump installation has been approved on ORNL drawing D-8645. The purpose of this installation is to supply approximately 1gph of distilled water from the fuel-gas condenser to the fuel-circulating pump. This water is pumped at sufficiently high pressure to keep the rotor housing of the circulating pump purged of fuel. Because of the compressibility of the water in the connecting water leg of the pulsafeeder purge-pump installation, delivery of distilled water is reduced from 1 to approximately 0.417 gallon

per hour. It is not anticipated that there will be sufficient radiation damage to decompose enough water in this system to cause the pump to gas-bind.

Main-Heat-Exchanger Leak-Detection System. A system for detecting leakage of fuel or boiler water into the leak-detector space in the tube sheet of the main heat exchanger has been approved in the memorandum to HRE file, dated October 25, 1951. The proposed system consists of a pressure tap and remote-reading pressure gage connected to the split tube sheet. If a leak develops, either the fuel or water side of the exchanger may be throttled or shut down. The resulting pressure readings of the leak-detector pressure gage will subsequently reveal which of the two sides is leaking.

Alternate Feed Pumps. A design for an alternate type of feed pump to replace the existing pulsafeeder pumps has been submitted for approval by the ORNL Engineering Department. This design is a simple piston pump with several innovations that are believed to be improvements of the commercial plunger pumps of the same general type. These innovations consist of the following:

1. Double-ball check valves are placed in the inlet and outlet pipes to provide a minimum amount of holdup in the pump cylinder.
2. The inlet check valves are built directly into the piston head, and hence inertia, as well as pressure differential, is available for actuation.
3. The suction inlet of the pump is at about the middle of the side of the cylinder. Fluid is introduced directly to a grooved annulus turned in the center of the piston, and hence leakage of high-pressure fluid is

HRP QUARTERLY PROGRESS REPORT

always back to the pump suction. The close fit between the lower half of the piston and cylinder inhibits leakage into the lower portion of the cylinder. Any leakage that does occur is subsequently flushed back to the dump tanks through a small check valve and drain line at the low point of the pump cylinder.

The pump piston is directly connected by a piston rod through a conventional packing gland to a double-acting hydraulic cylinder located vertically and beneath the pump. The drive fluid for this unit may be oil or other liquid supplied from an externally located source.

This unit is expected to have the following advantages over the pulsafeder pumps:

1. The thin diaphragms constituting the pumping units of the pulsafeder pumps are eliminated. If the pitting type of corrosion described by the chemists does occur in the HRE piping system, the lifetime of a thin diaphragm will be a very random probability. Also, the total number of flexures that such a diaphragm can endure without fatigue failure is unknown.

2. The loss of pumping efficiency in the pulsafeder pumps owing to the compression of water between heads is eliminated.

3. The holdup in the pumping head is lower.

This design is submitted on ORNL drawing D-10171.

Alternate Tube Bundle for the Main Heat Exchanger. Revised drawings of an alternate tube bundle for the main heat exchanger have been prepared. The new design will have the following major advantages over the existing design:

1. The tube ends are flared into the tube sheet before welding to prevent weld metal from partially obstructing the tube openings.

2. The inlet and outlet pipes have a gradual transition from 1 1/2-in. to 2 1/2-in. schedule-80 pipe for better fluid distribution and low pressure drop.

3. The slightly greater tube-bundle area will provide higher capacity.

4. The stay bolts inserted in the head liner will prevent distortion during welding and machining.

This design is submitted on ORNL drawing D-10130.

Test of Turbine-generator Set. A trip was made to the Worthington plant at Wellsville, New York to witness the test run of the turbine-generator set. The unit ran smoothly and the manufacturer, on the basis of a "power-pressure" test, confirmed his original guaranteed steam rates. The "power-pressure" test consisted of the following five steps: (1) calculate the nozzle areas (other than first stage) for maximum efficiency, (2) choose the first-stage nozzle to meet the guaranteed load points, (3) determine the amount of power out of each nozzle group by calculation, (4) test turbine with maximum steam possible through each group ("group" implies several openings in one nozzle), (5) compare power obtained from 3 and 4, and if the test power is the same or greater than the calculated power, the turbine is expected to meet the guaranteed performance.

The turbine-generator set will be further tested by several MIT students during the period from December 3 to 7, 1951. The tests will check the

manufacturer's steam rates and determine the operating characteristics of the turbine, generator, condenser, and auxiliary equipment.

Dumping, Purging, and Concentrating in the Fuel System. A memorandum was written on the subject, *Dumping, Purging, and Concentrating in the HRE Soup System*, dated October 22, 1951, which gives the minimum size of charge necessary for a specific fuel concentration and the minimum concentrations possible with the present fuel system.

Rupture-Disk Locations. All rupture-disk locations were analyzed from the standpoint of ease of remote removal, and recommendations were made to relocate the rupture disk in the core-tank dump line to facilitate its removal. A decision was made to leave the letdown valve in its present location provided a horizontal access hole is incorporated in the east wall of the reactor.

Corrosion Sampler. Two corrosion-sample retainers will be inserted in the ends of the removable elbow of the line adjacent to the main heat exchanger. The retainer is essentially a split sleeve held together by two rings, one of which has a conical spring section that is compressed by the ring-joint flange faces to prevent vibration. The sample holder and a typical sample are shown on ORNL drawing D-10128. If a velocity of 15 ft/sec is assumed for normal flow, the increased flow rate due to the restriction in the line will be approximately 23.6 feet per second. Seven samples are to be inserted in each retainer. Present plans call for two retainers made of type-347 stainless steel, and future plans call for two made of titanium. The samples are to be made of the following materials: types-316, -329, -347, and Carpenter-20 stainless steel; induction-melted

zirconium; induction-melted zirconium plus 5% tin; and titanium. Another drawing (B-10129) is being made to show a special flange that is really a reworking of a standard 1 1/2-in. 2500-lb stainless steel flange. The inside diameter is enlarged to compensate for the restriction, and therefore there is no increase in flow velocity.

HRE Flowsheets. The HRE flowsheet is being redrawn in five sections to show the available pertinent information. The five sections will comprise the high- and low-pressure fuel and D₂O systems and the power system. The final drawings will be reduced to 11 by 17 in. for incorporation in the HRE design data booklet.

PUMP LOOP DESIGN

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J. Brown	J. D. Maloney
	W. L. Ross

Westinghouse Model 100-A Pump Loops. Drawings have been completed and installation of eight pump loops along the south wall of the experimental area of Building 9204-1 has started. Six of the eight loops will have Westinghouse Model 100-A canned-rotor pumps of the type used in the HRE fuel system. These six loops will be fabricated from 1 1/2-in. schedule-80 type-347 stainless steel pipe. A pressurizer fabricated from 4-in. schedule-80 type-347 stainless steel pipe with immersion heaters cast in aluminum around the pipe will be connected to each loop. During operation at 1000 psi and 250°C it will be necessary to remove about 3 kw of heat from each loop. This will be accomplished by using a water spray on the loop, since this method has been successful on similar Model 100-A pump loops.

The loops will be used for testing fuel stability and the corrosion of

HRP QUARTERLY PROGRESS REPORT

various metals and alloys. Three ports for insertion of corrosion sample pins are located on each loop. Provisions have also been made for insertion of a corrosion sample in a short length of pipe in the main stream of the loop.

Westinghouse Model 30-A Pump Loop.

One of the eight pump loops will have a Westinghouse Model 30-A canned-rotor pump and the loop will be fabricated from 1 1/2-in. carbon steel pipe. The primary purpose of this loop will be to determine corrosion of hot water on steel similar to that used in the HRE reflector vessel.

Westinghouse Model 150-B Pump Loop.

The remaining loop will be used for testing a Westinghouse Model 150-B canned-rotor pump. This pump is a 150-gpm pump, and unlike the Model 100-A pump it has a built-in water-cooling coil and requires no oil for cooling the stator. This loop will be identical to the Model 100-A pump loops, except that the pump will be mounted in a vertical position.

Canned-Rotor 4000-gpm Pump Test Loop. In the long-range homogeneous reactor program emphasis is shifting from 4000-gpm circulating pumps to those of larger capacity, say, 20,000 gpm. However, a considerable amount of valuable information can be obtained from a 4000-gpm prototype of the larger pump. Of interest will be points of major wear or corrosion, suitability of large water-lubricated radial and thrust bearings, and experience in handling large equipment. One 4000-gpm pump test loop will probably be adequate for this work and for any component testing that may be desired.

The present plan for this test loop includes installation of a 4000-gpm circulating system made of 10-, 8-, and 6-in. stainless steel pipe, the

required flanges and fittings, a canned-rotor 4000-gpm pump, and the necessary auxiliaries for satisfactory loop operation. The loop will be approximately 25 ft long to accommodate flow-measuring devices. Procurement of major items is in progress, with delivery expected in May and June of 1952.

The loop and its auxiliaries are shown in the accompanying flowsheet, Fig. 8. This system will operate at a nominal pressure of 1000 psi and temperature of 250°C, and it will contain the necessary components to maintain these conditions as well as to supply from 1/4 to 1/2 gpm of seal water to flush loop solution from the armature and bearing chamber of the pump. In addition to the above, provisions are to be made to keep the dissolved oxygen content of the solution between 10 and 1000 ppm. The stability of the solution has been found to be dependent on this dissolved oxygen. A Dumping system is also included to facilitate filling and emptying the loop, which holds 120 gal of solution. Two panels similar to those used on the Model 100-A pump loops will house the instruments and controls. Most of the auxiliaries will be installed so that they can be easily operated and yet not interfere with the crane and equipment necessary for the removal of any of the heavy components of the loop.

It is intended that this loop will operate continuously at a constant solution concentration. Consequently, some means of overcoming the continuous 1/2-gpm flow of water into the loop from the pump bearing chamber is necessary. A letdown system is provided for this purpose in which about 2 gpm is relieved to atmospheric conditions through a back-pressure letdown valve. Approximately one-quarter of this quantity flashes to steam

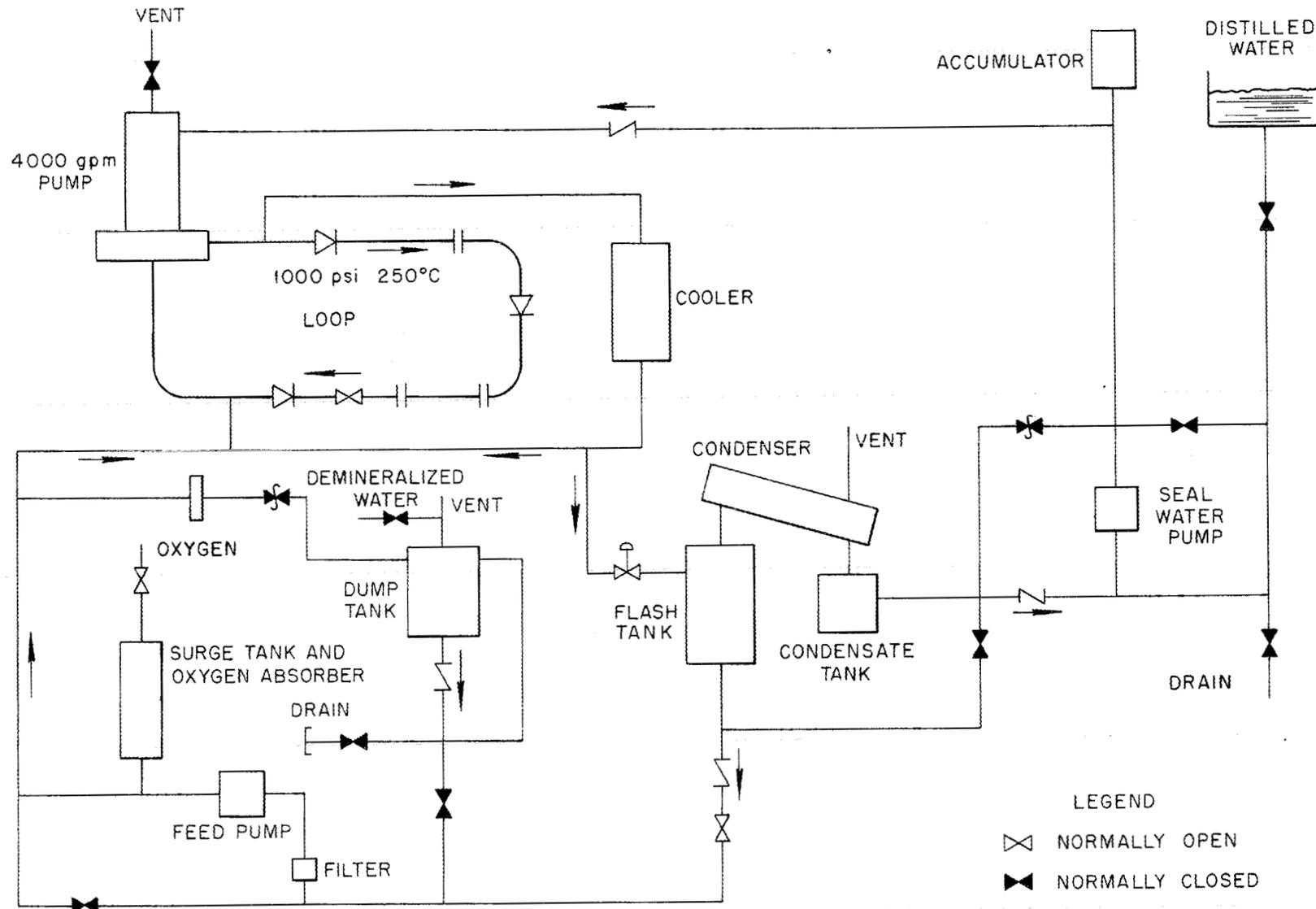


Fig. 8. Flow Sheet for 4000-gpm Pump Loop.

HRP QUARTERLY PROGRESS REPORT

and is condensed. The condensate is then pumped into the 4000-gpm pump as the seal water. The remaining three-fourths of concentrated solution is injected back into the loop with a high-pressure feed pump. Since this method provides a closed cycle, the over-all concentration will remain the same. The distilled water will be used for start-up only and therefore will have only a transient effect upon concentration.

The high-pressure piston pumps and letdown valve are also part of a system to keep the loop pressurized at 1000 psi. The letdown valve is set to open at the desired loop pressure while the seal water and feed pumps provide flow of liquid. The accumulator and surge tank are necessary to modify the pulses set up by these pumps. A rupture disk designed to break at 1500 psi will be installed on the loop proper to provide ultimate high-pressure protection in case the regular controls fail. A relief valve set at 600 to 700 psi will be installed between the rupture disk and dump tank to keep the entire contents of the loop from flashing into the dump tank. This could happen since the saturation pressure of the loop solution at 250°C is 580 psi.

The circulating pump adds approximately 260 kw of heat, which must be

removed from the system in order to maintain a constant operating temperature. Although part of this heat is removed by the seal-water condenser, the majority is taken out by a separate loop cooler. This heat exchanger consists of 100 ft of 3/4-in. pipe coiled and submerged in a tank of water. About 25 gpm of loop solution is shunted through this coil, and the heat transfer is controlled by the level of water in the tank. The steam boiled off is condensed by a water spray before being disposed of in the building drains. Since about 50 gpm of cooling water is required directly for pump cooling, this ample supply of water is subsequently available to operate the cooler.

Instruments and controls will be provided to (1) collect data to be used in the evaluation of the pump and other equipment that may be tested in the loop, (2) maintain automatic operation of the loop (controls on temperature and pressure, primarily), (3) assure the safety of operating personnel, and (4) protect equipment from abnormal operating conditions.

Layout and detail drawings of the loop and its auxiliaries are being prepared. The design should be complete by January 1, 1952.

CORROSION

SCOUTING STUDIES

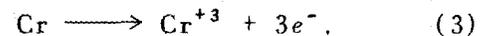
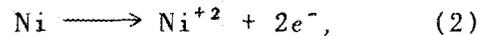
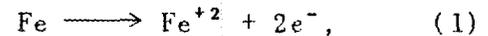
Study of Fundamental HRE Corrosion Problems (J. C. Griess). For the past few months the general mechanism of the corrosion process encountered in the HRE has been under investigation. The purpose of this study has been to find a means of determining the extent of corrosion when passivated type-347 stainless steel is exposed to uranyl sulfate solutions at 250°C. In all the experiments carried out to date the rate of corrosion has been comparatively slow and the process of determining the relative merits of different protective films has been time-consuming. Hence, a reliable, fast method of measuring the effectiveness of different protective films is desirable. If the reactants and the products involved in the corrosion process were known, it might be possible to use changes in the concentration of either as an accurate measure of the corrosion damage. Furthermore, an understanding of the corrosion mechanism might allow a more intelligent attack on the corrosion problem itself.

It has previously been pointed out that in the system uranyl sulfate solution (30 g of uranium per liter)—passivated stainless steel—air, changes in pH, uranyl sulfate, iron, and chromium concentrations do not give a quantitative estimation of the extent of corrosion. It is possible for an analysis of a given solution to show no detectable change in uranyl, hydrogen, ferric, ferrous, or chromic ion concentration after heating at 250°C in a pretreated steel vessel even though the steel has been attacked.

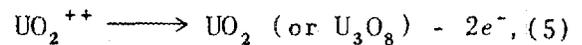
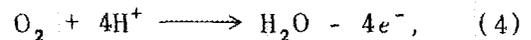
The corrosion encountered here is electrolytic in nature and the reactions

involved in the corrosion process appear to be as follows:

At the anodic areas



At the cathodic areas



In the presence of oxygen the cathodic reaction consists primarily of the reduction of oxygen. The anodic reactions cannot be identified with certainty since it has not been established that the elements that compose the alloy dissolve in the ratio in which they are present in the alloy. If chromium is oxidized it is quantitatively precipitated by hydrolysis. Iron apparently dissolves as ferrous iron, which, in the presence of a sufficiently strong oxidizing agent, is also hydrolytically precipitated as ferric oxide. If the nickel in the alloy dissolves, it will remain in solution unless it is carried down with the chromic and ferric oxides. Hence, anodic reactions 1 and 3 ultimately produce hydrogen ions (by hydrolysis), whereas cathodic reactions 4 and 6 consume hydrogen ions. (Cathodic reaction 5 produces hydrogen ions if U_3O_8 is the final product.) Since nickel is the minor constituent of the alloy, and since it should not hydrolyze at the pH values involved, there should be a very slight increase in the pH of the solution as the alloy is corroded.

HRP QUARTERLY PROGRESS REPORT

This change in a uranyl sulfate solution ($\text{pH} \approx 2.5$) is so small, however, that it is difficult, if not impossible, to detect unless the corrosion damage has been extensive.

If the corrosion process is slow, the cathodic reaction consists entirely of the reduction of oxygen. However, if the corrosion process is comparatively rapid, oxygen may not be able to diffuse to the cathodic surfaces fast enough to utilize the corrosion currents, and reactions 5 and 6 may take place. Indeed, in three cases where oxygen was present in low concentrations and the protective film on the steel was poor, analysis of the gas phase showed that hydrogen was present and that there was a decrease in the oxygen content. In none of these cases was there a measurable change in the uranium, iron, chromium, or hydrogen ion concentrations of the solutions. The nickel content varied between 10 and 20 ppm.

Some additional confirmation of the preceding statements was obtained from two experiments that were run at 250°C in the absence of oxygen. In each case hydrogen was found in the gas phase and some uranium was precipitated. Ferrous and nickelous ions were found in solution and the pH decreased. X-ray analyses showed that in each case the precipitated uranium consisted of an equimolecular mixture of UO_2 and U_3O_8 . The changes in the various constituents in solution were determined by chemical analyses. Since chromic ions were completely hydrolyzed and could not be determined by chemical analysis, it was necessary to assume some value for the amount of chromium dissolved from the alloy. It seemed reasonable to assume that chromium dissolved in the proportion in which it was found to be present in the alloy on the basis of the iron and nickel analyses. If this was done the material balances were poor. In one

experiment it was necessary to assume that chromium dissolved to the extent of about 50% its relative proportion in the alloy and in the other, 70%. When this was done good material balances were obtained in each case, and the equations given above quantitatively accounted for all changes observed in the solutions.

It was interesting to note in these two experiments that in the uranyl sulfate solution the ratio of nickel to iron was 0.167 in one run and 0.157 in the other. The ratio of nickel to iron in the steel itself was 0.148 ± 0.024 . Hence, there was an indication, at least, that the iron and nickel in the steel dissolve in approximately the correct ratio, but that chromium dissolved to a lesser extent.

At this time it appears that the corrosion which occurs at a passivated stainless steel surface on exposure to uranyl sulfate solutions at 250°C can be explained in the following manner. The protective film itself is chemically inert to the uranyl sulfate solution. However, at weak places in the film, ruptures or crevices develop and the steel itself comes in contact with the uranyl sulfate solution. When this happens, local cells with potential differences as large as 0.3 to 0.5 v are possible. In the presence of oxygen the cathodic reaction consists of the reduction of oxygen. At the anodic areas nickelous, ferrous, and chromic ions enter the solution. The chromic ions hydrolyze to yield chromic oxide and the ferrous ions are oxidized and hydrolyzed to ferric oxide. Hence, in static systems in the presence of oxygen the precipitation of chromic and ferric oxides tends to stifle the attack before it has proceeded to any appreciable extent. This process is probably repeated many times over the entire surface. Thus, under the conditions

given above, the protective film is self-healing and any corrosion damage is very slight and uniformly distributed over the surface exposed to the uranyl sulfate solution.

In a dynamic system the chance of stifling the attack in the presence of oxygen is less since the ferric ions may be swept away before they are hydrolytically precipitated at the site of corrosion. The above situation should be especially true in regions of great turbulence, and in these regions pitting might result.

In the absence of oxygen, ferrous ions that dissolve are never precipitated owing to the basicity of the ferrous ions. Apparently the precipitation of chromic oxide is insufficient to stifle the attack of the uranyl sulfate solution on the steel, and once corrosion begins at given locations attack continues at these areas, whereas the rest of the surface is cathodically protected from corrosion. Since oxygen is not available, the reduction of hydrogen and/or uranyl ions constitutes the cathodic reaction, and any reduced uranium hydrolyzes and precipitates. Under the above conditions the corrosion is localized and pits soon become apparent.

Protective films produced on steel by different methods are undoubtedly of different effectiveness, but it seems that any film will sooner or later develop breaks or pin holes and that the film must be self-healing to minimize corrosion damage and prevent precipitation of the uranium from solution. The presence of oxygen in the system certainly is desirable in this respect, but it does not necessarily represent as satisfactory a condition as might be ultimately achieved. For oxygen to be effective, the ferrous ions first formed must be oxidized and then hydrolytically precipitated. The oxidation is probably

fast, whereas the hydrolysis appears to be comparatively slow. Hence, if it were possible to precipitate the ferrous ions as fast as they were formed, the self-healing process would undoubtedly be more effective and would not depend on the presence of oxidizing conditions. Similarly an increase in the rate of hydrolysis of ferric ions would facilitate the self-healing process. This approach will be used for future work.

Preliminary experiments completed to date indicate that an analysis of the solution combined with an analysis of the gas phase is necessary for the interpretation of the changes taking place in the system. In systems that contain uranyl sulfate at a concentration of approximately 30 g of uranium per liter and a reasonable supply of oxygen, the consumption of oxygen and/or the production of hydrogen are directly related to the corrosion damage. Thus, in these cases the rate of corrosion can be followed by determining the changes in the gaseous phase. With this method it should then be possible to determine the relative merits of different protective films and the effectiveness of various inhibitors.

Studies with Organic Inhibitors in Uranyl Sulfate Systems (G. H. Cartledge and M. D. Silverman). Considerable data are available in the literature⁽¹⁾ concerning the use of organic inhibitors for the passivation and protection of steel surfaces. Most of these data were obtained at low temperatures and in systems quite different from those to be expected in the HRE. Although some work had been reported⁽²⁾ which showed that inhibition decreases with increasing temperature, it was believed

⁽¹⁾H. Uhlig, *Corrosion Handbook*, p. 905, Wiley, New York, 1938.

⁽²⁾A. H. Roebuck, *Naval Research Report*, NP-1859, Corrosion Laboratory, University of Texas, Austin, Texas.

HRP QUARTERLY PROGRESS REPORT

that at least brief experiments should be made under HRE conditions before assuming that inhibitors would be useless. Even though it was recognized that the organic molecules probably would not be stable under reactor radiation, the loss of their ability to provide corrosion inhibition does not necessarily follow.

The compounds selected were α, α -dipyridyl, phenyl thiourea, orthophenanthroline, dimethyl glyoxime, β -naphthoquinoline, diisoamyl sulfone, and diisobutyl sulfone. All these are known to form strong bonds with the main metallic components of stainless steel, to be thermally stable at 250°C or higher, to contain nitrogen and/or sulfur linkages that serve as focal points for chelation, and to show strong corrosion inhibition.

Type-347 stainless steel samples were degreased, washed, dried, and then placed in quartz ampoules containing 0.01 M solutions of the organics in uranyl sulfate (300 g of uranium per liter). These ampoules were sealed in air and rocked in a furnace for 40 hr at 250°C. The solutions were then analyzed and the steel samples examined.

All the steel samples showed evidence of corrosion, and analyses of the solutions substantiated this fact. Concentrations of nickel were in the range 250 to 350 ppm, and corresponding amounts of iron were also found (1600 to 2500 ppm). A comparison with blank runs, in which no inhibitor was used, showed that the inhibitors had very little effect, if any, on the corrosion rate.

Further experiments were conducted in an effort to determine whether failure of the inhibitors was due to breaking down of the organic molecule (e.g., oxidation by uranyl ion at 250°C) or to the rupture of a weak

chelation bond between the metal surface and the inhibitor. It was found that the organic compounds were stable in uranyl sulfate when held at 250°C for at least a week. This eliminated the first possibility. Efforts to study the second possibility by spectrophotometric means were unsuccessful because absorption measurements indicated that some complexing of the organic molecule by uranyl ion was occurring. Furthermore, interference in the ultraviolet by the large excess of uranyl ion present made interpretation of the spectral data in this region very difficult.

Additional experiments showed that the ferrous complexes of α, α -dipyridyl and orthophenanthroline were partly unstable and/or insoluble when heated at 250°C for 24 hr either in water or uranyl sulfate solutions.

Five-hour bombardments at 250°C in hole 12 at the full flux of the X-10 graphite pile showed that both pure compounds and ferrous complexes of orthophenanthroline and α, α -dipyridyl are partially decomposed in uranyl sulfate solutions either in the presence or absence of stainless steel.

Fundamental Corrosion Study (G. H. Cartledge). Further consideration of the data from the extensive corrosion-testing program for the HRE has intensified the conviction that there is need for a fundamental study of the details of the electrochemical processes in operation in uranium solutions in contact with metals. There has been much progress recently in the experimental study of passivity and the precise steps in the establishment of redox potentials in electrolytes. This work has suggested methods that may be applicable in uranium systems, and a new project in the fundamental study of this field is being planned.

STATIC TESTS

J. L. English J. Reed
A. R. Olsen S. H. Wheeler

Uranyl Sulfate Corrosion Studies.
Stagnant corrosion studies during the past quarter included the following:

1. The corrosion behavior of 150°C nitric-acid-pretreated type-347 stainless steel in 0.17 M uranyl sulfate at 150°C,
2. The corrosion behavior of untreated metals and alloys in 0.17 M uranyl sulfate at 150°C,
3. The effect of continuous exposure on chromic-acid-pretreated type-347 stainless steel in 0.42 M uranyl sulfate at 250°C,
4. The vapor phase corrosion of type-347 stainless steel above 0.17 M uranyl sulfate at 250°C,
5. The effect of oxygen treatment on pretreated type-347 stainless steel,
6. The effect of oxygen on uranyl sulfate stability in an untreated type-347 stainless steel system at 250°C.

Corrosion Behavior of 150°C Nitric-Acid-Pretreated Type-347 Stainless Steel in 0.17 M Uranyl Sulfate at 150°C. Investigations were made of the effectiveness of 150°C nitric acid pretreatments on type-347 stainless steel for corrosion protection in uranyl sulfate solutions at 150°C and the effect of initial surface condition on the corrosion resistance of the stainless steel. The tests were run in type-347 stainless steel autoclaves with solution capacities of 150 milliliters. The test specimens

were prepared by lathe-machining cold-rolled bar stock. Some of the specimens were then abraded on Nos.-80 and -120 grit papers.

The equivalent metal thickness loss on the machined specimens after 24 hr in 1% by weight of HNO₃ at 150°C was 0.002 mil; the thickness loss on the abraded sample was 0.003 mil for similar exposure. The uranyl sulfate tests were run for eight weeks at 150°C. The tests were examined each week and the uranyl sulfate solutions replaced.

The final corrosion rate on the machined specimen was 0.25 mil/yr as compared to 0.3 mil/yr for the abraded specimen. A slight pitting attack was observed on the latter, with maximum pit depths of 0.3 mil. Pitting attack on the machined specimen was almost negligible. Partial reduction of the uranyl sulfate solutions, to the extent of 18% per week, occurred during the first two weeks of the machined-specimen test. A reduction of about 10% in total uranium content was reported for the test solution containing the abraded specimen after one week of exposure. No further solution reduction was reported for any of the test solutions during the remaining periods of the tests.

The pretreatment of type-347 stainless steel at 150°C in 1% HNO₃ for subsequent exposure in uranyl sulfate at 150°C was less effective as a corrosion protection mechanism than HNO₃ pretreatment at 250°C for exposure in 250°C uranyl sulfate. For example, corrosion rates on type-347 stainless steel pretreated and exposed at 250°C averaged 0.05 mil/yr and less after eight weeks of test. The corrosion rate obtained on 150°C-pretreated and sulfate-exposed stainless steel was six times greater in magnitude for similar exposure time. The effect of machined vs. abraded

HRP QUARTERLY PROGRESS REPORT

surfaces was not pronounced with respect to corrosion resistance in 0.17 M uranyl sulfate at 150°C.

Corrosion Behavior of Untreated Metals in 0.17 M Uranyl Sulfate at 150°C. The corrosion resistance of five different metals and alloys in the untreated condition was determined in 0.17 M uranyl sulfate at 150°C. The materials included types-316 and -347 stainless steels, commercial grades of titanium and tantalum, and Carpenter-20 stainless steel. The stainless steel autoclaves in which the metals were exposed were initially pretreated in 1% HNO₃ at 250°C for 24 hr to minimize the effect of stainless steel corrosion products on the behavior of the test specimens. The tests were run for six weeks, with weekly replacement of the uranyl sulfate solutions and examination of the specimens for corrosion damage.

Titanium metal exhibited the best corrosion resistance in the group. The metals tested, listed in order of decreasing corrosion resistance, had the following corrosion rates (mil/yr):

Titanium	0.006
Tantalum	0.01
347 stainless steel	0.26
316 stainless steel	0.27
Carpenter-20 stainless steel	0.32

No definite tendency was shown by any of these materials to reduce the uranyl sulfate solutions under the test conditions. A few solutions exhibited a very slight reduction in total uranium content, but the data were not sufficiently conclusive to attribute this to actual reduction or to variations resulting from the analytical procedures used.

The test data indicated a reverse trend when sulfate-resistant alloys

were used in the uranyl sulfate system at 150°C. After exposure for six weeks, type-347 stainless steel showed a cumulative weight loss of 0.61 mg/cm², type-316 stainless steel containing an addition of 2% molybdenum for improved sulfate resistance showed a loss of 0.63 mg/cm², and Carpenter-20 stainless steel containing 2% molybdenum and 3% copper for still further improvement of sulfate-resisting properties showed a loss of 0.74 mg/cm². These differences are within the realm of experimental error and are not considered sufficiently significant at this time to state any definite conclusions.

Effect of Continuous Exposure on Chromic-Acid-Pretreated Type-347 Stainless Steel in 0.42 M Uranyl Sulfate at 250°C. A test series was run at 250°C in newly-machined stainless steel autoclaves using 0.42 M uranyl sulfate (101.4 g of uranium per liter) and machined samples of type-347 stainless steel. Six autoclaves were used so that by removing one autoclave from test each week continuous exposure for one to six weeks was obtained. Prior to the start of the tests, the autoclaves and specimens were pretreated for 24 hr in 2% CrO₃ at 250°C. The weight gains for the stainless steel specimens fluctuated from 0.15 to 1.02 mg/cm², but all specimens were coated with dull, black-brown films.

A summary of the test results follows:

1. The 2% CrO₃ pretreatment solutions exerted a more selective attack on nickel in the stainless steel than had been encountered previously in 1% HNO₃ pretreatment solutions. A maximum dissolved nickel concentration of 201 µg/ml was reported in the CrO₃ solutions as compared to 170 µg/ml, which is the

highest value observed thus far in HNO_3 pretreatment solutions.

2. A gradual dissolution of the CrO_3 pretreatment films from the specimen surfaces was visually apparent during the course of the tests. The rate of film removal was not time-dependent; i.e., the magnitude of film weight losses did not necessarily increase with increased exposure time. The metal surfaces, after film removal, were highly lustrous, metallic gray in color, and remained passive in the uranyl sulfate test solutions.

3. The corrosion rates calculated for those specimens showing actual weight losses after the pretreatment films had been completely removed during test were 0.02 mil/yr after 2 weeks and 0.26 mil/yr after six weeks. Pitting attack contributed to the over-all corrosion rate since both specimens exhibited numerous but shallow pits. The depths of these pits ranged from 0.3 to 0.5 mil.

4. The only solution reduction that occurred took place in the test that operated continuously for five weeks; the extent of this reduction was 8%. All other solutions remained stable during their respective exposure times, as determined by chemical analyses for total uranium content.

Vapor Phase Corrosion of Type-347 Stainless Steel Above 0.17 M Uranyl Sulfate Solutions at 250°C. A test specimen of type-347 stainless steel was pretreated in 1% HNO_3 at 250°C for 24 hr and then suspended in the vapor phase region above 0.17 M uranyl sulfate solution. The specimen and solution were heated to 250°C, and the test was continued for six weeks. The specimen was examined and the uranyl sulfate test solution replaced weekly.

The final corrosion rate was 0.01 mil/yr, which indicated very little

damage by exposure to saturated steam at 250°C. Chemical analyses of the test solutions disclosed no reduction in total uranium content for the six weeks.

Effect of Oxygen Treatment on Pretreated Type-347 Stainless Steel. Previous tests determined that the protective properties of nitric and chromic acid pretreatment films were destroyed if the specimens were permitted to remain exposed to air at room temperature for periods exceeding three days prior to exposure in uranyl sulfate at 250°C. After prolonged air exposure, pretreated specimens reacted in a manner similar to untreated specimens in that solution reduction was instigated. It was determined also that if the pretreated specimens were immersed in water or uranyl sulfate solution at room temperature, the air exposure could be extended to 14 days without incurring bad effects when the specimens were placed in the sulfate solution at 250°C.

The effect of exposure of both HNO_3 and CrO_3 pretreated type-347 stainless steel specimens to molecular oxygen rather than immersion in water or uranyl sulfate was investigated. The pretreatment consisted of heating the specimens for 24 hr at 250°C in either 1% HNO_3 or 2% CrO_3 . The oxygen exposure followed immediately for a period of 24 hr at room temperature. The specimens were then allowed to stand in air for 7 to 14 days, after which time they were placed in 0.17 M uranyl sulfate solutions and heated to 250°C. The salient facts obtained from these studies are as follows:

1. Exposure of nitric or chromic acid-pretreated type-347 stainless steel for 24 hr in oxygen at room temperature has the same effect on extending the life-expectancy of the films for use in uranyl sulfate at 250°C after prolonged exposure in air

HRP QUARTERLY PROGRESS REPORT

as immersion in water or uranyl sulfate at room temperature. In other words, a room temperature oxygen exposure immediately after pretreatment permits air exposures of treated surfaces for 14 days without loss of the protective nature of the pretreatment film when exposed to uranyl sulfate at 250°C. The implication of these data is that when uranyl sulfate is removed from a pretreated reactor component, the original protective film could be "stabilized" with oxygen to guarantee successful operation when the sulfate solution is returned to the system. This phenomenon remains to be demonstrated on a larger-than-laboratory scale.

2. The corrosion resistance of nitric- and chromic-acid-pretreated type-347 stainless steel treated 24 hr in oxygen, exposed to air for 14 days, and then exposed to 0.17 M uranyl sulfate at 250°C was nearly identical. After seven weeks the corrosion rate on the nitric-acid-pretreated stainless steel was 0.13 mil/yr as compared to the 0.17 mil/yr rate exhibited by the chromic-acid-pretreated specimen.

3. Dissolution of the chromic-acid-pretreatment film from the specimen was pronounced during operation at 250°C. The underlying metal surfaces were highly lustrous and continued to remain passive to the uranyl sulfate solution for the balance of the test. Thus, additional information is presented to support the belief that the bulk oxide films formed by the chromic acid pretreatment are not the real agent for imparting passive characteristics to the stainless steel.

Effect of Oxygen on Uranyl Sulfate Stability in Untreated Type-347 Stainless Steel at 250°C. A type-347 stainless steel autoclave with a total solution capacity of 1026 ml was equipped with a 5000-psi pressure gage and two sample cells (12 and 25 ml

capacity) constructed of stainless steel. The autoclave was electrically heated. The object of the test was to determine the ability of oxygen to maintain a stable uranyl sulfate—untreated type-347 stainless steel system under stagnant conditions at 250°C. Also, the corrosion rate of type-347 stainless steel was to be determined under these conditions.

Seven hundred and fifty milliliters of 0.17 M uranyl sulfate was placed in the autoclave, which was then sealed and pressurized with 500 psig of oxygen pressure at room temperature. The test was run continuously for 268 hr at 250°C, and from time to time solution samples were removed for gas and chemical analyses. The results of these analyses appear in Table 1.

The most important data resulting from this test were:

1. An untreated type-347 stainless steel system was operated satisfactorily for 268 hr in 0.17 M uranyl sulfate at 250°C with an initial oxygen pressure of 500 psig. No solution reduction occurred and corrosion attack was within tolerable limits.

2. An estimated 8.7 g of oxygen was consumed in the operation of the test, which involved a total internal surface area of 808 cm².

3. The calculated corrosion rate on type-347 stainless steel, based on the final dissolved nickel concentration, was 0.3 mil/yr. A weight gain of 0.15 mg/cm² for 268 hr was measured on the type-347 stainless steel test specimen in the autoclave.

Reflector Corrosion Studies. Reflector corrosion studies were continued during the past quarter with

TABLE 1

Analyses of Uranyl Sulfate Solution Samples from Test at 250 °C

CUMULATIVE TEST TIME (hr)	SOLUTION pH	TOTAL URANIUM (g/l)	NICKEL ($\mu\text{g/ml}$)	MANGANESE ($\mu\text{g/ml}$)	DISSOLVED OXYGEN (ppm)
0	2.2	39.6	1	1	
2	2.2	39.7	3	1	1026
26	2.1	39.8	9	1	609
124	2.1	39.6	20	1	311
148	2.1	39.8	21	2	324
172	2.1	40.5	27	3	999
196	2.1	40.5	27	7	900
268 ^(a)	2.0	41.0	44	5	794
274 ^(b)	2.1	39.3	43	4	

(a) Test stopped and cooled to room temperature, 28°C.

(b) 28°C.

emphasis placed upon stagnant heavy-water tests and the effect of oxygen partial pressure on corrosion resistance. The materials included were SAE-1030 mild carbon steel uncoupled and coupled with type-347 stainless steel, and the temperature of the tests was 200°C. Stainless steel autoclaves with solution capacities of 150 ml were used to contain the test solutions and samples.

Heavy-Water Studies. A limited quantity of heavy water was procured for stagnant corrosion tests to compare the corrosion behavior of reflector materials in heavy water with results obtained in natural water. Quartz rods were used to suspend the test specimens in the autoclaves and to insulate them from the autoclave mass. Hydrogen peroxide was added periodically to the test solutions in quantities sufficient to produce approximately a partial pressure of 25 lb in the system. The solubility

of oxygen in water under the test conditions was calculated to be 70 ppm. The partial pressure of oxygen, if actually obtained, was momentary since oxygen was undoubtedly consumed in the production of corrosion products. The dilution effect resulting from the addition of hydrogen peroxide to the heavy water was 0.6% per test run. This effect was cumulative since the original heavy water was used throughout the tests. The tests were operated for a total period of 807 hours. Every three to four days the specimens were examined and weighed and the hydrogen peroxide additions were made. The test results follow.

1. SAE-1030; 70 ppm oxygen:

Test Data

Initial solution pH	6.2
Average final solution pH	6.6
Cumulative weight loss, mg/cm ²	24.8
Final Corrosion rate, mil/yr	13.5

HRP QUARTERLY PROGRESS REPORT

The specimen was coated with a loosely adherent, brown-black scale at the end of each test period. The intensity of pitting attack progressed with exposure time, and at the end of 807 hr the attack was quite prolific, with maximum pit depths reaching 10 mils. The surfaces of the specimen after scale removal were dull black in color and etched in appearance.

2. SAE-1030; 70 ppm oxygen; 300 ppm trisodium phosphate:

Test Data

Initial solution pH	10.9
Average final solution pH	6.3
Cumulative weight loss, mg/cm ²	0.7
Final corrosion rate, mil/yr	0.4

The specimen had an extremely adherent, thin, semilustrous film. No bulk scale formations were observed, and with the exception of a few, small, stained areas, the surfaces were free of localized corrosion attack.

3. SAE-1030 coupled with type-347; 70 ppm oxygen:

Test Data (on SAE-1030 only)

Initial solution pH	6.2
Average final solution pH	7.3
Cumulative weight loss, mg/cm ²	20.7
Final Corrosion rate, mil/yr	11.3

The outer surfaces of the specimen were dull black in color, with an etched appearance. The area in contact with the type-347 stainless steel was relatively free of heavy scale accumulations but was pitted on the outer circumferential zone of contact. The pitting attack was no more intense, however, than that observed on the uncoupled specimen. The stainless

steel specimen did not show any indication of corrosion attack other than a slight weight gain.

4. SAE-1030 coupled with type-347; 70 ppm oxygen; 300 ppm trisodium phosphate:

Test Data (on SAE-1030 only)

Initial solution pH	10.9
Average final solution pH	8.8
Cumulative weight loss, mg/cm ²	5.7
Final corrosion rate, mil/yr	3.1

The carbon steel specimen was lustrous and bluish-tan in color, with a few randomly spotted, dull, stained areas. The area contacting the stainless steel was dull gray in color but did not show any significant pitting attack. The stainless steel specimen exhibited negligible corrosion attack.

These initial test results with D₂O systems slightly diluted with natural water show rather heavy corrosion effects for uncoupled and coupled SAE-1030 carbon steel. The magnitude of corrosion attack was drastically reduced in the case of the uncoupled specimen by the addition of 300 ppm of trisodium phosphate — the corrosion resistance was improved by a factor of nearly 25. In the case of SAE-1030 carbon steel coupled to type-347 stainless steel, the corrosion rate was reduced from 11.3 to 3.1 mil/yr by the addition of 300 ppm of trisodium phosphate. An important effect, however, was the very pronounced reduction in the intensity of localized corrosion attack.

A comparison between the corrosion rates on SAE-1030 carbon steel obtained in natural water and heavy water under similar test conditions is given in Table 2. Initial and final corrosion rates are listed for the specific test conditions.

FOR PERIOD ENDING NOVEMBER 15, 1951

TABLE 2

Comparison of the Corrosion Rates for SAE-1030 Carbon Steel Exposed in Natural Water and Heavy Water at 200°C

	NATURAL WATER		HEAVY WATER	
	EXPOSURE (hr)	CORROSION RATE (mil/yr)	EXPOSURE (hr)	CORROSION RATE (mil/yr)
Uncoupled: 70 ppm oxygen				
Initial rate	64	7.4	88	13.3
Final rate	797	3.0	807	13.5
Uncoupled: 70 ppm oxygen; 300 ppm trisodium phosphate				
Initial rate	64	1.4	88	2.5
Final rate	797	0.3	807	0.4
Coupled with type-347 stainless steel: 70 ppm oxygen				
Initial rate	64	4.6	88	15.7
Final rate	797	3.0	807	11.3
Coupled with type-347 stainless steel: 70 ppm oxygen; 300 ppm trisodium phosphate				
Initial rate	64	5.7	88	4.4
Final rate	797	1.6	807	3.1

The magnitude of corrosion attack in the heavy-water solutions was more intense in almost every instance. Comparable corrosion rates were obtained, however, in the case of coupled specimens with 300 ppm of trisodium phosphate present in the test solutions. With coupled specimens and 300 ppm of trisodium phosphate present, the corrosion rate for SAE-1030 carbon steel was 3.1 mil/yr in heavy water as compared with 1.6 mil/yr in natural water after approximately 800 hr of exposure.

The cause of increased corrosion attack in D₂O solutions is being further investigated.

Effect of Partial Pressures of Oxygen. Preliminary studies were started to investigate the effect of different partial pressures of oxygen on the corrosion resistance of SAE-1030 carbon steel at 200°C. The studies have been confined to natural water thus far. The general test procedure was daily inspection of samples and solutions and addition of hydrogen peroxide to supply 25- and 200-lb partial pressures of oxygen in the systems. The solutions were not changed during these tests, but they were filtered at the end of each test run to remove insoluble corrosion products. The oxygen concentrations

HRP QUARTERLY PROGRESS REPORT

corresponding to 25- and 200-lb partial pressures at 200°C were calculated to be 70 and 530 ppm, respectively.

For a period of 545 hr, the corrosion rates on SAE-1030 carbon steel in natural water at 200°C, containing 70 and 530 ppm of oxygen, were 4.9 and 0.4 mil/yr, respectively. A marked difference in appearance of the test specimens was apparent at the end of this time. The low-oxygen-concentration test specimen was coated with a uniform, dull-black film; the 530-ppm oxygen specimen was a lustrous, blue-green color, with a few, very small, stained areas. The addition of 300 ppm of trisodium phosphate to these types of test solutions resulted in a corrosion rate of 6.9 mil/yr in the 70-ppm oxygen solutions as compared with 0.2 mil/yr in the solutions containing 530 ppm of oxygen. In general, the same degree of difference in sample appearance was observed as was found on the specimens exposed in the absence of the trisodium phosphate. It should be mentioned that in the trisodium phosphate tests with the high oxygen concentrations, the concentration of phosphate ion was gradually decreased because of the necessity of adjusting the final solution volume to 125 ml before the start of the next test. The increase in solution volume per run was created by the addition of the hydrogen peroxide solution to produce the desired oxygen concentration. Regardless of the trisodium phosphate concentration in any particular test run, it was very evident that the high oxygen concentration was sufficient to greatly minimize corrosion attack.

These tests are being repeated with both natural and heavy water under more carefully controlled conditions. Galvanic couples between SAE-1030 and type-347 stainless steel will also be studied.

DYNAMIC CORROSION STUDIES

J. H. Gross C. G. Heisig
H. C. Savage R. A. Lorenz
R. E. Wacker

Three pump loops have been in operation during this report period. The mechanical aspects of the construction and operation of these loops are discussed in the chapter of this report on "Engineering Studies of Components." The experimental work has been primarily directed toward the determination of conditions for HRE start-up.

Since previous loop studies had shown that fuel stability in type-347 stainless steel at 250°C was dependent on the presence of an undetermined, adequate concentration of oxygen in the solution and had indicated that pretreatment had no effect on corrosion rate (other static studies do not bear this out), conditions for start-up with fuel had to be established to take these factors into account.

Fuel Stability. Nearly 5000 hr of operation with uranyl sulfate solution and varying concentrations of added oxygen have been accumulated. This experience indicates that the stability of uranyl sulfate solution is assured provided a certain amount of oxygen is in solution. The lower limit for oxygen content has not been established, although analyses have indicated concentrations as low as 20 ppm without concurrent evidence of precipitation. Also, in one run, daily oxygen analyses over an eight-day period showed the oxygen concentration varying over the range 32 to 112 ppm without evidence of precipitation. This suggests that the range of oxygen concentration is adequate, but there is no assurance that the concentration was not higher between analyses or that precipitation would

not have taken place after a longer period. The difficulty is that at the present time the oxygen is added by introducing a given pressure of oxygen gas into the vapor space of the pressurizer when the loop is cold. The oxygen pressure introduced can be varied, but the circumstances are such that this does not necessarily or consistently affect the concentration of oxygen found in the circulating solution, with the result that analyses have shown concentrations ranging from 20 to 3000 ppm. Means for adequately controlling oxygen concentration to make it possible to study its effect on solution stability and corrosion are being investigated.

Start-Up Conditions. The considerable number of hours of successful loop operation accumulated with oxygenated uranyl sulfate solution (40 g of uranium per liter) suggested that solution stability in a type-347 stainless steel system was reasonably assured. However, an examination of the data on the loop runs that had been made showed that no new loop had been started without a precipitation taking place in the initial operating period. It seemed desirable to determine whether this was a necessary or coincidental circumstance. Also, the stability studies with oxygenated fuel had been carried out in loops that had previously been pretreated; there was, therefore, a possibility that the stability observed might somehow have resulted from these pretreatments. After run A-8, A loop was equipped with a new, main-pipe circuit (the pressurizer was not changed) so that it would be possible to start up an essentially new system using only oxygenation to provide stability. Since operation of the old loop had been successful with only 25 psig of oxygen introduced into the pressurizer, and since it was desirable to operate at low oxygen concentration to minimize oxygen

consumption in mockup and HRE operation, start-up of the new A loop with 20 psig oxygen in the pressurizer was attempted. Precipitation occurred within 5 hours.

In view of the need for pretreatment as shown by the static test studies, the next attempt to run fuel in A loop was preceded by a 200-hr run with 250°C water oxygenated with 20 psig of oxygen introduced into the cold pressurizer to study the possibility that a similar surface preparation might be involved. However, the subsequent attempt to run fuel containing 40 g of uranium per liter with 20 psig of oxygen at 250°C resulted in precipitation in 36 hours. In this instance the precipitate was redissolved by running for brief periods with 50 to 500 psig of oxygen. Continuous successful operation then followed for 210 hr with 50 psig of oxygen pressure.

Thus it appears that the fuel solution is not stable in a new pump loop at 250°C; however, stable operation in the presence of 20 psig of oxygen pressure has been possible after extended operation at higher oxygen pressures. Unfortunately attempts to measure the oxygen concentration in the solution by analysis during the 20-psig tests were unsuccessful because the sample bombs leaked, so it is possible that the precipitations observed at the lower oxygen pressure were actually the result of poor mixing. Further study of this means of oxygen addition have shown that the pressure of oxygen introduced not only has no relation to the concentration found in the solution, but the results can vary widely from time to time under what are supposedly constant conditions. Again oxygen concentration control is necessary to obtain information on start-up conditions and to determine

HRP QUARTERLY PROGRESS REPORT

whether they differ from later operating conditions. Present indications are that more oxygen is required during the initial period, but this is not necessarily a result of the condition of the steel surface and may be caused by a small amount of organic impurity in the uranyl sulfate.

Operation at Reduced Temperature.

The new C loop was operated at 150°C with fuel solution containing 40 g of uranium per liter to provide comparison data at a lower temperature. The first test was run with helium pressurization to test whether oxygenation was as important at the lower temperature. It appears that it is not so important since the loop was operated successfully for 127 hr under these conditions -- much longer than in the comparable run at 250°C with 20 psig of oxygen. However incipient precipitation was indicated by pH changes at the end of the run, suggesting that oxygen is still necessary to solution stability although the concentration required might be a good deal less at the lower temperature. A fact that is not consistent, however, is that the general corrosion rate estimated from nickel build-up was about equal to the average rate for operation with oxygen at 250°C.

A second run of 950-hr duration was then made under a partial pressure of oxygen of 250 to 360 psig. During this

run there was no indication of precipitation. It is of particular interest to note that the general corrosion rate calculated from the build-up of nickel concentration in the solution was quite low during the first part of the run, but it then increased. During the last 300 hr the corrosion rate approached the average rate for 250°C operation. Thus it is apparent that the corrosion behavior of a loop may vary considerably with the age and/or the previous history of the loop.

Additives. Some short-term studies have been made of the effect on corrosion of the addition of the principal fission products (as oxides and sulfates) and CuSO_4 to the fuel solution. In view of the results obtained in the 150°C experiment in C loop, however, the results are quite questionable and therefore will not be discussed in detail. In both instances the corrosion seemed to be accelerated, but not markedly so. In fact, while the corrosion rate was higher immediately after the fuel containing the additive was put in the loop, changes of similar magnitude have been observed in changing from one batch of simple fuel solution to another, so the results are by no means conclusive. Further studies over extended periods of time will be required to make the results more meaningful.

RADIATION STABILITY

H. F. McDuffie

J. W. Boyle	D. M. Richardson
S. F. Clark	J. Ruth
F. J. Fitch	M. D. Silverman
J. A. Ghormley	A. W. Smith
W. E. Hill	A. C. Stewart
C. J. Hochanadel	H. H. Stone
W. F. Kieffer	F. H. Sweeton
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IRRADIATION EXPERIMENTS IN THE
X-10 GRAPHITE PILE

As indicated in the previous quarterly report,⁽¹⁾ a set of four pre-treated type-347 stainless steel bombs containing uranyl sulfate solutions (93% enrichment, 40 g of uranium per liter) was inserted into hole 60 of the X-10 graphite pile on July 23, 1951 and has been under continuous irradiation since that time for a total of 2900 hours. Prior to loading with uranyl sulfate, two of the bombs were pretreated with 2% chromic acid solution and two with 400 psi of oxygen pressure (measured at room temperature), and all four were heated to 275°C for 18 hours.

Initially, all four bombs were characterized by high equilibrium pressures of hydrogen and oxygen in the presence of neutron fluxes of the order of 5 to 8×10^{11} and required temperatures of around 290°C to effect recombination rapidly enough for safe operation (less than 5000-psi total pressure). Subsequently, all four bombs showed gradual declines in equilibrium pressure, which was compensated for by lowering the temperature. This phenomenon is now known not to be associated inseparably with solution instability, since analyses following similar runs have shown all the uranium

to be in solution. Rather, this decline in equilibrium pressure is now believed to be associated with the presence of fission products (as yet unspecified) that bring about the homogeneous recombination of hydrogen and oxygen in solution. A later section of this report discusses hydrogen-oxygen recombination in more detail.

During the eighth week of the present experiment, at around 1400 hr of total irradiation, one of the oxygen-pretreated bombs showed an abrupt decline of equilibrium pressure from 1075 to 490 psi. This indicated clearly the loss of uranium from solution, since the whole process took place within six hours. At the beginning of the next week, following the regular pile shutdown, the second of the oxygen-pretreated bombs failed to return to its previous equilibrium pressure, which indicated that it too had lost its uranium from solution. The striking agreement in behavior shown by these two bombs appears to be supported by the circulating test loop results reported by E. G. Bohlman at the HRP Group Leaders' Meeting on November 8, 1951. These test loop results at 150 and 250°C, with a partial pressure of oxygen above the solution to maintain the stability of the system, showed an accelerating corrosion process (as measured by the accumulation of soluble nickel in the solution), with the corrosion rate after around 1000 hr becoming quite high. It seems reasonable that a

⁽¹⁾"Radiation Stability," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 51.

HRP QUARTERLY PROGRESS REPORT

similar process occurring inside the bombs would, despite the stabilizing oxygen pressure, eventually become so rapid as to result in reduction of the uranium from the hexavalent to the tetravalent state, with accompanying precipitation of U_3O_8 and eventual loss of all uranium from solution.

The failure of both oxygen-pretreated bombs after eight weeks, although continuously protected by an oxygen-containing atmosphere, is in sharp contrast to the behavior of the chromate-pretreated bombs, which, after 17 weeks, are still showing reasonable equilibrium pressures of hydrogen plus oxygen. This superiority of chromate-pretreated bombs has been evident throughout the whole course of the radiation testing of HRE fuel, although not so dramatically as in the present experiments. Moreover, the ampoule experiments previously reported⁽²⁾ demonstrated the superiority of the chromate-pretreated specimens in that they withstood the action of uranyl sulfate solutions for one week at 250°C in the absence of oxygen (degassed ampoules), whereas untreated or nitrate-pretreated specimens were attacked after only one day.

Adequate support seems available for the conclusion that the combination of chromate pretreatment with a partial pressure of oxygen over the uranyl sulfate solution during the test affords very much better surface protection for type-347 stainless steel, both in the presence or absence of pile radiation, than is afforded by the combination of no pretreatment with a partial pressure of oxygen over the solution.

EFFECT OF COPPER IONS ON EQUILIBRIUM PRESSURES OVER HRE SOLUTION UNDER X-10 GRAPHITE PILE IRRADIATION

Through the study of hydrogen-oxygen recombination in the absence

of radiation (see "Catalytic Recombination" section in Part II of this report) it was discovered that small amounts of dissolved copper (as $CuSO_4$) would bring about the homogeneous recombination reaction in solution at a very rapid rate and that this reaction was quite temperature-sensitive. It immediately became important to learn whether this effect would be found when the hydrogen and oxygen were being continually produced by fission-fragment decomposition of water instead of being added initially from cylinders. An in-pile experiment, in which hole 12 of the X-10 graphite pile was used, was designed to confirm or deny the implications from the nonradiation studies.

Two untreated type-347 stainless steel bombs were used in the experiment. Each was loaded with uranyl sulfate solution (93% enrichment and 40 g of uranium per liter), and to each was added a calculated amount of copper sulfate. The amounts were calculated from the reaction-rate constants found in nonradiation studies and from the initial rates of gas production observed in previous studies with stainless steel bombs under neutron irradiation. The calculations were made so that the amount of copper added would be enough to give low equilibrium pressures at the full flux of hole 12. A temperature of 229°C was chosen for the initial test even though past experience with enriched solutions free from copper and exposed to the same flux would predict, by extrapolation, equilibrium pressures of 10,000 to 20,000 psi (far above the safe operating limits of the equipment) if a temperature as low as 229°C were used; because out-of-pile studies indicated that only small amounts of copper would be required to maintain low equilibrium pressures.

⁽²⁾"Radiation Stability," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending May 15, 1951*, ORNL-1057, p. 63.

TABLE 3

Experimental Data on Recombination Test Runs

RUN	Cu (M)	TEMP. (°C)	PRESSURE (psi)		
			STEAM	TOTAL (obs.)	EQUILIBRIUM
363	0.009	194	200	2200	2000
		209	270	1130	860
		229	400	700	300
		239	475	660	185
		249	567	670	103
		259	670	730	60
360	0.00625	209	270	2200	1930
		229	400	1100	700

The results of the initial tests were extremely gratifying in that the anticipated low equilibrium pressures were very closely approached in each bomb. Table 3 presents pertinent data concerning these runs, including results at temperatures other than 229°C. On Fig. 9 these data are presented to show their interrelationship as well as their relationship to pressures obtained in the absence of copper. On Fig. 10, which shows data from Run 363, the combined effects of gas equilibrium pressure plus steam pressure are indicated to give a total pressure whose temperature dependence shows the presence of a minimum.

This demonstrated ability of small amounts of copper ion to bring about the homogeneous recombination of hydrogen and oxygen at total equilibrium pressures of less than 1000 psi in the temperature region chosen for operation of the HRE suggests the possibility of being able to operate at full power *without gas bubble formation* or with any desired rate of gas evolution, depending on the copper concentration chosen. The significance of this to the safety and ease of

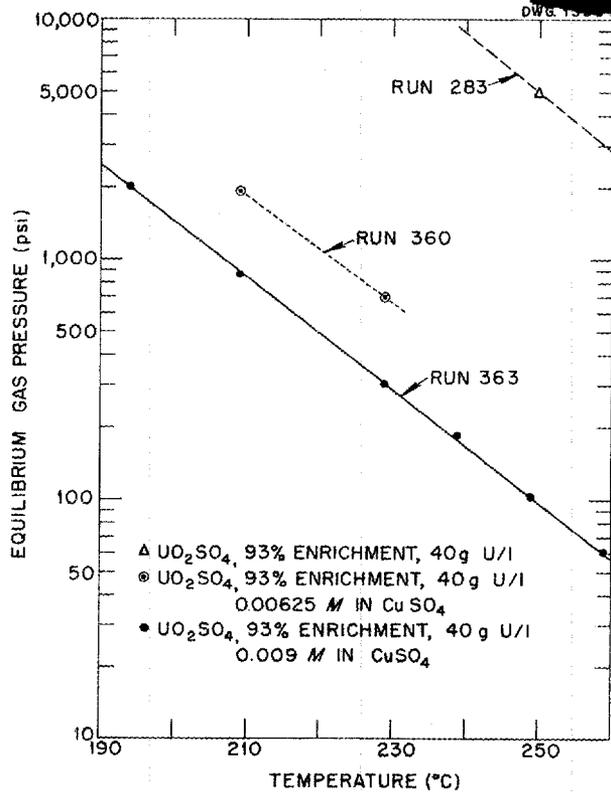


Fig. 9. Effect of Temperature and Copper on Equilibrium Gas Pressure. Irradiated at full flux in hole 12 of the X-10 graphite pile.

HRP QUARTERLY PROGRESS REPORT

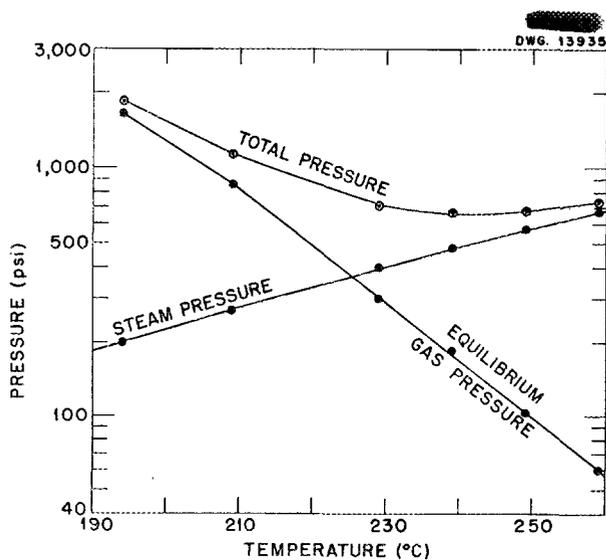


Fig. 10. Effect of Temperature on Pressure for the System Aqueous Uranyl Sulfate plus Copper Sulfate. Data from run 363.

operation of homogeneous reactors will depend on the control problems introduced by bubbles and by the performance of external recombiner systems under heavy load.

Further studies of this effect are in progress, including extension to the higher flux levels of the LITR and accurate determination of the roles of concentration and temperature.

DECONTAMINATION OF IRRADIATED TYPE-347 STAINLESS STEEL

Development of a satisfactory process for decontaminating those parts of the HRE that have been in contact with uranyl sulfate solution under irradiation is of obvious importance. It must be possible to remove all adsorbed fission products, uranium, and surface films without seriously corroding the underlying stainless steel if the HRE is to be of use over any extended period of time.

Through the cooperation of the Chemical Technology Division⁽³⁾ a very promising decontamination process has been developed. This process requires exposure for 1 hr at 25°C to an aqueous solution of 20% HNO₃ and 3% HF (both byweight) with minimal agitation to avoid stagnation of the liquid. The corrosion rate for type-347 stainless steel is 0.037 mil per hour.

An experiment demonstrating this process was carried out with a type-347 stainless steel bomb from Run 288 in which the usual 40 g of uranium per liter, 93% enrichment, UO₂SO₄ solution was exposed to the X-10 graphite pile flux for 12 days. The solution was then removed and the bomb rinsed with distilled water. A cooling period of 16 months preceded this decontamination study. It should be noted that the bomb used had been pretreated with 1% HNO₃ at 250°C for 24 hr and the top of the bomb had been cut off to expose the interior surface.

Table 4 presents some results of the decontamination process. In this process the bomb was placed in a beaker with 1000 ml of solution (stirred with a laboratory stirrer). After 2 hr a second fresh portion of solution was used for an additional 2 hr of treatment.

It can be seen from inspection of the table that the decontamination process was essentially complete after 1 hour. Mild agitation is considered necessary with respect to pretreated surfaces, since similar films on non-irradiated specimens were not removed by stagnant solutions.

Further studies are under way with additional type-347 stainless steel bombs that have been irradiated and allowed to cool for various periods of

⁽³⁾ Studies carried out by M. R. Bennett and F. Rogers.

FOR PERIOD ENDING NOVEMBER 15, 1951

TABLE 4

Decontamination of Irradiated Type-347 Stainless Steel Bomb

	FIRST PORTION OF LIQUID					SECOND PORTION OF LIQUID
	0	30	60	90	120	120
Time, min	0	30	60	90	120	120
Radiation from Bomb,* mr/min	1200	550	475	475	475	475
Film		Soft	Clean, bright	Clean, bright	Clean, bright	Clean, bright
Alpha Activity	Strong	Weak	None			
Solution Beta Activity, counts/min/ml						
Gross	0	7.37×10^3	8.84×10^3	9.29×10^3	9.29×10^3	1.75×10^3
TRE	0	5.71×10^3	6.77×10^3	6.77×10^3	6.77×10^3	112
UX	0	25	95	177	177	30
Ruthenium	0	248	332	402	402	None
Barium	0	40	150	150	150	72
Strontium	0	82	165	165	165	30
Zirconium	0	341	407	407	407	None
Iron, Nickel, Chromium	0				1.3×10^3	1.5×10^3
Solution Concentration, mg/ml						
Nickel	0	0.007	0.012	0.022	0.017	
Chromium	0	0.016	0.045	0.044	0.044	
Iron	0	0.12	0.24	0.30	0.37	
Manganese	0	0.008	0.10	0.011	0.019	

*Bomb removed from solution and activity read at contact with Cutie-Pie

time. Preliminary results indicate excellent confirmation of the data reported above. This information has been made available to groups working with the HRE mockup and the HRE itself for their consideration and use.

**RADIATION EFFECTS ON THE
HRE REFLECTOR SYSTEM**

In the previous quarterly report⁽¹⁾ results from the irradiation of natural

water containing 500 ppm of trisodium phosphate in SAE-1030 carbon steel bombs indicated low equilibrium pressures. Low corrosion rates had been reported by other groups.

As a final check D₂O was obtained from a drum scheduled for use in the reflector and was used in three irradiation experiments. The effects of 500 ppm of trisodium phosphate and saturated magnesium oxide were compared with the effect of heavy water

HRP QUARTERLY PROGRESS REPORT

TABLE 5

Radiation Effects on the HRE Reflector

SOLUTE	pH		GAS COMPOSITION		FINAL PRESSURE (psi)	PRECIPITATE
	INITIAL	FINAL	% H ₂	% O ₂		
None	6.2	7.35	60	18	32	Yes
500 ppm Na ₃ PO ₄	11.2	7.45	91	1.5	200	Yes
Saturated MgO	10.2	7.52	42	20	0	Yes

alone by using an exposure of ten days at a flux of 5 to 8 x 10¹¹ and temperatures of 100 to 200°C. Table 5 sets forth pertinent data for this run.

Precipitates were found in each bomb, as indicated by Table 5, and they were all magnetic (i.e., iron oxide). This unmistakable evidence of corrosion was confirmed by the excess hydrogen present in the two bombs that showed appreciable final pressure.

Similar experiments with D₂O from the same drum, carried out by other groups in the absence of radiation, led to the formation of similar precipitates. However, the corrosion rates encountered are considered tolerable for the HRE (see Table 2). Thus, no harmful effect of radiation was found, and the magnitude of the equilibrium pressure was satisfactorily low.

EXPERIMENTS AT HIGHER FLUXES

Apparatus for further experiments in the vertical hole of the LITR was completed, assembled, and tested during the previous quarter. Safety circuits were designed and constructed. Plans for the experiments were reviewed and

approved by the ORNL Pile Experiment Safety Committee. At the present time the experiment awaits the completion of electrical conduit and pipe-line installation by craftsmen and the availability of suitable reactor-control circuits that are now being installed. It is expected that experiments will begin early in December. The use of copper to recombine hydrogen and oxygen will provide a full-scale test of possible HRE operation and, at the same time, make for greater safety by keeping the equilibrium pressure at a low level. Subsequent experiments are planned to explore the relationship between temperature and precipitation of UO₄ at high fluxes. The vertical hole in the LITR is visualized as the most convenient facility for short-term tests.

Mechanical and electrical components for experiments in the horizontal beam holes of the LITR have been designed and tested. Since it is contemplated that long-term radiation-corrosion tests will be of primary interest in these facilities, considerable attention has been focused upon the development of safety circuits that will protect the reactor and experiment, give adequate information as to source of trouble, provide for flexibility

FOR PERIOD ENDING NOVEMBER 15, 1951

of operations, and eventually not require continuous attention by a technical man. Designs for such circuits have now been tentatively approved, and construction of the equipment is under way. It is expected that the choice of experiments in horizontal holes will be guided by prior experiments in the vertical hole.

PLANS FOR NEXT QUARTER

With specific reference to the HRE, the following items are under consideration:

1. Long-term experiments in hole 60 of the X-10 graphite pile will be continued with replacement of the present set of bombs by another. The effects of the use of copper and the

absence of pretreatment may be evaluated.

2. The amounts of copper required for HRE operation will be calculated and checked by experiments in the LITR.

3. The conditions required to avoid precipitation of UO_4 at high flux will be sought.

4. Long-term radiation-corrosion tests in the LITR will be initiated.

5. Recovery of uranium from irradiated, enriched, uranyl sulfate solution by use of ion exchange will be explored in connection with disposal of hot solutions from bomb experiments and may provide some data of interest to HRE operation.

HRP QUARTERLY PROGRESS REPORT

ENGINEERING STUDIES OF COMPONENTS

C. B. Graham, Section Chief

FUEL TEST LOOPS AND PUMPS

H. C. Savage C. G. Heisig
H. I. Kraig R. A. Lorenz
D. Schwartz

Fuel-Recirculating Test Loops. As previously reported,⁽¹⁾ there are three recirculating test loops in operation. All three loops, constructed of type-347 stainless steel as in the HRE, are being used to determine corrosion rates and the requirements for fuel stability under operating conditions of the HRE. These three loops, designated A, B, and C, have Westinghouse Model 100-A pumps for circulation of fuel at approximately 100 gpm. With 1-in. schedule-40 pipe, this gives flow rates of approximately 37 ft/sec as compared to approximately 18 ft/sec in the 1 1/2-in. schedule-80 pipe of the HRE.

After approximately 1700 hr of operation with uranyl sulfate (40 g of uranium per liter) at 250°C and 1000-psi pressure, loop A was removed and cut up for inspection of the interior surfaces. No serious corrosion effects were noted except at reduced sections (the impeller discharge opening and an orifice of 3/4-in. ID to restrict flow to approximately 100 gpm), where some pitting was found. Several precipitations of the fuel had occurred during this period. It was not until after several hundred hours of operation of this loop that the present method of using oxygen to maintain solution stability was discovered.

Loop A has been rebuilt and enclosed in a metal safety shield to allow operation of the loop with the

mixtures of hydrogen and oxygen gas that will be present during operation of the HRE. The effect of hydrogen and oxygen mixtures on corrosion rates and solution stability will be checked.

This loop, with the new recirculating line, has been operated approximately 400 hr since the last quarterly report, and thus there has been a total of approximately 2100 hr of satisfactory operation to date with the pump. The effect of various oxygen pressures inside the loop pressurizer has been investigated in an effort to determine the oxygen concentration required to maintain solution stability. No definite conclusions have been reached; however, the experience to date indicates that in a new, clean system an oxygen concentration of about 500 ppm is required at start-up. After a period of operation with high oxygen concentration (approximately 500 ppm), the fuel stability can be maintained in the loops with oxygen concentrations of about 20 ppm. The minimum oxygen requirements for fuel stability have not yet been determined.

Loop A is now operating under the following conditions:

Recirculating solution	uranyl sulfate (40 g of uranium per liter)
Solution temperature	250°C
Pressurizer temperature	250°C
System pressure	1000 psi (steam plus gas)
Gas composition	50 psi of oxygen and approximately 300 psi of helium.

(1) "Engineering Component Studies," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 56.

FOR PERIOD ENDING NOVEMBER 15, 1951

The present run (No. 16) is being made to compare corrosion rates with those obtained in loop C where the operating conditions are the same except that all the gas used (approximately 350 psi) is oxygen. Both loops A and C are operating with pressurizer temperatures of 250°C instead of the usual 285°C (1000-psi steam) to compare corrosion rates with previous runs where a 285°C pressurizer temperature was used.

The HRE mockup is now in operation with natural uranyl sulfate. In this system a start-up procedure (cleaning and passivation) is being investigated. In addition, the oxygen requirement and the method of maintaining the necessary oxygen concentration for solution stability and the corrosion rates that might be expected in the HRE are being evaluated under conditions that duplicate the operating conditions in the HRE.

Loop B has been operated for 1000 hr during the past quarter, and thus there has been a total of 2875 hr of satisfactory operation of this loop. Solution stability is maintained by keeping an oxygen pressure of 20 to 50 psi in the pressurizer. This oxygen is introduced into the recirculating line by taking a small amount of condensed steam, saturated with oxygen, from the top of the pressurizer and introducing it continuously (at approximately 0.5 gph) into the rear of the pump. All operation of this loop has been with the following conditions:

Line temperature	250°C
Pressurizer temperature	285°C
System pressure	1000 psi

It is being operated to check corrosion rates by using the following solutions in different runs: (1) uranyl sulfate (40 g of uranium per liter), (2) uranyl sulfate (40 g of uranium per liter)

plus simulated fission products, (3) uranyl sulfate (40 g of uranium per liter) plus simulated fission products and copper (approximately 1500 ppm). Copper was added on the assumption that at some future date it might be used in the HRE as a catalyst in the recombination of the hydrogen and oxygen generated during operation.

It was possible to maintain solution stability with small amounts of oxygen with all the solutions listed. However, corrosion rates were increased with solutions 2 and 3.

Loop C has operated satisfactorily for 1350 hr since the last quarterly report. For the initial run of 950 hr the line and pressurizer were operated at 150°C with fuel (40 g of uranium per liter) at 150°C. A pressure of approximately 300 psi above steam pressure was maintained with oxygen in the pressurizer. This had a twofold purpose: to ensure solution stability and to maintain positive pressure above the vapor pressure at the pump inlet to ensure liquid lubrication of the pump bearings. The 150°C run was made to compare corrosion rates with similar runs at 250°C. The initial corrosion rates were lower than comparable runs at 250°C; however, the corrosion rate increased to a value comparable to the 250°C runs after approximately 600 hr of operation. For further investigation of corrosion rates as a function of time, temperature, and oxygen concentration, longer runs under a given set of conditions are planned (500 to 1000 hr).

Loop C is now operating at 250°C throughout, with a system pressure of 1000 psi and with solution stability maintained by adding 350 psi of oxygen to the pressurizer. The corrosion results of this run will be compared with the results from loop A in which only 50 psi of the 350 psi of gas

HRP QUARTERLY PROGRESS REPORT

pressure is oxygen. Thus an attempt is being made to evaluate the effect of excess oxygen on the corrosion rate in a recirculating test loop.

A fourth loop, *D*, with a modified Westinghouse pump that includes a seal unit between the pump and motor end, has been operated for short periods with recirculating water. This loop is being used at present to check the operating characteristics of a shaft seal designed by the Engineering Department. The seal is effected by means of a Stellite No. 6 face running against No. 14 Graphitar. Positive seating of the two surfaces is maintained by spring loading. Water on the outside of the seal is kept at approximately 50-psi pressure above the recirculating liquid on the inside by means of a differential pressure cell and controller. At present there is leakage through the shaft-seal unit. Some of this leakage may be through the gaskets.

Two additional loops, designated *E* and *F*, are being constructed of 1 1/2-in. schedule-80 type-347 stainless steel pipe to give a velocity of approximately 18 ft/sec when pumping 100 gpm. These loops are approximately 11 ft long instead of the usual 5 ft to provide sufficient length for the installation of orifice flow meters in the loops. Other parts of the loop are similar to those used in loops *A*, *B*, and *C*.

The initial purpose of these two loops is to check Westinghouse Model 100-A pumps to determine the feasibility of pumping high-concentration fuel (200 to 400 g of uranium per liter) that has a density of 1.2 to 1.4 for use in the HRE and future test loops.

Instruments will be provided on these loops for measuring flow rates and head and motor characteristics,

and an attempt will be made to increase pump output. By increasing line voltage and improving the cooling of the pump stator, the motor horsepower may be increased as much as 30%. If the motor output cannot be increased sufficiently, it will be necessary to sacrifice pumping capacity and head. This can be done by decreasing the impeller diameter. An improved corrosion-testing arrangement has been provided to allow for more samples and closer evaluation of flow conditions.

Both of these loops should be completed by December 15. The two model 100-A pumps are already on hand; however, one of them has a leak in the Inconel can separating the rotor chamber from the stator. At present this leak has not been located and the extent of the repair work that will be necessary is not known.

Present plans call for six additional fuel-recirculating loops for corrosion and solution stability test work. These loops will allow testing of uranium solutions other than the sulfate. They will have Westinghouse Model 100-A pumps for recirculating the fuel and will be similar to the present loops *A*, *B*, and *C*. All major drawings for these loops are complete and fabrication of all components except the fuel systems has begun. The fuel systems will be fabricated as soon as loops *E* and *F* are completed (approximately December 15). The present shipping schedule calls for the first Model 100-A pump to be shipped the latter part of December, and one pump will be shipped every two weeks thereafter until six pumps have been delivered. It is felt that the loops will be ready for installation of the pumps as they arrive.

Water-Recirculating Test Loop. This water-recirculating loop will be used to check corrosion rates in

FOR PERIOD ENDING NOVEMBER 15, 1951

material used in the HRE D₂O-reflector system. It is constructed of 1 1/2-in. schedule-80 ASTM A-210 carbon steel pipe and ASTM A-106 Grade-B steel fittings, as far as possible. These steels are very similar to the steel used in the HRE pressure shell. For parts for which neither of the above steels was available SAE-1020 steel is being used. The loop is approximately 50% complete and should be ready for operation by December 15.

This loop will have a Westinghouse Model 30-A pump like that used for the reflector system of the HRE for recirculating the water. This pump will be equipped with a type-347 stainless steel diaphragm in place of the standard Inconel diaphragm. Thus, an evaluation of the type-347 stainless steel diaphragm can be made to determine whether it should be used for future pumps of this type. This pump is scheduled for shipment from Westinghouse November 15.

Westinghouse Model 100-A Pump. Seven totally enclosed Westinghouse Model 100-A centrifugal pumps are now on hand, and four of these pumps have been operated for a total of approximately 6700 hours. About 5200 hr of this operating time have been accumulated with the pumps equipped with Stellite No. 98M2 and No. 6 journals with No. 14 Graphitar bearings. All these pumps are being used in the fuel-recirculating test loops. One pump is now operating in the HRE mockup and another has just been installed in the HRE.

The pumps have given satisfactory service except in one or two instances in which thrust loads were excessive. With the present method of eliminating thrust loads by hydraulic balance and the use of tantalum seal rings, no thrust wear is encountered. The tantalum rings replaced type-347 stainless steel rings that corroded

and/or eroded and allowed the hydraulic-thrust balance point to shift.

Pump operation has been under HRE conditions as far as possible. These conditions are:

Solution pumped	uranyl sulfate (40 g of uranium per liter)
Solution temperature	250°C
System pressure	1000 psi.

Except in isolated instances in which foreign particles were allowed to reach the bearings, essentially no wear of the radial surfaces of bearings or journals has been found. To reduce the possibility of foreign particles (dirt, scale) reaching the bearings, a small flow of clean feed (condensed steam saturated with oxygen) is introduced at the rear of the pump. This is accomplished in the loops by a small by-pass line that connects the top of the pressurizer with the rear of the pump. The steam is condensed and cooled in passing through a water-cooled, jacketed section of the line before reaching the pump. This feed serves a dual purpose in that the oxygen carried over with steam passes through the pump, in solution, into the recirculating line and maintains the solution stability.

In the HRE mockup and the HRE itself, a 1-gph pulsafeeder is used to feed clean water to the rotor cavity and thus to the bearings.

On all pumps the thrust load is eliminated by proper location of the impeller with respect to the welded pads on the inside of the front and rear walls of the impeller housing. In some cases it has been found necessary to increase the clearance between the impeller hub and seal rings to achieve balance. Increasing the clearance of the rear seal rings tends to relieve forward thrust.

HRP QUARTERLY PROGRESS REPORT

Westinghouse Pump Bearings. Based on present experience, the Stellite No. 98M2 journal, No. 14 Graphitar bearing combination is very satisfactory. Present bearings, as received from Westinghouse, contain two longitudinal lubrication grooves and two radial grooves on the thrust face. Bearings with and without these longitudinal grooves or with only one groove have been used in the pumps to date. All have given satisfactory service, but it is believed that a no-groove bearing, adequately lubricated, might be safer in that it would be less likely to trap foreign particles that would start bearing wear.

The weak point in the bearings is that they are not capable of carrying the thrust loads that may be developed in the pump. This thrust load is eliminated on each pump by positioning the impeller as previously mentioned. However, since there is no long-term guarantee that the thrust load is permanently eliminated - wear around the impeller hub seal rings will change the thrust balance - a self-aligning radial and thrust bearing has been designed to carry larger loads. This bearing can be installed in a standard Model 100-A pump and is expected to be capable of carrying the maximum thrust loads developed by the pump. All drawings are complete and have been sent to the shop for fabrication. This bearing will be Stellite No. 98M2 against No. 14 Graphitar.

The investigation of metal bearings is continuing. Stellite No. 98M2 journals against Stellite No. 98M2 bearings have been used in the Model 100-A pumps with excellent results. It is felt that a metal-to-metal combination with hardness greater than Rockwell C-60, if properly designed, will give longer service than the present metal-to-No. 14 Graphitar combination. In addition, chemical tests of uranyl

sulfate stability indicate that it would be desirable to eliminate graphite from the recirculating system, although solution stability has been maintained in the recirculating test loops that have Graphitar pump bearings. Approximately 1500 hr of operation have produced no measurable radial wear. A water-lubricated Stellite No. 6 journal against a Stellite No. 98M2 bearing (with no longitudinal lubrication grooves) is now running in a test stand. With a load of approximately 19 psi, no wear was observed after 72 hours. It is planned to increase this load to approximately 38 psi.

The metal-to-metal bearings are quite sensitive to any misalignment. For this reason a self-aligning bearing housing for use in the present Model 100-A pump has been designed and is now in the shop for fabrication. If this device operates satisfactorily, Stellite bearings could be used interchangeable between various Model 100-A pumps.

One-gpm Pulsafeeder Pump. The test of the pumping heads of a Lapp 1-gpm pulsafeeder pump has been discontinued. The all-welded pumping head on this unit has now been installed on the HRE mockup. This head was operated for 2200 hr under HRE conditions of approximately 0.8 gpm against a discharge head of 1000 psi with uranyl sulfate (40 g of uranium per liter) at 80 to 120°C as the recirculating liquid. No leakage was detected through the diaphragm of this unit. Fuel stability was maintained throughout the entire operation, although no oxygen was used. It appears that at this temperature (80 to 120°C) solution stability is maintained without oxygen or that the decomposition rate is so low that a much longer operating time would be needed to detect instability.

OPERATION OF THE HRE MOCKUP

J. S. Culver C. W. Keller

Stability of the Letdown System.

An excellent discussion of the vortex-stability problem has been prepared by Smith and Katz.⁽²⁾ Data for this report were collected from tests with the mockup. Also, a fairly complete discussion of the testing and development of the letdown system was presented in the last quarterly progress report.⁽¹⁾

The surge tanks and 1/8-in. constrictions previously included in the systems were removed to simplify the systems, even though it meant a slight increase in minimum tolerable liquid flow for stability in the letdown stream. This increase is permissible, since, if the flow of the pulsafeeder pump does not fall below 1.0 gpm, the letdown system will be stable at all gas-flow and temperature conditions expected to be encountered in the reactor. Normal reactor conditions are considered to be an operating temperature of 250°C and a gas flow of 200 cc/sec at 1000 psi. This is based on 50 ev per molecule at 1000-kw power level.

To confirm the reproducibility of the data collected from tests with the mockup, the actual letdown heat exchanger to be used in the reactor was tested in the mockup and found to have the same performance characteristics as the one previously tested in the mockup.

A recommendation by the Physics Group⁽³⁾ to change the core outlet design was tested to observe the effects, if any, on the stability of the letdown system. Here again the minimum liquid flow for stability in

the letdown system increased slightly but did not exceed the 1.0-gpm tolerance. The pulsafeeder now delivers about 1.5 gpm, which gives a large safety factor.

Revisions of the Mockup for Operation with Fuel. In an effort to keep the mockup as nearly a replica of the reactor fuel system as possible, it was rebuilt and several new components were added. Figure 11 shows a schematic layout of the apparatus. Pressure and level controllers, as well as the boiler control circuits, are essentially identical to those on the reactor. The oxygen system is new to the mockup and so is the gas bleed valve that relieves gas from the pressurizer. The present oxygen absorber is designed for 100 ppm by weight in the circulating stream. However, during start-up the present procedure calls for 500 ppm. This large flow causes oxygen to be forced back into the pulsafeeder head, the check valves become very noisy, and the pumping ceases. If these large flows are found necessary, the absorber or its connections will have to be redesigned to correct this condition.

The gas bleed valve is intended to remove gas from the pressurizer and is controlled by a thermocouple in the top of the pressurizer and a temperature controller. When gas is present, the temperature drops below the 285°C steam temperature. When this occurs, the valve opens and bleeds off the gas until the temperature returns to the set value of 285°C.

In a test the system was brought up to 1000 psi by admitting the helium to the steam space in the pressurizer. The gas supply was then shut off, and the water in the pressurizer was brought up to 285°C. The thermocouple in the top of the pressurizer indicated a temperature of 210°C.

⁽²⁾J. M. Smith and D. L. Katz, *Performance of the Letdown System of the HRE*, ORNL CF 51-8-287.

⁽³⁾T. A. Welton, *Pressurizer Design*, ORNL CF 51-8-31.

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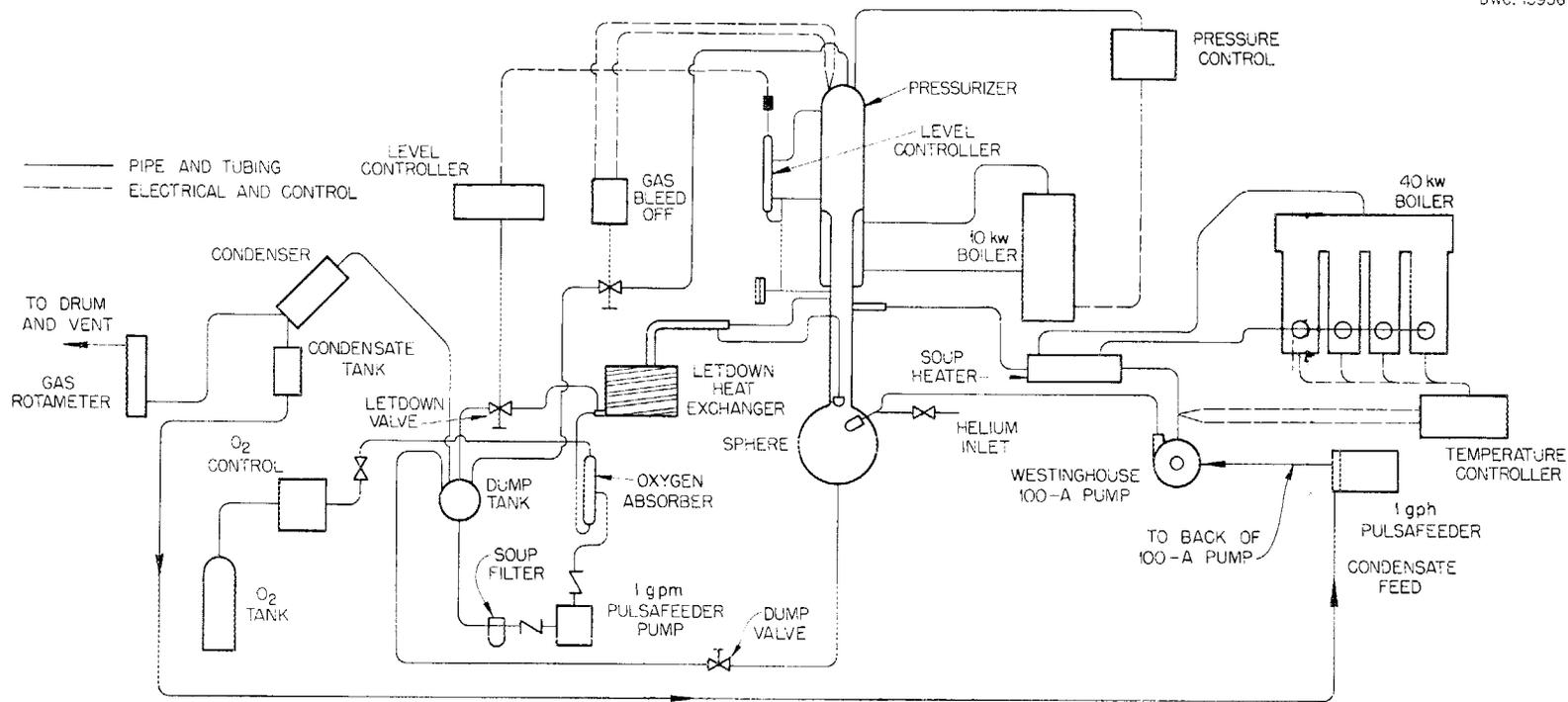


Fig. 11. Piping Layout of HRE Mockup.

With the bleed valve open, the temperature reached 280°C in 4 hours. On this basis, the instrument group is considering a larger valve for the reactor.

Operation of the Rebuilt Mockup. The entirely new system was started up and, after some "debugging" of the components, operated successfully with water. This was followed by a series of chemical washings to remove dirt, scale, etc.

The cleaning process involved alternate washes with 3% trisodium phosphate at 150°C for 3 hr and 5% nitric acid at 80°C for 4 hours. Analyses of these solutions were made, and the treatment was finished with a distilled water rinse at 250°C.

The cleaning process was followed by a distilled water run with about 400 ppm of oxygen at 250°C. This was continued for about 72 hours. On November 20 uranyl sulfate solution (600 g of uranium per liter) was added gradually to the distilled water to bring the concentration in the circulating stream up to 40 g of uranium per liter over a period of 12 hours. Oxygen was added continuously to maintain 400 to 500 ppm during this period. After one week of continuous operation, the oxygen is being reduced progressively to ascertain the minimum flow necessary to maintain solution stability.

HOMOGENEOUS REACTOR CORES

I. Spiewak J. I. Lang
J. A. Haford R. H. Wilson

Flow in the HRE Core. An evaluation has been made of the mixing to be expected in the HRE core. This work was carried on in a transparent lucite model of the spherical core tank. Observations were made by

studying dye concentration changes in various portions of the sphere.

The outstanding characteristic of the flow distribution is a stagnant region in the shape of a cylindrical annulus coaxial with the sphere outlet. This extends from top to bottom of the sphere at an average diameter of 8 inches. A more complete description of the flow pattern is found in ORNL-990.⁽⁴⁾

A complete analysis of the data obtained in the model for the variable density conditions prevalent in actual operation shows that safe performance is probable at 250°C outlet temperature and full power. These observations were made with various concentrations of methanol solutions and with hot water. The maximum temperature in the stagnant region is estimated at 275.6°C. The major cooling mechanisms were found to be liquid mixing, convection caused by density differences, and the effect of gas bubbles. This work has been reported elsewhere.⁽⁵⁾

The stagnant region has been eliminated successfully with the use of cylindrical tapered rods based on the sphere wall and extending through the stagnant region in horizontal planes. An objection to their use in the HRE is the possibility of failure caused by stress-corrosion or fatigue. The use of these rods is being investigated only as a possible alternative. They are described more fully elsewhere.⁽⁶⁾

A sample rod made of type-347 stainless steel has been tested in one of

⁽⁴⁾I. Spiewak and J. O. Bradfute, "Mixing in the HRE Core," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending February 28, 1951*, ORNL-990, p. 31.

⁽⁵⁾I. Spiewak and J. O. Bradfute, *Effect of Density Differences on Flow in the HRE Core*, ORNL CF 51-10-165, Oct. 17, 1951.

⁽⁶⁾I. Spiewak and J. O. Bradfute, *Use of Baffles in the HRE Core Tank*, ORNL CF 51-8-232, Aug. 29, 1951.

HRP QUARTERLY PROGRESS REPORT

the pump loops for 282 hr under flow conditions more rigorous than those anticipated in the HRE core. There is no evidence to date of incipient failure. There was some erosive damage near the tip of the rod during the first 100 hr of the test when a precipitation occurred in the fuel. Further damage is not visible under the microscope. There appears to be no corrosion thus far at the base of the rod where the maximum bending stresses exist. The number of vibratory cycles thus far is about 10^8 , whereas the conventional endurance limit exists at about 10^6 cycles (if corrosion does not occur). Thus, there is indication that a fatigue failure is highly improbable.

Intermediate Core Development. A program is being initiated for testing models of intermediate reactor core connections. The two basic types of flow proposed are the HRE-type rotational flow and straight-through flow from bottom to top of the reactor.

The first type of flow is being studied in detail at the University of Tennessee. Some tests are planned at ORNL with a 12-in. sphere equipped with four tangential inlets and two polar outlets. This sphere will have plastic windows for flow-pattern studies, and extension of the University of Tennessee work on pressure drop is planned. It is expected that the four inlets will give better insight into the effect of the number of inlets on flow and pressure drop. To date, only one or two inlets have been used on models.

The straight-through type of flow will be studied in a 12-in. cylindrical model with conical entrance and exit sections. Inasmuch as this sort of design is known to produce stagnant regions, the inlet cone will be provided with a number of baffles designed to eliminate stagnation. It is also planned to try to obtain a velocity

distribution that would approximate the flux in a reactor. The ideas for baffling that will be tried are:

1. Entry through a number of small holes drilled in a plate mounted normal to the cylinder axis. These holes can be arranged to produce a desired velocity distribution and may be tilted if a rotational component is desired.

2. Entry through a number of concentric cones mounted in the main conical inlet to the cylinder. These, it is hoped, will provide uniform flow through the test section. If a rotational component is desired, sheet metal strips can be mounted between cones, or an airfoil section can be inserted before the cones.

3. Tangential entry close to the apex of the inlet cone or at a pipe preceding the inlet. It is hoped that this mode of entry will eliminate stagnant areas.

It is believed that these model studies, coupled with the University of Tennessee work, will allow a decision to be made as to the best core flow pattern for future homogeneous reactors.

Gas Separators. The straight-through type of core in the intermediate and large-scale homogeneous reactors will have gas present outside of the core in the circulating system. Even if the liquid-phase catalyst is used, it will probably be necessary to effect some separation in the external system.

Preliminary work has been carried out with models in the 100-gpm flow range, and two basic designs that have been examined appear promising. The first type is basically a pipe with axial flow and tangential inlets and outlets. The gas is centrifuged

toward the center, where it collects in a vortex and is withdrawn. An attempt is made to recover the rotational energy in the outlet. This pipe gas separator is summarized in a memorandum that will be issued soon. The second design is merely a loop in which the gas is again thrown toward the center and withdrawn from pipe taps. This was investigated by an MIT Practice School group, and their report is being prepared.

RECOMBINERS

J. A. Ransohoff R. Van Winkle

The flow sheet for the fuel off-gas recombiner has been modified during the last quarter, and a mockup of the new system has been tested and operated with gas flows of 0.025 to 15 cfm of the mixture $2H_2 + O_2$ STP. The principal changes in the flow sheet are: (1) installation of auxiliary steam generators to supply about 5 lb/hr (1.6 scfm) of steam to the gas lines between the first condenser and the burner and between the burner chamber and the catalytic recombiner and (2) elimination of the unsatisfactory control method that regulated the steam and gas flow to the burner nozzle by controlling the amount of cooling water sent to the first condenser.

This system has been found to recombine $2H_2 + O_2$ at all flow rates between 0.025 and 15 cfm in the burner chamber. It has also been demonstrated that flash-backs from the burner to the first condenser no longer occur when gas flow is suddenly reduced from the maximum to 0.25 cfm. Such flash-backs had been observed frequently in the previous equipment, but it has since been shown that they occurred because the recombiner system being tested then was open to the atmosphere with little restriction of flow between the outside atmosphere and the burner nozzle.

A program of explosion testing has been started for the purpose of observing peak pressures reached when explosions of hydrogen and oxygen occur in various closed vessels at various ambient pressures and atmospheres of explosive gas.

The feasibility of recombining hydrogen and oxygen by bubbling through copper sulfate solutions is being investigated in preliminary tests.

It is well known that the gas velocity through the burner nozzle must be kept greater than some minimum value, approximately 30 ft/sec, to prevent the flame from striking back. In the original flow sheet of the recombiner system it was proposed to keep the flow of gas to the burner above this minimum by allowing some steam to pass through the first condenser when gas flows were low. This was to be accomplished by using an air-operated valve to regulate the amount of cooling water sent to the condenser. The valve was operated automatically by a differential pressure controller that measured the pressure drop across a flow nozzle in the gas line between the condenser and the burner. It was found that this system worked well for steady flows of gas, but in the case where gas flow was reduced very rapidly from 15 cfm to 1 cfm several minutes elapsed after the cooling water was throttled before the condenser heated sufficiently to pass through enough steam to dilute the gas and maintain the desired minimum flow through the burner nozzle. At such times, several back-flashes would occur before the minimum flow through the nozzle was restored. Although these back-flashes were always quenched in the condenser, the overheating of the burner nozzle during the brief period of low flow caused warpage and partial closing of the

HRP QUARTERLY PROGRESS REPORT

holes of the burner nozzle by oxidation.

By installing auxiliary steam generators that continuously inject a constant flow of about 1.6 scfm of steam (5 lb/hr) into the gas leaving the first condenser and the burner chamber, the need for controlling the composition of the gas leaving the first condenser has been eliminated. This system operates smoothly at all flows of hydrogen and oxygen up to the maximum design value of 15 cfm. At very low flows (0.025 to 0.1 cfm) the burner does not operate continuously, because the mixture of gas and steam flowing through the nozzle is non-combustible at these flows. Since the burner walls are cold, the mixture becomes combustible in the burner chamber when steam condenses. The intermittent burning causes small pulsations in pressure in the burner chamber when it is operating at very low gas flows. It has been found that when excess oxygen is present in the atmosphere of the burner chamber, the mixture of $2\text{H}_2 + \text{O}_2 + \text{steam}$ is burned much more smoothly at the nozzle. This condition will prevail in the

HRE, because oxygen will be added to the fuel solution.

Although the burner will recombine the gas at all flows, it is sometimes more desirable to turn off the spark plugs and react the gas in the catalytic recombiner, which can be used to handle flows from 0 to 0.12 cfm without having the catalyst temperature exceed 400°C . Gas going to the catalytic recombiner is diluted by steam from the second auxiliary steam generator to prevent the formation of localized hot spots in the catalyst.

Operating experience on the mockup indicates that the HRE fuel off-gas recombiner system will operate smoothly and safely with little attention from the operators. A test program has been outlined for the HRE recombiner systems in which the flow nozzle for measuring gas flow will be calibrated and the whole recombiner system will be operated as a unit to test its performance at various flows from 0.025 cfm to 15 cfm. In addition, the performance of the D_2O catalytic recombiner system will be tested.

CHEMICAL CONTROL

W. H. Davenport R. H. Powell

ELECTROMAGNETIC DENSITOMETER

The most suitable point in the HRE for the installation of a Densitrol instrument for continuous specific-gravity measurement appears to be across the main heat exchanger. Flanges have been provided on the lines entering and leaving the heat exchanger at points close to the exchanger so that the instrument, after adequate testing, may be connected to the system.

Two instruments are being developed; one for use at an average operating

temperature of 50°C and one for use at 250°C. The lower temperature instrument might be installed as shown in Fig. 12. A small heat exchanger would be required to cool the stream before it entered the Densitrol, and a restricting valve placed after the Densitrol would be required to limit the flow to the range 0.1 to 0.3 gpm. There is a drop in pressure across the heat exchanger of 40 psi. The instrument designed for use at 250°C would be installed in a similar manner, except that the small heat exchanger would not be necessary.

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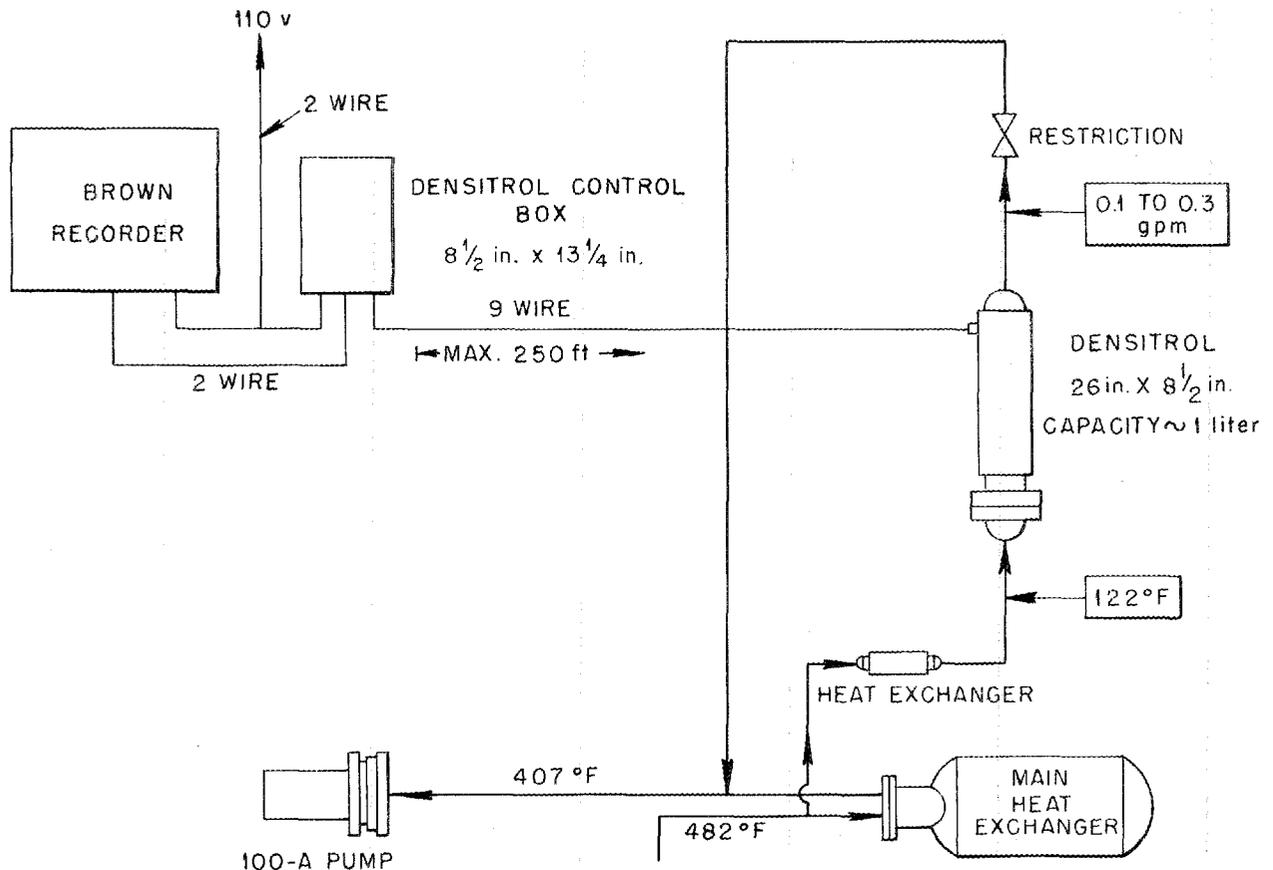


Fig. 12. Proposed Densitrol-Installation Flow Diagram.

HRP QUARTERLY PROGRESS REPORT

The advantages of using a low-temperature instrument are: (1) the lower temperature-density coefficient at lower temperatures permits greater fluctuations in operating temperature, (2) the higher solution densities at low temperatures permit greater weight in the plummet and, hence, more rugged construction, (3) the development and testing are nearer completion for the low-temperature instrument than for the high, owing chiefly to the more rugged construction. The chief disadvantage is that an additional heat exchanger is required to cool the stream. This results in greater holdup and also cuts down on the already limited space that is available around the HRE.

The advantages and disadvantages are exactly reversed if a high-temperature instrument is considered, that is, the disadvantages are: higher temperature-density coefficient, lower solution density, etc. The development of a high-temperature instrument has been delayed chiefly by the difficulty of fabricating a satisfactory plummet at ORNL and partly by a holdup in fabrication of the position-detecting coil by a subcontractor of the Precision Thermometer and Instrument Company.

The instruments are being fabricated by Precision Thermometer and Instrument Company, with modifications suggested by ORNL to meet the HRE conditions. The status of development and testing of these instruments is given in the following sections.

Development of a Densitrol for Use at an Average Operating Temperature of 50°C. Two instruments with pyrex plummets were received from the manufacturers. One instrument, which was used for laboratory testing, is wired at several points with plastic insulated wire and could not be used in a radiation field. The second has

glass-insulated wiring. Both instruments have differential transformers wound on Bakelite forms. A substitute transformer wound on a lavite form has been ordered.

The sampling chamber, with the plummet removed, has been tested hydraulically to 2000 psi. Pyrex plummets had been tested to at least 4000 psi, previously.⁽¹⁾ Laboratory testing was carried out by using a small test loop in which 2 liters of a uranyl sulfate solution was circulated at atmospheric pressure by using a small centrifugal pump. A 2-liter flask heated by a spherical mantle was included in the system to provide temperature control. Separate studies were made of each of the solution variables - flow rate, concentration, temperature, and bubble content.

Flow was varied from 0.1 to 0.33 gpm, and temperature was varied from 40 to 60°C, with the instrument set for an average operating temperature of 50°C and the automatic temperature compensator set for the temperature-density coefficient of uranyl sulfate at 50°C. Uranium concentration was changed by dilution from about 40 to about 26 g of uranium per liter. Densities were checked at each concentration by using a pycnometer.

In every case the specific gravity recorded by the Densitrol deviated from the expected value by no more than ± 0.0002 g/ml. This would amount to an error of plus or minus 0.5% in the determination of uranium in solutions with a concentration of 30 g of uranium per liter.

Volumes of air were introduced into the line entering the sampling chamber. When there was no throttling on the

⁽¹⁾W. H. Davenport, Jr., and R. H. Powell, "Chemical Control," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 75-83.

outlet side of the chamber, a 15-cc volume of air caused the plummet to assume false positions that led to erroneous results. These errors, for the same volume of air, were reduced to momentary pulsations by throttling on the outlet side of the chamber. The flow was reduced a factor of 3 by the restriction. The operation of the instrument in the laboratory was considered satisfactory.

The low-temperature instrument is being installed in the mockup. If the mockup tests indicate that the operation of the instrument is satisfactory, a low-temperature Densitrol will be considered feasible for use in the HRE. Before installation, however, the Bakelite-form, differential transformer will have to be replaced with the lavite-form transformer that is now on order.

Development of a Densitrol for Use at an Average Operating Temperature of 250°C. One high-temperature Densitrol is on order. The high-temperature instrument differs from the low-temperature instrument, primarily, in the choice of material used in plummet construction. Components in the control box have different electrical values, but these changes present no difficulty. Pyrex is not a satisfactory plummet material, since it is attacked markedly by uranyl sulfate solutions at 250°C. The development of plummets fabricated from other materials has been undertaken at ORNL. Stainless steel and titanium have been considered, with titanium appearing to be more favorable owing to its higher tensile strength-to-weight ratio. The difficulty in fabrication stems from the fact that the wall of the plummet must be sufficiently thin to give the plummet an over-all density comparable to the uranyl sulfate solutions through which it moves. The wall must also be heavy enough to withstand external pressures as high as 2000 psi.

Increased collapse strength has been gained by pressurizing the instrument internally with an inert gas. A type-347 stainless steel plummet with a collapse pressure of 300 psi has been pressurized internally to 900 psi.

It seems possible that the permissible *differential* between external and internal pressure would be increased by increasing the internal pressure, since the higher internal pressure would give the wall a greater spring factor. An experiment is under way to see whether this is the case. A dummy type-347 stainless steel plummet has been fabricated. After pressurization to 1000 psi with nitrogen, the dummy will be inserted in a bomb constructed from 1 1/2-in. schedule-80 pipe. The testing bomb can then be attached to a dead-weight pressure tester to determine the collapse pressure of the plummet.

As a preliminary to the fabrication of a titanium plummet, two dummy assemblies with 0.025-in. cylindrical wall thickness and 1-in. OD were made by R. J. Fox of the Research Shops for tests of welds. The welding of each of these experimental dummies was undertaken by P. Patriarca of the Metallurgy Division. A successful weld was made on the second one by employing the heliarc technique and using a helium atmosphere in a dry-box equipped with a rotating stage. The weld withstood an internal hydraulic pressure up to 4000 psi; however, the test dummy ruptured at a point near, but not at, the weld. Subsequently, the titanium plummet, Figs. 13 and 14, which had been machined at the Research Shops, was successfully welded at the rim. The titanium plummet has been hydraulically tested for bursting strength up to 2500 psi at room temperature and will be tested for collapse strength after pressurizing. Both argon and carbon dioxide are being

HRP QUARTERLY PROGRESS REPORT

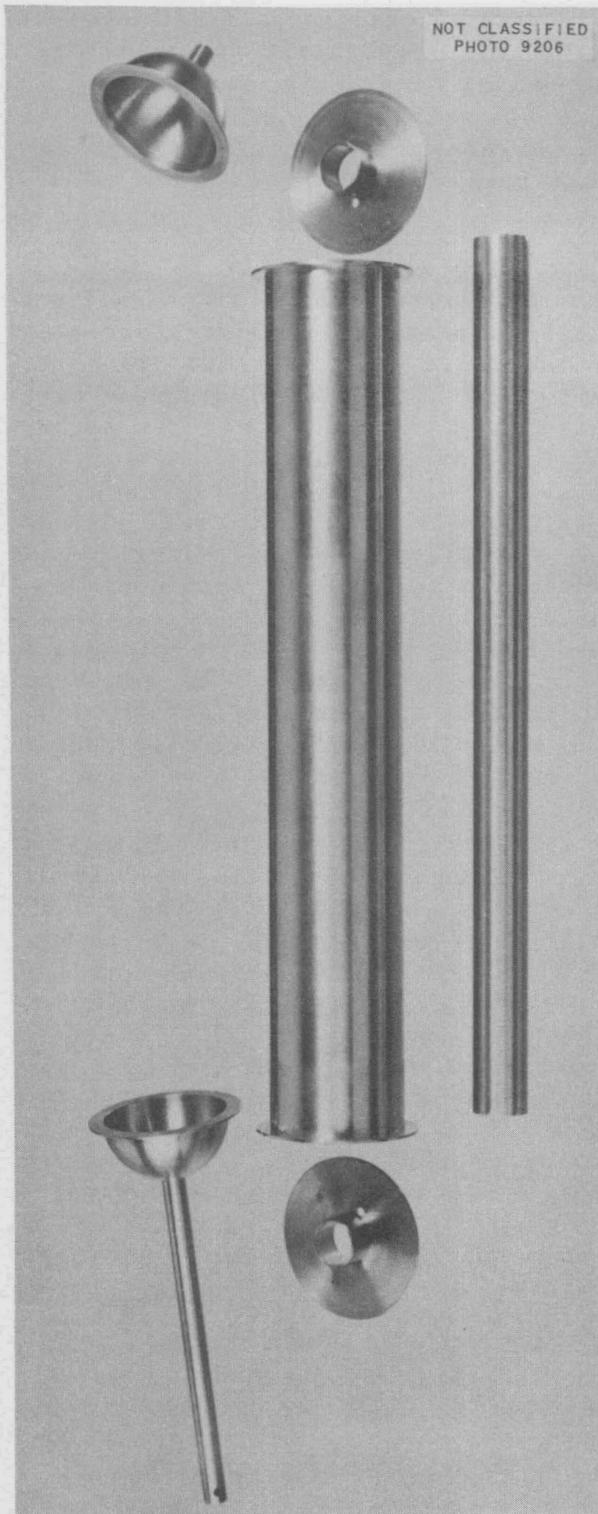


Fig. 13. Component Parts of Titanium Plummet Before Welding. Unassembled.

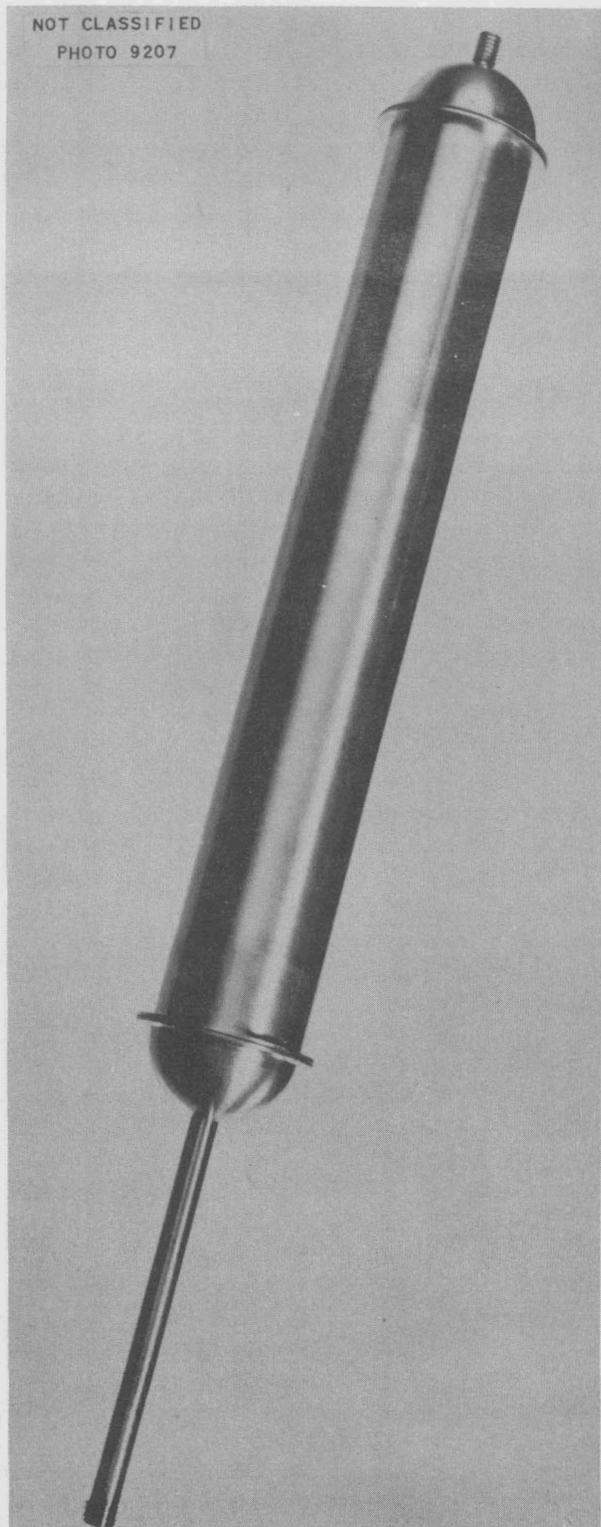


Fig. 14. Component Parts of Titanium Plummet Before Welding. Assembled.

considered for pressurizing. After these tests have been completed a successful weld must be made at the filling point. The filling point is at the screw nut shown in Fig. 13. The wall thickness of the end hemispheres is 0.020 in.; wall thickness of the long cylinder is 0.025 inch. The titanium and stainless steel collars for weight adjustment are not shown. The 4000-psi rupture strength of the dummy assembly indicates the possibility of pressurizing a titanium plummet to a higher pressure than had been originally contemplated.

The titanium was fabricated from the purest titanium available commercially; however, the use of titanium alloys is being considered to provide even greater strength.

Q MEASUREMENT

The major problem in the measurement of the Q of a high-frequency coil as affected by changes in uranium concentration is in developing a suitably corrosion- and radiation-resistant electrical insulator for the coil, which will be immersed in the high-pressure, high-temperature fuel solution.

The bomb⁽²⁾ designed for testing material strength and performance of various Q -coil and insulator units has been altered to use independent gasketing (2 gaskets) of the ceramic with 18-gage platinum O rings. Also the shape of the ceramic collar of the Q -coil base has been revised to fit the bomb illustrated in Fig. 15.

Of the glazes tested by gasketing the glazed Q -coil unit, none has been found that will not crack during gasketing with either 3/16-in.-thick gold O rings or with 0.040-in.-thick

platinum O rings. The 0.040-in.-platinum O rings were used in the bomb illustrated in Fig. 15, whereas 3/16-in.-thick gold O rings had been used in the previous bomb.⁽²⁾

The failure of the glazes during gasketing in the most recent tests has led to the necessity of examining materials other than true ceramics. The prospective use of high-temperature fused material, such as spinels, corundum, or any of the synthetic minerals, obviously presents new problems. It was hoped that these problems could be avoided by the use of powdered, compressed, fired materials that could be satisfactorily glazed and gasketed. However, it is now deemed advisable to consider the use of synthetic materials. To date, the following materials have been corrosion-tested in boiling 0.17 M uranyl sulfate for the purpose of eliminating those materials not possessing chemical stability in the fuel solution at relatively low temperature. J. English⁽³⁾ of the Reactor Experimental Engineering Division has reported the results shown in Table 6.

Stupalith 2209 is now being tested in contact with 0.17 M uranyl sulfate solution at 250°C under a steam pressure of 565 psi by English.

In addition, synthetic corundum and synthetic spinels are being examined for their chemical corrosion stability in boiling 0.17 M uranyl sulfate. These materials are normally thought to be extremely difficult to dissolve in common mineral acids, they possess a hardness of 8 on Mohs' scale, and they are highly infusible. If any of the corundum and spinels have the requisite chemical (and radiation) stability in the fuel, it may be possible to secure a specially formed thimble with a collar suitable

(2) W. H. Davenport, Jr., and R. H. Powell, "Q Measurement," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending May 15, 1951*, ORNL-1057, p. 90.

(3) Personal Communication, November 12, 1951, from J. L. English to R. H. Powell.

HRP QUARTERLY PROGRESS REPORT

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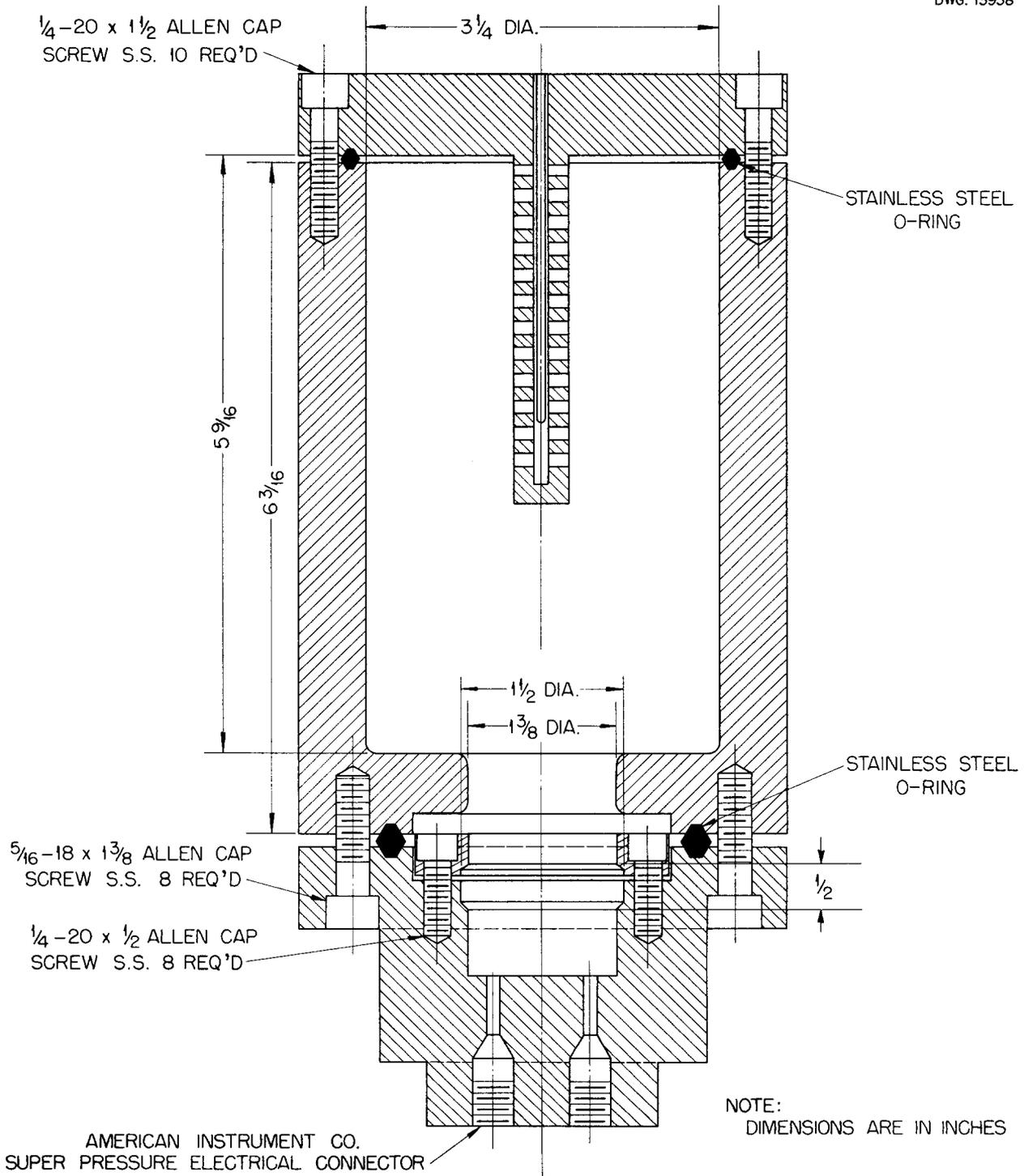


Fig. 15. Revised Q-Coil Test Bomb.

TABLE 6

Corrosion Studies in Boiling 0.17 M Uranyl Sulfate

MATERIAL	TIME OF TEST (hr)	CORROSION RATE (mils/yr)	SAMPLE CONDITION
Stupalith 2209*	276	0.8	No change from original
Petalite (fused natural mineral)	105	17.3	Slight etched effect
Cordierite**	127	47	Relatively unaffected
Zirconium Oxide	65	15	Yellow, powdery surfaces
Chromite**	127	255	Black, flaky surfaces
Cordierite (natural)	127	302	White, powdery surfaces
Barium mica**	190	500	Crumbly surfaces
Stupalith 2417*	43	611	Yellow and powdery
"Spinel" Cordierite**	85	1131	White and flaky
Fosterite**	85	1285	Yellow, powdery surfaces
Boron mica**	71		Sample disintegrated

*Obtained from Stupakoff Ceramic and Manufacturing Company, Latrobe, Pa.

**Synthetic material supplied by Dr. Robert A. Hatch, U. S. Bureau of Mines, Electrotechnical Laboratory, Norris, Tenn.

for gasketing. Such a thimble might be made in the shape of a small beaker with a gasketing lip or collar attached, so that a suitable metallic coil could be inserted into the annular space of the object and the fused spinel or fused corundum used as the electric insulator for the Q coil in the measurement of the Q relationship with the fuel system. It is recognized that many of the synthetic spinels and synthetic corundum (ruby and sapphires) have high mechanical stresses formed during their syntheses. H. H. Willard has been consulted on this matter and is contacting Linde Air Products Co., New York on the feasibility of the manufacture of such a thimble. If it is feasible and if this laboratory's test for chemical and radiation stability are favorable, an attempt will be made to secure suitable forms and gasket the forms to a metal pipe section.

At present, the following synthetic materials obtained from the Guardian

Manufacturing and Supply Company in New York are being corrosion-tested under boiling fuel conditions by English: ruby, white sapphire, golden sapphire, blue spinel, titania, tourmaline.

Room-temperature, normal-pressure experiments are being conducted to measure the Q to uranyl sulfate concentration relationship at higher concentrations than hitherto employed. Measurements up to the concentration of 400 mg of uranium per milliliter are planned.

The glazed Q-coil units recently made by E. Cantrell of the Chemistry Research Shops are being used for these experiments. These glazed Q-coil ceramic units differ from the earlier Q-coil units⁽⁴⁾ in that they are constructed in two parts. The base

⁽⁴⁾W. H. Davenport, Jr., and R. H. Powell, "Analytical Chemical Control of the Homogeneous Reactor Solution," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950*, ORNL-925, p. 273.

HRP QUARTERLY PROGRESS REPORT

collar and plug, which serve to enclose the two electrical leads connecting the resonating Q coil, are machined from natural 1137-grade Lava. The Q coil is encased by a moulding technique in a cylinder with open ends through which liquid may flow in and around. The electric leads emerge from the outside wall of the cylinder and fit into two holes provided in and base plug and collar. The present cylinder is 1 1/16-in. long and has a 1/4-in.-diameter annular space centrally traversing the long axis of the open-end cylinder. The cylinder walls are 1/4-in. thick. Both pieces, that is, the base and the cylinder encasing the electrical coil, are united and bonded by the glaze used. Accordingly, great strength has been incorporated in the ceramic base, and the Q "quality" of the electric coil has been greatly improved (a Q of 135 in air was obtained with 20 mega-

cycles r-f in contrast to values of 60 to 80 in earlier Q -coil units). The entire unit was glazed in one operation. The collar glaze cracked during gasketing but the ceramic withstood the gasketing pressure applied in the sealing of the bomb head.

RADIATION-RESISTANT GLASSES

Neutron-absorbing, cadmium borofluosilicate, optical glasses⁽⁴⁾ have been examined for changes in the optical spectrum after exposure in the X-10 graphite pile. The findings after the first radiation exposure have been reported,⁽¹⁾ and a second irradiation of the glasses is continuing in their former position in hole 60. Measurement of any further changes following a second radiation exposure will be made when the glasses are removed from the pile.

TABLE 7

Chemical Composition of Neutron-Absorbing Glasses

GLASS CODE	1 M	2 M	3 M	4 M
Melting temperature, °C	1300	1400	1250	1400
Density, g/cm ³	3.365	4.632	4.288	4.278
Cationic %				
CaF ₂	10.0	10.0	10.0	10.0
CdO	8.0	46.0	27.0	37.0
SiO ₂	10.0	40.0	20.0	40.0
AlO _{1.5}	2.0	4.0	3.0	3.0
BO _{1.5}	70.0	0.0	40.0	10.0
Weight %				
CaF ₂	21.2	8.5	12.6	9.5
CdO	27.9	64.3	55.7	58.1
SiO ₂	16.3	26.1	19.3	29.4
AlO _{1.5}	1.4	1.1	1.2	0.9
BO _{1.5}	33.1	0.0	11.2	2.1
Composition by Analysis				
Weight %				
CdO		60.0	55.6	54.3
SiO ₂		27.6	19.2	30.1
BO _{1.5}			10.3	1.9

TABLE 8

Corrosion Tests in Boiling 0.17 M Uranyl Sulfate

GLASS CODE	TIME OF TEST (hr)	CORROSION RATE (mils/yr)	SAMPLE CONDITION
1 M	162		Sample disintegrated
2 M	162	538	Yellow with powdery surface
3 M	162	187	Flaky surfaces
4 M	162	186	Powdery surfaces

The glasses⁽¹⁾ heretofore identified as Glasses 1, 2, 3, and 4 (ORNL Identification code) can now be characterized chemically by the information given in Table 7 which was furnished by Melnick *et al.*⁽⁵⁾

A corrosion test⁽³⁾ has been performed on unirradiated glasses cut from the melt described by chemical analysis in Table 7. These tests were also performed by English by boiling the glass specimens in 0.17 M uranyl sulfate solution. The specimens were checked for weight loss, and prior to

each weighing they were washed thoroughly in distilled water and dried to constant weight. The original uranyl sulfate test solution was used throughout each individual test. The corrosion data are summarized in Table 8.

The results of the boiling corrosion tests clearly removed all the glasses tested from consideration for possible use in contact with 0.17 M uranyl sulfate solutions. One of the glasses (Code 2 M) might be useful if not in contact with fuel solutions; however, its resistance to further change in the characteristics of its spectrum under radiation will not be known until after the completion of the second irradiation test, which is under way.

⁽⁵⁾L. M. Melnick, H. W. Safford, K. W. Sun, and A. Silverman, "Neutron-Absorbing Glass: CdO-SiO₂-B₂O₃ System," *J. Am. Ceram. Soc.* 34, 84 (March 1951).

HRP QUARTERLY PROGRESS REPORT

PHYSICS

T. A. Welton, Leader

NONLINEAR HRE KINETICS WITH GAS PRODUCTION

P. R. Kasten

Some experimental data concerning the gas holdup volume to be expected in the core of the HRE for various gas-production rates has been presented in previous HRP quarterly reports, and an analytic study of the gas residence time has been made by F. N. Peebles of the University of Tennessee. The purpose here is to present the mathematical system describing the dynamics of the reactor when gas is generated throughout the core volume and, on the basis of the above, to evaluate the parameters associated with gas formation.

To obtain an over-all picture of the response of the reactor to reactivity changes, the relations between power, temperature, reactivity, gas volume, rate of gas generation, pressure, and fluid density must be known. As reported previously,⁽¹⁾ the time-dependent nuclear power and temperature equations are

$$\frac{d\sigma}{dt} = \lambda_0 [k(1 - \beta) - k_c] \sigma + \sum_i \lambda_i c_i, \quad (1)$$

$$\frac{dc_i}{dt} + \lambda_i c_i = \lambda_0 \beta_i k \sigma, \quad (2)$$

$$\sum_i \beta_i = \beta, \quad (2a)$$

(1) "Reactor Physics," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950*, ORNL-925, p. 78.

$$\frac{dT}{dt} = SP_0 [\sigma - 1], \quad (3)$$

where σ is the power relative to base power, or P/P_0 , and the other symbols have the same meaning as in ORNL-925.⁽¹⁾

The effects of gas bubbles and pressure on the reactivity will be considered here, therefore,

$$k_c = k_{c0} + \alpha(T - T_0) + \epsilon [v_g - v_g(0)] + g(p - p_0), \quad (4)$$

where

p = absolute pressure within the reactor vessel, lb/in.²,

T = temperature, °C,

v_g = vapor-gas fraction of reactor volume,

g = coefficients for the above variables, or $\partial k / \partial x$, where x is the variable.

Since the total volume of the bubbles is the volume of the dry gas divided by the partial pressure of the dry gas within the bubbles,

$$v_g = V_{dg} / V_r p_{dg}, \quad (5)$$

where

v_g = fraction of reactor volume composed of gas and vapor,

V_{dg} = volume of dry gas at T (°C) and p (lb/in.²),

V_r = volume of reactor core,

p_{dg} = partial pressure of the dry gas at T and p
 $= 1 -$ (partial pressure of water vapor at T).

The vapor pressure of water, p_w , can be approximated near 232°C by

$$p_w = 7.75 T - 1376, \quad (6)$$

with p_w in lb/in.² when T is in °C; hence, with $V_r = 50$ liters,

$$v_g = \frac{V \frac{273 + T}{505} \frac{1000}{p}}{V_r (p - 7.75T + 1376)}$$

$$= 0.0000396 \frac{V(273 + T)}{(p - 7.75T + 1376)}, \quad (7)$$

where V is the volume in milliliters of the dry gas in the reactor at 1000 psi and 232°C.

V is a time-dependent function determined by the rate at which gas is generated within and removed from the reactor vessel, or

$$\frac{dV}{dt} + aV = b \int_0^\infty F(s) \sigma(t - s) ds, \quad (8)$$

where

a = average reciprocal time a bubble stays in the vessel,

b = rate at which bubbles are produced when the reactor is operating in the steady state at P_0 power,

$F(s)$ = normalized distributed delay function for bubble formation.

If the liquid flow rate in the gas letdown line does not vary appreciably, any decrease in fluid density within

the reactor core must be accompanied by a net emission of liquid, or

$$\frac{dp}{dt} = - \frac{Av\rho_1}{V_r}, \quad (9)$$

where

ρ = fluid density, lb/ft³,

A = area of pressurizer pipe, ft²,

V_r = volume of reactor, ft³,

ρ_1 = density of liquid forced into pressurizer, lb/ft³,

v = variation of fluid velocity in pressurizer pipe from normal value, ft/sec.

The velocity variation v of the liquid in the pressurizer pipe is dependent upon the driving and resisting forces, or

$$\frac{m}{Ag_c} \frac{dv}{dt} = \Delta p - cv|v| - dv, \quad (10)$$

where

m = mass of liquid in pressurizer pipe = $AL\rho_1$,

A = area of pipe,

L = length of pipe,

g_c = conversion factor, 32.2 ft·lb mass per lb force·sec²,

Δp = variation of pressure drop across pressurizer pipe from steady-state value, psi,

t = time, sec,

c, d = constants.

To complete the system, a relation of the form $\rho = f(p, T, v_g)$ is required. With $v_g(0)$ small, $T_0 = 232^\circ\text{C}$, and $p_0 = 1000$ psi, this relation is

$$\rho = \rho_1(1 - v_g), \quad (11)$$

HRP QUARTERLY PROGRESS REPORT

where

$$\rho_1 = 51.1 + (p - p_0) [(4.74 \times 10^{-6} T) - (7.05 \times 10^{-4})] - 0.0898 (T - T_0). \quad (12)$$

The parameters will be evaluated for reactor operation at 1000 kw, 1000 psi, and mean flow temperature of 232°C. When v_g is small, the coefficients in Eq. 4 become

$$\alpha = 0.001,$$

$$\epsilon = 0.0224 T - 3.36,$$

$$g = 1.113 \times 10^{-6} (0.0474 T - 7.05).$$

On the basis of 50 ev per water molecule decomposed, 155 cc/sec of dry gas or 272 cc/sec of saturated gas will be formed. From data presented previously,⁽¹⁾ the above corresponds to about 200-cc gas holdup distributed throughout the core liquid. Hence, $a = 1.36/\text{sec}$, $b = 155 \text{ ml/sec}$, $V(0) = 114 \text{ ml}$, and $v_g(0) = 0.0040$. In the above, bubbles were introduced at the circumference of the sphere. Peebles performed some analytical studies on gas residence time, assuming uniform bubble formation throughout the liquid, and his computations indicated the percentage gas holdup to be from 0.1 to 0.3. Assuming 0.25% gas holdup, $a = 2.18/\text{sec}$, $v_g(0) = 0.0025$, and $V(0) = 71 \text{ ml}$.

The bubble-time delay function, $F(s)$, in Eq. 8 is not known accurately, so three cases will be presented. If there is no time delay in bubble formation, Eq. 8 resolves to

$$\frac{dv}{dt} + aV = b \sigma(t). \quad (13)$$

If there is some average time τ that can be associated with delay in bubble formation, then

$$\frac{dV}{dt} + aV = b \sigma(t - \tau). \quad (14)$$

Probably $F(s)$ is of the form

$$A [e^{-\mu s} - e^{-\nu s}],$$

where $\nu > \mu$, in which case Eq. 8 can be represented by the following three first-order equations:

$$\frac{dV}{dt} + aV = bA [g(t) - q(t)],$$

$$\frac{dg}{dt} + \mu g = \sigma(t), \quad (15)$$

$$\frac{dq}{dt} + \nu q = \sigma(t).$$

The remaining constants have been given elsewhere and appropriate values are summarized in the following:

$$\lambda_0 = 10^4/\text{sec},$$

$$\lambda_0 \beta k_{co} = 75.5/\text{sec},$$

$$SP_0 = 5.13^\circ\text{C}/\text{sec},$$

$$c = 0.00496 \text{ psi}\cdot\text{sec}^2/\text{ft}^2$$

$$a = 0.212 \text{ psi}\cdot\text{sec}/\text{ft},$$

$$\frac{A}{V_r} = 0.0238/\text{ft},$$

$$\frac{m}{Ag_c} = \frac{L\rho_1}{g_c} = 0.000863 \rho_1 \text{ psi}\cdot\text{sec}^2/\text{ft}.$$

The above equations describe the complete mathematical system. While an analytic solution of the above cannot be obtained for an impressed Δk on the system, the equations are readily integrable numerically, so the time behavior of the variables can be plotted if the need arises.

OVER-ALL STABILITY OF THE HRE

T. A. Welton

Calculations strongly indicate that the HRE possesses no instability that can assert itself in a time shorter than a few seconds. For example, the delayed neutrons strongly damp any power oscillations, and the friction in the pressurizer pipe damps the mechanical oscillation of the core-pressurizer system, at least in the range of possible operating powers. In all these investigations, a model with constant heat removal has been used. This is presumably valid for investigation of the short-time behavior but gives no description of actual operation with heat removal by a boiler. The question of the stability of the complete HRE system (nuclear-thermal-mechanical) is of considerable interest, when it is considered that in normal operation the turbine inlet valve will act as a control rod for the reactor. Although it is clear that such a system has an equilibrium operating point, detailed investigation is required to find the conditions under which the equilibrium is stable.

The complete set of equations describing the time variation of the variables of the system is a very complicated array of nonlinear integro-differential equations. In making a stability analysis it is almost essential that the equations be written as differential equations, and the total number of time derivatives entering must furthermore be made rather small (ten being a large number) if great complication is to be avoided. The following set of assumptions gives a simple, yet moderately reasonable, approach:

1. The effects of decomposition gas are ignored (presence of a homogeneous catalyst assumed).

2. The reactivity of the reactor is simply proportional to the core temperature. This, of course, neglects inertial effects in the pressurizer, as well as the variation of statistical weight over the core volume.

3. The temperature of the fuel, while inside the reactor, rises at a constant rate when the reactor power is constant.

4. The temperature of the fuel entering the reactor is equal to the temperature of the steam in the boiler plus a constant temperature difference, which arises from the heat-transfer requirements in the boiler plus the pump losses.

These conditions are described by the following equations:

$$\dot{P} = \frac{1}{\tau} [\delta - \beta - \alpha \bar{T}] P + \frac{\beta}{\tau} \bar{P}, \quad (1)$$

$$\bar{T} = T + f\Delta, \quad (2)$$

$$T(t) + \Delta(t) = \int_0^{\infty} ds F(s) T(t-s) + \epsilon \int_0^{\infty} ds G(s) P(t-s), \quad (3)$$

$$\dot{T} + f\dot{\Delta} = -\lambda\Delta + \epsilon P. \quad (4)$$

The symbols used in these equations are defined as follows:

P = instantaneous reactor power,

τ = prompt-generation time,

β = fraction of delayed neutrons,

δ = excess reactivity under external control,

α = temperature coefficient of reactivity,

\bar{T} = mean, instantaneous, reactor temperature,

HRP QUARTERLY PROGRESS REPORT

\bar{P} = average over past of reactor power with the delayed-neutron distribution function,

T = reactor inlet temperature,

Δ = instantaneous temperature rise between inlet and outlet,

ϵ = coefficient for converting from energy input to temperature rise,

f = fraction of Δ that must be added to T to obtain the mean core temperature,

$F(s)$ = probability per unit range of s that fluid entering the core has residence time s ,

$$G(s) = \int_0^{\infty} ds' F(s + s'),$$

$$\lambda = \text{replenishing rate for the core} = \frac{1}{\int_0^{\infty} s ds F(s)}$$

Equation 1 is the usual power equation; Eq. 2 defines mean reactor temperature; Eq. 3 gives outlet temperature as a linear operation on the past of the inlet temperature as well as the power history while the fluid was traversing the reactor; and Eq. 4 is the continuity equation for energy. It expresses the fact that the mean reactor temperature must rise at a rate determined by the difference of power produced and power extracted. Some additional simplification can be gained by the following plausible assumptions: (1) the flow in the core can be assumed to provide complete mixing, (2) the transit time through the boiler will be neglected. These assumptions do not change Eqs. 1 and 2.

The assumption of complete mixing yields

$$F(s) = \lambda e^{-s},$$

$$G(s) = e^{-\lambda s}, \quad (5)$$

$$f = 1.$$

Under this assumption, Eqs. 3 and 4 become identical and Eq. 3 will henceforth be ignored.

The description of this simplified reactor system requires for completion a relation between power removed from the fuel in the boiler and the power removed from the boiler in the form of steam. Since $\lambda\Delta/\epsilon$ is the net power leaving the reactor and hence removed in the boiler,

$$\dot{T} = \eta \left[\frac{\lambda\Delta}{\epsilon} - R \right], \quad (6)$$

where η is the reciprocal heat capacity of the boiler contents (analogous to ϵ for the core), and R is the rate of removal of heat energy from the boiler in the form of steam.

The law of variation of R must also be specified to complete the description. Four simple possibilities are presented.

1. $R = \lambda\Delta/\epsilon$ so that $\dot{T} = T_0 = \text{constant}$, obtained by venting the boiler to atmospheric pressure, for example.

2. $R = P_0 = \text{constant}$, obtained by properly changing the setting of the turbine inlet valve as T varies.

3. $R = P_0 + [(\partial R/\partial T)_v (T - T_0)]$, obtained by using a fixed setting of the turbine inlet valve, with $(\partial R/\partial T)_v$ being the rate of increase of steam power with temperature for a fixed valve setting.

4. $R = P_0 + [(\partial R/\partial T)_p (T - T_0)]$, obtained by controlling the turbine

inlet valve for constant electrical-power output, with $(\partial R/\partial T)_P$ being the appropriate derivative.

Although case 3 is the procedure planned for the normal operation of the HRE, cases 1 and 4, which are easy to try, and case 2, which is easy to calculate, are included.

A further simplification and some numerical values are required at this point. Equation 1, for reactor power, can be considerably simplified because the generation time τ is extremely short in comparison with the period of any possible unstable motion, and the term \dot{P} can therefore be neglected. The HRE system with D₂O reflector, 230°C mean core temperature, 100-gpm flow rate, and power P_0 (in megawatts) will be assumed. Under these conditions

$$\begin{aligned} \beta &= 8 \times 10^{-3}, \\ \alpha &= 6.5 \times 10^{-4}/^\circ\text{C}, \\ \lambda &= 0.125 \text{ sec}^{-1}, \\ \epsilon &= 5.7 \text{ }^\circ\text{C}/\text{megawatt}\cdot\text{second}, \\ \eta &= 1.0 \text{ }^\circ\text{C}/\text{megawatt}\cdot\text{second}. \end{aligned}$$

The turbine tests are not yet complete, but it is clear that $(\partial R/\partial T)_V$ is a positive number and $(\partial R/\partial T)_P$ is a negative number. Simple thermodynamic arguments yield the following plausible values:

$$\left(\frac{\partial R}{\partial T}\right)_V = 10 \frac{P_0}{T_0} \left(\frac{\partial R}{\partial T}\right)_P = -10 \frac{P_0}{T_0},$$

where the first factor of 10 arises from the variation of vapor pressure with temperature according to the Clawsius-Clapeyron equation, and the second factor of -10 is essentially the reciprocal mechanical efficiency of the HRE system. The quantity P_0 is

considered to be 1 megawatt and T_0 is the operating steam temperature (absolute). With $T_0 = 500^\circ\text{K}$, the values become

$$\left(\frac{\partial R}{\partial T}\right)_V = - \left(\frac{\partial R}{\partial T}\right)_P = 2 \times 10^{-2} \text{ megawatts}/^\circ\text{C}.$$

One further simplification is possible. The quantity \bar{P} will be related to P by the assumption of a single group of delayed neutrons with a mean decay constant μ . This definition would then be:

$$\dot{\bar{P}} + \mu\bar{P} = \mu P \quad (7)$$

A very reasonable value for μ would be of the order of 0.1 sec^{-1} . The results cannot be drastically affected by taking $\mu = \lambda = 0.125 \text{ sec}^{-1}$, and, for simplicity, this assumption has been made.

The reactor system has now been completely defined, and the final step is to linearize the equations of motion (Eqs. 4, 6, 7, and 1) with \dot{P} omitted. Equilibrium values of variables are denoted by a subscript 0, and deviations of the variables from equilibrium are denoted by a prefixed δ . All terms containing the product of two deviations are dropped. The resulting equations are (power in megawatts, temperature in $^\circ\text{C}$):

$$\begin{aligned} \alpha P_0 (\delta T + \delta \Delta) &= -\beta (\delta P - \delta \bar{P}) \\ \delta \dot{T} + \delta \dot{\Delta} &= -\lambda \delta \Delta + \epsilon \delta P \quad (8) \end{aligned}$$

$$\delta \dot{\bar{P}} + \lambda \delta \bar{P} = \lambda \delta P$$

$$\delta \dot{T} = \frac{\lambda \eta}{\epsilon} \delta \Delta - \eta \nu \delta T$$

where $\nu = \infty, 0, 2 \times 10^{-2}$, and -2×10^{-2} , respectively, for the four cases.

HRP QUARTERLY PROGRESS REPORT

If the possible exponential time variations (e^{pt}) are sought, the quantity p must satisfy

$$\begin{vmatrix} aP_0 & aP_0 & +\beta & -\beta \\ P & p + \lambda & -\epsilon & 0 \\ 0 & 0 & -\lambda & p + \lambda \\ p + \eta\nu & \frac{-\lambda\eta}{\epsilon} & 0 & 0 \end{vmatrix} = 0, \quad (9)$$

or

$$p^3 + ap^2 + bp + c = 0, \quad (10)$$

with

$$a = \eta\nu + \frac{\lambda\eta}{\epsilon} + \lambda + \frac{\alpha\epsilon P_0}{\beta},$$

$$b = \lambda\eta\nu + \frac{\alpha(\epsilon + \eta) P_0 \lambda}{\beta} + \frac{\alpha\epsilon\eta\nu P_0}{\beta},$$

$$c = \frac{\alpha\epsilon P_0 \lambda \eta}{\beta} \left[\nu + \frac{\lambda}{\epsilon} \right].$$

For the first case, Eq. 1 degenerates to a quadratic with roots

$$p = -\frac{\alpha\epsilon P_0}{\beta}, -\lambda, \quad (11)$$

so that the case of constant inlet temperature always yields stability. For the other three cases, the usual condition for stability is that a , b , and c be positive and that ab be greater than c . In the following table, the values of a , b , c are given for the three cases:

Case	a	b	c	ab
2	0.610	0.068	0.00127	0.0415
3	0.630	0.080	0.00243	0.0504
4	0.590	0.056	0.00011	0.0330

Each case is stable, but in case 4 stability is marginal because of a near cancellation occurring in the value of c . A slightly larger value of $|\nu|$ would yield instability. In general, case 1 is certainly stable; cases 2 and 3 are stable by a large margin, with no possibility of negative values for a , b and c ; and case 4 is either definitely unstable or marginally stable. Further studies are planned with a more realistic reactor system, but the work described here indicates strongly that a fixed opening of the turbine inlet valve (which will actually be achieved by the turbine governor when the alternator is synchronized with the 60-cycle supply) will lead to stable operation. At the same time, an attempt to operate the turbine inlet valve in such a way as to hold the delivered power constant is very likely to lead to unstable operation unless suitable anticipation is incorporated in the governing mechanism.

KINETIC CALCULATIONS FOR HOMOGENEOUS REACTORS

W. C. Sangren

The systems of equations that arise in the study of the kinetics of the homogeneous reactor contain one or more nonlinear equations, and it has been necessary to resort to non-analytical methods to obtain detailed approximate solutions. Three methods have been used: (1) numerical integration with desk computers, (2) numerical integration with the SEAC (the National Bureau of Standards' Eastern Electronic Digital Computer), and (3) a semianalytical method involving a perturbation technique. The following sections indicate the types of results that have been obtained by the three methods used. It is planned to present the detailed results in a separate report. In general, the conclusion and results

obtained by J. M. Stein⁽²⁾ are confirmed. A table of symbols is given at the end of this section.

Hand Computations. Five systems of differential equations have recently been integrated with the aid of desk computers. The following system was the first one investigated:

$$\dot{T} = S(P - P_0),$$

$$\dot{C} = -\lambda C + \frac{\beta}{\tau} P,$$

$$\dot{P} = -\frac{\alpha}{\tau} (T - T_0) P + \frac{\delta - \beta}{\tau} P + \lambda C,$$

where $\lambda = 0.08$, $\alpha = 0.001$, $\delta = 0.01$, $\beta = 0.0075$, $\tau = 0.0001$, $P_0 = 1000$, and $S = 0.00573$. These results appear in ORNL-1121.⁽³⁾

The following system:

$$\dot{T} = S(P - P_0)$$

$$\dot{P} = -\frac{\alpha}{\tau} (T - T_0) P + \frac{\delta - \beta}{\tau} P + \frac{\beta}{\tau} P_0$$

in which the constants given previously are used, was integrated partly to compare the assumption of a constant source due to delayed neutrons with the assumption of one averaged group of delayed neutrons. The comparative results for power appear in Fig. 16. It is apparent that a constant source due to delayed neutrons is, for this δ , a good assumption.

⁽²⁾J. M. Stein (ed.), "Physics," *Homogeneous Reactor Experiment Report for the Quarter Ending February 28, 1950*, ORNL-630, p. 21; "Reactor Physics," *Homogeneous Reactor Experiment Feasibility Report*, ORNL-730, p. 48; "Reactor Physics," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950*, ORNL-925, p. 50.

⁽³⁾W. C. Sangren, L. H. Thacker, H. T. Williams, and P. M. Wood, "Numerical Calculation of a Power Surge," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 102.

Systems 1 and 9, as listed under SEAC computations, were calculated with both the SEAC and desk computers. The hand computations were carried out before the SEAC computations, since it was desirable to have these results both as a means of checking the machine results and as a method of estimating magnitudes.

The most recent hand computation was carried out on System 14 (listed in the following section). In this case it was thought desirable to shock the pressurizer system only and follow the early motion of the neutron and pressurizer systems. The results brought out nothing unexpected.

The five systems of differential equations listed in this section were integrated by the Runge-Kutta method. For the more difficult systems, such as Systems 1, 9 and 14, one computer can calculate at about the rate of 0.3 sec per system per month.

SEAC Computations. The following set of equations dealing with the thermal, nuclear, and pressurizer systems form the basis for the computations performed on the SEAC:

$$1. \quad \dot{T} = S(P - P_0)$$

$$2. \quad \dot{P} = \frac{1}{\tau} \left[\left(\frac{\partial k}{\partial \rho} \right) (\rho - \rho_0) + \delta - \beta \right] P + \frac{\beta}{\tau} P_0$$

$$3. \quad \dot{\rho} = -\frac{A\rho_0}{V} U$$

$$4. \quad \dot{U} = \frac{A}{M_r} (p - p_0) - \frac{B}{M_r} U - \frac{E}{M_r} U|U|$$

$$5. \quad \rho - \rho_0 = \frac{1}{v_s^2} (p - p_0) - \left[\left(\frac{\partial \rho}{\partial T} \right) \right] (T - T_0)$$

From the computational viewpoint it is desirable to replace Eqs. 1 through

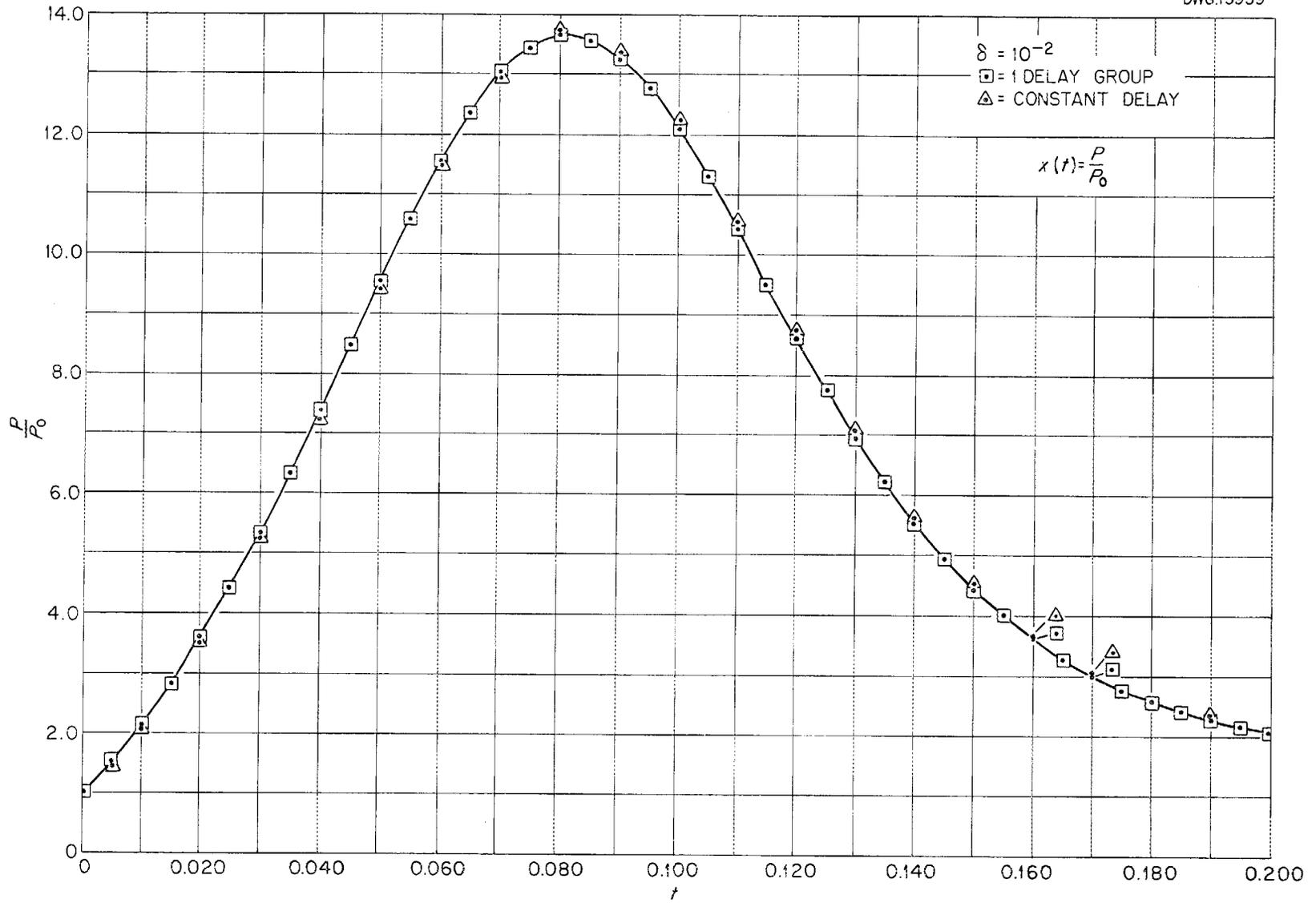


Fig. 16. Power as a Function of Time for a δ Step Function of 0.01.

5 by a corresponding set with fewer constants or parameters. By using Eq. 5 in Eq. 4 and letting

$$y = \frac{1}{SP_0}(T - T_0),$$

$$x = P/P_0,$$

$$v = \frac{1}{\tau} \left[\frac{\partial k}{\partial \rho} \right] \frac{A\rho_0}{V},$$

$$Z = \frac{1}{\tau} \left[\frac{\partial k}{\partial \rho} \right] (\rho - \rho_0),$$

the following set of equations is obtained:

$$6. \quad \dot{y} = x - 1$$

$$7. \quad \dot{z} = -v$$

$$8. \quad \dot{x} = zx + \frac{\delta - \beta}{\tau} x + \frac{\beta}{\tau}$$

$$9. \quad \dot{v} = -\alpha_1 v - \alpha_2 v|v| + \omega_H^2(z + \omega_n^2 y)$$

$$\omega_H^2 = \frac{A^2 \rho_0}{VM} v_s^2,$$

$$\omega_n^2 = \frac{1}{\tau} \left[\frac{\partial k}{\partial T} \right] SP_0,$$

$$\alpha_1 = \frac{B}{M},$$

$$\alpha_2 = \frac{E A\rho_0}{M \tau V} \left[\frac{\partial k}{\partial \rho} \right].$$

Thirteen such systems were computed on the SEAC. Eqs. 6 and 7 and the initial conditions $x(0) = 1$, $z(0) = 0$, $y(0) = 0$, and $v(0) = 0$ are used in all the systems. The systems were completed by adding one of the following pairs of differential equations:

(8) ₁ $\dot{x} = 375x + zx$	(9) ₁ $\dot{v} = 2.5(10^4)z + 1.25(10^6)y$
(8) ₂ $\dot{x} = 300x + zx + 75$	(9) ₂ $\dot{v} = -0.3v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₃ $\dot{x} = 300x - zx - 75$	(9) ₃ $\dot{v} = -0.01v v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₄ $\dot{x} = 300x + zx + 75$	(9) ₄ $\dot{v} = -0.3v - 0.01v v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₅ $\dot{x} = 100x + zx$	(9) ₅ $\dot{v} = 2.5(10^4)z + 1.25(10^6)y$
(8) ₆ $\dot{x} = 25x + zx + 75$	(9) ₆ $\dot{v} = -0.1v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₇ $\dot{x} = 25x + zx + 75$	(9) ₇ $\dot{v} = -0.3v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₈ $\dot{x} = 25x + zx + 75$	(9) ₈ $\dot{v} = 0.01v v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₉ $\dot{x} = 25x + zx + 75$	(9) ₉ $\dot{v} = -0.3v - 0.01v v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₁₀ $\dot{x} = -25x + zx + 75$	(9) ₁₀ $\dot{v} = -0.3v - 0.01v v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₁₁ $\dot{x} = -5x + zx + 75$	(9) ₁₁ $\dot{v} = -0.3v - 0.01v v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₁₂ $\dot{x} = 50x + zx + 75$	(9) ₁₂ $\dot{v} = -0.3v - 0.01v v + 2.5(10^4)z + 1.25(10^6)y$
(8) ₁₃ $\dot{x} = 100x + zx + 75$	(9) ₁₃ $\dot{v} = -0.3v - 0.01v v + 2.5(10^4)z + 1.25(10^6)y$

HRP QUARTERLY PROGRESS REPORT

where

$$\left[\frac{\partial k}{\partial \rho} \right] = 0.0074,$$

$$V = 1.75,$$

$$L = 5.9,$$

$$A = 0.037,$$

$$v_s^2 = 7.05(10^6),$$

$$\omega_n^2 = 50,$$

$$\omega_H^2 = 2.5(10^4),$$

$$\tau = 10^{-4},$$

$$\beta = 0 \text{ or } 0.75(10^{-2}),$$

$$\alpha_1 = 0 \text{ or } 0.1 \text{ or } 0.3,$$

$$\alpha_2 = 0 \text{ or } 0.01,$$

$$\delta = 0.50(10^{-2}) \text{ or } 10^{-2} \text{ or } 1.25(10^{-2}) \text{ or } 1.75(10^{-2}) \text{ or } 3.75(10^{-2}).$$

For convenience in identification each system is named according to the number which is a subscript for its equation (Eq. 8 or 9).

A fourteenth system with

$$(8)_{14} \quad \dot{x} = -75x + zx + 75$$

and

$$(9)_{14} \quad \dot{v} = 2.5(10^4)z + 1.25(10^6)y,$$

and the initial conditions $x(0) = 1$, $z(0) = 0$, $y(0) = 0$, and $v = -10^5$, was computed with a desk computer.

The general system 6, 7, 8, 9 with initial conditions was programmed for solution by the Heun method on the SEAC. The parameter values, the integration interval (of order 10^{-4}

sec), and the interval at which the results were to be printed out were read into the machine independently of the main routine. Since it was not necessary to change the main routine from system to system, there is the possibility of using, in the future, the main routine with different values of the parameters. The range of integration was either from $t = 0$ to $t = 0.3$ sec or $t = 0$ to $t = 0.4$ second. The total machine time, including 1 hr for checking the programming and coding, was about 5 hr for all thirteen systems. However, the actual computation time per system was less than 20 seconds. The remaining machine time was taken up by the printing out of the results and, to a small extent, by reading the routine and parameter values into the machine. One hundred values of x and 50 values for each of y , v and z were printed out. Typical results are shown in Figs. 17 through 22.

Analysis. Since Eqs. 6 through 9 along with the initial conditions form the basis for the SEAC computations, it is desirable to obtain analytic approximations to the solutions of this general system and then to compare them with some of the computed results. Since the initial value of z is zero and the damping due to velocity proves to be relatively unimportant, a first approximation can be obtained by solving the linear system consisting of Eqs. 6 and 7, and

$$\dot{x} = \frac{\beta}{\tau} + \frac{\delta - \beta}{\tau} x,$$

$$\dot{v} = \omega_H^2(z + \omega_n^2 y).$$

It is easy to see that $x_1 = A_1 l^{\psi t} + A_2$ and $z_1 = B_1 \cos \omega_H t + B_2 \sin \omega_H t + B_3 + B_4 t + B_5 l^{\psi t}$, where $\psi = (\delta - \beta)/\tau$ and the A 's and B 's are constants depending on the parameters.

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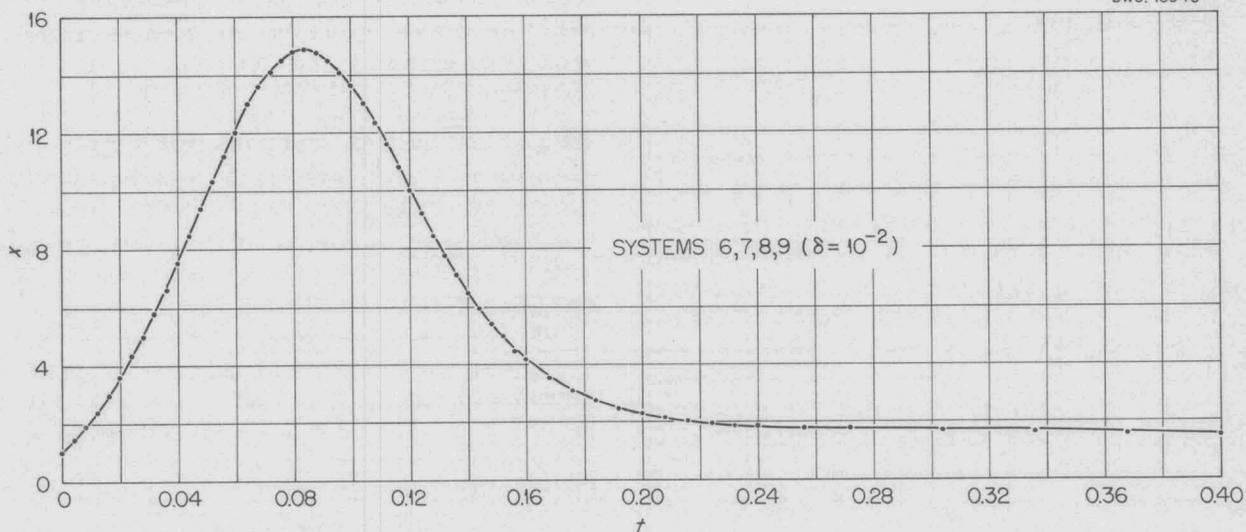


Fig. 17. Power as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients.

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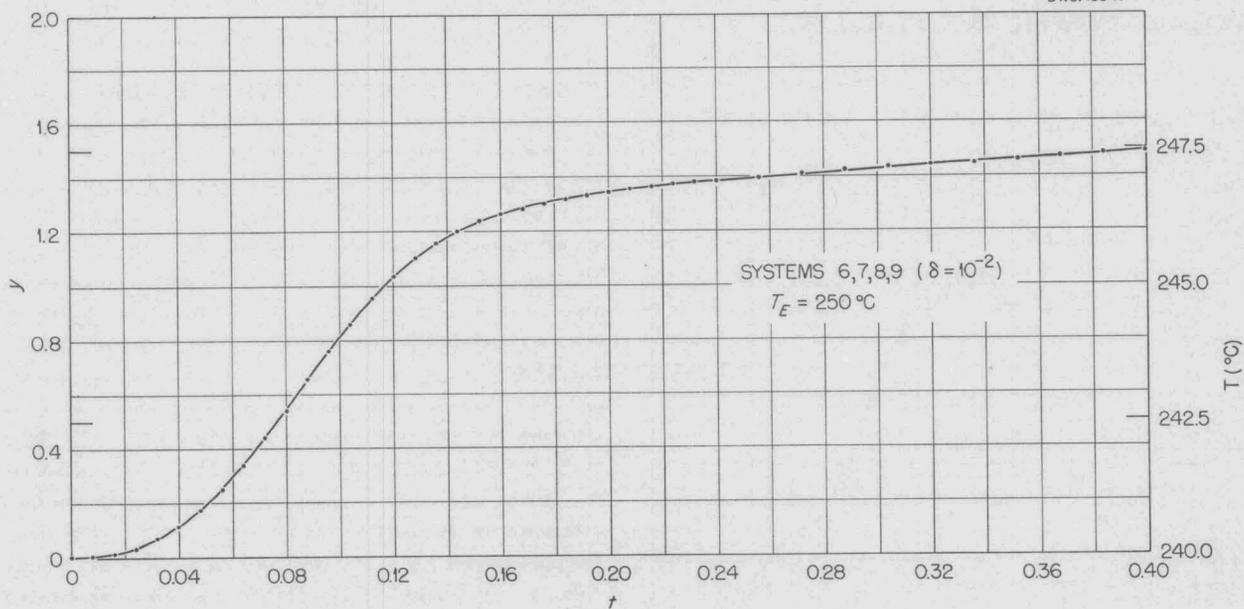


Fig. 18. Temperature as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients.

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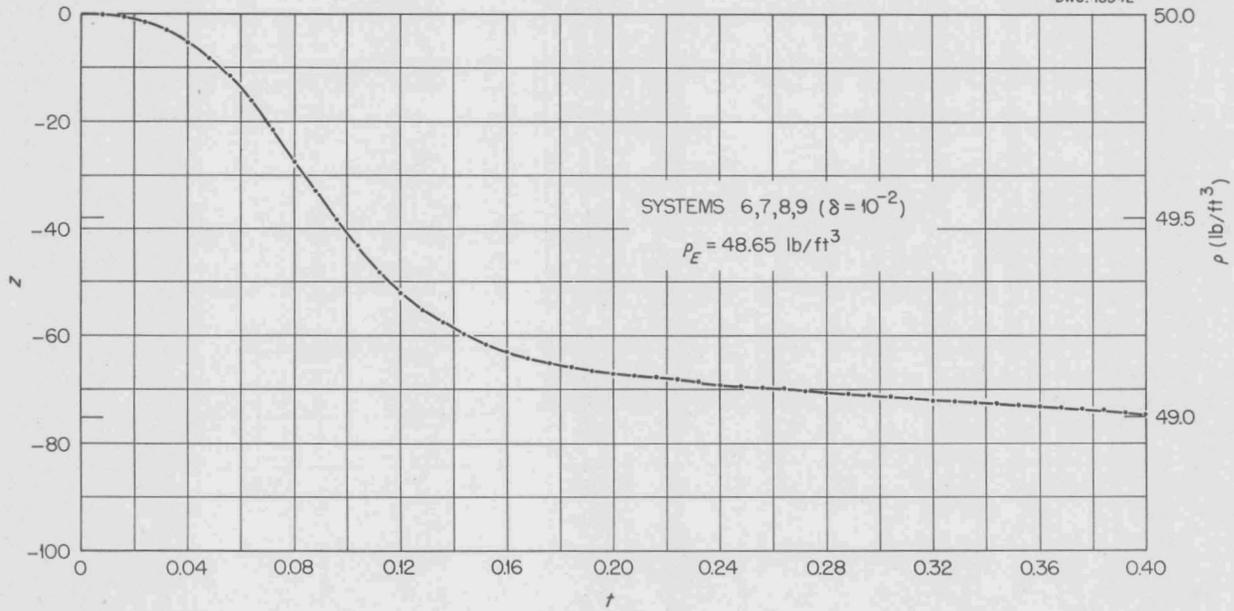


Fig. 19. Density as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients.

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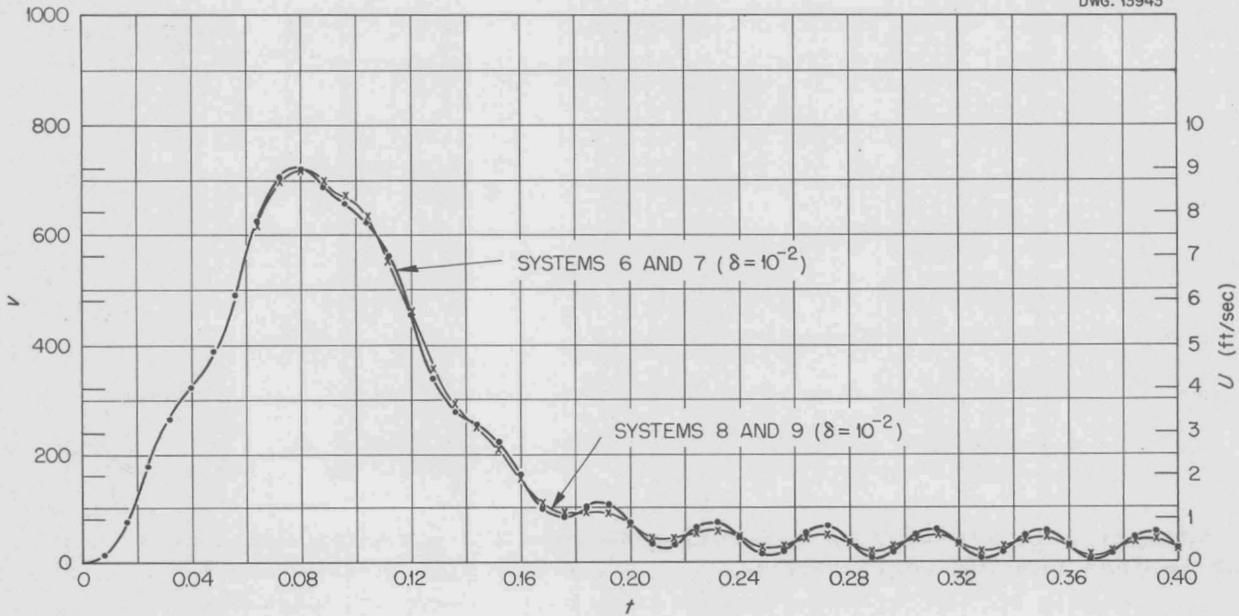


Fig. 20. Velocity as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients.

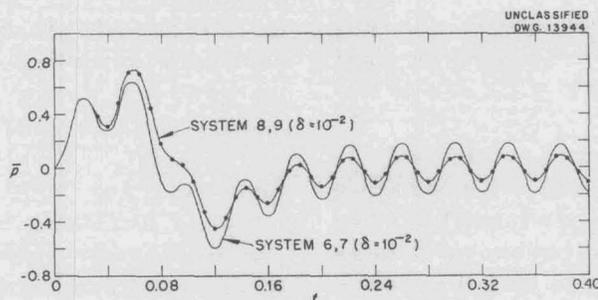


Fig. 21. Pressure as a Function of Time for a δ Step Function of 0.01 for Various Damping Coefficients.

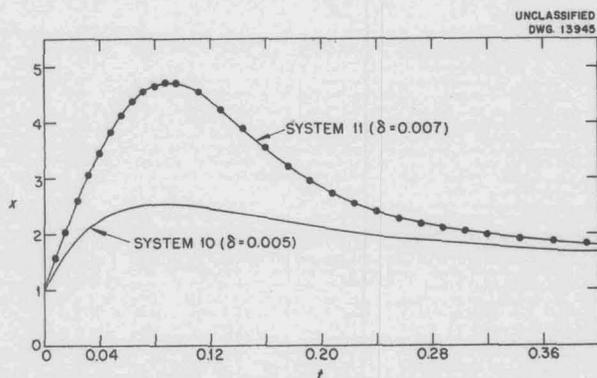


Fig. 22. Power as a Function of Time with δ Step Functions of 0.005 and 0.007.

It is apparent that such first approximations can be useful only for the early rise in x before the z has any importance. A second and better approximation can be obtained by substituting x_1 and z_1 into the right-hand side of Eq. 8 and then integrating to obtain x_2 . By using Eqs. 6, 7, and

$$\dot{v} = \omega_H^2(z + \omega_n^2 y),$$

second approximation formulas can be derived for y , z , v and $\bar{p} = z + \omega_n^2 y$. The formulas for x_2 , y_2 and z_2 take the forms:

$$x_2 = f_1 + f_2 t + f_3 t^2 + f_5 l^{\psi t} + f_6 l^{2\psi t} + f_7 t l^{\psi t},$$

$$y_2 = a_1 + a_2 t + a_3 t^2 + a_4 t^3 + a_5 l^{\psi t} + a_6 l^{2\psi t} + a_7 t l^{\psi t},$$

$$z_2 = c_1 + c_2 t + c_3 t^2 + c_4 t^3 + c_5 l^{\psi t} + c_6 l^{2\psi t} + c_7 t l^{\psi t} + c_8 \cos \omega_H t + c_9 \sin \omega_H t,$$

where the f , a and c are constants that depend on the parameters.

The formulas for x , y , z , and v and p have been evaluated by using the

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constants that were used with SEAC computations. The formulas with subscript 1 lead to numbers that are close to the SEAC numbers only during the time from the beginning of the x rise to about half the total x rise. The formulas with subscript 2 lead to numbers which are close to the SEAC numbers during the time from the

beginning of the x rise to slightly beyond the maximum x rise. This time proves to be long enough to also obtain maximum \bar{p} values. The SEAC results and the formula results are compared in an over-all fashion in Figs. 23 and 24.

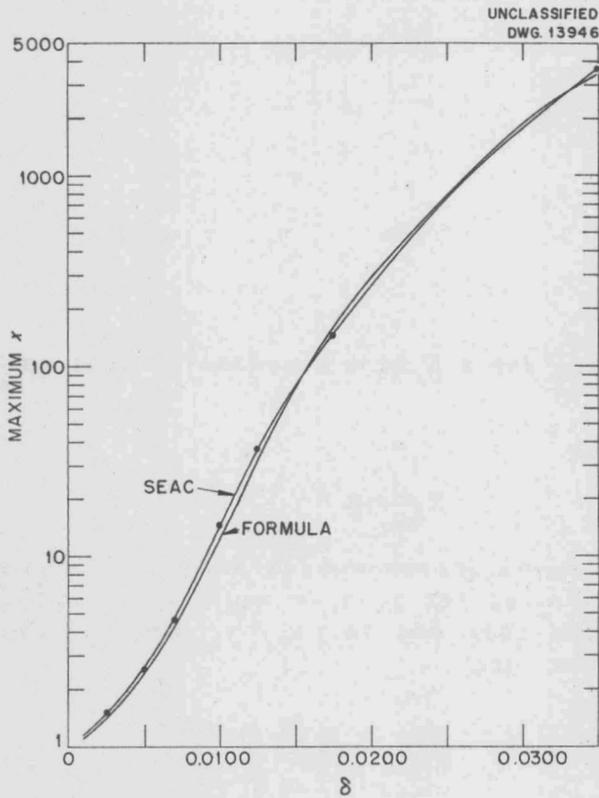


Fig. 23. Power vs. δ Step Functions.

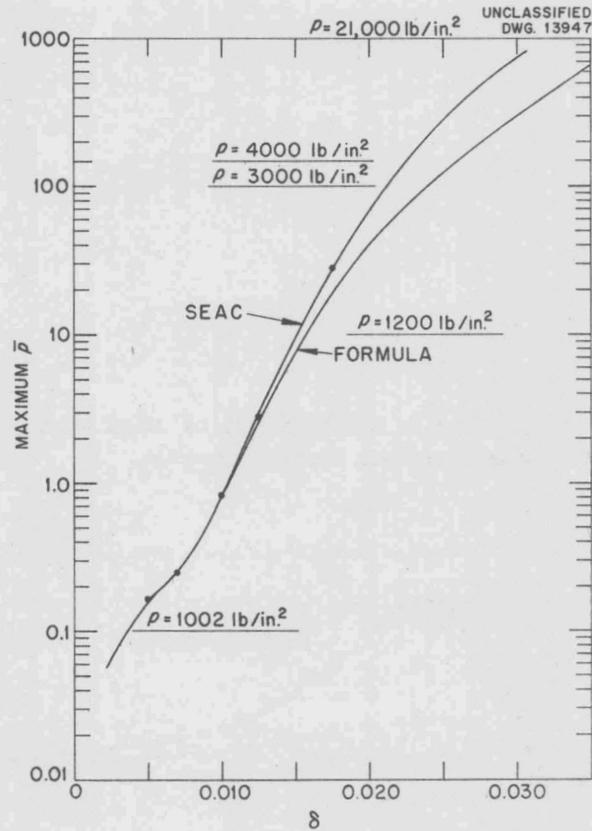


Fig. 24. Pressure vs. δ Step Functions.

TABLE OF CONSTANTS AND VARIABLES

P = power level of reactor, kw	$z = \frac{1}{\tau} \left[\frac{\partial k}{\partial \rho} \right] (\rho - \rho_0)$
P_0 = initial (and equilibrium) power level, 1000 kw	δ = step change in reactivity
$x = P/P_0$	p = pressure in core, lb/in. ²
T = temperature, °C	p_0 = initial pressure, 1000 lb/in. ²
T_0 = initial temperature, 240°C	V = volume of core
T_E = equilibrium temperature	A = area of relief pipe opening to pressurizer
S = reciprocal heat capacity, °C/kw·sec	v_s = velocity of sound in core
$y = \frac{1}{sP_0} (T - T_0)$	M = mass of coolant in core
$a = \frac{\partial k}{\partial T} =$ temperature coefficient of reactivity, 10 ⁻³ /°C	M_r = mass of coolant in relief pipe
τ = lifetime of prompt neutrons, 10 ⁻⁴ sec	$\omega_H^2 = \frac{A\rho_0}{VM} v_s^2, 2.5 \times 10^4$
$\omega_n^2 = \frac{aSP_0}{\tau}$	B, E = constants determined by pipe flow losses
β = bulk or average fraction of delay neutrons, 0.0075	U = velocity of fluid in relief pipe
λ = delay constant for assumed single group of delayed neutron emitters, 0.08	$v = \frac{1}{\tau} \left[\frac{\partial k}{\partial \rho} \right] \frac{AP_0}{V} U$
C = lumped concentration of delayed neutron emitter	$\alpha_1 = \frac{B}{M}$
k = material multiplication constant	$\alpha_2 = \frac{E}{M} \frac{A\rho_0}{\tau V} \left[\frac{\partial k}{\partial \rho} \right]^{-1}$
ρ = density of core fluid, lb/ft ³	$\bar{p} = z + \omega_n^2 y = \frac{1}{\tau v_s^2} \left[\frac{\partial k}{\partial \rho} \right] \cdot (\rho - \rho_0)$
ρ_0 = initial density, 50 lb/ft ³	$\psi = \frac{\delta - \beta}{\tau}$
ρ_E = equilibrium density	L = length of pressurizer pipe
$(\partial k / \partial \rho)$ = density coefficient of reactivity, ft ³ /lb, 0.0074	



**MODIFICATION OF THE PRESSURIZER DESIGN
TO ELIMINATE MECHANICAL INSTABILITY**

R. E. Aven and G. T. Trammell

It has been pointed out previously⁽⁴⁾ that at zero power the core vessel plus the pressurizer constitute a system in which damped density oscillation in the core can occur. The core density satisfies the following equation:

$$\ddot{\rho} + K\dot{\rho} + \omega_H^2\rho = 0 \quad (1)$$

where ω_H is the frequency of the resonator and K is the damping coefficient due to fluid friction. However, if the HRE is operating at power, the reactivity variation associated with the density oscillation has the effect of introducing an antidamping term in the above motion with coefficient

$$K' = \frac{\beta \omega_n^2}{\tau \omega_H^2},$$

and unless $K > K'$ the density oscillations will build up to a limiting amplitude that may be troublesome.

Some modifications have been made in the pressurizer design that will insure that $K > K'$. The pressurizer and the main outlet pipe have been made common up to the turn-off of the main flow line to the heat exchanger. By this procedure, the "eddy viscosity" associated with the turbulent main flow greatly increases the damping of the pressurizer flow compared with that possible with laminar flow. In addition, a damper in the form of a perforated cylinder has been inserted

(4)R. E. Aven, "Fluid Friction Coefficients in the Pressurizer Tube and Their Effects on the Reactivity of the Core Materials," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 107.

in this common flow line to further increase the pressurizer damping. These modifications do not increase the friction losses of the main circulating flow or adversely affect the ability of the pressurizer to limit large power and pressure excursions.

Under these conditions, it is easy to show that

$$K = \frac{2S \int_0^{L'} \frac{F(x) dx}{A^2(x)}}{\rho \int_0^L \frac{dx}{A(x)}} \quad (2)$$

where

S = main flow rate (volume per unit time)

x = distance along pressurizer pipe, measured from core edge

L' = distance from core edge to turn-off of main flow

L = distance from core edge to liquid surface in pressurizer

$A(x)$ = cross-sectional area of pipe at position x

ρ = fuel density

The quantity $F(x)$ is defined by

$$\frac{\partial p}{\partial x} = -F(x) U^2(x), \quad (3)$$

where $\partial p/\partial x$ is the pressure gradient at x and $U(x)$ is the mean fluid velocity at x . It has been assumed in obtaining Eq. 2 that for small high-frequency variations of fluid velocity about some mean value the friction factor does not change, but that the factor in the pressure drop, ρv^2 , actually changes instantaneously as

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v changes. An explicit expression for $F(x)$ is

$$F = \frac{\rho f}{2L}, \quad (4)$$

where f is the usual friction factor and L is the equivalent diameter.

For the calculation of K' , the following quantities are needed:

$$\omega_H^2 = \frac{c^2}{V \int_0^L \frac{a x}{A}} V = \text{core volume,}$$

where c^2 = squared sound speed in fuel,

β = fraction of delayed neutrons,

τ = prompt generation time,

ω_N^2 = rate of decrease of prompt-rise rate when heat removal is discontinued.

For the purpose of calculation, the pressurizer tube has been divided into the following ten sections:

1. Entrance region from the core to the pressurizer pipe.
2. Angular area between the pressurizer pipe and the gas-pipe nose.
3. Vaned section of the vaned nose.
4. Lower 1 3/4-in.-tube section.
5. Lower supporting-web section.
6. Middle 1 3/4-in.-tube section.
7. Upper supporting-web section.
8. Upper 1 3/4-in.-tube section.
9. Section of pipe including the gas-pipe take-off and the 1 1/2-in.-elbow fuel outlet
10. Pressurizer tube from section 9 to the pressurizer.

The following table shows the dimensions of these sections:

TABLE 9

Dimensions of Pressurizer Tube Sections

SECTION	A (ft ²)	LENGTH (ft)	D _e (ft)	f
1	0.0179	0.0834	0.0606	0.0255
2	0.0262	0.0834	0.0834	0.0233
3	0.0412	0.279	0.112	0.0218
4	0.0425	1.26	0.0974	0.0225
5	0.0386	0.115	0.098	0.0225
6	0.0425	1.72	0.0974	0.0225
7	0.0386	0.115	0.098	0.0225
8	0.0425	0.333	0.0974	0.0185
9	0.0252	0.188		
10	0.0459	1.73		
Average Area	0.03555			

The following results were obtained:

$$K' = \frac{\beta \omega_N^2}{\tau \omega_H^2} = \frac{75}{0.84} \cdot \frac{(48)V}{c^2} \int_0^L \frac{dx}{A},$$

where

V = volume of the reactor core, 1.767 ft³,

c^2 = velocity of sound in the fluid, 10,670,000 ft²/sec,

$$\int_0^L \frac{dx}{A} = \sum_{i=1}^{10} \frac{L_i}{A_i} = 144 \text{ ft}^{-1}.$$

Thus

$$K' = 0.102, \quad (5)$$

$$K = \frac{2S \int_0^{L'} \frac{F(x)}{A^2} dx}{\rho \int_0^L \frac{dx}{A}}$$

where $S = 0.2228 \text{ ft}^3/\text{sec}$ (100 gpm),

$$\frac{S}{\rho} \int_0^{L'} \frac{F(x)}{A^2} ds = \frac{S}{\rho} \sum_{i=1}^8 \frac{f_i L_i \rho}{2D_i A_i^2} = 69.8,$$

$$K = 0.972. \quad (6)$$

These calculations show the damping to be well above the amount needed to counteract the effects of the anti-damping.

CRITICALITY CALCULATIONS FOR HOMOGENEOUS REACTORS

L. C. Biedenharn and P. M. Wood

The reactivity calculations reported previously⁽⁵⁾ and in other sections of this report were based on the following approximate formula, which is derived in LA-524.⁽⁶⁾

$$K_{eff} = \eta p f \cdot \frac{1}{\nu_1 \nu_2} [1 + \nu_2 p_{12} (\nu_1 - 1)]$$

$$\nu_2 p_{12} = \frac{\nu_x + \nu_2}{\nu_x^{-1}} \cdot \frac{1}{1 - \frac{\Sigma L_0^2}{\tau}}$$

Here ν_1 and ν_2 are eigenvalues of one-velocity critical systems or, more precisely, the number of neutrons required to be emitted per absorption in the core to achieve criticality; the subscripts 1 and 2 refer to fast and slow groups, respectively. The constants for group one are taken to be the same for reflector and core (if both are at the same temperature) and are completely specified for our purposes by the Fermi age-in-water τ . For group two the transport mean free path is assumed to be the same for core and reflector, and it is essentially that of water. The thermal cross sections of the core and reflector then serve to determine ν . The quantity ν_x is the eigenvalue of a one-velocity critical problem, with core constants of group two and reflector absorption adjusted to match the diffusion length to that of group one. Aside from Σ , which is the macroscopic reflector absorption cross

(5) T. A. Welton, H. T. Williams, L. H. Thacker, P. M. Wood, "Criticality Calculations," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 84.

(6) R. P. Feynman and T. M. Welton, *Calculations of Critical Masses Including the Effect of the Distribution of Neutron Energies*, LA-524 (Jan. 21, 1947).

HRP QUARTERLY PROGRESS REPORT

section for group two, the other constants have their usual significance. In the terminology of LA-524,⁽⁶⁾ this equation represents the first lower two-group approximation; the lower here refers to a lower bound criticality in the limit of zero inelastic scattering.

To get some estimate of the accuracy of this approximation for water-moderated systems, the critical concentration of 93.4% enriched uranium (in the form of uranyl sulfate) in a spherical water-moderated infinite-water-reflected reactor at 20°C has been calculated by this and other methods and the results compared. The other methods employed were: the upper two-group approximation, the two-group diffusion theory, and the method of Greuling.⁽⁷⁾ In addition, various three-group approximations (extensions of the techniques of LA-524⁽⁶⁾) were used, but the resulting increase of accuracy did not compensate for the much larger effort required. Greuling's method is the most accurate of all the methods (particularly for the low uranium concentrations of interest here) and was regarded as the standard of accuracy. The value of τ for the other two methods was, in fact, taken to be the mean square slowing-down distance given by Greuling's three-group slowing-down kernel.

The results are presented in Fig. 25. It can be concluded from this work that the approximate formula given here was of sufficient accuracy for the previous calculations⁽⁵⁾ and is the best simple approximation to use. Although the excellent agreement of the results of this method with the results of Greuling's method is to some extent the result of a cancellation of errors, it seems reasonable

⁽⁷⁾E. Greuling, *Theory of Water-Tamped Water Boiler*, LA-399 (Sept. 27, 1945).

to expect that this cancellation may persist for other similar systems. The errors are, in any event, small compared with the inaccuracies of the constants.

EFFECT OF CIRCULATION ON THE IN-OUR RELATION FOR THE HRE

R. E. Aven

If $U(\lambda_i)$ is defined as the ratio of delayed-neutron reactivity contribution of the i^{th} group in a circulating-fuel reactor to its contribution in a static-fuel type, then $U(\lambda_i)$ is given by

$$U(\lambda_i) = 1 - \frac{e^{\lambda_i t_2} - 1}{\lambda_i t_1} \cdot \frac{\int_0^\infty F(s) (1 - e^{-\lambda_i s}) ds}{e^{\lambda_i t_2} - \int_0^\infty f(s) e^{-\lambda_i s} ds} \quad (1)$$

where

t_1 = residence time in reactor,

t_2 = residence time in outside loop,

λ_i = natural-decay constant of the i^{th} delayed-neutron group,

$F(s) ds$ = probability that the residence time, s , of a particle is in the range ds .

In deriving the equation for $U(\lambda_i)$, the following assumptions have been made: (1) uniform activation inside core and zero activation in outside loop, and (2) uniform effect of emitted neutrons inside core and zero effect of emitted neutrons in outside loop.

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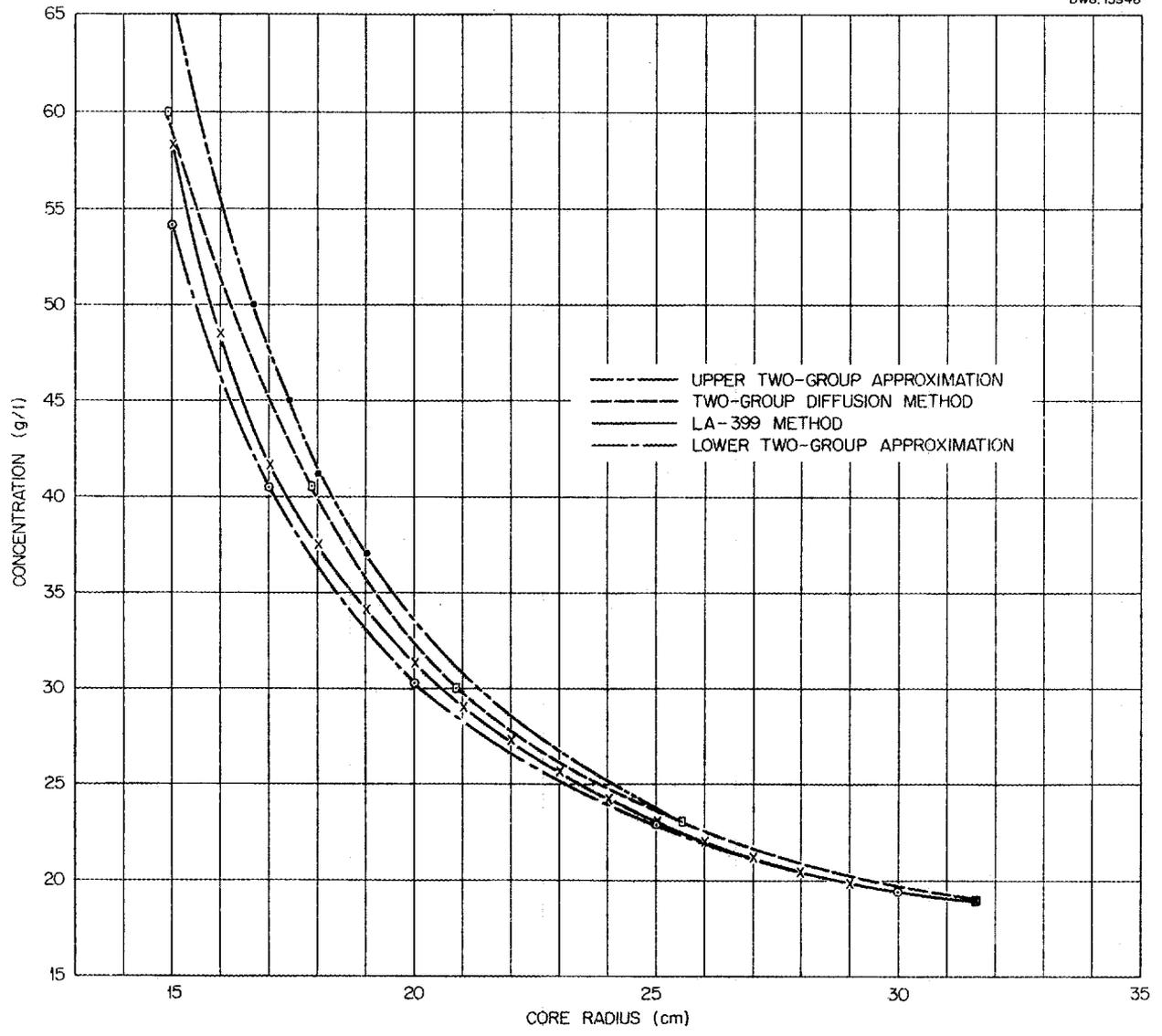


Fig. 25. Uranium Concentrations Required for Criticality as a Function of Core Radius. H₂O core, infinite H₂O reflector, 20°C, 93.4% enriched uranium.

Let

$$\dot{C}_i + \lambda_i C_i = N, \quad (2)$$

- N = number of fragments per second being produced per unit volume,
- V = core volume,
- v = rate of flow,
- C_i = number of fragments per unit volume at inlet with decay constant λ_i.

and

$$\left\{ e^{\lambda_i t_2} - \int_0^{\infty} [F(s)] e^{-\lambda_i s} ds \right\} C_i = N \int_0^{\infty} F(s) ds \left[\int_0^s e^{-\lambda_i (s-s')} ds' \right],$$

then

HRP QUARTERLY PROGRESS REPORT

where s' = time a particle spends in the reactor, and

$$\int_0^s e^{-\lambda_i(s-s')} ds' = \frac{1 - e^{-\lambda_i s}}{\lambda_i} .$$

Solving for C_i ,

$$C_i = \frac{N \int_0^\infty [F(s)] (1 - e^{-\lambda_i s}) ds}{\lambda_i e^{\lambda_i t_2} - \int_0^\infty F(s) e^{-\lambda_i s} ds} .$$

The total production of fragments is NV per second, which is also equal to the total decay per second. The decay per second outside the core is

$$C_i e^{\lambda_i t_2} \nu (1 - e^{-\lambda_i t_2}) \\ \equiv \frac{C_i V}{t_i} (e^{\lambda_i t_2} - 1) .$$

If $U(\lambda_i)$ is defined as the ratio of the decay rate inside the core to the total decay rate, then

$$U(\lambda_i) = \frac{NV - \frac{C_i V}{t_i} (e^{\lambda_i t_2} - 1)}{NV} \\ = 1 - \frac{C_i}{N} \cdot \frac{e^{\lambda_i t_2} - 1}{t_i} ,$$

but

$$\frac{C_i}{N} = \frac{\int_0^\infty F(s) (1 - e^{-\lambda_i s}) ds}{\lambda_i e^{\lambda_i t_2} - \int_0^\infty F(s) e^{-\lambda_i s} ds} .$$

Therefore,

$$U(\lambda_i) = 1 - \frac{e^{\lambda_i t_2} - 1}{\lambda_i t_1} \\ \frac{\int_0^\infty F(s) (1 - e^{-\lambda_i s}) ds}{e^{\lambda_i t_2} - \int_0^\infty F(s) e^{-\lambda_i s} ds} . \quad (1)$$

If complete mixing is assumed, then

$$F(s) = \frac{1}{t_1} e^{-s/t_1} .$$

By substituting for $F(s)$ in Eq. 1 and solving for $U(\lambda_i)$, the following equation is obtained:

$$U(\lambda_i) = 1 - \frac{1 - e^{-B\lambda_i t_1}}{1 + \lambda_i t_1 - e^{-B\lambda_i t_1}} \quad (3)$$

where $B = t_2/t_1 = 0.29$ for the homogeneous reactor. If slug flow is assumed then

$$F(s) = \delta(s - t_1) .$$

J. M. Stein and E. R. Mann have shown that for slug flow the equation for $U(\lambda_i)$ is

$$U(\lambda_i) = 1$$

$$+ \frac{e^{-\lambda_i t_1} - 1}{\lambda_i t_1} \left[\frac{e^{B\lambda_i t_1} - 1}{e^{B\lambda_i t_1} - e^{-\lambda_i t_1}} \right] . \quad (4)$$

Equations 3 and 4 are plotted for $B = 0.29$, with $U(\lambda_i)$ as ordinate and $\lambda_i t_1$ as abscissa (Fig. 26).

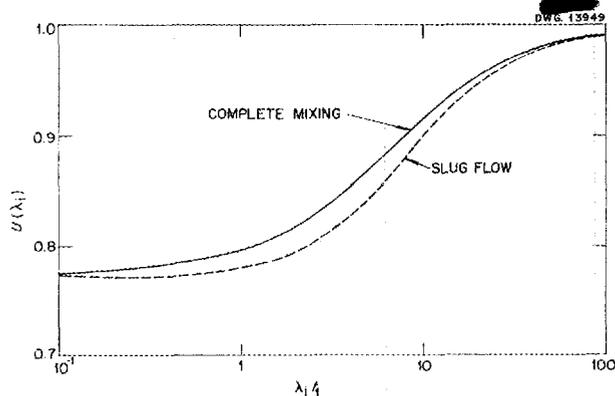


Fig. 26. Ratio of Decay Rate in Core to Total Decay Without Circulation.

Residence time in the reactor may be calculated from the relation

$$t_1 = \frac{V}{v'} \quad (5)$$

where V = volume of core, ft^3 ,

v' = rate of flow, ft^3/sec .

Table 10 gives residence times for various rates of flow.

TABLE 10
Residence Time in the Reactor vs. Rate of Flow

RATE OF FLOW (gpm)	RESIDENCE TIME (sec)
130	6.09
100	7.93
80	9.92
60	13.22
40	19.83
30	26.44
10	79.30
5	158.7
0	∞

By determining the value of $\lambda_i t_1$, the corresponding value of $U(\lambda_i)$ may be read from Fig. 26. The product of $U(\lambda_i)$ and the percentage of delayed-neutron reactivity contribution of the static fuel gives the percentage of delayed-neutron reactivity contribution for the i^{th} group. The sum of the contributions from all delayed-neutron groups gives the total reactivity contribution at the corresponding flow rate. These values are tabulated in Table 11 for a flow rate

TABLE 11

Total Reactivity Contribution of Delayed-Neutron Groups at a Flow Rate of 100 gpm

λ_i (sec^{-1})	$\lambda_i t_1$ $t_1 = 7.93 \text{ sec}$	$U(\lambda_i)$	REACTIVITY CONTRIBUTION FROM STATIC FUEL (%)	REACTIVITY CONTRIBUTION FROM CIRCULATING FUEL (%)
14.0	111.1	0.990	0.0283	0.0280
1.61	12.8	0.930	0.0963	0.0896
0.456	3.62	0.846	0.2730	0.2310
0.154	1.22	0.802	0.2411	0.1934
0.0315	0.250	0.780	0.1880	0.1466
0.0122	0.097	0.776	0.0283	0.0219
Total			0.8550*	0.7105

*The value of $\beta = 0.855\%$ is based on the delayed neutron activity of the water boiler.

HRP QUARTERLY PROGRESS REPORT

of 100 gpm. In Table 12 are listed the delayed-neutron contributions for various flow rates, and Fig. 27 shows this graphically. Tables 11 and 12 give values calculated with complete mixing assumed.

The assumption of complete mixing is probably the best simple assumption to make, but for purposes of comparison the calculated values for the

TABLE 12

Delayed-Neutron Contributions at Various Flow Rates

RATE OF FLOW (gpm)	TOTAL REACTIVITY CONTRIBUTION OF DELAYED NEUTRONS (%)
130	0.7020
100	0.7105
80	0.7169
60	0.7261
40	0.7409
20	0.7678
10	0.7899
5	0.8114
0	0.855

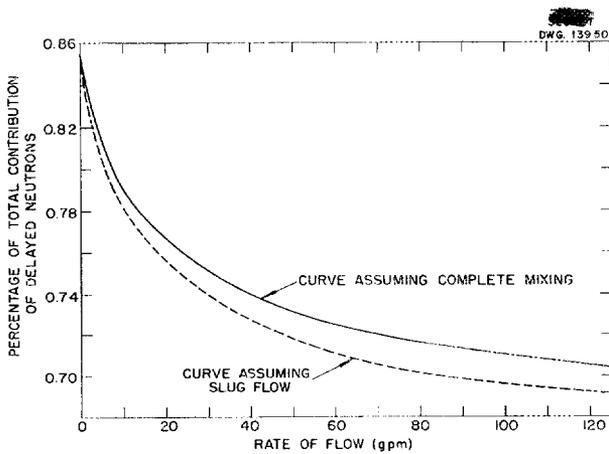


Fig. 27. Percentage of Total Contribution of Delayed Neutrons as a Function of Flow Rate.

percentage contribution of the delayed neutrons, assuming slug flow, are also plotted on Fig. 27.

The equation for the excess reactivity of the system, δ , in terms of rise rate p may be derived by a slight extension of the previous derivation.

$$\delta = \tau p + \beta - \sum_i \beta_i \lambda_i t_1 \left[\frac{1}{1 + (p + \lambda_i) t_1 - e^{-B(p + \lambda_i) t_1}} \right], \quad (6)$$

where τ = prompt generation time,
 β = total fraction of delayed neutrons (assumed equal to 0.00855),
 $p = 1/T$ where T = period of the reactor.

For various values of p the excess reactivity has been calculated and plotted (Table 13 and Figs. 28 and 29).

The rate of change of reactivity at criticality (i.e., $p = 0$) is given by the equation:

$$\delta'(0) = \tau + \sum_i \frac{\beta_i}{\lambda_i} - \sum_i \frac{\beta_i \Delta_i}{\lambda_i} + \sum_i \beta_i \Delta_i t_1 \left\{ \frac{B}{1 - e^{-B\lambda_i t_1}} - \frac{1}{1 + \lambda_i t_1} - \frac{B + \frac{e^{-B\lambda_i t_1}}{(1 + \lambda_i t_1)^2}}{\frac{e^{-B\lambda_i t_1}}{1 + \lambda_i t_1}} \right\}$$

TABLE 13

Excess Reactivity as a Function of the Reciprocal of the Reactor Period

ρ	δ FOR 0-gpm FLOW	δ FOR 60-gpm FLOW	δ FOR 100-gpm FLOW
0 (criticality)	0	0.00127	0.00145
0.01	0.00079	0.00190	0.00206
0.02	0.00131	0.00230	0.00246
0.04	0.00201	0.00285	0.00301
0.06	0.00250	0.00324	0.00339
0.08	0.00288	0.00354	0.00369
0.10	0.00319	0.00378	0.00393
1	0.00654		0.00668
10	0.00893		0.00893
100	0.01688		0.01688

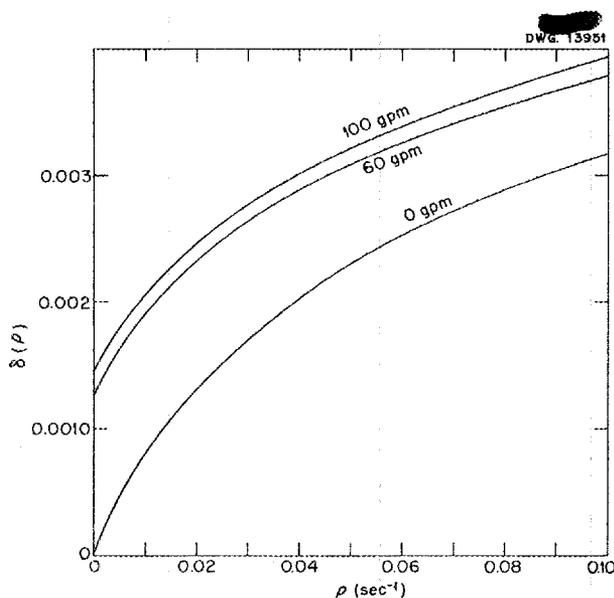


Fig. 28. Excess Reactivity.

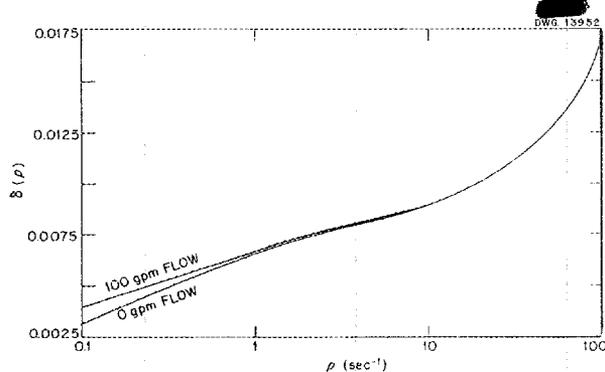


Fig. 29. Excess Reactivity.

TABLE 14

Rate of Change of Reactivity at Criticality as a Function of Flow Rate

FLOW RATE (gpm)	$\delta'(0)$
130	0.0815
100	0.0816
80	0.0816
60	0.0817
30	0.0823
5	0.0867
0	0.1052

where $\Delta = 1 - U(\lambda)$. Values for $\delta'(0)$ are given for various flow rates in Table 14, and Fig. 30 shows a plot of $\delta'(0)$ vs. flow rate.

HRP QUARTERLY PROGRESS REPORT

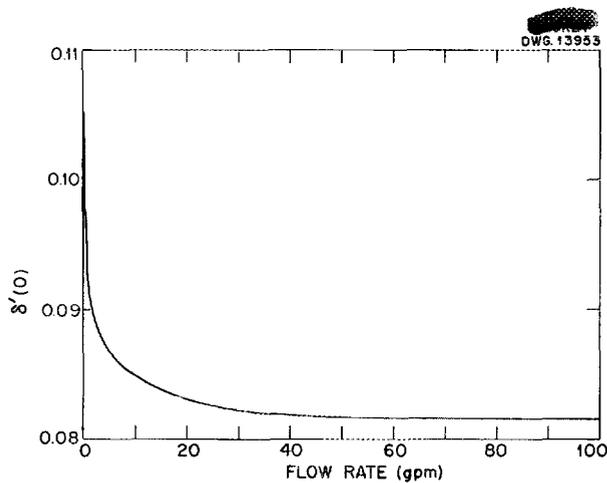


Fig. 30. Rate of Change of Reactivity at Criticality.

NUCLEAR CONSTANTS FOR THE HRE

H. T. Williams

It seemed desirable to recalculate the "nuclear constants" that are useful in the work on the kinetics of the HRE in order to assign the "best possible" values and estimate the limits of error. Since it appears probable that the HRE will eventually be operated with a natural-water reflector, the quantities of interest were calculated for that case also.

The approximate method described in LA-524⁽⁶⁾ was used for the solution of the two-group problem.

In estimating the limits of error the following facts were considered:

1. Two-group theory is not strictly valid for an H_2O - D_2O system; the size of the error is uncertain. The error arising from this factor is probably of the same order as that resulting from the uncertainty in the ratio of the fast-diffusion constants for heavy and natural water. (For the purpose of estimating errors, this ratio was allowed to range from 0.5 to 1.5.)

2. Certain of the two-group constants and nuclear constants used in the calculations are not known with sufficient accuracy. For example, a 1.4% error in η (number of neutrons produced per neutron absorbed in fuel) changes the critical concentrations by about 3 grams per liter. These uncertainties in fuel concentrations in turn affect the other constants to be calculated.

3. No clean-cut, accurate method is known for determining the over-all effect of the steel core tank. All the constants calculated were found to be quite sensitive to the various types of boundary conditions that were tried at the core-reflector interface.

In tabulating the results, the conditions for which the calculation was made appear on the right. The notation is as follows:

C = fuel concentration, grams of uranium per kilogram of H_2O ,

K = effective multiplication constant of reactor ($K = 1$ for criticality),

T = average temperature in core, $^{\circ}C$,

T_R = average temperature in reflector, $^{\circ}C$,

ρ = average density of H_2O in core, g/cm^3 ,

τ = prompt generation time, sec.

Operation with D_2O Reflector

Amount of excess reactivity needed to overcome the poisoning effect of the steel core vessel:

$$\frac{\Delta K}{K} = (4.5 \pm 1.5)\%$$

$$T = 230^{\circ}C$$

$$T_R = 164^{\circ}C.$$

Critical concentration:

C (Critical) = 43.0 ± 6.1 g of U per kg of H_2O

= 35.4 ± 5 g of U per liter of H_2O

$T = 230^\circ C$

$T_R = 164^\circ C$.

Density coefficient of reactivity at constant temperature, averaged from $\rho = 0.823$ to $\rho = 0.883$:

$$\left(\frac{\partial K}{\partial \rho}\right)_T = 0.65 \pm 0.07 \text{ cm}^3/\text{g}$$

$T = 230^\circ C$

$T_R = 164^\circ C$

$C = 43$ g/kg.

Temperature coefficient of reactivity at constant density, averaged from $T = 230^\circ C$ to $T = 180^\circ C$:

$$\left(\frac{\partial K}{\partial T}\right)_\rho = -(7.7 \pm 0.83) \times 10^{-5} \text{ }^\circ C^{-1}$$

$T_R = 164^\circ C$

$C = 43$ g/kg.

Prompt neutron generation time:

$$\tau = (7.0 \pm 0.7) \times 10^{-5} \text{ sec}$$

$T = 230^\circ C$

$T_R = 164^\circ C$

$C = 43$ g/kg.

Amount of reactivity controlled by the reflector (or reactivity change made by dumping reflector at operating temperature):

$$\frac{\Delta K}{K} = (24.5 \pm 3)\%$$

$T = 230^\circ C$

$T_R = 164^\circ$

$C = 43$ g/kg.

Reflector temperature coefficient of reactivity at constant core temperature, averaged from $T_R = 164^\circ C$ to $T_R = 100^\circ C$:

$$\left(\frac{\partial K}{\partial T_R}\right)_T = -(1.4 \pm 0.5) \times 10^{-4} \text{ }^\circ C^{-1}$$

$T = 230^\circ C$

$C = 39.4$ g/kg.

or

$\Delta(\text{Critical mass})$

$$\frac{\Delta T_R}{\Delta K} = 0.84 \pm 0.30 \text{ g of U per } ^\circ C.$$

Operation with H_2O Reflector

Amount of excess reactivity needed to overcome the poisoning effect of the steel core vessel:

$$\frac{\Delta K}{K} = (5 \pm 1)\%$$

$T = 230^\circ C$

$T_R = 164^\circ C$.

Critical concentrations:

C (Critical) = 34.1 ± 2.7 g of U per kg of H_2O

$T = 20^\circ C$

$T_R = 20^\circ C$.

C (Critical) = 54.2 ± 4.3 g of U per kg of H_2O

$T = 230^\circ C$

$T_R = 164^\circ C$.

Density coefficient of reactivity at constant temperature, averaged from $\rho = 0.854$ to $\rho = 0.794$:

$$\left(\frac{\partial K}{\partial \rho}\right)_T = 0.81 \text{ cm}^3/\text{g}$$

$T = 250^\circ C$

(No estimate of error)

$T_R = 175^\circ C$

$C = 59.8$ g/kg.

HRP QUARTERLY PROGRESS REPORT

Temperature coefficient of reactivity at constant density, averaged from $T = 250^\circ\text{C}$ to $T = 260^\circ\text{C}$:

$$\left[\frac{\partial K}{\partial T} \right]_{\rho} = 5.3 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$$

$$T_R = 175^\circ\text{C}$$
$$C = 59.8 \text{ g/kg.}$$

Prompt-neutron generation time:

$$\tau = (4.97 \pm 0.31) \times 10^{-5} \text{ sec}$$

$$T = 230^\circ\text{C}$$
$$T_R = 164^\circ\text{C}$$
$$C = 54.2 \text{ g/kg.}$$

Amount of reactivity controlled by reflector (reflector dumped at operating temperature):

$$\frac{\Delta K}{K} = (19.3 \pm 2.5)\%$$

$$T = 230^\circ\text{C}$$
$$T_R = 164^\circ\text{C}$$
$$C = 54.2 \text{ g/kg.}$$

EFFECTIVENESS OF HRE CONTROL PLATES

P. M. Wood

The reactivity controlled by the HRE control plates in both heavy and natural water was calculated using ordinary two-group diffusion theory. The method used was the following.

The reactivity of the reactor with 48.73 g of uranium per kg of H_2O and

a heavy-water reflector was calculated (with a reasonable choice of constants) without taking into account the core vessel.

$$K_{eff} = 1.02417$$

The presence of the steel core vessel was found previously to lower the reactivity about 4%. Subtracting this,

$$K_{eff} = 0.98417.$$

The reactivity of the reactor with the core completely surrounded by a shell that absorbs all thermal neutrons but no fast neutrons was calculated letting the fast flux go to zero at the reflector boundary and the thermal flux go to zero at the core boundary.

$$K_{eff} = 0.89632$$
$$\Delta K_{eff} = 0.98417 - 0.89632 = 0.08785.$$

The fraction of the core surface covered by the two control plates is ~ 0.328 . Assuming that the effectiveness of the plates is proportional to the fraction of the core surface area they cover, their effect is $0.328 \times 0.08785 \times 100\% = 2.88\%$ K_{eff} for both plates or 1.44% per plate.

A similar calculation for the natural-water reflected reactor at 52.90 g of uranium per kg of H_2O (42 g/l) gave the result of 1.31% K_{eff} per plate. The results for the two cases are surprisingly close.

CONTROLS

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L. P. Inglis J. E. Owens

E. E. Mason D. Toombs

W. P. Walker

Major emphasis for the quarter has been on adjustment and calibration of instruments for installation in the reactor, but some development work has also been done. Installation of instruments in the HRE is virtually complete and the system is now being checked.

The integrating unit for registering total reactor energy was built and operated satisfactorily. The unit is basically a watt-hour meter with the appropriate proportionality factor to connect the meter reading with reactor power and time. The current coil of the meter is supplied with a constant current from the regulated instrument supply, and the voltage coil is connected to the arm of a potentiometer across the same source. The reactor energy will be obtained from either of two detectors -- one detects the flux level and the other the temperature differential across the heat exchanger. These quantities are recorded on regular strip-chart instruments, and the potentiometers used with the integrators are connected to the balancing motors of the recorders. Thus, the voltage fed to the integrator is proportional to flux or temperature difference, as the case may be, and hence the register of the watt-hour meter will be proportional to flux and time or temperature difference and time (since the flow is constant, this is proportional to power extracted and time).

Since the watt-hour meter runs too slowly at low voltages, a switch is automatically closed and the current

increased when the instrument indicates below 10% of the full scale. An accuracy of 3% is maintained over 98% of the instrument scale, but the integrator fails to operate accurately on the low 2% of the instrument scale.

A series of tests were run to determine the most satisfactory type of thermocouple and installation for use with the reactor, since for efficient operation it is necessary to determine temperatures accurately and quickly. Several different types of thermocouples were installed in a short length of 1-in. stainless steel pipe covered with 1 in. of asbestos insulation. Steam at atmospheric pressure was run through the pipe, and the temperature of the various thermocouples was measured against time. As a reference, a bare thermocouple was inserted into the center of the pipe to give the actual steam temperature.

From this experiment (Fig. 31) it could be seen that the silver-soldered and spot-welded thermocouples gave the fastest determination of temperature. However, this type of thermocouple would be difficult to replace after the reactor had been running. Therefore, the most feasible thermocouple is the special bayonet in a deep well. The deep well for the bayonet is welded so that it projects down the center of the pipe. The special bayonet is a 20-gage iron-constantan thermocouple with fittings to hold it in the well.

The thermocouples must be electrically insulated from the well if two

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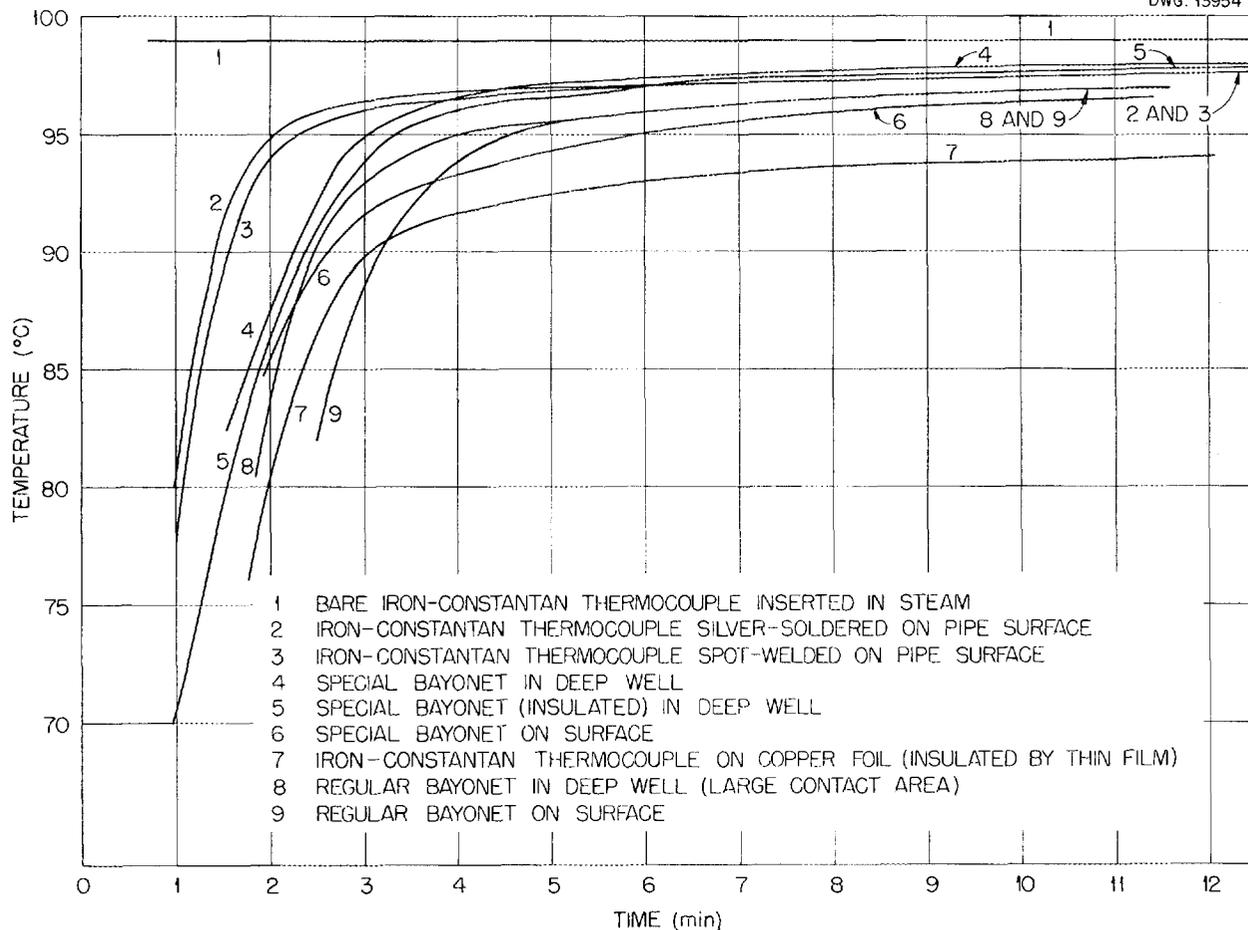


Fig. 31. Thermocouple Transient Response.

thermocouples that buck are used for an instrument. A thin layer of insulating cement on the end of the special bayonet gave good results (Fig. 31).

The oxygen system of the reactor is provided to replace the oxygen in solution that is lost through the let-down system. If the oxygen in solution is 500 ppm by weight and the flow of fuel through the letdown valve is 1½ gal/min, the amount of oxygen to be supplied is 20 cc/min at a working pressure of 1200 psi.

The oxygen flow is controlled by valve 712R, which is controlled by

FRCA-88, and FRCA-88 is actuated by the air output of the differential pressure cell across the capillary (Fig. 32). To ensure a continuous flow of oxygen and at the same time prevent an open path from the hot fuel to the outside of the shield, it is necessary to use two valves, an intermediate oxygen tank for a reservoir, and a single-pole, double-throw pressure switch (PC-86). Under normal flow conditions valve 712A would be closed and the reservoir would have oxygen at about 1300 psi discharging through the capillary tube, at the point where the pressure drop across the capillary is measured by a Foxboro differential pressure cell, to valve 712B, and on

reactor power to building steam, until a safe time interval has elapsed. This time interval is defined as the time required to flush the condenser hot well. On the reverse process, the building condensate return line is closed immediately upon the opening of the reactor steam line.

There is a possibility that pulsafeeder pump stoppage may cause rather violent fluctuations in the vortex as the letdown valve starts letting down pure gas. To prevent this, an interlock has been provided to start the D₂O timer if the fuel pulsafeeder stops while the reactor is operating. Since the fuel circulating pump is a convenient way of determining reactor operation, shutdown is initiated if the pulsafeeder stops while the circulating pump is running. This control

may be transferred to a fuel-flow indicator on the pulsafeeder line if experience shows such an instrument advisable.

For convenience of the operator in flushing out the high-pressure system, a valve has been added in the line from the fuel dump tank to the fuel pulsafeeder. This enables the operator to pump pure water from the condensate weigh tank into the high-pressure system for flushing or rapid dilution.

The separate pulsafeeders previously planned for the reflector system have been replaced by a dual-head unit. These heads operate in the same manner as the two pumps, both pump on initial filling and one cuts out (by means of an oil by-pass valve) when the reflector level is up.

Part II

ALTERNATE SYSTEMS

SOLUTION CHEMISTRY

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R. D. Brown E. V. Jones
H. O. Day K. S. Warren
 H. W. Wright

STABILITY OF PLUTONIUM SULFATE IN URANYL SULFATE SOLUTION

An investigation of the stability of plutonium sulfate in an aqueous solution of 1.26 *M* uranyl sulfate has been conducted over temperatures ranging from 25 to 240°C. A stock solution that contained 0.386 g of plutonium per liter of the concentrated uranyl sulfate was used for all the work to date. The method of preparing this stock solution is given in some detail in the following section.

Preparation of Plutonium Sulfate Stock Solution. A 5-ml aqueous solution that contained 0.132 g of plutonium as the nitrate was received as the end-product of the Hanford purification process. This amount of material was made 4 *M* with respect to nitric acid and extracted twice with 5 ml of TBP solvent.⁽¹⁾ After washing the TBP phase with 10 ml of 4 *M* HNO₃, the plutonium was extracted with 1 *M* H₂SO₄. Heating the resulting acid extract with excess H₂SO₄ served to precipitate Pu(SO₄)₂, and after the liquid was decanted off, the residue was heated to fuming until the solid had assumed a uniform coral-pink color. The solid was taken up in a minimum amount of water, precipitated with 30% H₂O₂, washed, and redissolved in sulfuric acid. The peroxide precipitation was repeated twice, and the precipitate was redissolved each time.

(1) TBP solvent consisted of 15 vol % of tributyl phosphate and 85 vol % of a petroleum fraction designated as AMSCO-123-15 (boiling range 368 to 400°F, American Mineral Spirits Company).

The solid was then precipitated with concentrated sulfuric acid. Careful evaporation to near-dryness of the residue was followed by complete solution in 10 ml of distilled water. This solution was 0.15 *M* in H₂SO₄, as determined by free-acid analysis. One-half milliliter of the solution was added to 9.0 ml of aqueous uranyl sulfate (333.3 g of uranium per liter), and the mixture was diluted to 10.00 milliliters. The resulting plutonium sulfate stock solution contained 461 g of uranyl sulfate and 0.695 g of plutonium sulfate per liter. The resulting free acid in this stock solution, as calculated from the dilution ratio employed, was 0.0075 *M* and the solution could be considered essentially neutral.

Apparatus and Procedure. The heating oven for the small samples of plutonium sulfate—uranyl sulfate stock solution was a cylindrical block of aluminum heated by a Nichrome-ribbon spiral wrapped around the block, with adequate insulation enclosing the unit. A number of 1/8-in. holes were drilled near the center and parallel with the axis of the cylinder for receiving the sealed tubes containing the samples. The sealed tubes were prepared from 3-mm-OD pyrex tubing and were vibrated in a vertical position in the oven by fastening the ends to the armature of a buzzer. Continuous shaking was maintained during a run in this manner, and the desired oven temperature was controlled within ±1°C by means of a thermocouple and a Brown Elektronik.

About 0.03 ml of the stock solution of plutonium—uranyl sulfates was drawn

HRP QUARTERLY PROGRESS REPORT

TABLE 15

Stability of Plutonium Sulfate in 1.26 M Uranyl Sulfate Solution

TEMPERATURE (°C)	TIME OF HEATING (hr)	AMOUNT OF PLUTONIUM REMAINING IN SOLUTION (g/l)		
		SAMPLE 1	SAMPLE 2	AVERAGE
25	not sealed	0.385		0.385
80	18	0.360	0.354	0.357
90	19	0.342	0.302	0.322
110	45	0.030	0.016	0.023
165	96	0.015	0.029	0.022
195	20	0.0048	0.0058	0.0053
240	22	0.0062	0.0077	0.0069

up in a 120-mm length of 3-mm-OD tubing, sealed at the end on both sides of the drop, and inserted in the oven, shaker unit. After equilibrium was established, as determined by experimentally varying the time of heating, the tube was centrifuged and opened. About 80% of the liquid was removed with a medicine dropper; care was taken not to disturb the remainder of the centrifuged solution at the bottom of the tube. A 20- μ l portion of the solution was diluted to 10.0 milliliters. Determination of the plutonium still held in solution was finally made on an aliquot by using standard procedures and counting techniques.

Supplementing the analytical method for stability determinations just described was a direct, visual-observation technique in which a buzzer was used for shaking a single, horizontal, glass tube in an electrically heated, thick-walled, capillary tube. During heating, the use of a telescope permitted continuous visual scanning of the sample for changes in color, the appearance of additional

phases, such as solid particles, and other phenomena by either transmitted or reflected light. The rapidity of the formation of a tan-yellow precipitate could be noted, and this information greatly facilitated subsequent work with the cylindrical aluminum heater.

Results. Work with a stock solution that contained 0.386 g of plutonium ion per liter of a practically neutral uranyl sulfate solution (300 g of uranium per liter) produced the data in Table 15.

These data indicate that in the neighborhood of 100°C over 90% of the plutonium ion originally present in solution is precipitated. The data are in agreement with those obtained by W. E. Tomlin⁽²⁾ at approximately 165 and 250°C with plutonium sulfate prepared by an ion-exchange method.

(2)W. E. Tomlin, "Chemical Processing," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 171.

FISSION-PRODUCT SOLUBILITIES IN URANYL SULFATE SOLUTIONS AT HIGH TEMPERATURES

Lanthanum Sulfate and Yttrium Sulfate. By using the well-known silica-tube synthetic method described previously,⁽³⁾ the work of Lietzke and Stoughton⁽⁴⁾ on the solubilities of lanthanum sulfate and yttrium sulfate in aqueous uranyl sulfate solutions has been extended to higher concentrations of uranyl sulfate.

The solubility data are given in Tables 16 and 17 and are shown along with those of Lietzke and Stoughton

TABLE 16
Solubility of Lanthanum Sulfate in 1.26 M Uranyl Sulfate

TEMPERATURE (°C)	La ₂ (SO ₄) ₃ (wt %)
78	4.39
91 and 149 (Double point)	3.97
148	3.80
150	3.75
150.5	3.70
151	3.60
152	3.46
154	3.25
160	2.69
168	2.30
178	1.85
202	1.22
222	0.88
Two liquid layers at 291°C	0.57

⁽³⁾C. H. Secoy, "The System of Uranyl Sulfate-Water. II. Temperature-Concentration Relationships Above 250°," *J. Am. Chem. Soc.* 72, 3343 (1950).

⁽⁴⁾M. H. Lietzke and R. W. Stoughton, *The Measurement of the Solubility of Fission Product Sulfates at High Temperatures and Pressures*, ORNL-970 (March 13, 1951).

in Figs. 33 and 34. Compiled data at 250°C, including extrapolation values, are given in Table 18.

TABLE 17
Solubility of Yttrium Sulfate in 1.08 and 1.26 M Uranyl Sulfate Solutions

IN 1.08 M UO ₂ SO ₄		IN 1.26 M UO ₂ SO ₄	
TEMPERATURE (°C)	Y ₂ (SO ₄) ₃ (wt %)	TEMPERATURE (°C)	Y ₂ (SO ₄) ₃ (wt %)
208	4.32	212	4.31
215	3.41	221	3.62
217	3.44	224	3.43
230	2.78	231	2.99
245	2.12	237	2.74
(a)	1.43	(b)	2.34
(a)	1.08	(b)	2.14

(a) Two liquid layers at about 277°C. No crystals up to 320°C. Held at 320°C for two hours.

(b) Two liquid layers at about 270°C. No crystals after several hours above 280 to 310°C for 2.14 wt % Y₂(SO₄)₃ solution.

TABLE 18
Comparative Solubilities of Yttrium Sulfate and Lanthanum Sulfate at 250°C

Y ₂ (SO ₄) ₃		La ₂ (SO ₄) ₃	
UO ₂ SO ₄ (M)	SOLUBILITY (wt %)	UO ₂ SO ₄ (M)	SOLUBILITY (wt %)
0.126	0.16	0.126	0.015
1.26	2.34	1.26	0.57

As indicated by the data, lanthanum sulfate and yttrium sulfate show negative temperature coefficients of solubility. These sulfates also have strong tendencies to supersaturate, and the temperatures recorded are those at which the crystals dissolved completely upon very slow cooling.

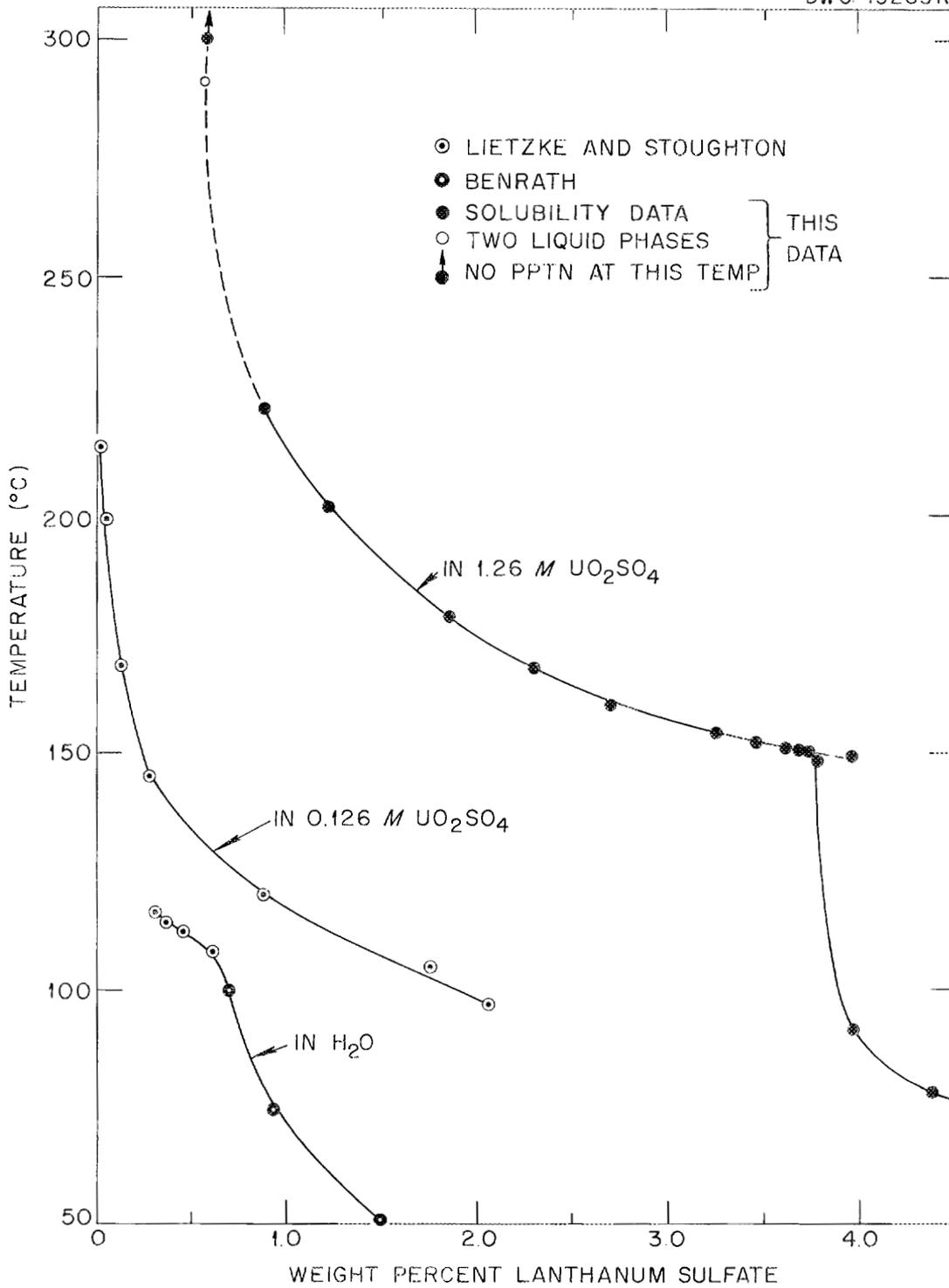


Fig. 33. Solubility of Lanthanum Sulfate in Aqueous Uranyl Sulfate.

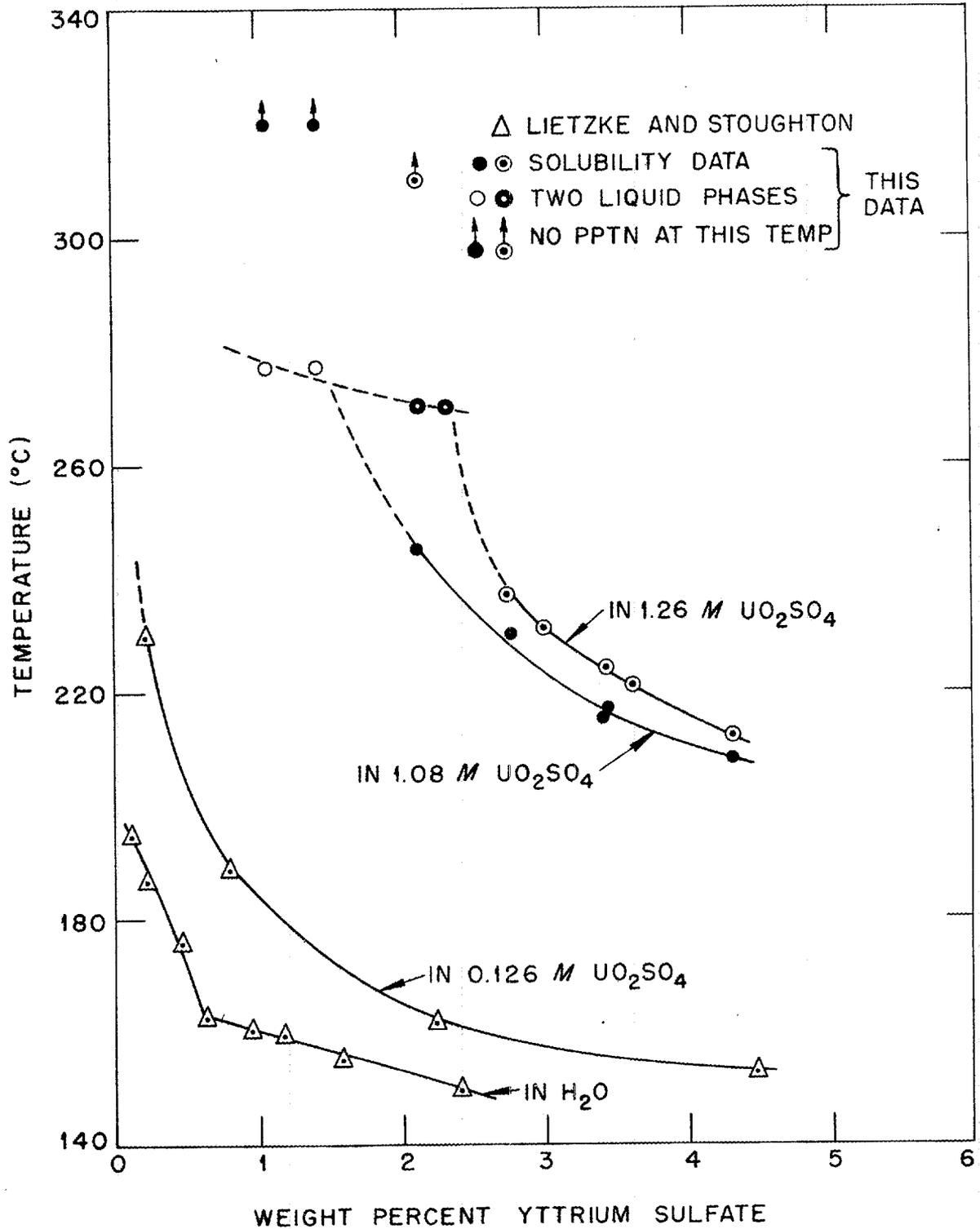


Fig. 34. Solubility of Yttrium Sulfate in Aqueous Uranyl Sulfate.

HRP QUARTERLY PROGRESS REPORT

Cesium Sulfate. The solubility of Cs_2SO_4 in $1.26\text{ M UO}_2\text{SO}_4$ was studied in the same manner. The solubility data are given in Table 19, along with the data of Lietzke and Stoughton for the solubility of Cs_2SO_4 in water,⁽⁴⁾ and Fig. 35. Cesium sulfate shows a positive temperature coefficient of solubility, and the temperatures recorded are those at which the crystals dissolved upon very slow heating. The data show a surprisingly low solubility in $1.26\text{ M UO}_2\text{SO}_4$ in comparison with that in water. At 190°C the solubility is about 196 times greater in water. Possibly there is no complexing of cesium sulfate with uranyl sulfate but compound formation of low solubility.

TABLE 19

Solubility of Cesium Sulfate

IN WATER		IN $1.26\text{ M UO}_2\text{SO}_4$	
TEMPERATURE ($^\circ\text{C}$)	Cs_2SO_4 (wt %)	TEMPERATURE ($^\circ\text{C}$)	Cs_2SO_4 (wt %)
23	63.5	170(?)	0.30
175	71.8	181	0.33
211	73.5	190	0.37
270	75.0	218	0.44
292	75.5	249	0.49
		290	0.54
		Two liquid layers at 293°C , much undissolved	0.78

Ceric Sulfate. Preliminary tests showed that ceric sulfate hydrolyzed rapidly in hot water but was somewhat soluble in $1.26\text{ M UO}_2\text{SO}_4$, with little or no hydrolysis, and showed a negative temperature coefficient of solubility. Further investigation indicated that the solubility is less than 0.014% at room temperature. This low solubility and the negative temperature coefficient of solubility make the silica-tube synthetic method unsuited

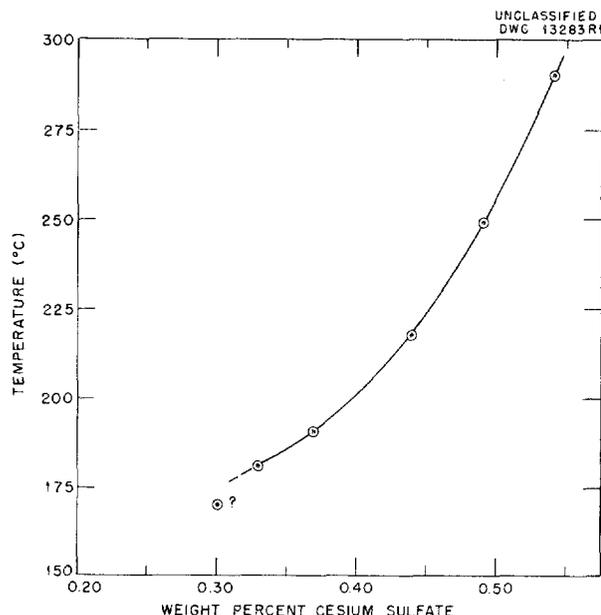


Fig. 35. Solubility of Cesium Sulfate in $1.26\text{ M UO}_2\text{SO}_4$.

for this study, and it was discontinued. This problem will be attacked in the future by using the filter-bomb method.

Molybdenum Oxide. Preliminary tests showed that MoO_3 is appreciably soluble in $1.26\text{ M UO}_2\text{SO}_4$ at room temperature. Two samples of 0.014 and 0.97 wt % were heated in the rockers in silica tubes. There was little, if any, change up to 70°C . Above this temperature a white precipitate slowly formed. In the latter sample the precipitate of unknown composition was very bulky. At about 190°C the solution was clear and two liquid layers formed at 300°C . On cooling, the bulky, white precipitate reappeared at about 115°C . At 250°C 1% or more of MoO_3 is completely soluble in $1.26\text{ M UO}_2\text{SO}_4$.

Zirconium Sulfate. Zirconium sulfate was prepared from c.p. zirconyl chloride by double precipitation with concentrated hydrochloric acid, final washing with the same acid, and bringing to dryness and to constant weight with an excess of sulfuric acid.

Two solutions of $Zr(SO_4)_2$ containing 6.53 and 11.15 wt % in 1.26 M UO_2SO_4 remained stable when heated up to about 280°C, but at that temperature an irreversible change began that yielded a considerable mass of white precipitate, which remained when the tubes cooled to room temperature.

Cadmium Sulfate. Cadmium sulfate shows a negative temperature coefficient of solubility and considerable supersaturation. The evidence seems conclusive that solutions with up to 20.0 wt % of $CdSO_4$ in 1.26 M UO_2SO_4 give the two liquid layers at about 310°C, with no crystals forming. Another sample with 25.83 wt % of $CdSO_4$ dissolved at 263°C.

SOLUBILITY OF CUPRIC FLUORIDE IN URANYL FLUORIDE SOLUTION

A study of the solubility of cupric fluoride in uranyl fluoride solution at 100 to 300°C was undertaken to determine the phase stability of an aqueous uranyl fluoride solution by utilizing cupric ion as a catalytic recombiner for hydrogen and oxygen.⁽⁵⁾ Preliminary tests confirmed the results of earlier investigations that showed appreciable hydrolysis of cupric fluoride in water at 100°C. However, a more stable system might be expected in aqueous uranyl fluoride owing to complex formation.

Solutions were prepared by adding Baker's technical grade $CuF_2 \cdot 2H_2O$ (containing stoichiometric cupric and fluoride ions and very few spectrographic impurities) to solutions of high-purity Harshaw UO_2F_2 . These solutions were run in silica tubes in the usual manner.⁽⁶⁾ Cupric ion was

determined after the runs for each sample, which was completely soluble at room temperature, to check the reversibility of the systems.

The data given in Table 20 indicate solubility values of cupric fluoride well in excess of the limits necessary for catalytic recombination of hydrogen and oxygen at 250°C in 0.126 and 1.26 M UO_2F_2 solutions. The solubility processes involved are reversible and possess a negative temperature coefficient of solubility in the 100 to 300°C range. There was some slight attack of the silica tube at about 250°C, which was evidently due to cupric fluoride since no attack occurred in runs containing only uranyl fluoride solution.

CONDUCTIVITY OF URANYL SULFATE SOLUTION

The conductivity of uranyl sulfate solution has been investigated at 0°C in concentrations ranging from 0.0005 to 0.0974 N and at 25°C in concentrations ranging from 0.0025 to 2.5 N.

Conductivity data have been calculated from resistance measurements made in a standard conductivity cell having a cell constant of 1.1135 by means of a Leeds and Northrup Jones conductivity bridge. The accessory equipment consisted of a Hewlett-Packard sine wave, audiosignal generator, a General Radio null detector, and a Dumont 208-B oscilloscope. The bridge was well shielded to reduce the inductance and capacitance effects of stray current; however, it was not possible to control room humidity and temperature as recommended by the manufacturer of the conductivity bridge.

The cell was immersed in an oil-filled constant-temperature bath controlled by a mercury-type thermostat and mercury-to-mercury

⁽⁵⁾See "Radiation Stability" in Part II of this report.

⁽⁶⁾See previous section in this chapter on "Fission-Product Solubilities in Uranyl Sulfate Solutions at High Temperature."

HRP QUARTERLY PROGRESS REPORT

TABLE 20

Solubility of Cupric Fluoride in Uranyl Fluoride Solutions

UO ₂ F ₂ (M)	CuF ₂ (wt %)	SOLUBILITY			
		At 150°C	4 hr at 220 to 260°C	16 hr at 270°C	2 hr at 300°C
0.126	0.20	Soluble	Soluble		
0.126	0.33	Soluble	Borderline solubility		
0.126	0.59	Incomplete solubility	Much crystalline precipitation		
1.26	0.59	Soluble	Soluble	Soluble	Soluble
1.26	0.92	Soluble	Soluble	Soluble	Borderline solubility
1.26	1.37	Soluble	Much crystalline precipitation		
1.26	2.16	Soluble	Much crystalline precipitation		

relay. Cooling for 0°C measurements was accomplished by using a small refrigerating unit operating through a copper coil suspended in the oil bath. Measurements were made at the specified temperature to ±0.005°C, as measured by a Leeds and Northrup thermohm, with a Bureau of Standards certificate used in conjunction with a Mueller type of resistance bridge and high-sensitivity galvanometer.

The standard KCl solutions of 0.1 and 0.01 demal were prepared from recrystallized KCl according to the data of Jones and Bradshaw.⁽⁷⁾ Baker and Adamson reagent-grade KCl was further purified by dissolving in conductivity water and filtering to remove any insoluble matter; it was then crystallized out by evaporating and cooling, again dissolved in conductivity water, and the solution

saturated with Cl₂ prepared from c.p. HCl and KMnO₄. The solution was then boiled vigorously to remove the Cl₂, and the KCl was precipitated with HCl prepared from c.p. sulfuric and hydrochloric acids. The solution was then evaporated to dryness, taken up in conductivity water, and, after two recrystallizations, dried and fused in a platinum dish in an inert atmosphere.

The solutions of UO₂SO₄ were prepared by dilution from a pure stock solution (available in the laboratory) containing 298 g of uranium per liter. After this was done a question arose regarding the accuracy of the U/SO₄ ratio in this sample and a new sample of uranyl sulfate was prepared by precipitating the uranyl sulfate from the stock solution with c.p. acetone and redissolving in conductivity water, again precipitating with redistilled (middle fraction) acetone, and redissolving in conductivity water after several evaporations to remove the acetone resulting from the decomposition of the acetone complex. This

(7) G. Jones and B. C. Bradshaw, "The Measurement of the Conductance of Electrolytes. V. A. Predetermination of the Conductance of Standard Potassium Chloride Solutions in Absolute Units," *J. Am. Chem. Soc.* 55, 1780 (1933).

sample will be used to check some of the results already obtained.

Tables 21 and 22 show the equivalent conductivity of uranyl sulfate at 0 and 25°C. Figure 36 shows a plot of \sqrt{c} vs. Λ at the temperatures indicated.

TABLE 21

Equivalent Conductivity of Uranyl Sulfate

CONCENTRATION (eq./liter)	Λ (0°C)	Λ (25°C)
0.0005	62.90	---*
0.001	54.54	
0.0025	43.63	78.71
0.0125	26.54	45.65
0.025	20.91	33.80
0.0974	13.26	21.37
0.250		16.88
2.504		6.1

*See Table 22 for values at lower concentrations.

TABLE 22

Equivalent Conductivity of Uranyl Sulfate and Nickel Sulfate

CONCENTRATION (eq./liter)	Λ $\frac{1}{2}$ NiSO ₄ (25°C) ^(a)	Λ $\frac{1}{2}$ UO ₂ SO ₄ (25°C) ^(b)
0.0005 N	118.7	120.0
0.001	113.1	95.9
0.005	93.2	64.2
0.01	82.7	49.6
0.02	72.3	37.0
0.05	59.2	26.2
0.10	50.8	21.2

(a) K. Murata, "Electrical Conductance of Nickel Sulfate Solution and Ionic Conductance of Nickel," *Bull. Chem. Soc. Japan* 3, 47 (1928).

(b) Values taken from graph and work of Dittrich on conductivity of uranyl sulfate. C. Dittrich, "Die Uranylsalze vom physikalisch-chemischen Standpunkte aus betrachtet," *Z. physik. Chem.* 29, 449 (1899).

Uranyl sulfate behaves as a weak electrolyte at these temperatures. No anomalies appear in the curves; the conductivity increases with dilution in a continuous fashion. It is interesting to compare the conductivity of this solution with that of nickel sulfate.

From this data it appears that UO₂SO₄ is similar in equivalent conductance to NiSO₄ at higher dilutions, but it is a weaker electrolyte than the latter since it shows a much lower equivalent conductivity at higher concentrations.

Because it is a weak electrolyte it has not been possible to calculate the equivalent conductance at infinite dilution, Λ_0 , by application of the Onsager equation, nor are sufficient data available to calculate Λ_0 by empirical means.

VAPOR-PRESSURE STUDIES OF URANYL SALT SOLUTIONS

The vapor-pressure measurements of aqueous uranyl sulfate and uranyl nitrate were made with a 5000-psi Baldwin pressure gage that had been calibrated against a dead-weight piston gage. The accuracy of the Baldwin pressure gage was about ± 2 to 3 psi; therefore for higher accuracy of future work, a 2000-psi Baldwin gage was obtained and calibrated. The temperatures at which the pressure measurements were made were measured with a platinum resistance thermometer and controlled by a nickel resistance thermometer and a Leeds and Northrup duration-adjusting type of controller. Details of the thermostat and control instruments are given in the previous report in this series.⁽⁸⁾

(8) H. O. Day, Jr., "Vapor Pressures of Uranyl Salt Solutions," *Homogeneous Reactor Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 122.

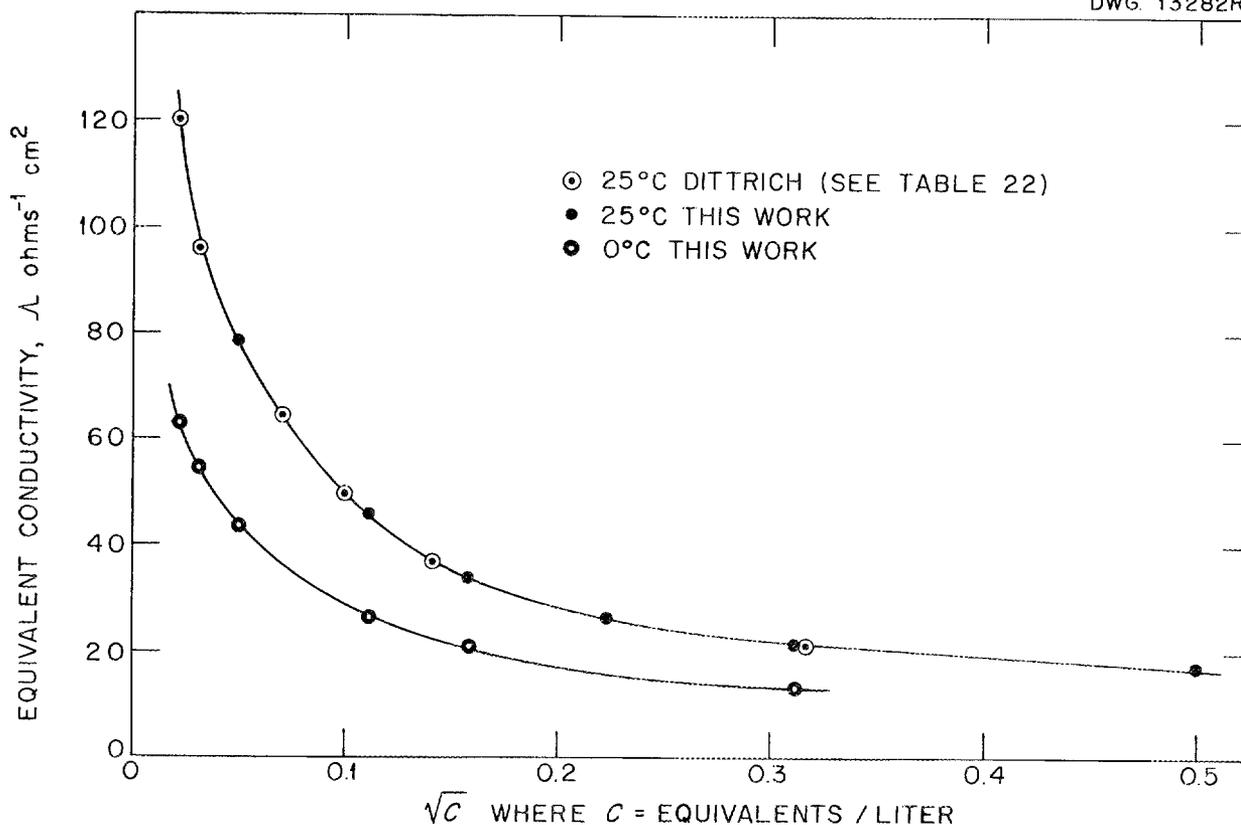


Fig. 36. Conductivity of Uranyl Sulfate.

A given solution was placed in a silica tube that fitted firmly into a standard, American Instrument Company, stainless steel, pressure bomb. Only vapor came in contact with the steel, and apparently very little corrosion occurred. The vapor-pressure measurements given in Table 23 were made on 6.84 (0.198 M) and 32.82 (1.248 M) wt % uranyl sulfate solutions, 37.81 (1.378 M) wt % uranyl nitrate solutions, and dissolved water for comparison.

Unfortunately, no degassing equipment was available at the time the measurements were made and, consequently, all samples contained dissolved air. This factor led to some

erratic results since the amount of air in a sample is a function of sample volume, sample concentration, external pressure, and room temperature.

The pressures that are reported to one decimal are the average of several readings and do not imply that accuracy. Temperature was controlled to $\pm 0.02^\circ\text{C}$.

After maintaining the solutions at temperatures above 200°C for six-day periods and observing no pressure increase, a very slight, yellow, crystalline solid was found in the 6.84 wt % solution. This solid was identified

TABLE 23

Vapor Pressures of Uranyl Sulfate and Uranyl Nitrate Solutions

TEMPERATURE (°C)	VAPOR PRESSURE* (psi)						
	WATER (literature)	WATER (experimental)	6.84 wt % UO ₂ SO ₄	32.82 wt % UO ₂ SO ₄		37.81 wt % UO ₂ (NO ₃) ₂	
				RUN 1	RUN 2	RUN 1	RUN 2
200	225.54	250.5	247	252.5	239.3	237.9	221.7
225	369.90	393.7	391.2	395	385.8	371.7	365.4
250	576.91	601.7	602.7	602.7	585	562.2	572.7
275	862.80	893.7	898	891.4	876.4	836.7	865.3
300	1246.12	1275.7	1272	1275.7	1261.3	1224.7	1246.2
325	1748.68	1778.7	1772.7	1774.7	1725.7(?)	1704.7	
350	2398.39	2429.7	2418.7	2428			

* All experimental samples contained air.

by X-ray diffraction as uranyl ortho-silicate⁽⁹⁾ or some similar structure. No precipitation occurred in the more concentrated solution.

It is known that uranyl nitrate solution decomposes at elevated temperatures, and it was considered of interest therefore to measure the vapor pressures of uranyl nitrate solution to determine the effect of this decomposition upon the pressure. The results given in Table 23 are very erratic owing to dissolved air but, in any case, are surprisingly low compared to the values of uranyl sulfate solution.

The vapor pressure differences between water and the various solutions are rather small as expected and of practically no consequence from an

⁽⁹⁾W. L. Marshall and J. S. Gill, "X-Ray-Diffraction Data for the Compound Uranyl Ortho-silicate Trihydrate," *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1950*, ORNL-1036, p. 15.

engineering viewpoint. Apparatus for degassing the solution has been provided so that more accurate vapor pressure data can be obtained. In hopes of obtaining data accurate enough for the determination of activity coefficients, a dynamic type of apparatus is being considered. Details will appear in a future report. For the present, however, effort will be concentrated on the degassing and measurements of pressure at the higher temperatures and on the compound manometer system described in a previous report for vapor pressures measured up to approximately 150°C.

SULFATE ANALYSIS OF PRODUCTION-GRADE URANYL SULFATE

Alternate methods for sulfate analysis of production-grade uranyl sulfate have been studied in an effort to eliminate the uncertainties involved in the standard, barium sulfate, gravimetric procedure and to determine

HRP QUARTERLY PROGRESS REPORT

sulfate within $\pm 0.15\%$. After a consideration of the various methods that might be investigated, the following conclusions were reached:

1. None of the methods involving initial removal of uranium were to be considered, since preliminary analyses gave results 10% below the standard. (These low values were due to ammonium sulfate occlusion and subsequent sublimation upon drying at 900°C .)

2. Gravimetric methods involving other reagents or precipitates would be postponed, since these alternates might introduce as many variables as the current method.

3. Initial concentration of effort would be on an ion-exchange method involving a cation exchanger and on removal of uranium bulk with hydrogen peroxide and subsequent titration or gravimetric analysis for sulfate.

Use of Hydrogen Peroxide. The use of hydrogen peroxide for the initial removal of uranium before barium sulfate precipitation has been investigated to a small extent. Uranium was precipitated using both a large excess of 3% hydrogen peroxide and three times theoretical hydrogen peroxide. Attempts were made to titrate directly the sulfuric acid produced; however, erratic results were obtained, possibly owing to the small amount of uranyl ion still present in the filtrate or to the peroxide present after slight boiling of the filtrate. The standard gravimetric method was used on the remaining filtrates and comparative results with those obtained by the direct precipitation from uranyl sulfate solution are given in Table 24.

An examination of the data indicates insufficient agreement between the various analysts and therefore the lack of agreement is probably a matter

of individual technique. Further exploration of the use of hydrogen peroxide would still involve the bulk of the barium sulfate uncertainty and, for that reason, will not be investigated further.

TABLE 24
Comparative Sulfate Analyses of a
Uranyl Sulfate Solution

METHOD	$\text{SO}_4^{=}$ (%)
Standard gravimetric precipitation from UO_2SO_4 solution (Thomason)	8.553
Standard gravimetric precipitation from UO_2SO_4 solution (Stephens)	8.962 8.952
Standard gravimetric precipitation from UO_2SO_4 solution (Day, Gill)	8.275(?) 8.375 8.414
Use of excess H_2O_2 , precipitation from filtrate (Jones)	8.437 8.449
Use of three times theoretical H_2O_2 , precipitation from filtrate (Jones)	8.384 8.367 8.399
Use of Dowex 50, titration of eluent (Day, Gill)*	8.497 8.503

* See following section on "Ion-Exchange Method."

Ion-Exchange Method. The ion-exchange method involves the selective adsorption of uranyl ion on a cation exchange resin and subsequent titration of sulfuric acid in the element. Some of the first work involving other cations was done by Samuelson⁽¹⁰⁾ and more recently work has been described by MacNevin *et al.*⁽¹¹⁾ The method has been extended to include the uranyl cation and offers much promise in that a single acid-base titration

⁽¹⁰⁾O. Samuelson, "Om Avändningen av basutbytande ämnen i den analytiska kemien III," *Kem. Tid.* 52 115-125 (1940).

⁽¹¹⁾W. N. MacNevin, M. G. Riley, and T. R. Sweet, "On Ion-Exchange Experiment for Quantitative Analysis," *J. Chem. Education* 28, 389 (1951).

of the eluent is involved, and the procedure is much faster than a gravimetric process. A detailed report of the procedure has been written and will be distributed upon request. A summary follows.

Clear Dowex 50, 12% crosslinkage, 200 to 400 mesh, was treated with a large excess of 3 M H_2SO_4 and then washed free of acid. Analytical results indicated that it was unnecessary to go through an extensive preparation of resin involving alternate washes of HCl, NaOH, and ethanol.

The column used for the final runs consisted of an 18-cm-long, 2-cm-diam., pyrex tube containing a No. B Corning sintered-glass filter disk near the bottom. The tube was reduced in diameter just below the filter and connected to an 18-cm-straight, 2-mm-ID, capillary tube. A 1/2-in.-long rubber tube, with a pinchcock, was attached to the end of the tube for flow control of the solution. No stopcock was included since sulfate might have adsorbed on the grease. About 16 cc of wet resin was added to each column.

A diluted sample was prepared by dissolving a known amount of water-washed (dried at 350°C) Mallinckrodt $UO_3(HNO_3 < 0.033 \text{ mole } \%)$ in a standard amount of H_2SO_4 . A sample was run through a column at 8 cc/min, the column was washed free of $SO_4^{=}$, and the total eluent was titrated for H_2SO_4 . At this flow rate the resin capacity was about 3 to 4 milliequivalents per cubic centimeter of wet resin. A sample could be run in about 20 min, not including titration times, and about six samples could

be run per column before regeneration with 3 M H_2SO_4 .

Eight exploratory samples containing known amounts of sulfate were run in order to test the method and determine ideal column size. Analytical deviations, sometimes as much as 0.3%, were probably due to development of technique and to the different type of columns employed.

The final results are given in Table 25, and they indicate agreement within $\pm 0.15\%$, with exception of the samples containing a high deficiency in sulfate. Even in these latter cases it is questionable whether the $\pm 0.2\%$ deviation is greater than titration accuracy. The bulk of this work was done with one type of resin in order to expedite the program; however, other resins such as Dowex 50, 12% crosslinkage, 60 to 100 mesh, might be equally or more efficient.

TABLE 25

**Titration Analysis for Sulfate after
Ion-Exchange Removal of Uranium**

Exploratory runs are not included

SAMPLE NO.	RATIO SO_4/U	$SO_4^{=}$ IN SAMPLE (mmoles)		
		ADDED	ANALYTICAL RESULT	DEVIATION (%)
1	1.0	2.441	2.439	-0.08
2	1.0	2.403	2.404	+0.04
3	1.0	2.569	2.566	-0.12
4	1.2	2.283	2.282	-0.04
5	1.2	2.691	2.691	0
6	1.2	2.315	2.316	+0.04
7	0.8	2.582	2.587	+0.19
8	0.8	2.670	2.676	+0.22
9*	0.8	2.825	2.830	+0.18

* Using Dowex 50, 8% crosslinkage, 60 to 100 mesh.

HRP QUARTERLY PROGRESS REPORT

CORROSION

J. L. English
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URANYL SULFATE CORROSION STUDIES

Two alternate metals that have shown excellent corrosion resistance in uranyl sulfate solutions at elevated temperature are titanium and Bureau of Mines zirconium containing approximately 5% of tin. One important advantage in the use of either of these materials is that an initial pretreatment in dilute HNO_3 or CrO_3 at 250°C is not required to ensure solution stability in the system. During the past quarter studies were made of (1) the corrosion of titanium metal, including welded titanium tubing, titanium in concentrated uranyl sulfate, effect of oxygen on the corrosion of titanium, and galvanic corrosion effects between titanium and type-347 stainless steel; (2) the corrosion of Bureau of Mines zirconium, including resistance-melted zirconium-tin alloys, induction-melted zirconium-tin alloy, crystal-bar zirconium-tin alloy, and consumable-arc-melted zirconium.

Titanium Metal. The scope of the titanium corrosion-testing program has been somewhat limited in the past owing to the unavailability of sufficient metal for testing purposes. Work thus far has been conducted with sample quantities of hot-rolled sheet and bar and extruded and welded tubing. More recently, suitable material was procured to permit the fabrication of a 25-ml capacity all-titanium test autoclave. As a result of the continued success of titanium as a corrosion-resistant material in uranyl sulfate solutions, orders have been placed for metal in quantity sufficient

to fabricate liners and autoclaves approaching 1000 ml in capacity. In the interim, most of the stagnant titanium corrosion tests, of necessity, have been conducted in pretreated stainless steel autoclaves of 150-ml solution capacity.

Welded Titanium Tubing. A 2000-hr test was completed with a specimen of welded and annealed $\frac{1}{2}$ -in.-OD titanium tubing, procured from the Rem-Cru Corporation. After welding and drawing to size the tubing was annealed at 1200°F . The corrosion test consisted of exposing the specimen in $0.17\text{ M UO}_2\text{SO}_4$ at 250°C in a CrO_3 -pretreated stainless steel autoclave. At the end of the 2000-hr period, in which the specimen was examined weekly, the corrosion rate was determined to be less than 0.01 mil/yr. The sample was lustrous and had a pink-bronze color. Examination at high magnification disclosed no signs of corrosion damage.

Titanium in Concentrated Uranyl Sulfate. A titanium autoclave of 20-ml total capacity, fabricated from commercial-grade, hot-rolled, titanium bar, was obtained from B. Zemel of the Chemistry Division. A machined specimen from the same material was used in the corrosion test. The test solution was 6 ml of $1.71\text{ M UO}_2\text{SO}_4$ containing 407.2 g of uranium per liter. The pH of the solution was 1.0. After 227 hr of operation at temperature, the sample showed a weight gain of 0.014 mg/cm^2 . No reduction in total uranium content was reported by chemical analyses on the solution before and after the test. The specimen developed a pale-blue,

highly lustrous, color during the exposure, and final examination at 200X revealed complete freedom from corrosion damage.

A titanium autoclave of 25-ml total capacity was fabricated from a 2-in.-OD, hot-rolled bar of Alloy RC 130A obtained from the Rem-Cru Corporation. The alloy designation indicates the addition of approximately 7% manganese to the titanium. The corrosion test specimen was machined from ½-in.-OD, commercial-grade, hot-rolled titanium bar that was procured from the Allegheny Ludlum Company. The specimen and 15 ml of 1.71 M UO_2SO_4 were placed in the autoclave and heated to 250°C. After 800 hr of operation, during which the specimen was examined and the solution replaced weekly, a weight gain of 0.09 mg/cm² was observed. No reduction in total uranium concentration has been detected thus far. The specimen was a lustrous, pale-blue color with a few scattered deposits of fine, white oxides. The test is being continued.

Effect of Oxygen. An electrically heated, stainless steel autoclave of 1-liter capacity was partially filled with 750 ml of 0.17 M UO_2SO_4 . A test specimen of ½-in.-OD, commercial-grade, hot-rolled titanium bar was suspended in the solution by means of a quartz hook. The sealed system was then pressurized with 500 psig of oxygen at room temperature, after which the autoclave was heated to 250°C. Solution samples were withdrawn periodically and analyzed for total uranium content. At the end of 100 hr, the specimen showed a weight gain of 0.05 mg/cm². Microscopic examination at 200X disclosed no signs of corrosion attack. The appearance of the specimen did not change throughout the test; the original metallic luster was retained.

Galvanic Corrosion Effects. A bimetallic corrosion test specimen was

prepared by fitting a solid, titanium-metal insert into a type-347 stainless steel ring. The titanium insert was machined from ½-in., hot-rolled, commercial-grade titanium supplied by the Allegheny Ludlum Company. The total exposed area of the steel specimen was nearly five times greater than that of the titanium. The assembled specimen was suspended by a quartz hook in 350 ml of 0.17 M UO_2SO_4 contained in a stainless steel autoclave. After sealing, the autoclave was pressurized with 500 psig of oxygen at room temperature and heated to 250°C. During operation of the test solution samples were withdrawn daily for total uranium analyses. At the end of 173 hr the test was stopped. No reduction in uranyl sulfate solution occurred during this time. The corrosion specimen was taken apart, and weights of the individual components were determined. The titanium specimen lost 0.2 mg/cm² and the corrosion rate was 0.9 mil/yr. The steel sample lost 0.1 mg/cm² during the run, corresponding to a corrosion rate of 0.2 mil/yr. Thus, under the conditions of the test, titanium metal was slightly anodic to the steel. The steel specimen was highly lustrous and gray-black in appearance at the end of the test. The titanium specimen retained its original metallic luster except for one small area adjacent to the stainless steel that was pale purple in color. No indication of crevice corrosion was visible to the naked eye. However, at 200X, there were indications of mild, localized, corrosion attack on the titanium immediately adjacent to the steel. This attack evidenced itself by the presence of shallow, clean-appearing pits, located predominantly on the edges of the specimen. Tests of this type are being repeated.

Zirconium. A limited amount of work was completed during the past

HRP QUARTERLY PROGRESS REPORT

quarter with zirconium-tin alloys exposed to uranyl sulfate solutions at 250°C. The materials investigated included Bureau of Mines zirconium containing 3 to 5% tin additions and crystal-bar zirconium containing a nominal 5% tin addition. As in the case of the titanium corrosion tests, these stagnant zirconium corrosion studies were conducted in pretreated stainless steel autoclaves of 150-ml solution capacity.

Very recently, approximately 100 lb of zirconium and zirconium-tin alloy metal ingots, rod, and plate were received from Bureau of Mines in Albany, Oregon. Fifty pounds of this material was a 5% tin alloy of zirconium. Aside from use of the material for regular corrosion test specimens, it is planned to fabricate all-zirconium autoclaves and liners in order to conduct corrosion tests with solution volumes approaching 500 milliliters.

Results of recently completed corrosion tests on the Bureau of Mines zirconium-tin alloys are presented below.

Resistance-Melted Zirconium-Tin Alloy. Samples of resistance-melted zirconium containing 3 and 5% tin additions were run for 30 weeks in 0.17 M uranyl sulfate at 250°C. The alloys were hot-forged and rolled after melting. The cumulative weight changes on the specimens are given in Table 26.

The corrosion behavior of the two specimens was entirely different. The 3% tin alloy showed a progressive weight increase with time, whereas the 5% tin alloy lost weight steadily. The corrosion rate on the 5% specimen was 0.04 mil/yr after 30 weeks of operation. Both specimens were coated with dark brown, semilustrous, thin films.

Induction-Melted Zirconium-Tin Alloy. Two samples of induction-melted zirconium containing a nominal

TABLE 26

Corrosion of Resistance-Melted Zirconium-Tin Alloy

CUMULATIVE EXPOSURE TIME (weeks)	CUMULATIVE WEIGHT CHANGE (mg/cm ²)	
	3% Sn	5% Sn
1	+0.03	-0.02
2	+0.05	+0.03
3	+0.06	+0.02
4	+0.07	-0.03
5	+0.10	-0.05
6	+0.13	-0.05
7	+0.11	-0.12
8	+0.14	-0.12
9	+0.12	-0.17
10	+0.13	-0.15
11	+0.14	-0.17
12	+0.18	-0.17
13	+0.20	-0.19
14	+0.21	-0.20
15	+0.16	-0.24
16	+0.21	-0.25
18	+0.22	-0.32
20	+0.23	-0.46
22	+0.26	-0.44
24	+0.31	-0.47
26	+0.28	-0.39
28	+0.33	-0.45
30	+0.37	-0.37

5% tin addition were tested in 0.17 M UO₂SO₄ at 250°C. Sample 1 was induction-melted sponge metal that was forged and hot-rolled at 1800°F. The sample was etched in 5% hydrogen fluoride before test exposure. Sample 2 was Bureau of Mines sponge metal that was induction-melted and forged at MIT. This specimen was also etched in 5% hydrogen fluoride before testing. Corrosion data for the two samples appear in Table 27.

In cases where solution reduction occurred, the test specimen was returned, untreated, to a newly-pretreated autoclave and the test

TABLE 27
Corrosion of Induction-Melted
Zirconium-Tin Alloy

CUMULATIVE EXPOSURE TIME (weeks)	CUMULATIVE WEIGHT CHANGE (mg/cm ²)	
	SAMPLE 1	SAMPLE 2
1	-0.04	-0.02
2	0.00	+0.02
3	-0.03	+0.06
4	-0.02	+0.14
5	-0.02	+0.10
6		+0.21
7	-0.03	+0.06
8	-0.02	+0.08
9	-0.02	+0.06
10	+0.01	+0.06
11	0.00	+0.08
12	-0.01	+0.08
13	0.00	+0.06
14	+0.01	+0.06
15	+0.79*	+0.02
16		+0.04
17	+0.59*	
18		-1.75
19	+0.06	
21		+0.08
23		+0.08
25		+0.08
27		+0.12
29		+0.04
31		+0.08

* The test solution precipitated.

continued. The abrupt weight loss on Sample 2 after 18 weeks was unexplained; no reduction in the uranyl sulfate test solution was reported at this time nor in the following week when the sample reverted to its original trend of slight weight increase. Both specimens exhibited thin, uniform, dark-brown films at the end of their respective exposure times. In general, the behavior of these specimens was better than that of the resistance-melted zirconium containing 5% tin.

Arc-Melted Crystal-Bar Zirconium-Tin Alloy. A specimen of arc-melted crystal-bar zirconium containing approximately 5% tin has been exposed to 0.17 M UO₂SO₄ for 25 weeks at 250°C. This material was forged and rolled at 1450°F after melting and was identified as BMI 927. The specimen was etched in 5% hydrogen fluoride before the test was started. Corrosion data accumulated thus far appear in Table 28.

The specimen was coated with a mottled, gray and black film at the end of the test. When solution reduction occurred during the seventh week, the sample was returned to new uranyl sulfate test solution without an initial cleaning to remove adhering uranium oxides. The final corrosion behavior of this specimen was similar

TABLE 28
Corrosion of Arc-Melted Crystal-Bar
Zirconium-Tin Alloy

CUMULATIVE EXPOSURE TIME (weeks)	CUMULATIVE WEIGHT CHANGE (mg/cm ²)
1	-0.04
2	0.00
3	-0.04
4	-0.02
5	-0.02
6	-0.03
7	+0.05*
8	-0.02
9	0.00
10	-0.02
11	0.00
12	-0.01
13	+0.06
15	+0.05
17	+0.06
19	+0.06
21	+0.09
23	+0.06
25	+0.12

* Reduction of test solution.

HRP QUARTERLY PROGRESS REPORT

to that of the induction-melted zirconium containing 5% tin addition.

Consumable-Arc-Melted Zirconium. Stagnant corrosion tests were conducted on two samples of unalloyed consumable-arc-melted zirconium to determine the effect of changing the uranyl sulfate test solution weekly, as compared to using the original sulfate solution throughout the test. The zirconium was melted from Grade-C sponge metal by the consumable-arc process. The ingot was then forged and swaged in air at 700°C. Prior to testing the specimens were etched in 10% HNO₃ - 5% HF mixtures. The uranyl sulfate test solutions were 0.17 M; the temperature of the tests was 250°C. The corrosion data obtained thus far are listed in Table 29.

The specimen exposed with weekly solution changes gradually developed a white-colored layer of surface oxides that was uniform on all areas. In the test using the original solution throughout the sample was semilustrous with no bulk oxide formations. The greater magnitude of weight increase on the former sample was attributed to the fresh supply of

oxygen obtained weekly in the new test solutions.

URANYL FLUORIDE STABILITY AND CORROSION STUDIES

During the past quarter static corrosion tests were continued using 0.17 to 1.26 M UO₂F₂ contained in type-347 stainless steel bombs to determine the effect of CrO₃- and HNO₃-pretreatment films on the corrosion resistance of stainless steel and the effect of dissolved oxygen on the solution stability of UO₂F₂.

Corrosion Resistance of Pretreated Stainless Steels. Specimens of CrO₃-pretreated types-309, -316 (ELC), -321, and -347 stainless steel were exposed at 250°C in 1.26 M UO₂F₂ contained in CrO₃-pretreated bombs. The solutions in the bombs were changed and the specimens inspected and weighed weekly. The tests were continued for a period of one week after initial uranium reduction was observed. In all instances further reduction occurred, accompanied by a decrease in pH. Partial uranium reduction occurred in the tests containing types-316 and -347 stainless steel samples after five weeks of exposure. Partial uranium reduction occurred in the tests containing types-309 and -321 samples after 10 and 17 weeks of exposure, respectively. The fact that precipitation occurred over a wide range of exposure periods (5 to 16 weeks) was possibly influenced by the initial condition of the bomb surfaces or faulty pretreatment films rather than differences in test specimen types. A gradual diminution of the bulk oxide films was observed on all the samples as exposure time was increased. Corrosion data are given in Table 30.

A sample of HNO₃-pretreated type-347 stainless steel was exposed at

TABLE 29

Corrosion of Consumable-Arc-Melted Zirconium

CUMULATIVE EXPOSURE TIME (weeks)	CUMULATIVE WEIGHT GAIN (mg/cm ²)	
	SAME SOLUTION	WEEKLY SOLUTION CHANGE
1	1.15	0.51
2	0.91	0.95
3	1.06	1.21
4	1.25	1.50
5	1.35	1.88
6	1.61	2.20
7	1.86	2.75
8	2.04	3.01
9	2.20	3.38
10	2.32	3.60

FOR PERIOD ENDING NOVEMBER 15, 1951

TABLE 30

Corrosion Data for CrO₃-Pretreated Stainless Steels Exposed to
1.26 M UO₂F₂ at 250°C

CUMULATIVE EXPOSURE TIME (weeks)	CUMULATIVE WEIGHT CHANGE (mg/dm ² /mo)*				CORROSION RATE (mil/mo)			
	STAINLESS STEEL TYPE				STAINLESS STEEL TYPE			
	309	316	321	347	309	316	321	347
1	0.0	+8.03	-6.52	+4.65	0.0		0.0032	
2	-3.26	-1.99	-14.10	-10.40	0.0016	0.0001	0.0070	0.0052
3	-22.60	-9.65	-21.00	-70.50	0.0112	0.0048	0.0103	0.0349
4	-34.50	-160.8	-19.93	-123.7	0.0171	0.0795	0.0099	0.0612
5	-62.30		-23.40		0.0309		0.0116	
6	-131.8		-24.90		0.0652		0.0123	
7	-166.8		-22.60		0.0824		0.0112	
8	-184.0		-20.60		0.0910		0.0102	
9	-123.5		-22.65		0.0610		0.0112	
10			-23.80				0.0118	
11			-22.60				0.0112	
12			-26.70				0.0132	
13			-29.1				0.0144	
14			-32.0				0.0158	
15			-37.2				0.0184	
16			-76.3				0.0376	

*Mg/dm²/mo = milligrams per square decimeter per month.

250°C to 1.26 M UO₂F₂ contained in a HNO₃-pretreated bomb. The solution was changed every two weeks and the sample inspected and weighed. Chemical analyses indicated that no uranium reduction occurred in the test solutions for 12 weeks of cumulative exposure. The bulky, pretreatment film partially flaked off and exposed isolated areas of bare metal. Corrosion data are given in Table 31.

Another series of tests was run at 150°C to determine the effect of UO₂F₂ concentration on the corrosion resistance of HNO₃-pretreated type-347 stainless steel samples. Two tests were run in HNO₃-pretreated type-347 stainless steel bombs at each of the following UO₂F₂ concentrations:

TABLE 31

Corrosion of HNO₃-Pretreated Type-347
Stainless Steel by 1.26 M UO₂F₂
at 250°C

CUMULATIVE EXPOSURE TIME (weeks)	CUMULATIVE WEIGHT LOSS (mg/dm ² /mo)	CORROSION RATE (mil/mo)
2	4.95	0.0025
4	5.55	0.0027
6	4.52	0.0022
8	1.23	0.0006
10	2.21	0.0011
12	2.26	0.0011

0.42, 0.84, and 1.26 M. The bombs were opened weekly for inspection and solution sampling. The tests were run

HRP QUARTERLY PROGRESS REPORT

TABLE 32

Corrosion Data for HNO₃-Pretreated Type-347 Stainless Steel Exposed to 0.42 and 0.84 M UO₂F₂ at 150°C

CUMULATIVE EXPOSURE TIME (weeks)	CUMULATIVE WEIGHT CHANGE (mg/dm ² /mo)			CORROSION RATE (mil/mo)		
	I*	II*	III*	I*	II*	III*
1	97.1	72.0	191.5	0.048	0.036	0.095
2	103.8	98.8	209.0	0.051	0.049	0.104
3	112.0	94.8	212.0	0.056	0.047	0.105
4	125.0	103.5	292.0	0.062	0.051	0.145
5	111.8	101.8	296.1	0.056	0.051	0.147
6	112.0	104.8	362.2	0.056	0.052	0.179
7	115.5	119.0	420.0	0.057	0.059	0.208
8	138.5	136.0	426.1	0.069	0.068	0.211

* Samples I and II were exposed to 0.42 M UO₂F₂. Sample III was exposed to 0.84 M UO₂F₂.

until uranium reduction occurred or until a total of eight weeks of exposure time was accumulated. Uranium precipitation occurred in three of the tests after one week of exposure; two of the bombs contained 1.26 M UO₂F₂ and one bomb contained 0.84 M UO₂F₂. No uranium reduction occurred in the other three bombs during the entire eight weeks of exposure. Corrosion data for the samples exposed to solutions in which no reduction occurred are given in Table 32. The average corrosion rate for the two samples exposed for eight weeks to 0.42 M UO₂F₂ was 0.07 mil/mo; the corrosion rate for the sample exposed to 0.84 M UO₂F₂ was 0.21 mil/mo.

Effect of Dissolved Oxygen on the Solution Stability of Uranyl Fluoride. Preliminary tests are being run at 150 and 250°C to determine the effect of dissolved oxygen on the solution stability of 0.17 and 1.26 M UO₂F₂ contained in type-347 stainless steel bombs. Partial pressures of oxygen varying from 10 to 500 psi are maintained in the bombs by the addition of hydrogen peroxide. Visual inspection of several short-time tests indicate that dissolved oxygen may be beneficial in stabilizing the uranyl fluoride solutions. Chemical analyses of test solutions are incomplete, and quantitative results will be reported at a later date.

RADIATION STABILITY

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J. W. Boyle	D. M. Richardson
S. F. Clark	J. Ruth
F. J. Fitch	M. D. Silverman
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T. J. Sworski	

RADIATION DECOMPOSITION OF HOMOGENEOUS REACTOR FUEL SOLUTIONS

Initial Yields of Gas from Pile-Irradiated Uranyl Solutions. The effects of enrichment, concentration, temperature, added solutes, and radiation dose (nvt) on the production of gases by the decomposition of water are being determined for uranyl sulfate and uranyl fluoride. The technique being used involves irradiation of a sample of the solution contained in a small diameter silica ampoule and subsequent determination of the hydrogen and oxygen gas produced. Irradiations are carried out in hole 12 of the X-10 graphite pile. Small amounts of a gas that is condensable at liquid nitrogen temperature are usually observed. The amount is independent of dose, and the gas has been identified as CO₂ that was probably formed from impurities present in the solution.

Initial yields of hydrogen in terms of G moles H₂ formed per 100-ev energy absorbed in the solution, are presented in Table 33.

As can be seen, these G values are low when compared with the reported⁽¹⁾ yields of 2 to 3 molecules of H₂ per

(1) F. C. Lanning and S. C. Lind, "Chemical Action of Alpha Particles from Radon on Aqueous Solutions," *J. Phys. Chem.* 42, 1229 (1938).

100 ev for alpha particle decomposition of water, and they are also lower than previously reported values of 2 to 2.5 for enriched uranyl sulfate solutions. The broader scope of the present studies and the good agreement between data from two separate teams of investigators presently engaged in this work suggest that values in the neighborhood of 1.5 are maximal for uranyl sulfate solutions (40 g of uranium per liter, 93% enrichment) at 250°C. Probably the most striking feature of the table is the effect of KBr (bromide ion) in raising the G value for unenriched solutions. It is believed that this effect is the result of suppression of a back reaction (recombination to H₂O) rather than any direct effect on water decomposition. The data indicate that G values for unenriched solutions tend to be lower at higher temperatures, as shown by Table 33. Furthermore, Fig. 37 indicates that the apparent G values are dependent upon the type and amount of radiation received. These effects appear when more than 5% of the energy input comes from sources other than fission recoils (i.e., fast neutrons and gamma rays). For highly enriched solutions, where more than 95% of the energy input comes from fission recoils, there does not appear to be a temperature dependence and bromide ion does not raise the G values. All these observations are consistent with a temperature-dependent (gamma-induced?) back reaction proceeding via

HRP QUARTERLY PROGRESS REPORT

TABLE 33

Initial Yields of H₂ from Pile-Irradiated Uranyl Solution

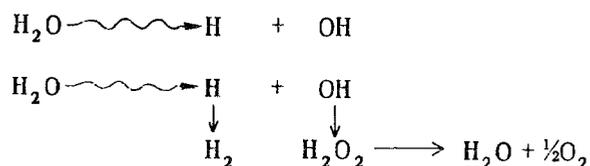
SOLUTE	ENRICHMENT		ADDED SOLUTE	G VALUES				
	g of U per liter	g of U ²³⁵ per liter		30°C	100°C	120°C	150°C	250°C
UO ₂ SO ₄ (Depleted)	202					0.6		
UO ₂ SO ₄ (Natural)	38.1					1.0		
	44.6	0.316		0.98	0.94		0.76	
	44.6	0.316	0.01 M KBr	1.23			1.17	
	227					0.94		
	297	2.11				0.87		
	297	2.11		1.01	0.95			
	437					0.725		
UO ₂ SO ₄ (Enriched)	40.7	37.75				1.50		
	102	37.75				1.35		
	202	37.75				1.12		
	40.7	37.8					1.56	1.44
	40.7	37.8	0.02 M KBr				1.68	
	204	190				1.03		
UO ₂ F ₂ (Natural)	44.6	0.316		1.03	0.71		0.64	
	44.6	0.316	0.01 M KBr				1.32	
	297	2.11		1.16	0.97		1.05	0.48
	297	2.11	0.02 M KBr					1.0

a radical mechanism (H + O₂) that is suppressed by bromide ion. Further investigation of these details is in progress.

Examination of Fig. 38 shows further a marked lowering of the apparent G value as the concentration of uranium is increased and the U²³⁵ content is maintained constant. This decrease in G values may also be understood as resulting from a change in the relative energy input from fission recoil as compared with fast neutrons and gamma rays.

With irradiation at low temperatures, the amount of oxygen gas found is too

low to balance the hydrogen, as illustrated by Figs. 39 and 40. It is believed that the deviation from a 2:1 ratio is caused by the presence in the solution of hydrogen peroxide that is undecomposed because of the low temperature.



Traces of organic impurities can also react with the OH radicals or H₂O₂ to bring about a deficiency of oxygen gas.

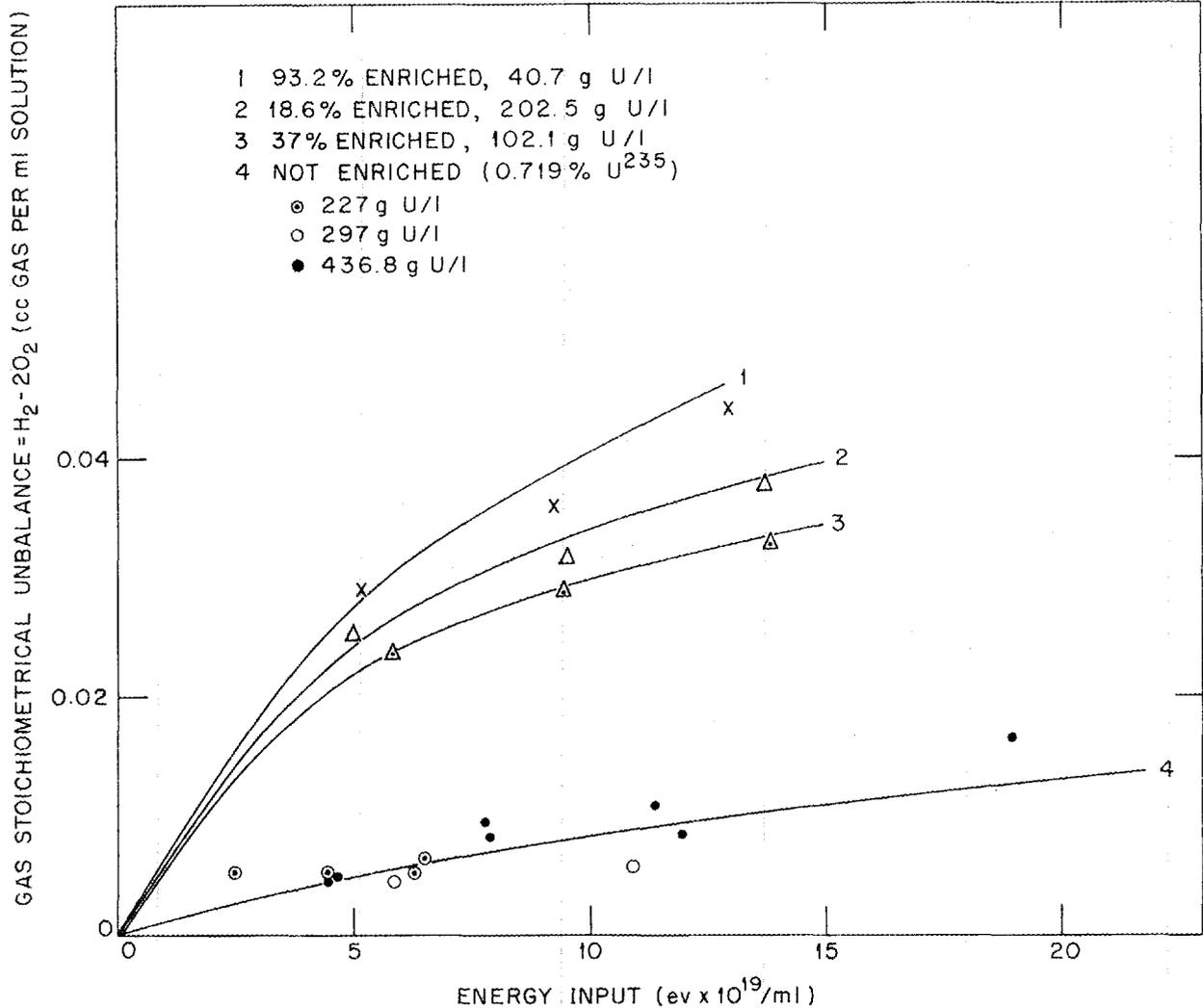


Fig. 37. Hydrogen-Oxygen Unbalance in Irradiated Uranyl Sulfate Solutions as a Function of Energy Input.

In one experiment a solution containing 44.6 g of uranium per liter was irradiated for 15 min at 30°C and then titrated with ceric sulfate. The peroxide found was approximately equivalent to the excess hydrogen.

Measurement of Rate of Energy Absorption in Water and in Uranium Solutions Irradiated in The X-10 Graphite Pile. In order to calculate

a yield for products obtained by irradiating uranyl solutions in the X-10 graphite pile, it is necessary to know the total energy absorbed in solution from gamma rays and neutron scattering and the energy contributed by the fission process. The rates of energy absorption in water and in solutions containing three concentrations of U²³⁵ were measured by using an adiabatic calorimetric method. The calorimeter and method were similar to

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OWG. 13957

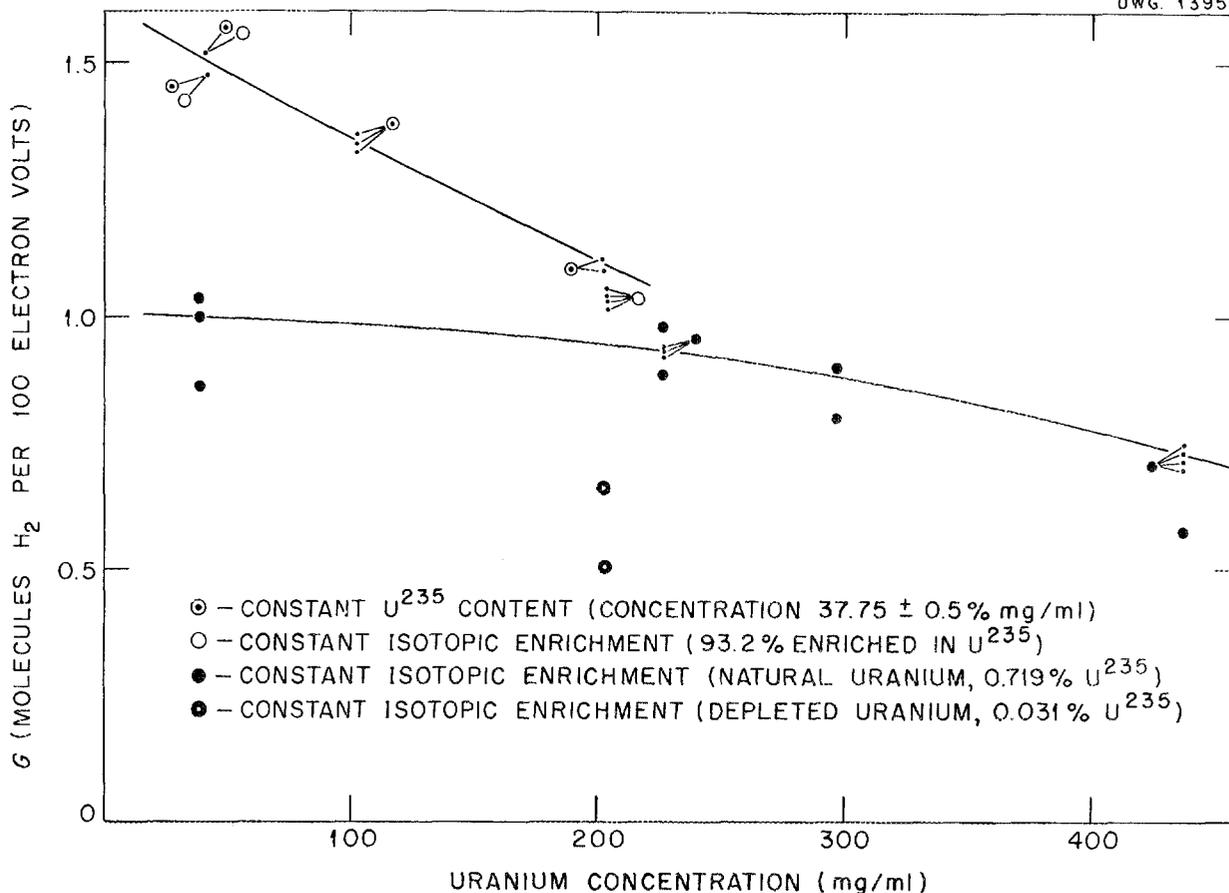


Fig. 38. Hydrogen Yield per Unit Energy Input as a Function of Concentration for UO_2SO_4 Solutions.

those used previously for gamma rays.⁽²⁾ The results are listed in Table 34. The fission energy absorbed in solution was also calculated from the thermal flux determined by using a manganese monitor and the following equation:

$$\begin{aligned} \text{Total ev/ml} = & \text{specific activity of} \\ & \text{monitor} \times [3.446 \times 10^{15} \\ & \text{ev (mg of } U^{235} \text{ per ml)}] \\ & + 0.5804 \times 10^{15} \text{ ev.} \end{aligned}$$

⁽²⁾"Radiation Chemistry," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870.

The specific activity of Mn^{56} was measured in a 1-mg sample of a 0.70% Mn alloy of Al-Mn-Co obtained from the Analytical Chemistry Division. The values obtained by this method were found to be 6 to 11% lower than those based on calorimetric data, and a correction is included in the equation to give values consistent with calorimetric data.

The value measured for the enriched solution is ~ 25% below that obtained by extrapolation of the values measured for the natural uranium solutions. This can be accounted for in part by self-shielding in the solution and in

DWG. 13958

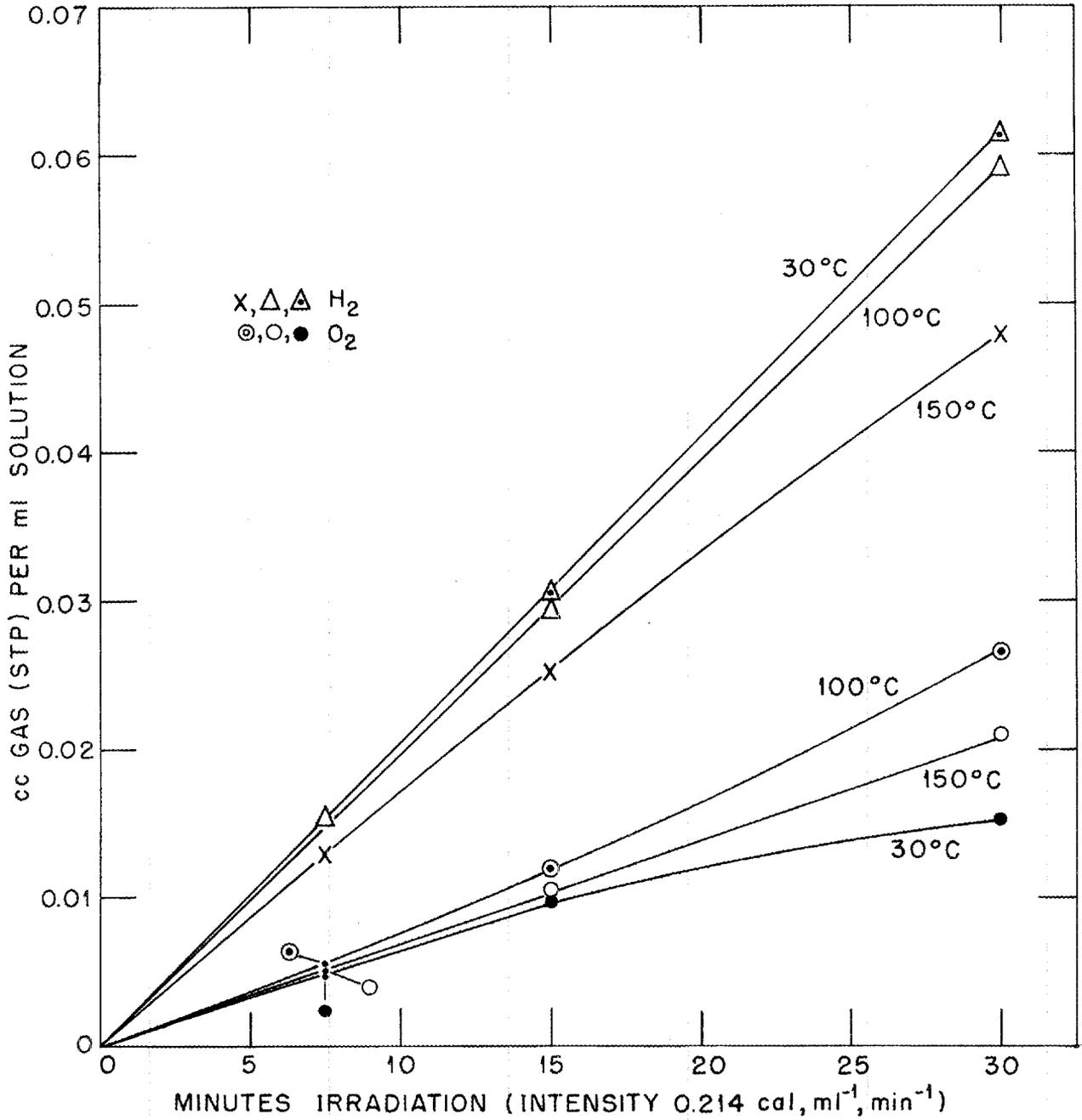


Fig. 39. Gas Production From Pile-Irradiated UO₂SO₄ Solutions Containing 44.6 g Natural Uranium per Liter.

HRP QUARTERLY PROGRESS REPORT

TABLE 34

Energy Absorption in Uranyl Solutions Irradiated in the Maximum Flux in Hole 12 in the X-10 Graphite Pile

	WATER	URANYL SULFATE	URANYL SULFATE	URANYL NITRATE
Uranium per liter, g	0.0	44.6	297.0	42.32
Uranium ²³⁵ per liter, g	0.0	0.316	2.11	39.44
Temperature, °C	38	37	33	38
Solution ^(a) density, g/ml	1.00	1.06	1.39	1.06
Solution ^(b) specific heat, cal/g/°C	1.00	0.95	0.73	0.95
Rate of temperature rise, °C/min	0.076	0.201	0.888	12.8
Pile power, mw	3.85	3.65	3.55	3.80
Rate of energy absorption in solution, cal, ml ⁻¹ , mw·min ⁻¹	0.0202	0.0582	0.266	3.55

(a) Data from Lietzke, Wright, and Marshall (August 1951).

(b) Data from *Project Handbook*, Vol. I, CL-697. The sulfate solutions were assumed to have the same specific heat as the nitrate solution.

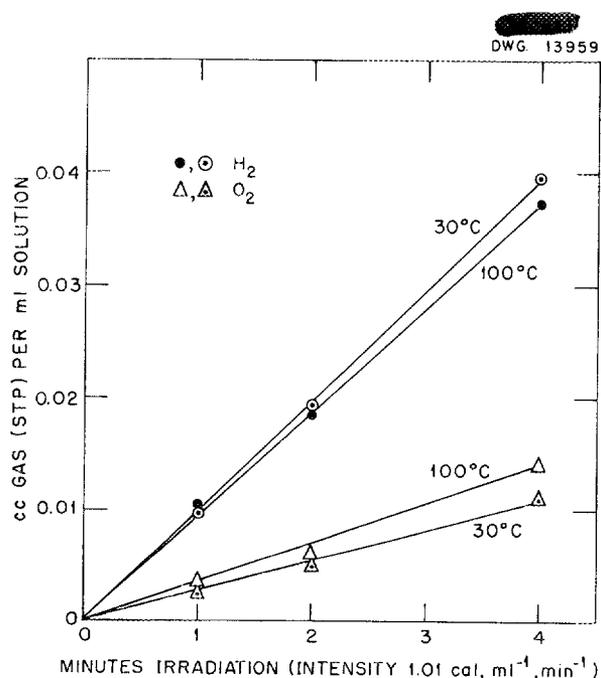


Fig. 40. Gas Production From Pile-Irradiated UO₂SO₄ Solutions containing 297.0 g Natural Uranium per Liter.

part by a precipitate that was observed when the calorimeter was opened. The value obtained for water is close to that reported by Ghormley,⁽³⁾ 0.0202 cal, ml⁻¹, mw·min⁻¹ and that of Richardson,⁽⁴⁾ 0.0209 cal, ml⁻¹, mw·min⁻¹.

HOMOGENEOUS RECOMBINATION OF HYDROGEN AND OXYGEN

In the previous report⁽⁵⁾ the two reactions - homogeneous reduction of uranyl sulfate by hydrogen gas and reoxidation of reduced uranium by

(3) Report of the Chemistry Division for the Months March, April, and May 1947, Mon-N-311.

(4) D. M. Richardson, *Calorimetric Measurement of Radiation Energy Dissipated by Various Materials Placed in the Oak Ridge Pile*, ORNL-129 (October 1, 1948).

(5) H. F. McDuffie et al., "Radiation Stability," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 51.

oxygen - were demonstrated, and plans for experiments to demonstrate hydrogen-oxygen recombination by uranyl sulfate were given.

During the last quarter these experiments have been carried out with great success. Preliminary kinetic data have been included in the latest Chemistry Division quarterly progress report⁽⁶⁾ and results of tests under pile-irradiation have been discussed in the chapter on "Radiation Stability" in Part I of this report. Further kinetic studies to establish accurately the effects of temperature, ion concentration, gas composition, and pressure are in progress and will be reported later.

In summarizing the present knowledge, the following points can be made:

1. A 2:1 mixture of hydrogen and oxygen reacts smoothly and homogeneously with uranyl sulfate solution from 0.0625 to 2.5 M in concentration at temperatures from 200 to 290°C and at gas pressures up to 1500 psi in excess of steam pressure.

2. The rates of recombination in the presence of 0.17 M UO_2SO_4 at temperatures of 250 to 290°C are rapid enough to account for recombination of all the gas formed when solutions of 93% enrichment are exposed to the full flux of the X-10 graphite pile (5 to 8×10^{11}) and, under these con-

ditions, to provide equilibrium pressures in the range of 1000 to 5000 psi. This provides a satisfactory explanation for the temperature dependence observed in all past irradiation studies.

3. A number of substances other than uranyl sulfate have been found somewhat effective in promoting recombination, including ions of Cu, Sn, Tl, Fe, and Cr.

4. Copper appears outstandingly effective in that it shows a recombination rate in the neighborhood of 100,000 times that shown by uranyl sulfate alone at the same temperature.

5. The variety of substances that have been shown capable of effecting homogeneous recombinations has suggested the hypothesis that certain fission products (unspecified - possibly including iodine) will also be found effective. The gradual accumulation of these substances would account for the slow, downward drift of equilibrium pressures observed in radiation experiments but not connected with loss of uranium from solution.

6. A valuable by-product of the kinetic studies on recombination has been the development of a simple equation that appears to describe satisfactorily the time dependence of pressure for uranyl sulfate solutions in the metal bombs being irradiated. This equation is of the same form as that for the so-called "secular equilibrium" in radiochemistry.

⁽⁶⁾"Radiation Stability," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1951*, ORNL-1153.

HRP QUARTERLY PROGRESS REPORT

CATALYTIC RECOMBINATION

D. W. Kuhn A. O. Ryon
A. A. Palko

FULL-SCALE CATALYTIC RECOMBINER

Recombination of hydrogen and oxygen on a platinum catalyst has been effected at a rate of 14 scfm of hydrogen-oxygen mixture. The capacity of this recombiner is therefore sufficient to handle the maximum gas production of the HRE, and it thus provides an alternate primary recombiner should the flame recombiner fail.

The reactor consisted of a 4-in. pipe jacketed by a 5-in. pipe and contained 1.9 lb of catalyst in a bed 4-in. deep. Cooling water was passed through the jacket at the rate of 4.1 lb/min. Flow rates were: steam, 92 scfm; hydrogen-oxygen mixture, 13.8 scfm. This gave a mixture containing 13.1% hydrogen-oxygen and a space velocity of $216,000 \text{ hr}^{-1}$. The percentage of conversion was 99.96. Other data on this run are as follows:

Temperatures, °C	
Gas in	160
Catalyst	
Head	295
Center	700
Tail	715
Reactor wall, catalytic recombiner side	415
Gas out	563
Cooling water	
In	27
Out	98
Pressure at head of catalytic recombiner, psig	17.2
Pressure drop across catalytic recombiner, psi	6.6

About 20% of the heat of reaction was transferred to the cooling water, and the remainder served to raise the temperature of the off-gas. The heat liberated by the reaction for the feed

rate given above was 160,700 Btu/hr or 47.1 kw. The energy could be converted to useful work at reasonably good thermodynamic efficiencies, since the steam leaves the catalyst at high temperature.

It should be made clear at this point that the dimensions, space velocities, etc., are not the recommended figures for the alternate HRE catalytic recombiner. The unit that was used in this test is somewhat undersize but was extended to the full-scale flow conditions just to see what the ultimate capacity of such a small unit might be. Apparently the capacity of the unit is even greater than 14 cfm of hydrogen-oxygen, but two undesirable features in the above data are the high pressure drop across the catalyst and the high space velocity. Both these factors may be improved by using a larger diameter reactor. For example, if an 8-in. pipe is packed with a 4-in. bed, the pressure drop would be reduced to less than 1 psi, and the space velocity would be about $50,000 \text{ hr}^{-1}$, which is quite reasonable. Further, if it is desired not to remove part of the heat of reaction by a water-cooled jacket, the reactor could be made adiabatic and the maximum temperature within the unit controlled by using sufficiently dilute gas mixtures. A discussion of temperature control is presented in the next section.

REMOVAL OF HEAT FROM THE CATALYST

Three series of experiments have been completed that furnish information concerning the control of temperature in a catalytic reactor and the removal of heat of reaction. As a result of this work, it has been shown that the

FOR PERIOD ENDING NOVEMBER 15, 1951

heat of the hydrogen-oxygen recombination can be removed from a catalytic reactor without difficulty.

One set of results was obtained with the jacketed, 4-in. pipe reactor described above. A second experiment was carried out in a jacketed 1/2-in. pipe, whereas the third reactor was a tube-and-shell heat exchanger containing seventeen 1/4-in. pipes with catalyst packed inside the 1/4-in. pipes and coolant circulated through the shell. The results of these tests are given in Table 35.

From these data it is seen that a 1/2-in. pipe reactor, jacketed in this

case with a 1 1/2-in. pipe, is easily cooled and that the temperature of the off-gas can, if desired, be held to a low value even when the temperature in the center of the bed reaches 650°C. If it is desired to prevent the interior of the catalyst bed from reaching high temperatures, this may be accomplished by diluting the gas, as shown in Table 35.

It may also be noted from the table that some work has been done by using a catalyst very low in platinum content, 0.01% Pt rather than 0.3% Pt. Measurements of catalyst conversion efficiencies with these two catalysts have not yet been completed, but it is

TABLE 35

Operational Data for Experimental Recombiners

RUN NO.	TEMPERATURES (°C)					COOLING WATER FLOW RATE (lb/min)	GAS FLOW RATES (cfm) (0°C, 1 atm)		H ₂ + ½ O ₂ (%)	SPACE VELOCITY (hr ⁻¹)
	GAS IN	MAX. IN CAT.	GAS OUT	COOLING WATER			STEAM	H ₂ + ½ O ₂		
				IN	OUT					
4-in. pipe reactor; 856 g of 0.3% Pt-on-Al ₂ O ₃ ; 4-in. bed										
83 A1	156	170	150	85	115	1.47	94	0.46	0.49	194,000
83 A2	156	171	160	No cooling		0	94	0.46	0.49	194,000
83 B1	153	338	282	63	130	3.0	93.6	4.2	4.3	200,000
83 B2	156	336	319	No cooling		0	93.6	4.2	4.3	200,000
83 C1	159	609	493	25	82	4.1	96	10.2	9.6	217,000
83 C2	162	606	568	No cooling		0	96	10.2	9.6	217,000
83 D1	160	715	563	27	98	4.1	92	13.8	13.1	216,000
1/2-in. pipe reactor; 14.5 g of 0.3% Pt-on-Al ₂ O ₃ ; 4-in. bed										
76 A	152	292	175	127	132	0.81	2.10	0.11	5.0	244,000
76 B	143	474	170	118	124	0.93	0.98	0.11	10.1	120,000
76 C	144	652	210	122	137	0.81	1.07	0.21	16.4	141,000
1/2-in. pipe reactor; 14.5 g of 0.01% Pt-on-Al ₂ O ₃ ; 4-in. bed										
75 A	140	448	135	116	123	1.06	1.00	0.11	9.9	122,000
75 B	143	650	172	123	147	0.93	1.08	0.21	16.3	142,000
Seventeen 1/4-in. pipes in bundle; 294 g of 0.3% Pt-on-Al ₂ O ₃ mixed with 300 g of Al ₂ O ₃ ; 24-in. bed										
70 A	102	150	99	93	130	3.0	6.83	0.93	12.0	20,000
67 A	117	180	102	94	148		1.82	0.46	20.2	6,200

HRP QUARTERLY PROGRESS REPORT

indicated that at low space velocities (of the order of $50,000 \text{ hr}^{-1}$) the percentage conversion is equally good by using either catalyst. If a low-platinum catalyst could be substituted for the 0.3% Pt catalyst, a considerable saving on catalyst cost would be realized.

COMPARISON OF PLATINUM WITH PALLADIUM

The question of the relative merits of platinum and palladium as catalysts for the hydrogen-oxygen reaction has been raised. A few simple tests have been conducted on each type of catalyst to compare activity at room temperature when the catalyst is dry with activity when the catalyst is wet.

The catalysts, purchased from Baker and Company, Inc., Newark, New Jersey, were each in the form of cylindrical Al_2O_3 pellets, 1/8 in. diam by 1/8 in. long, with the noble metal coated on the surface of the pellets. Chemical analyses of these catalysts were: 0.3% Pt, 0.020% Cl; and 0.3% Pd, 0.025% Cl. Thirty grams of catalyst was packed inside the inner tube of a pyrex condenser to form a bed 6 1/2 in. long by 5/8 in. in diameter. A mixture of 180 cc/min of electrolytic gas ($2\text{H}_2 + \text{O}_2$) and 2670 cc/min of helium was passed through the catalyst under various conditions, as indicated in Table 36. The temperatures shown were taken at the hottest point within the catalyst, which was 1/4 in. from head of bed.

TABLE 36

Comparison of Platinum and Palladium as Recombination Catalysts

TIME AFTER STARTING FLOW OF GAS (min)	PLATINUM				PALLADIUM			
	RUN 1, DRY CAT. (no cooling)	RUN 2, DRY CAT. (cooling water run through jacket of condenser)	RUN 3, CAT. WET AT START (cat. cooled)	RUN 4, WATER DRIPPING ON CAT. THROUGHOUT RUN (cat. cooled)	RUN 5 (same as Run 1)	RUN 6 (same as Run 2)	RUN 7 (same as Run 3)	RUN 8 (same as Run 4)
0	22°C	21°C	12°C	19°C	29°C	18°C	18°C	19°C
1	170	148	13	19	80		16	
2					204			
3	306	217	15	19		180		
4					312		14	
5		214	28	19		191		
7			60	19				
8								
9								
10	358	208	150	19		192	14	
15					368		25	19
17							55	
20	370	208	198	19			134	
25							166	
30					370	196		19
60				19			198	19
90				19				19

FOR PERIOD ENDING NOVEMBER 15, 1951

From these parallel experiments on the two types of catalyst, it is seen that both catalysts are active at room temperature when dry and that the reaction begins immediately. In Runs 3 and 7 the catalyst was initially flooded with water, but no more water was added after starting the gas mixture through the bed. Here no reaction occurred until portions of the catalyst became dry, after which the heat of reaction quickly dried a large portion of the bed. The wet, platinum catalyst responded more rapidly than the palladium. Reaction on the wet platinum

catalyst became evident after 7 min had elapsed, whereas 17 min were required for comparable reactivity in the palladium. Finally, if by some means the catalyst is maintained wet, no reaction will occur for an indefinite period of time. This was shown not only by the absence of any temperature rise but also by measurement of the volume of gas mixture entering and leaving the reactor. These measurements showed zero per cent conversion in Runs 4 and 8 and 100% conversion in all other runs once the reaction had begun.

HRP QUARTERLY PROGRESS REPORT

SLURRY STUDIES

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L. E. Morse
J. P. McBride

Interest in slurries as reactor fuels is centered in the development of an aqueous uranium trioxide slurry suitable for use at temperatures near 250°C and containing 100 to 300 g of uranium per liter. The objective of this program in the past has been the attainment of a stable slurry that would not settle out when the reactor is shut down. It now appears that the objective will be difficult to achieve, and the goal of the program has been shifted toward obtaining an easily redispersed slurry without regard to stability.

URANIUM TRIOXIDE CHEMISTRY

Uranium trioxide is stable as the monohydrate in water between 60 and 300°C, and this hydrate can exist in any one of at least four different crystalline modifications, depending on its mode of preparation and the temperature under consideration. Two of the modifications, the alpha and beta, are stable at temperatures below 185°C and the others, gamma and delta, are formed in water at temperatures above 185°C. The crystal structure of the alpha and beta forms is orthorhombic, the gamma is rhombic, and the delta is triclinic.

Since the alpha and beta modifications of uranium trioxide monohydrate are only stable at temperatures below 185°C, they are ruled out as equilibrium states under the contemplated conditions of reactor operation. These materials are, however, of considerable interest since they represent the starting point for preparing the stable gamma and delta forms. During the past quarter slurries made from both the gamma and delta modifications of

uranium trioxide monohydrate have been prepared and their properties studied. It was found that slurries prepared from the gamma form exhibited less tendency toward packing, on heating, than those prepared from the delta form. At present it is felt that gamma uranium trioxide monohydrate represents a very promising starting material for the preparation of slurry fuels. Figure 41 summarizes the methods of preparing gamma and delta uranium trioxides.

Alpha $\text{UO}_3 \cdot \text{H}_2\text{O}$, the starting material for the preparation of $\gamma \text{UO}_3 \cdot \text{H}_2\text{O}$, is formed by decomposing uranium peroxide, $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, in air at 300°C, to "amorphous" UO_3 and then hydrating the product in water at a temperature between 77 and 185°C. $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ exists in two forms, depending on its method of preparation from uranyl nitrate solution. When uranyl nitrate is added to excess hydrogen peroxide solution, a very viscous precipitate that is difficult to filter and consists of microcrystalline, needle-like crystals is obtained. On the other hand, the addition of insufficient hydrogen peroxide for complete precipitation to uranyl nitrate yields an easily filterable, rapidly settling, precipitate consisting of large agglomerates of microcrystalline cubes. Either of these materials on firing at 300°C and hydration at 90°C yields $\alpha \text{UO}_3 \cdot \text{H}_2\text{O}$, which appears as large agglomerates of small, irregular-shaped particles under the microscope. The heating of $\alpha \text{UO}_3 \cdot \text{H}_2\text{O}$ in water at 250°C for about 60 hr yields $\gamma \text{UO}_3 \cdot \text{H}_2\text{O}$. This material is yellow-orange in color and appears under the microscope as rods about 1 μ in diameter and 10 to 20 μ long. This material shows no tendency to agglomerate, pack, or

HRP QUARTERLY PROGRESS REPORT

TABLE 37

Summary of Uranium Oxides

COMPOUND	CRYSTAL SHAPE	COLOR	pH OF SLURRY (250 g of U per liter)	SOLUBILITY IN H ₂ O (mg of U per liter)	HYDRATION NUMBER (n)	BEHAVIOR OF SLURRY (250 g of U per liter) ON HEATING AT 250°C	
						AGGLOMERATES	CAKES
α UO ₃ ·nH ₂ O	Irregular	Yellow	6.4	8.7	2.09	Unstable	Unstable
β UO ₃ ·nH ₂ O	Irregular	Yellow	3.6 unwashed 5.8 washed	9.0	2.08	Unstable	Unstable
α or β UO ₃ ·nH ₂ O	Irregular		6.4	1.5	0.81 to 1.06	Unstable	Unstable
γ UO ₃ ·nH ₂ O	Rods	Orange- yellow	6.3	1.4 at 25°C 1.0 at 90°C	0.83 to 0.90	No	No
δ UO ₃ ·nH ₂ O	Platelets	Dark brown	6.1	2.6 at 24°C 4.5 at 95°C	1.06	No	Slightly
UO ₄ ·nH ₂ O	Needles or cubes	Cream		0.5 at 30°C 1.4 at 80°C	Unknown	Unstable	Unstable

100°C, and almost completely at 250°C in a short time. The material formed on hydration at 250°C did not resemble either the γ or δ UO₃·H₂O and is being studied further as a possible fuel.

Bentonite, kaolin, and bismuth oxide were investigated as slurry stabilizing and antipacking agents. None of these materials seemed to stabilize slurries of δ UO₃·H₂O, nor did they appreciably alter the packing characteristic. No effect on inhibiting crystal growth has been observed (Table 38). An attempt was made to improve the properties of δ UO₃·H₂O as a fuel material by heat treating it at 600°C for 48 hours. This had only a slight effect on the properties of a slurry prepared from the material. These results are summarized in Table 39.

The preparation of a stable uranium slurry requires that the solids present be of very small particle sizes. It

has been reported that small amounts of beryllium and zirconium oxide have the property of stabilizing aluminum oxide crystals with respect to growth. The applicability of these materials for inhibiting growth of heated uranium slurries was investigated by igniting a mixture of uranyl nitrate and beryllium nitrate at 600°C. The material was ground in a ball mill and the fines collected by sedimentation and dried. This material, which has a mole ratio of 0.3 mole BeO to 1.0 mole of UO₃, was used to prepare a slurry containing 250 g of uranium per liter. After heating for 60 hr at 250°C and settling for 24 hr, the ratio of settled solids volume to total volume was 0.4%. This represents the most stable, high-uranium-concentration slurry prepared to date.

MAGNESIUM URANATE STUDIES

Magnesium uranate was considered briefly as a desirable fuel, since

TABLE 38

Stability of UO_3 Slurries Containing Additives

Slurry: 250 g of uranium per liter as UO_3

Heating cycle: 250°C for 60 hr in sealed quartz tubes, without agitation

Sedimentation time: 24 hr

URANIUM OXIDE	ADDITIVE	RATIO OF SETTLED SOLIDS VOLUME TO TOTAL VOLUME	REMARKS
$8 UO_3 \cdot H_2O$	None	0.15	Settled rapidly without packing
$8 UO_3 \cdot H_2O$	None	0.36	Settled rapidly without packing
Heat treated at 600°C for 48 hr	30 g of dialyzed bentonite of particle size below 25 $m\mu$	0.28	UO_2^{++} reduced to U(IV); settled rapidly without packing
	30 g of kaolin of particle size below 200 $m\mu$	0.32	Settled rapidly without packing
	Bismuth oxide	0.26	Formation of bismuth uranate indicated; settled rapidly without packing

TABLE 39

Effect of Heating and Kaolin Addition on Slurry Particle Size

Composition: 250 g of uranium per liter as UO_3

Heating: 60 hr at 250°C

PARTICLE DIAMETER (microns)	PERCENTAGE OF UO_3 LESS THAN STATED PARTICLE SIZE		
	UNHEATED SLURRY	HEATED SLURRY	HEATED SLURRY CONTAINING KAOLIN
2.5	10.0	5.0	5.0
5	37.5	11.0	8.0
10	64.0	25.0	22.5
15	78.5	39.0	37.5
20	85.5	49.5	42.5
25	91.5	55.0	50.0

slurries of this material should possess a high pH. An attempt to prepare magnesium uranate by addition of ammonia to a solution of magnesium chloride resulted in a compound containing 72.6% uranium and 1.6% magnesium rather than the 72.9 and 7.5% calculated for magnesium uranate. Heating slurries of this material resulted in color and pH changes. At room temperatures the substance had a solubility of 14 mg of uranium per liter.

A study was made of the possibility of increasing the pH of uranium trioxide slurries by addition of magnesium oxide. A uranium trioxide slurry with a pH of 5.8 was spiked with magnesium oxide in the ratio of 1 mole of MgO to 20 moles of uranium trioxide. This increased the pH to

HRP QUARTERLY PROGRESS REPORT

10, but after boiling for 1 hr the pH fell to 6.6. Successive additions of magnesium oxide raised the initial pH, which gradually decreased on boiling. Up to a 1:5 mole ratio of magnesium oxide to uranium trioxide, the pH finally dropped to close to the original on boiling; at higher magnesium oxide concentrations the pH

dropped more slowly and became constant at 8.5. On being heated to 250°C, the pH of this slurry dropped to 7.5 and bad caking of the solids occurred. Because of the caking that takes place with magnesium uranate slurries, this material is not considered to be a promising fuel and will not be investigated further.

SLURRY PUMPING STUDIES

CIRCULATING SLURRY EXPERIMENTS

A. S. Kitzes

Apparent Viscosity of UO_3 Slurries. Equipment has been constructed for measuring the apparent viscosity of various UO_3 slurries. Conventional rotational viscometers could not be used because the UO_3 slurries settle too rapidly. Consequently, the equipment consists of a length of tubing through which the slurries are forced from a reservoir by air. The pressure drop across the tube is measured for various rates of flow at constant temperature. The apparent viscosity can then be determined from a plot of the shear diagram. Agitation is provided to keep all the particles suspended. The equipment is now being calibrated by using glycerine and various sucrose solutions.

Abrasion Tests. In ORNL-1121,⁽¹⁾ it was reported that dry $UO_3 \cdot H_2O$ abraded types-347 and -321 stainless steel at the rate of 0.5 mil/hr when allowed to fall freely between a stationary metal specimen and a softer metal rotating disk separated by 0.005 inch.

Results of a test in which a slurry containing $UO_3 \cdot H_2O$, 100 g of UO_3 per liter, was pumped between the stationary specimen and rotating disk indicated that type-347 stainless steel is abraded at the rate of 0.2 mil/hr or approximately one-third of the rate at which the specimen was abraded by dry oxide.

These qualitative tests have been discontinued since the data proved

⁽¹⁾A. S. Kitzes *et al.*, "Slurry pumping Studies," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 156.

conclusively that oxide slurries will abrade stainless steel if the clearance between moving parts is small.

Temperature Cycle Loop. Several runs were made in the temperature cycle loop described in ORNL-1121.⁽²⁾ Slurries, containing as high as 200 g of oxide per liter of water, were pumped through the stainless steel loop at a velocity of 10.5 ft/sec with a centrifugal pump. Results of periodic heat-transfer measurements indicated that the over-all heat-transfer coefficient was independent of the oxide concentration in the slurry and approximated within the experimental error the value obtained when pumping distilled water through the loop. The heat-transfer coefficient did not drift with time, indicating no film formation on the heat transfer surfaces.

Chemical analysis of samples drawn off periodically showed a build-up of iron and U^{+4} in the solids, no change in the nickel or chromium content of the solids, and a slight increase in the pH of the slurry. Data are too meager to draw any definite conclusions. No evidence of erosion of the pump volute and rotor was found by visual inspection of these parts. Tests are being continued with a slurry of pH greater than 6.

BOILING EXPERIMENTS

A. S. Kitzes W. Q. Hullings
R. B. Gallaher C. A. Gifford

A boiling-slurry reactor has a major advantage over the companion circulating type in that there are no pumping problems. An experimental

⁽²⁾*Ibid.*, p. 160.

HRP QUARTERLY PROGRESS REPORT

program was initiated this quarter to determine qualitatively some of the problems associated with boiling a slurry. It is anticipated that difficulties may arise from three sources: (1) lack of stability of the slurry with resulting lack of uniformity, (2) foaming, (3) nonuniform bubble formation. Preliminary results have been obtained only on the first two problems.

Stability and Uniformity of Boiling Slurry. In order to determine to what extent the slurry becomes inhomogeneous while boiling, a glass system was set up in which $\text{UO}_3 \cdot \text{H}_2\text{O}$ slurries of varying concentrations and particle sizes were refluxed without agitation at 100°C and atmospheric pressure.

In these early tests, samples taken periodically from the flasks indicated no change in particle size,

no variation in solids content, no foaming, and fairly uniform bubble formation, provided there was no settling of the particles. In those cases where the boiling rate was too slow because of insufficient heating capacity to keep the particles suspended, the settled particles caked and caused "bumping" and erratic bubble formation.

Slurries, concentrated up to 250 g per liter, were boiled successfully for days.

Foaming. No foaming was evidenced in boiling several different hydrated uranium oxide slurries at 100°C and atmospheric pressure, except in one case. Apparently this one oxide had picked up some grease during processing that caused the foaming. Additional tests are being planned to determine the effect of other impurities in initiating foaming.

BOILING REACTOR STUDIES

R. N. Lyon, Section Chief

R. B. Briggs P. R. Kasten

P. C. Zmola

Further investigations were undertaken this quarter to determine the feasibility and possible operating characteristics of a boiling homogeneous reactor. These investigations include actual reactor tests as well as non-nuclear experiments.

"Supo", at Los Alamos, was operated under boiling conditions in cooperation with Dr. King and his Los Alamos group. Boiling was accomplished by shutting off the water flow through the internal cooling tubes so that the reflux condenser removed most of the heat generated. The unit was operated at atmospheric pressure to a power of 6 kw, which corresponds to a power density of approximately 0.5 kw per liter.

The results of this "Supo" experiment are quite encouraging, since they clearly demonstrate that a boiling homogeneous reactor is not inherently unstable. A comprehensive analysis of the data obtained has not yet been completed but will be presented as soon as possible.

The Department of Engineering of the University of California at Los Angeles is engaged in an analytical and experimental research program, under Atomic Energy Commission contract, for the investigation of factors governing transient density changes in a heated liquid subjected to heating fluctuations. Their experimental system consists of a dilute aqueous electrolyte heated throughout its volume by resistance heating. The power applied to the liquid is pulsed and a transient density change takes

place. The objectives of the experiment are to obtain a record of this transient density change, to establish limits for an analytical expression describing density as a function of time, and to control the time lag associated with given density change.

Some experiments have already been performed at atmospheric pressure, and the design of equipment for high pressure studies (up to 1000 psi) has been completed. A steady power density of 0.5 kw per liter with pulses to 5 kw per liter was used for the atmospheric tests.

The design of a small, boiling homogeneous reactor for a short-term experimental study has been initiated. Present plans call for a power output of up to 100 kw (2 kw per liter) with the unit operating over a range of pressures up to 150 psi. A vertical thimble, inside of which may be placed a movable boron rod that can be oscillated, or a flux measuring instrument will pass through the center of the reactor.

This experiment is expected to yield information that will indicate possible maximum power densities, height of the liquid level, and flux distribution in a boiling homogeneous reactor. Oscillating the boron rod will provide data for obtaining the ratio of the percentage of delayed neutrons to the prompt neutron generation time and will give an indication of the mean density variation with power and time.

HRP QUARTERLY PROGRESS REPORT

Most of the required equipment has been assembled for an experiment to obtain information on vapor formation and liquid entrainment. The liquid under observation is heated in a sealed pressure vessel (designed for 2000-psi operation) to the desired pressure, whereupon a rupture disk releases the pressure and allows the fluid to flash through an orifice. The pressure and temperature of the liquid will be recorded against time during the escape period, and the total amount of liquid entrained will be measured. Water will be used

during the preliminary tests, but eventually the working fluid will be uranyl sulfate solution.

A small qualitative experiment has been planned to assess the effects of fission fragments on bubble formation. Liquid containing fissile material, either supersaturated with gas or in a superheated condition, will be placed in a beam of neutrons. Visual observation will determine whether fission fragments are effective as nuclei for bubble formation.

HOMOGENEOUS REACTOR CHEMICAL PROCESSING

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The chemical processing involving the fewest unknowns for treating a homogeneous plutonium producer, which uses a uranyl sulfate-heavy water fuel, would consist of the following steps: removal of the fuel from the reactor in one batch, evaporation of the fuel solution to recover heavy water, conversion to a natural water system, 18-day decay of neptunium to plutonium, and finally, separation of plutonium, uranium, and fission products by tributyl phosphate solvent extraction.

HEAVY-WATER RECOVERY

The first step in the chemical processing of a homogeneous plutonium producer would consist of heavy-water recovery. The alternate procedure of carrying out solvent extraction for a heavy-water system is not desirable, since the inventory of heavy water would be greatly increased and excessive heavy-water losses would be encountered unless elaborate precautions were taken. It is now proposed that heavy-water recovery be accomplished by evaporating the uranyl sulfate to a slurry and drying the slurry for removal of residual water. This drying operation is being studied in the laboratory to determine the optimum drying temperature and time.

Preliminary data for heavy-water recovery upon drying uranyl sulfate at temperatures of 200 to 400°C have been obtained. It was found that about 1%, by weight, of water remained with the uranyl sulfate after drying at 200°C for 6 hours. The water content of the uranyl sulfate was

then reduced to 0.1% by drying at 400°C for only 3 hours. However, partial decomposition of the sulfate ion occurred at the higher temperature.

The apparatus for this work consisted of a tube furnace and a vitreous-sil combustion tube in series with an absorption train. A 1-g sample of uranyl sulfate was used. A dry, inert gas was used as a sweep, and the moisture lost by the uranyl sulfate was determined by direct weighing after absorption in an anhydron-pack absorption tube. A packing of silver ribbon at the outlet end of the combustion tube served to absorb the oxides of sulfur resulting from the decomposition of uranyl sulfate.

PLUTONIUM CHEMISTRY

The type of chemical process selected for a homogeneous plutonium producer will depend to a large extent on whether the plutonium in the reactor is present in solution or as a precipitate. The behavior of trivalent and tetravalent plutonium in the system uranyl sulfate-sulfuric acid-water, at various temperatures, has been previously reported. During this period the behavior of plutonyl ion was investigated.

A stock solution of plutonyl nitrate was prepared and added to 1 M UO_2SO_4 to a concentration of 0.46 mg/ml. In these experiments the sulfuric acid concentration was varied and the solutions heated at 250°C for 68 hours. Table 40 summarizes the data obtained in the experiments.

HRP QUARTERLY PROGRESS REPORT

TABLE 40

Solubility of Plutonium in $1M UO_2SO_4 \sim H_2SO_4$ on Heating at $250^\circ C$

Solution: $1M UO_2SO_4$ containing
0.46 mg of Pu(VI) per
ml

Heating: 68 hr at $250^\circ C$

$H_2SO_4(N)$	Pu SOLUBILITY (mg/ml)
0.024	0.065
0.28	0.079
0.60	0.162
0.93	0.354

This table shows that the plutonyl state exhibits a higher solubility than the tri- and tetravalent states. The x-ray-diffraction pattern of the precipitates formed showed the material to be plutonium dioxide. Further, a valence state analysis of the supernatant from one of the solubility determinations showed the plutonium in solution to be 82% plutonium(VI) and 18% plutonium(III) and plutonium(IV). From this analysis it is concluded that plutonyl ion is reduced to tetravalent plutonium at elevated temperatures in uranyl sulfate, and that the tetravalent plutonium precipitates. Accordingly, the values indicated in Table 40 are a measure of the solubility of tetravalent plutonium and not plutonyl ion. The conditions of this experiment are not representative of those prevailing in a homogeneous reactor, since no partial pressure of oxygen was maintained. It is conceivable that oxygen would oxidize plutonium to the hexavalent state under the conditions of reactor operation.

In these experiments plutonyl sulfate was prepared by oxidizing a stock solution of plutonium nitrate with an excess of silver peroxide. The silver was then precipitated with hydrochloric acid and separated by centrifuging. The oxidized plutonium was placed on a Dowex-50 resin column and after washing with water and $0.5N H_2SO_4$, the plutonium was eluted with $6N H_2SO_4$.

SOLVENT EXTRACTION

Although it is not yet known how plutonium will behave in an aqueous homogeneous plutonium producer, it is definite that plutonium and uranium must be isolated and decontaminated from the fuel solution after it is discharged for re-enrichment. Even if plutonium precipitates and is completely removed from the reactor by filtration, the discharged fuel solution will contain appreciable quantities of neptunium²³⁹. This neptunium will be allowed to decay to plutonium, which must then be isolated from the uranium and fission products.

At present, solvent extraction is the optimum method of isolating the plutonium and decontaminating the uranium for return to a diffusion plant. It would be desirable to make the separation after only 15 to 20 days of cooling instead of the present cooling period of 90 days. The 15- to 20-day cooling period is necessary to permit the decay of neptunium to plutonium, since neptunium is not recovered by the solvent extraction process.

A study of the solvent extraction of short-time cooled material has been initiated. Samples of natural uranium were irradiated in the X-10 graphite pile, and one test was made of the

FOR PERIOD ENDING NOVEMBER 15, 1951

efficiency of solvent extraction after 15 days of cooling. The results of this test indicated that the present Purex process will not give adequate decontamination from neptunium. A decontamination factor of only 10 was obtained for this element over one cycle of solvent extraction.

It is not yet known what effect the presence of short half-lived fission products, not present after 90 days of cooling, had on the decontamination, but certainly nothing followed the uranium and plutonium to the extent of the neptunium breakthrough.



APPENDIX



BEARING OPERATION AT LOW VALUES OF THE SOMMERFELD NUMBER

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An investigation concerning the operation at low values of the Sommerfeld number of bearings made of unusual materials was begun on August 26, 1951 at the University of Tennessee by the Department of Mechanical Engineering under Subcontract No. 392 for the Oak Ridge National Laboratory.

The fuel circulating pump is a most important and critical piece of equipment in a homogeneous nuclear reactor system. In the form most generally envisioned for the pump, the journal bearing is an essential element. Journal bearing design normally calls for materials and lubricants proven by long experience and is based on hydrodynamic theory. Operation at relatively high values of the Sommerfeld number⁽¹⁾ is usually expected.

In a homogeneous reactor the leakage problem makes the canned-rotor type of pump highly desirable. The use of this type of pump, however, introduces problems of bearing design. The circulating fuel mixture, which normally would be the lubricant in a canned-rotor pump, is highly corrosive. This limits the choice of material for the bearing to a relatively small group, and the materials presently known to be satisfactory from the standpoint of corrosion resistance

have physical properties that make them generally undesirable in normal bearing practice. The lubricants generally used for the bearings in a canned-rotor pump have low viscosities of the order of 0.25 centipoise at operating temperatures that may approach 150°C.

The objectives of this investigation include, but are not limited to, the following four problems.

1. The life-expectancy of bearings constructed of unusual materials according to the design presently used for the Westinghouse 100-A pump is to be determined.

2. Basic data on the characteristics of submerged bearings are to be obtained, with emphasis upon improvement of bearing performance in the Westinghouse 100-A and similar pumps through better design. This effort is to include studies of the effect of radial clearance on lubricant flow in submerged bearings and the extent of hydrodynamic film development; resistance to failure owing to abrasive particles that may contaminate the lubricant; the effect of bearing surface finish and precision on the minimum Sommerfeld number; and the effect of the presence of the thrust face of a composite bearing on the performance of the radial section of the bearing.

3. Studies will be made of materials that are satisfactory from the standpoint of corrosion, with emphasis on the improvement of bearing performance in the Westinghouse 100-A and similar pumps through the use of more satisfactory materials. This problem is to include studies of the

$$^{(1)} S_n = \left(\frac{ZN}{P} \right) \left(\frac{r}{c} \right)^2,$$

where

S_n = Sommerfeld number,
 Z = absolute viscosity,
 N = journal speed,
 P = unit bearing load,
 r = journal radius,
 c = radial clearance.

HRP QUARTERLY PROGRESS REPORT

relative compatibility in and recoverability from boundary lubrication conditions of various material combinations, and the relative resistance to abrasion from particles that may contaminate the lubricant.

4. An evaluation of the findings of 1, 2 and 3 will be made in an effort to extend the hydrodynamic theory of lubrication to include the more elusive variables outlined.

SCHEDULE OF EXPERIMENTAL STUDIES

The experimental work to be conducted in connection with this investigation is to be divided into two phases. Phase I will include the following series of tests.

Test Series No. 1. Tests will be made to evaluate the life-expectancy of bearings constructed of Stellite Nos. 3, 6, and 98M2 and type-18-8W stainless steel designed for use in the Westinghouse 100-A pump.

Test Series No. 2. An evaluation will be made of the relative compatibility between various combinations of the materials to be used in Test Series No. 1. Stellite No. 98M2 against No. 14 Graphitar will be used as a basis for comparison.

Test Series No. 3. The effect of the surface finish and surface finish-to-clearance ratio on the minimum Sommerfeld number will be determined.

Phase II will include the following series of tests.

Test Series No. 4. Studies will be made of the lubricant flow characteristics in bearings with a longitudinal flow path. This series of tests will include the effect of groove arrangement and thrust face geometry.

Test Series No. 5. Experiments will be designed to study the performance of the integral thrust face of a composite bearing.

Test Series No. 6. A study will be made of the bearing life as it is affected by contamination of the lubricant. The size and hardness of abrasive particles and the ratio of particle size to the radial clearance will be investigated, and the relative abrasion resistance of the materials listed in Test Series No. 1 will be determined.

EXPERIMENTAL FACILITIES

Two test stands have been designed for these studies. One test stand has been completed and is being calibrated, and the second unit is about 60% complete. These units are based on the equipment design used by the General Electric Engineering and Consulting Laboratory, with modifications to improve accuracy of measurement and increase component life.

The test stands were designed to permit experimentation at atmospheric temperature and pressure. Recent experiments have shown that the temperature coefficients of static friction of metals are rather small and the harder the surface the lower the temperature coefficient.⁽²⁾ In view of the materials being proposed for canned-rotor pump bearings, it is felt that the expense and lack of flexibility associated with high-pressure and high-temperature bearing tests is not justified in the immediate investigation. The test equipment has been designed to permit a speed range of 466 to 4660 rpm and total bearing load of 400 lb, and the

(2) I. Simon, H. O. McMahon, and R. J. Bowen, "Dry Metallic Friction as a Function of Temperature Between 4.2°K and 600°K," *J. Applied Phys.* 22, 177-184 (1951).

FOR PERIOD ENDING NOVEMBER 15, 1951

Sommerfeld number in tests can be made to equal that expected in a pump by adjustment of these two variables.

The tests units, which were designed for the studies included in Phase I, will require alteration in load application and instrumentation for the studies scheduled in Phase II.

A Brush Surface Analyzer has been procured for the determination of surface finish. This equipment permits an exploration of the surface finish, plots the actual asperity height, and gives a rms roughness value. This is felt to be necessary because it has been observed that the ratio of the actual asperity height to the rms roughness may vary over a rather wide range, depending on the procedure and technique used to finish the bearing surfaces. Thus, a group of surfaces with the same rms roughness may ex-

hibit a rather wide deviation in maximum asperity height.

Considerable time has been spent on experimentation in finishing Stellite bearing surfaces to establish a technique of finishing the bearing surfaces with as low a maximum asperity height as practical.

ESTIMATED SCHEDULE OF ACTIVITIES

Construction of test unit No. 2 should be complete by January 5, 1952. Test work previously outlined is tentatively scheduled as follows:

Test Series No. 1	January 1	January 30
Test Series No. 2	January 21	February 16
Test Series No. 3	February 18	March 22
Test Series No. 4	March 14	April 12
Test Series No. 5	April 14	May 10
Test Series No. 6	May 12	June 7

[REDACTED]

SECURITY INFORMATION

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SECRET

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