ORNL-826

ORNL 826

This document consists of 158
pages.
Copy 101 of 121. Series A

1

Contract No. W-7405, eng 26

ORNL-826

HOMOGENEOUS REACTOR EXPERIMENT

C. E. Winters, Project Engineer

QUARTERLY PROGRESS REPORT for Period Ending August 31, 1950

Photostat Price \$ 24.30

Microfilm Price \$ 7.50

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

DATE ISSUED **OCT 24 1950**

OAK RIDGE NATIONAL LABORATORY
operated by
CARBIDE AND CARBON CHEMICALS DIVISION
Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

10 001

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

~~SECRET~~

ORNL 826
Progress Report
Reactors

Internal Distribution:

1	G. T. Felbeck (C&CCD)	21	E. J. Murphy	36	C. B. Graham
2-3	706-A Library	22	F. C. VonderLage	37	J. L. English
4	706-B Library	23	C. E. Winters	38	W. R. Gall
5	Biology Library	24	E. H. Taylor	39	L. R. Quarles
6	Health Physics Library	25	A. H. Snell	40	E. P. Blizzard
7	Metallurgy Library	26	A. Hollaender	41	E. D. Shipley
8-9	Training School Library	27	F. L. Steahly	42	R. S. Livingston
10-13	Central Files	28	M. T. Kelley	43	C. P. Keim
14	C. E. Center	29	M. M. Mann	44	C. D. Susano
15	C. E. Larson	30	J. H. Gillette	45-46	Central Files (O.P.)
16	W. B. Humes (K-25)	31	J. A. Lane	47	K. Z. Morgan
17	W. D. Lavers (Y-12)	32	R. N. Lyon	48	D. W. Cardwell
18	L. B. Emlet	33	J. M. Stein		
19	A. M. Weinberg	34	C. H. Secoy		
20	J. A. Swartout	35	G. H. Clewett		

External Distribution:

49-60 Argonne National Laboratory
61-68 Atomic Energy Commission, Washington
69 Battelle Memorial Institute
70-73 Brookhaven National Laboratory
74 Bureau of Ships
75 Carbide & Carbon Chemicals Division (Y-12)
76 Chicago Operations Office
77-80 General Electric Company, Richland
81 Hanford Operations Office
82-83 Idaho Operations Office
84 Iowa State College
85-88 Knolls Atomic Power Laboratory
89-91 Los Alamos
92 Massachusetts Institute of Technology (Kaufmann)
93 National Advisory Committee for Aeronautics
94-96 NEPA Project
97-98 New York Operations Office
99 North American Aviation, Inc.
100 Patent Branch, Washington
101-115 Technical Information Division, ORE
116-117 University of California Radiation Laboratory
118-121 Westinghouse Electric Corporation

DO NOT
PHOTOCOPY

~~SECRET~~

TABLE OF CONTENTS

I. SUMMARY	C. E. Winters	6
II. ENGINEERING DESIGN	W. R. Gall	9
Shielding		10
Reflector Purification		12
Emergency Cooling System		12
Control Rod Mechanisms		12
Soup Pressurizer		16
Steam Generator		20
Power Equipment		20
Reflector Dumping Time		23
Miscellaneous Equipment		23
D ₂ O cooler		23
Soup to soup heat exchanger		23
III. ENGINEERING DEVELOPMENT	C. B. Graham	27
Introduction		28
The Soup Dump Tank System		30
Soup Recirculating Test Loop		32
Pump and circulating tests		32
Bearings for 100A pump		33
Pressurizer and level and pressure control		33
Soup feed pump		34
Soup heat exchanger		34
Ring and Groove Type Pipe Joints		35
Removal of Gas from the HRE		37
High pressure stainless steel model of the core		37
Gas holdup		37
Cooling of core		40
IV. CONTROL AND SIMULATOR	L. R. Quarles	43
Control		44
Simulator		50
V. REACTOR PHYSICS	J. M. Stein	54
Shielding		55
Induced Activity		60
VI. RECOMBINATION OF HYDROGEN AND OXYGEN	G. H. Clewett	64
Introduction		65
Composition Limits for Explosions in Hydrogen-Oxygen-Steam Mixtures		66
Pilot Tests of Primary Recombiner		68
Preliminary burner tests		69
Pilot plant layout		70
Operation of pilot layout		72
Thermal Recombination of Hydrogen and Oxygen		73
Catalytic Recombination of Hydrogen and Oxygen		75

TABLE OF CONTENTS (Cont'd)

VII. CHEMICAL STUDIES	C. H. Secoy	77
Solubilities of Fission Product Sulfates		78
Chemical Control		80
Determination of uranium concentration		80
Determination of oxidizing power		83
Determination of other properties		84
Experimental and developmental — An electromagnetic densitometer		85
Phase Rule Studies		89
Introduction		89
Experimental		89
The data and discussion		91
Slurry Problems		98
Radiation Chemistry		104
VIII. CORROSION	J. L. English	106
Summary		107
Introduction		108
Protective Treatments on Stainless Steels		109
Nitric acid pretreatments		115
Chromic acid pretreatments		122
The use of oxygen partial pressures		123
Corrosion Resistance of Stainless Steels		125
Corrosion Resistance of Zirconium		127
Corrosion of crystal bar zirconium		127
Corrosion of bureau of mines zirconium		128
Zirconium welding		140
Irradiation-Corrosion Tests		141
Corrosion of Bearing Materials		143
Stellite alloys		143
Titanium carbide		145
Hastelloy C		145
Durhy		146
Carboloy 44A		146
Graphitar		147
Durimet		147
Type 410 stainless steel		148
Rexalloy		149
Corrosion Resistance of Reflector Materials		150
Effect of water pH on corrosion resistance of SAE 1030		150
Effect of hydrogen peroxide on corrosion resistance of SAE 1030		151
Effect of sodium dichromate on corrosion resistance of carbon steel		152
Effects of sodium chromate on corrosion resistance of carbon steel		152
Effect of 2S aluminum on contact corrosion of carbon steel		153
Corrosion resistance of boral in water		156
Miscellaneous Corrosion Tests		157
Tantalum		157
Titanium		157

LIST OF FIGURES

Fig. 1	Proposed HRE Shield Arrangement	11
Fig. 2	D ₂ O Purification System	13
Fig. 3	Emergency Cooling System	14
Fig. 4	Safety Plate Assembly	15
Fig. 5	Sectional View of Shim $\mathbb{R}$	15
Fig. 6	Shock Absorber, Bearings and Rod Arrangement	17
Fig. 7	Control Rod Drive Mechanism	18
Fig. 8	Soup Pressurizer Heating System	19
Fig. 9	HRE Steam Generator	22
Fig. 10	Operation of Reactor at Fractional Loads	25
Fig. 11	Reflector Fluid Level During Emergency Dump	26
Fig. 12	Gas Outlet Details	38
Fig. 13	Calibrated Cylinder	39
Fig. 14	Holdup vs. Gas Flow at Vortex Pressure	41
Fig. 15	Gas Flow vs. Gas Holdup in Steel Sphere for Different Bottom Injection Rates	42
Fig. 16	Block Diagram of Simulator	51
Fig. 17	Flux Distribution in Barytes Concrete Shield	62
Fig. 18	Thermal Recombination as a Function of Flow Rate	74
Fig. 19	The pH of Aqueous Uranyl Fluoride at 25°	93
Fig. 20	The Density of Aqueous Uranyl Fluoride at 25°	93
Fig. 21	The System, Uranyl Fluoride-Water	94

I. SUMMARY

The detailed design of most of the larger and more important portions of the equipment within the reactor shield is either completed or is on the drawing board. The principal exception is the "off-gas" system, which includes the dump condensers, the recombiners, and the fission gas traps. The heavy items such as the forged steel reflector vessel, the soup heat exchanger and the pumps are on order. Most of the remaining parts of the system will be fabricated in local shops.

Six bids for the HRE building and site development were received by the AEC. J. A. Johnson, Inc., the successful bidder, was given formal notice to proceed on August 21. Completion of the building for occupancy is scheduled for December 21, 1950.

The design of the shield and the equipment arrangement within the shield has started. Preliminary calculations indicate that the upper limit of induced activity in equipment is reasonable. Unless boron is included in the concrete mixture the induced activity in the shield will deny human access adjacent to equipment for repair or replacement. The present shield specifications call for a density of at least 3.1, and a water content, if possible, of 7% with the incorporation of 1% of boron. Mixtures of Portland cement, limonite, barytes, and columanite meet all of these specifications. With these specifications the shield thickness would be seven feet, allowing two feet between the reactor and the external soup equipment, and five feet on the outside of all equipment containing fresh soup.

The most significant engineering development result in the past quarter is the successful operation of a test loop containing uranyl sulphate at 250°C and 1000 psi, pumped by a Model 30 Westinghouse canned rotor pump. This loop operated for three weeks before it was shut down for the installation of additional equipment for test. A disassembly of the pump disclosed some wear on the bearings and a slight amount of cavitation in the impeller. Tests on the soup concentrator control system, in its unfinished state, demonstrated that the concentration could be predicted and controlled to ± 1 gm/l ($\pm 3\%$). It is predicted that when the system is finished, concentration can be controlled and measured to ± 0.25 gms U/l ($\pm 1\%$) which should be more than adequate for temperature control of the reactor. Other engineering test experiments indicate that the high pressure fuel feed pump is satisfactory. When care is

used in assembly, modified standard oval ring joints for high pressure pipe lines appear to be leak free. Simulated gas holdup measurements on the core continue to indicate that the core will contain a maximum of 0.5% by volume of gas. A full scale soup test loop is under construction and should be completed and tested during the next quarter, along with the emergency dump system, and several of the smaller heat exchangers.

Extensive corrosion experiments in the absence of radiation have been performed. Results are given in Part VIII of this report. Stainless steel with proper surface preparation indicates less than one mil per year of corrosion. A demonstration of the adequacy of stainless steel, at least in the absence of radiation, is indicated by the successful operation of the test loop as described before. The quality of recent Bureau of Mines Zr appears to have greatly improved, to the extent that zirconium sufficient to make a reactor core tank has recently been requested through the AEC. It is very doubtful that a feasible Zr core tank can be ready for the initial HRE startup, therefore dual emphasis on corrosion of zirconium and stainless steel will continue.

The program to study variables affecting solution stability in the presence of radiation is unfortunately not as far advanced as other phases of the program. Sixteen experiments have been performed, five of which were unsuccessful in that the uranyl sulphate was reduced and had precipitated. The most encouraging result was that 11 experiments were successful, and that extenuating circumstances existed for all the unsuccessful cases. It appears that if the early experiments in the HRE are to be completely successful, more information concerning the control of the corrosion-radiation-solution stability variables must be available. An expanded program to acquire these answers is now in effect.

Experiments to define the explosibility of hydrogen, oxygen, steam mixture indicate that mixtures containing 30% of $2H_2 + O_2$ are potentially explosive; mixtures below this figure apparently are not explosive. Experiments have indicated a design for a high temperature flame type burner-recombiner for gases that will operate over a range of rates of about 50:1. Recombination experiments using thermal and catalytic types have been conducted on small scale. Larger scale tests are planned so as to allow selection of best type for final installation.

A program to measure the solubility of fission product sulphates at high temperatures has been initiated. The collected information will allow predictions to be made as to the operating cycle of the solutions before some sort of reprocessing will be necessary to prevent gross precipitation of fission products.

A survey has been made of the methods available for the chemical analysis and control of homogeneous reactor soup. Further work will be required before final procedures can be adopted and standardized.

The specifications for the reactor nuclear and process instruments have been virtually completed. Detailed design of the instrument panel, control console, and safety interlock system will be completed during the next quarter. The nuclear instruments for this installation will be essentially identical to those for the MTR except that the high speed servo system has been eliminated. An analogue computer or reactor simulator is under construction. The simulator, when finished, should represent an excellent tool for studying the dynamic stability of all circulating fuel type reactors.

Long Range Program. A separate long range reactor study and planning group has been established at ORNL. While all types of reactors are to be studied, the first detailed study will concern large aqueous homogeneous type reactors for power plutonium, power breeding, or straight power producing type reactors. The first report of this group will be issued separately during the first week in September.

Phase rule studies of uranyl fluoride-water system is reported as well as recent results of the slurry program.

II. ENGINEERING DESIGN

SHIELDING

The biological shield for the HRE serves the following functions:

- (a) Reduction to instrument tolerance level of all radiation emanating from the reactor.
- (b) Compartmentalization of equipment within the shield to improve accessibility for maintenance or replacement purposes.

Preliminary estimates indicate that seven feet of barytes concrete or the equivalent is sufficient to serve function (a) for the reactor tank itself with somewhat lesser thicknesses required for other components of the reactor. It is also estimated that approximately one foot of barytes is adequate protection against induced activity in any of the component pieces of equipment after shutdown, draining, and decontamination. Hence, if each item is separated by at least one foot of shielding from other equipment, function (b) is served. A tentative shield and equipment arrangement is illustrated in Fig. 1. In this arrangement overall dimensions of the shield are shown to be 22 ft by 24 ft, the outer two feet being mortared blocks and the interior being stacked blocks. The overall height of the shield has not yet been established, but it is expected to be approximately 20 ft.

It is planned to first install the supporting structure and reactor equipment on the foundation after which the shield will be constructed around it starting at the center and working outward.

Results of approximate calculations of the upper limits of the induced activities in principal items of soup system equipment are given in Table I.

TABLE I

ITEM (Description)	SATURATION ACTIVITY (Curies)	SATURATION ACTIVITY AFTER ONE DAY SHUT- DOWN (Curies)	BARYTES CONCRETE SHIELD THICKNESS REQUIRED TO REDUCE TO 0.1 R/Hr (Inches)
Reflector Shell	6800	280	22*
Heat Exchanger	130	3.	5.8
Pump	590	24.	9
Pipe per foot	4.8**	1.7**	6.2

* Thickness required to reduce intensity of radiation to .1 r per 8-hr day

** Activity due to delayed neutrons only

It can be seen that 2 ft of barytes concrete is sufficient to reduce the radiation from induced activity in the reflector tank to 0.1 r per 8-hr day. Detailed calculations based upon a careful evaluation of expected service conditions will substantially lower the activities reported in Table I.

REFLECTOR PURIFICATION

Due to corrosion of the reflector vessel, of the reactor core tank, and of the control plates, the heavy water reflector system will eventually become contaminated with metallic ions. It is proposed to periodically purify the reflector fluid stored in the dump tanks by a distillation process as shown on Fig. 2. When desirable, D_2O may be distilled at a rate of 0.1 gpm, and the resulting sediment will be allowed to collect in the still. This sediment can then be removed from the system by a drain-off to the outside of the shield. The still vapor will be condensed on the surface of the gas header and flow to the dump tanks.

EMERGENCY COOLING SYSTEM

Figure 3 outlines principal features of an emergency cooling system designed to function in event of complete failure of all services to the reactor. It consists of jackets on all D_2O and soup dump tanks and on the D_2O vapor header connected in parallel with each other and supplied with water by a convection loop. Other items of the loop are a surge tank at the top of the shield, fin tubes for dissipation of heat and two vertical 2-in. pipes connecting the dump tank jackets with the surge tank and the fin tubes. Water heated in the jackets will rise through the "hot leg" to the surge tank and return through the fin tubes and the "cold leg."

CONTROL ROD MECHANISMS

Figures 4 and 5 illustrate the construction of the safety plate assemblies designed to serve as a quick-acting safety mechanism to allow time for dumping to be effective in event of a scram. Each assembly consists of four curved

13

FIG 2

D₂O PURIFICATION SYSTEM

14

SECTIONAL VIEW
OF SHIP

FIG. 5

plates fitted around approximately 120° of circumference of the core tank and suspended on a 1 in. stainless steel rod from a magnet housed in a 4-in. pipe above the reflector tank. There will be two safeties of this type and one "regulating" rod which will be simply a rod containing Boral.

The Boral absorber plates are enclosed in aluminum plates with bevelled edges. These plates are fastened together and hung on the 1-in. supporting tube by aluminum plates as shown in Fig 6. The whole aluminum and boral assembly is fastened to the 1-in. stainless steel tube by a non-rotating disconnect as close as possible to the plates. The stainless steel tube is joined to a solid stainless rod to which the magnet armature is attached. This armature is removable through the housing in order to remove shock absorber and bearings for servicing.

A section of the complete mechanism is shown in Fig. 7 .

Data on the drive mechanism are as follows:

Total travel	18 in.
Total weight rods, plates, and armature	26.1 lb
Release time of magnet	0.010 sec
Initial acceleration of rods	6.38 g
Acceleration after 3 in. travel	1 g
Time for first 3 in. travel	0.054 sec
Stopping distance for shock absorber	1 in.

SOUP PRESSURIZER

It is proposed to maintain a pressure of 1000 psia in the reactor core by heating with high pressure steam. A 15-inch long section of the pressurizer will be jacketed with a 6-in. pipe, and saturated steam at pressures up to approximately 1500 psia will be supplied to the jacket. The steam will be contained in a closed system and will be generated by a small high pressure boiler having a 10 kw electrical heat input. Condensed steam from the jacket will flow by gravity to the boiler.

Figure 8 is a simplified flow diagram of the boiler and pressurizer system.

FIG. 6
SHOCK ABSORBER, BEARINGS
& ROD ARRANGEMENT

MOTOR DRIVE

- (A) Vertical gear motor (3 phase induction - reversible instantaneous) to fit within 5" sch 40 pipe as shown
- (B) Jetz Mfg Co's gear motor type M1-1/2 H₁ motor - 3 phase - 220V output at gear reducing shaft 40 rpm - 48" - 031 HP Max OD = 4 3/4"
- (C) Gear box to be vented to prevent oil or grease leakage due to pressure differences inside & outside
- (D) Cap of motor housing to be 5" XX strong pipe cap & to contain 12 kovar glass terminals & 1 spark plug
- (E) Gear motor to be "welded in" housing as shown

DRIVE SCREW

1/2-10 Acme
Travel - 18"

Time of travel $\frac{18 \text{ in}}{30 \text{ rev/min} \times 4 \text{ in/rev}} = 4 \frac{1}{2} \text{ min}$
Rate of travel $\frac{18 \text{ in}}{4 \frac{1}{2} \text{ min}} = 4 \text{ in/min}$

FIG 7
CONTROL ROD DRIVE
MECHANISM

16. 017

FIG. 8
SOUP PRESSURIZER HEATING SYSTEM

The time required to bring the pressurizer to 1000 psia is influenced considerably by the size of the vessel used for the boiler, because the mass of metal comprising the boiler increases rapidly as the boiler diameter increases. Size of the boiler is not yet determined, but it is estimated that a 4-in. diameter boiler will require 55 minutes and an 8 in. one will require 120 minutes to bring the pressure up to 1000 psia. Heat losses from the system during normal operation are estimated to be about 1.5 kw.

Liquid level in the pressurizer is maintained by a control based on a weighing device which detects changes in weight of a small tank connected to the pressurizer vessel by two 3/8 in. diameter 40 in. long tubes.

STEAM GENERATOR

Complete drawings and specifications for the steam generator have been issued for bids and A. O. Smith, Inc., is the successful bidder. Data for this exchanger is given in Table II. Figure 9 shows the calculated performance of the exchanger in terms of steam pressure versus total reactor power.

POWER EQUIPMENT

Some studies have been made to determine the most practical power generating equipment to propose for use in the homogeneous reactor experiment. The equipment would consist of a steam turbogenerator set and condenser. The rating of the turbine will be 150 kw at 200 psia throttle pressure and 2 in. Hg absolute exhaust pressure with saturated steam at the throttle. The generator would be 150 kw, 0.8 power factor, 460 volt three-phase air-cooled. Use of a turbine will necessitate installation of a vacuum pump to remove air from the condenser and a condensate pump to remove water. However, the condenser will be designed to condense steam from a pressure reducing valve without vacuum when it is not desired to operate the turbine.

To predict the net output of the system when the reactor is operated either above or below its rated 1,000 kw level necessitates data on the operating characteristics of the turbine-generator at other than its rated pressure

TABLE II

Homogeneous Reactor Experiment
Equipment Design Data Sheet

Heat Exchanger

Item No. 3
Drawing Nos. D-7559
D-7564
D-7565

Heat Load	1000 kw	
	Soup	Water
Inlet Temp., (°F)	482	382
Outlet Temp., (°F)	407	382 (sat. steam)
Inlet pressure, (psi)	1000	200
Outlet pressure, (psi)	980 (approx.)	200
Design pressure, psi	2000	600
Design Temperature (°F)	500	500
Inside dia. of shell	26 1/4 in.	O. D. 28 in.
Shell thickness	7/8 in.	

Tubes: - 112 tubes 1/2 in. O. D. 18 BWG (0.049 in. wall)
110 in. avg. effective heat transfer length. U bend tube bundle.

Double tube sheet. Leak detection between tube sheets.

Feedwater heater and dry pipe in steam space.

Normal water level - 3 in. above center line (500 lb water at 382°F)

Total volume of soup: 5.37 liters

Total heat transfer area, outside tubes: 67 ft²

Steam outlet: 4 in. schedule 60

Feedwater inlet 1 in. schedule 40.

Soup inlet and outlet 1 1/4 in. schedule 80.

Remote reading liquid indicator (1 in. connections).

Feedwater control from same connections.

All welded construction. Completely stress relieved and radiographed.

NO. 318. 20 DIVISIONS PER INCH BOTH WAYS. 180 BY 200 DIVISIONS.

CODER BOOK COMPANY, INC.

NORWOOD, MASSACHUSETTS

DES. 9742

FIG. 9

HRF STEAM GENERATOR

PRESSURE-LOAD CHARACTERISTICS

SOUP TEMP. 482°F
HEAT TRANSFER SURFACE
67.50 FT.
SOUP VELOCITY 15.8 FT./SEC.

and rated steam flow. Normally steam turbines are operated at fractional loads with full throttle pressure. Behavior of a turbine when throttle pressure is increased but rate of steam supply decreased could be known with certainty only by testing of an actual unit, since each control valve nozzle arrangement, blade design, etc., would offer a different set of characteristics. Turbines equipped with nozzle control as well as throttle control would obviously exhibit better efficiencies at the fractional loads. The engine efficiencies shown in Table III and Fig. 10 have been estimated on the basis of Westinghouse performance data with a correction factor applied for variation in the throttle pressure.

REFLECTOR DUMPING TIME

Figure 11 gives results of an estimate of dumping time for the D_2O reflector. It is seen that to dump from 6 in. above the core tank to bottom of the core tank required approximately 22 sec.

MISCELLANEOUS EQUIPMENT

D_2O COOLER

A heat exchanger has been designed which cools the reflector fluid from $302^{\circ}F$ to $282.8^{\circ}F$ by heating boiler feedwater from $101^{\circ}F$ to $194^{\circ}F$. The exchanger is a double pipe type consisting of 16 10-ft lengths of 1-in. schedule 40 pipe inside $1\frac{1}{4}$ -in. schedule 40 pipe connected in series by concentric return bends at each end.

SOUP TO SOUP HEAT EXCHANGER

A high pressure exchanger has been designed to cool soup flowing from the core tank by exchange with that being returned to the core tank.

TABLE III

Output of 150 kw Turbogenerator (Rated at 200 psia/2 in. Hg abs)
at Fractional Reactor Heat Releases

FRACTIONAL LOAD	REACTOR HEAT RELEASE (kw)	THROTTLE STEAM ¹ PRESSURE (psia)	ENGINE ² EFF. (%)	OVERALL THERMAL EFF. (%)	GROSS GEN. OUTPUT (kw)	NET GEN. ³ OUTPUT (kw)
5/4	1250	148	47.7 ⁴	13.3%	166	146
4/4	1000	200	47.7	14.1	141	121
3/4	750	256	43.5	13.4	100	80
1/2	500	332	37.1	11.9	60	40
1/4	250	430	20.0 ⁴	7.3	17	

1. Steam pressure determined from analysis of heat transfer relationships in heat exchanger. Steam temperature was found to be almost linear relationship with reactor heat release.
2. Engine efficiencies taken from Westinghouse data for two-stage straight condensing turbine rated at 150 kw when supplied with steam at 200 psia and exhausting at 2 in. Hg abs. Efficiencies at 3/4 and 1/2 loads taken from Westinghouse fractional load data (see 4, below).
3. Net generated output assumed to be gross output minus 20 kw. The plant requirements for pumping, etc. for both steam cycle and reactor apparatus having been roughly estimated at this value.
4. Engine eff. obtained by extrapolation of curve.

FIG. 10.
OPERATION OF REACTOR AT FRACTIONAL LOADS
 150 KW RATED CAP TURBINE (200 PSIA/2" Hg abs)

Helium expanded & compressed
adiabatically, constant mass of
 D_2O vapor in reflector vessel
expanded adiabatically

FIG. 11

REFLECTOR FLUID LEVEL DURING EMERGENCY DUMP

III. ENGINEERING DEVELOPMENT

INTRODUCTION

As described below a number of experimental facilities have been operated to develop satisfactory components for the HRE. Results, thus far, are very encouraging and are discussed under the following headings:

- A. Dump Tank System
- B. Soup Recirculation Test Loop
 - 1. Pump and circulating tests
 - 2. Bearings for 100A pump
 - 3. Pressurizer and level and pressure controls
 - 4. Soup feed pump
 - 5. Soup heat exchanger
- C. Ring and Groove Type Pipe Joints
- D. Removal of Gas from HRE

The major points to be covered in the next quarter include:

- A. Completion of the design and installation of the off gas system, and demonstration of its operability.
- B. Continued operation of the "Recirculating Test Loop" after connection of the soup feed pit, resulting in information on:
 - 1. Operation of the soup feed pump,
 - 2. Operation of the heat exchanger,
 - 3. Operation of the "let down" valves,
 - 4. Operation of the level and pressure controls,
 - 5. Thermal stability of the soup, corrosion, pump operation, etc., for relatively long periods of operation.
- C. Operation of the 100 gpm (100A) pump and gas removal system at 250°C and 1000 psi pressure. The high pressure pump and sphere will be installed in the mock-up and operated first with water and possibly later with soup to prove
 - 1. That changes in viscosity, temperature and pressure will not adversely effect gas removal or hydraulic behavior of the core,
 - 2. Satisfactory operation of the 100A pump,
 - 3. Temperature and pressure effects when dumping the soup.

- D. Completion of the mock-up. This facility now consists of dump tanks, concentration system and steel for supporting the boiler and IOOA pump. As various components are delivered or released from other experiments they will be installed in the mock-up, resulting in an essentially complete reactor except for shield. In this way satisfactory operation of the reactor as a whole may be demonstrated (except for critical experiments). Most of the mock-up will be dismantled and moved to the HRE site approximately February 1, 1951, where it will be used.

THE SOUP DUMP TANK SYSTEM

The soup dump system has been installed in the mock-up and a preliminary concentration test has been run in which a known amount of water and sodium sulfate (to simulate UO_2SO_4) was charged into the system and evaporated. Samples were taken from the dump tanks at various times during the evaporation to be analyzed for $\text{SO}_4^{=}$ concentration for comparison with the concentrations indicated by the weight of condensate collected in the condensate tanks using a Baldwin strain gage type of load cell to weigh one of the two condensate tanks.

The initial $\text{SO}_4^{=}$ concentration was 7.28 grams per kilogram H_2O (which is equivalent to 13.5 g U^{235} per liter at 250°C if the solution were UO_2SO_4). At the maximum concentration, the equivalent U^{235} concentration was measured to be 32.4 grams per liter by chemical analysis, while the load cell indicated a concentration of 31.6 grams of U^{235} per liter--an error of 0.8 grams per liter. Table I shows results at several points during evaporation, dilution and re-evaporation.

In this system there are two principal sources of error, condensate hold-up in the condenser and accuracy of the load cell. The precision of the load cell used in this initial test was $\pm$ one pound, which corresponds to $\pm$ two pounds of water since half of the water collected is weighed by the load cell. A new load cell has been recently obtained whose accuracy is $\pm$ 0.25 pound. With the new load cell, it is hoped that U^{235} concentrations may be correctly indicated within $\pm$ 0.2 or 0.3 grams U^{235} per liter at the expected operation concentrations. Specific resistances of two condensate samples taken during this test were 160,000 and 174,000 ohm cm which is considered adequate purity for this system.

TABLE I

	CALCULATED RESULTS FROM LOAD CELL READINGS		CHEMICAL ANALYSIS OF SAMPLES	
	CALC. $\text{SO}_4^{=}$ CONCENTRATION ($\text{g}/\text{SO}_4^{=}/\text{kg H}_2\text{O}$)	EQUIVALENT U^{235} CONCENTRATION ($\text{g/l at } 250^\circ\text{C}$)	MEAS. $\text{SO}_4^{=}$ CONCENTRATION ($\text{g}/\text{SO}_4^{=}/\text{kg H}_2\text{O}$)	EQUIVALENT U^{235} CONCENTRATION ($\text{g/l at } 250^\circ\text{C}$)
Initial sample	7.28	13.5	7.29	13.6
During first evaporation	10.52	19.6	10.62	19.8
During first evaporation	15.50	28.9	16.40	30.5
Maximum concentration	16.92	31.6	17.40	32.4
After diluting	10.04	18.7	10.10	18.8
Second evaporation	12.09	22.5	12.34	23.0

SOUP RECIRCULATING TEST LOOP

PUMP AND CIRCULATING TESTS

The Westinghouse totally enclosed centrifugal pump to be used in the recirculating systems has been described in previous Homogeneous Reactor Feasibility reports. In the test work now in progress a Model 30 pump with chrome plated shafts (at the front and rear bearing surfaces) and graphitar No 14 bearings is being used. The pump test loop consists of approximately 20 ft of pipe for recirculation and a pressurizer.

The initial test consisted of approximately 75 hours operation at 250°C and 1000 psi with pumping rates between 30 and 45 gpm (approximately 17 ft/sec in the 1 in. recirculating line). After 50 hours of operation with distilled water, the system was preheated with 0.1 M HNO_3 for 12 hours at 250°C and 1000 psi and uranyl sulfate (40 g/l) added. After 24 hours operation (250°C and 1000 psi), all uranyl sulfate had precipitated. The solution was badly discolored and contained a brownish precipitate. At this point the Westinghouse pump was dismantled for inspection. The front chrome plated bearing surface was worn to the extent that the original clearance of 0.0015 in. had increased to 0.0045 in. Except for a slight darkening of the rotor and impeller, all other parts of the pump, including the rear bearing surfaces, were in good condition. The pump was reassembled with a new rotor and front graphitar bearing.

The precipitated uranium oxide was removed from the recirculating line and pressurizer with nitric acid. The inside surfaces of the recirculating line and pressurizer appeared quite dirty, and it was concluded that the system was not clean enough prior to the original nitric acid pretreatment. (Tests indicate that the nitric acid pretreatment to prevent uranium precipitation is not effective if the metal surface is not cleaned thoroughly to remove all oxides, grease or other films.) Therefore, the inside surfaces of the high pressure system (excluding pump) were cleaned with a 0.1 M HCl-HgNO_3 solution, the pump installed, and the nitric acid pretreatment repeated.

Uranyl sulfate (40 g/l) was then added to the high pressure test system and to date has operated 460 hours at 250°C and 1000 psi with no sign of uranium precipitation. The pumping rate was approximately 40 gpm. The pump was disassembled for the second time and found in good condition. Maximum

bearing wear was approximately 0.001 in. In order to test other bearing materials the original rotor has been reworked to include bearing surfaces of hardened 410 stainless steel and will be placed in service when operation is resumed. It is planned to continue the present test as long as necessary to prove solution stability and satisfactory pump operation.

BEARINGS FOR 100A PUMP

The model 100A Westinghouse pump for recirculating soup in the HRE was supplied with titanium carbide bushings and graphitar No 14 bearings. Static corrosion tests indicate that these bushings are not satisfactory for operation in uranyl sulfate at 120°C. Replacement bushings of Stellite No. 6 have been ordered. This pump will be operated for several weeks in the mock-up where it will circulate water.

A bearing testing device has been built to investigate Stellite, 410 stainless steel and possibly other materials for pump bushings under running conditions.

A Stellite bushing is now running in this device but has not operated for a long enough period to be conclusive. The bushings in the 100A pump will be changed as soon as the bearing test indicates that a suitable material has been found.

PRESSURIZER AND LEVEL AND PRESSURE CONTROL

The pressurizer in the high pressure recirculating system consists of a 6-in. I.D. tank approximately 25 in. long. The temperature (285°C) and corresponding pressure of 1000 psi is maintained with electric heaters. The heaters are controlled with a Foxboro circular chart controller actuated by a Baldwin-Southwark pressure cell connected to the vapor space of the pressurizer. This unit is now controlling at 1000 psi.

A level indicator-controller has been designed for the pressurizer, and a pilot model has been installed on the "test loop" pressurizer. This device consists of a small side tank connected to the pressurizer by flexible tubing. Changes in weight (level) in the side tank are transmitted, mechanically, to

a strain gage type weighing device which is connected to the level indicating instrument. This device will be operated in the near future, and is expected to be a very reliable and rugged means of level control.

SOUP FEED PUMP

The soup feed pump has been received and set up. To date the pump has been operated with water to gain experience and determine operating characteristics. The pump now on hand has a bolted head design. However, a second pump has been ordered with all welded heads and a welded replacement head has been ordered for the present pump. This will provide pumps for both the soup and reflector systems.

Tests to date indicate that the pumping capacity is slightly low (approximately 0.8 gpm at 1000 psi instead of the specified 1 gpm), but this rate is adequate and can be increased. The capacity will be increased if only minor adjustments are required, and the pump will then be connected to the test loop system where it will feed soup through the soup dump heat exchanger into the test loop.

SOUP HEAT EXCHANGER

A soup heat exchanger has been designed and fabricated. This heat exchanger is to be installed on the high pressure test loop between the soup recirculating system and the soup feed pump. Its purposes are twofold: (1) to recover heat from the soup which is continuously let down from the high pressure system, and (2) to lower the temperature of the soup before it reaches the let down valve, thus reducing the corrosion problem in this valve. The present design consists of a double tube with a 1/2-in. O.D. inside a 1/2-in. pipe. The unit is 100 ft long and is coiled on a 4-ft diameter. Calculations indicate that this exchanger will lower temperature of the soup flowing to the dump tanks from 482°F to 212°F, while raising the feed temperature from 176°F to 450°F. At a flow rate of 1 gpm this amounts to a heat recovery of 39 kw.

The heat exchanger and soup feed pump will be connected to the heat loop in approximately two weeks, so that the exchanger, valves, and controls may be studied under simulated operating conditions.

RING AND GROOVE TYPE PIPE JOINTS

Two stainless steel ring joints have been in operation in the test loop for approximately 600 hours and have operated satisfactorily. One 6-in. joint is used on the top of the pressurizer, operating at 285°C, and the second (1-in. size) in the test loop. Both joints have been disconnected several times and have not leaked when connected. The above joints do not have provision for leak-detection.

A 1-1/2 in. 1500 lb_s ring and groove type flanged joint of special Taylor Forge design was tested in a furnace, with hydrostatic pressure, for leakage. This joint differs essentially from the standard ring and groove type joint in that the gasket groove is wider so as to fit a "clover leaf" cross-section ring gasket. This gasket is designed for leak-detection and probably has greater resiliency than the standard ring gasket. For leak-detection purposes, the gasket was drilled so that external pressure could be applied to the space at the bottom of the groove when the joint was assembled.

For testing, the bolted joint, consisting of two blind flanges (316 stainless steel) and a gasket (304 stainless steel), was installed in a furnace. Two separate pressure systems, located external to the furnace, were connected with 1/8-in. diameter tubing to the gasket groove and the space inside the gasket ring. Hydrostatic pressure was applied through these external systems such that the gasket groove pressure was approximately 1600 psi, and the pressure inside the ring was about 1300 psi at a furnace temperature of about 550°F. Air was evacuated from both systems prior to pressurizing. Twenty-one cycles, alternate heating and cooling, were run on the joint during a period of 33 days with little or no apparent leakage.

A consistent small increase in pressure inside the ring gasket was observed without a corresponding decrease in the ring joint groove pressure. Since this increased pressure could not have come from leakage from the higher pressure joint groove, it is believed that the increase was caused by the decomposition of grease which entered the system through a hydrostatic pump used to fill the system. It is calculated that a pressure decrease of 200 psi (1600 to 1400 psi) would represent a leakage of approximately 0.1 cm³ from the entire gasket groove system. The data indicate that leakage, if any, for 33 days of testing was considerably lower than this volume, although the exact

amount of increase in pressure due to decomposition is not known. This gasket is now considered satisfactory and a special report will be issued in the near future when more precise data has been obtained from the degreased system.

REMOVAL OF GAS FROM THE HRE

HIGH PRESSURE STAINLESS STEEL MODEL OF THE CORE

Early in June the stainless steel model of the HRE core was completed and installed. The internal geometry of this vessel is the same as the reactor itself but the wall thickness is much greater to allow it to be safely operated continuously at 1000 psi without the pressurized reflector vessel surrounding it.

The first runs on this heavy core were made with a special outlet equipped with a Lucite window (see Fig. 12). The entire outlet assembly was first tested on an existing plastic sphere and found to be comparable with previous designs.

Illuminating the interior of the sphere proved to be somewhat of a problem but was finally solved by directing the beam from a focussed light source into the window and viewing the vortex with a mirror. Due to the optical characteristics of the hemispherical surface on the lower end of the window only the portion of the vortex void adjacent to the window could be observed.

Visual observations indicate that the stainless steel vessel operates as well as its plastic predecessors as regards size of the void and its alignment with the gas outlet. As expected, the pressure drop was somewhat higher than on previous models due to the smaller inlet pipe and smaller outlet annulus.

GAS HOLDUP

Holdup measurements were made by means of a 1-1/2-in. calibrated Pyrex pipe into which the stream of gas and water was directed (see Fig. 13). The water was returned from the bottom of the glass tube to the pump suction through a rotameter. When gas is admitted to the sphere through the inlet stream the level in the calibrated glass tube rises by the volume displaced by the bubbles. This system works well but measures total bubble volume in the sphere and external circuit as well. Since operating pressures were higher than on previous experiments the amount of dissolved air was greater. Wherever throttling occurred, air came out of solution and added to the measured volume.

FIGURE 12
GAS OUTLET DETAIL

FIGURE 13
CALIBRATED CYLINDER

In an attempt to reduce this effect flow was regulated by a by-pass valve installed at the main circulating pump. A small pump was added to boost the return stream from the glass cylinder (which was at atmospheric pressure) into the circulating pump suction. This allowed the system to operate at higher inlet pressures (90-100 psi) and yet have all valves open in the circulating loop. Thus the only pressure drops encountered were in the sphere itself and the necessary piping. In spite of this improvement some bubbles still appear in the glass return line to the pump, with the result that all holdup measurements are conservative.

In interpreting the results obtained with this apparatus one is still faced with the problem of choosing the pressure to be used in calculating gas flows. Since a large portion of the measured gas volume is at or near vortex pressure, one might arbitrarily use this pressure (30-50 psi depending on gas flow) to calculate inlet flow rate. The air is actually admitted at inlet water pressure (80-90 psi) but rapidly expands to the lower pressure as it progresses through the sphere. If this pressure is used, flow figures must be correspondingly reduced. When the mockup is available, this problem will virtually disappear because the pressure differential will be small compared to the operating pressure of 1000 psi.

The important value in gas holdup measurements is the percentage of total core volume occupied by gas bubbles. The percentage holdup was found to be almost proportional to gas flow, varying from 0 - 0.5% as the gas flow increased from 0 - 500 cc/sec based on vortex pressure (see Fig. 14). Calculations in report ORNL-730 indicate that 1% is permissible.

COOLING OF CORE

Earlier experiments on mixing and cooling the central cylindrical portion of the reactor suggested the possibility of injecting cold solution into the bottom of the sphere which, according to experiments with dye streams, would rapidly diffuse in the central region and cool it (see report, *Mixing in the HRE* by Graham, Wilson and Culver, ORNL-794). This raised the question of the effect of such a stream on the gas holdup characteristics of the system. To test this, a by-pass from the inlet stream with a flow meter and regulating valve was installed (see Fig. 13), and holdup tests were run as before with varying amounts of water introduced at the "south pole." Results showed no ill effects and even a slight improvement in holdup figures (see Fig. 15).

DWG. 97129

100 040

I V. CONTROL AND SIMULATOR

CONTROL

Further study of the control problem has confirmed the basic methods suggested in the *Feasibility Report* (ORNL-730). The nuclear instrumentation as shown in Figure II.- 14 (Dwg. 9038) of that report is essentially a smaller version of the MTR instrumentation. The full flux range will be covered by two fission chambers operating counting rate meters, the higher level one having a recorder, a compensated chamber operating period and log N instruments, the log N being provided with a recorder, and two boron safety chambers feeding power level instruments. The sigma bus will be fed by the period and level circuits. The components of this phase of the instrumentation are given in Table I.

TABLE I

INSTRUMENT	NUMBER OF INSTRUMENTS
Log counting rate	2
Indicators	2
Recorder	1
A-1 Amplifier	2
A-1A Preamplifier	2
Log N and Period	1
Indicators	1
Recorder	1
Period Amplifier	1
Compensated Ion Chamber Supply	1
Sigma Amplifiers	3
Preamplifiers	2
Magnet Amplifier	3
Power Level	2
Power Level Recorder (2 point)	1
Fission Chambers	2
3 in. Boron Chambers	2
Compensated Ion Chamber	1

In addition to nuclear induced scrams, critical situations in the process cycle will also initiate scrams. The danger signals and interlocks necessary for safe operation of the system are being studied at the present time.

The process instrumentation is indicated on the several flow sheets of ORNL-730. The pertinent data on these are given in Table II.

Additional consideration has been given the level detector for the soup pressurizer and a weighing system has been designed consisting essentially of a small side tank connected by flexible tubing to the pressurizer and a Baldwin tension cell for weighing this tank and its contents. The experimental model should be ready for test within a few days.

The soup concentration will be determined by two methods. The first involves determining the weight of water in the condensate tank and using this as a concentration indicator. A temporary mock-up of this has been tested with satisfactory results. The tension cell which will be used in the final assembly has been received and will be tested in the near future. The second instrument for determining the concentration utilizes the hydrometer principle. This instrument is being assembled and will be ready for testing in a day or so.

TABLE II 46

No.		MEASURING ELEMENT AND VENDOR	RANGE	RECEIVER TYPE	CONTROL TYPE	CONTROLLED VARIABLE
1	Level Pressurizer	Baldwin Tension Cell	0-10 in.	RC	Proportional Pneumatic	Hi & Lo Alarm Soup Level By Valve
2	Pressure Pressurizer	Fox.-Baldwin Press Cell	0-2000 psi	RC	On-off Electric	Hi Alarm Power to Heaters
3	Temp-Soup Pressurizer	T.C. IC. (Brown)	0-300°C	RS Multipoint	None	Hi Alarm
4	Temp-Soup Out Core	T.C. IC (Brown)	0-300°C	I Circular Scale	2 Position Elec.	Hi & Lo Alarm Shim Rods
5	Temp-Soup Core	T.C. IC (Brown)	0-300°C	RS Multipoint	None	
6	Temp-Soup Out Exchanger	T.C. IC (Brown)	0-300°C	RS Multipoint	None	
7	Temp-Soup Out Pump	T.C. IC (Brown)	0-300°C	RS Multipoint	None	
8	Temp-Soup in Dump Tank	T.C. IC (Brown)	0-300°C	RS Multipoint	None	
9	Press Condensate Tank	Baldwin 200 psi Press Cell	(Abs.) 0-50 psi	RC (Fox)	Proportional Pneumatic	Hi & Lo Alarm Cooling H ₂ O to Condenser
10	Press Diff. Soup to Reflector	Baldwin 2000 psi Press Cell	0-300 psi	RC (Fox)	Proportional and Derivative Pneumatic	Hi & Lo Alarm Supply and Dur.
11	Concentration Weight-Condensate	Baldwin 0-182 kg Tension Cell	0-75 kg	I (Fox)	None	
12	Concentration Transmitting Hydrometer	Float and Induction Pick-up		I		
13	Level Reflector	Fox D P Cell	0-30 in.	RC (Fox)	Proportional Pneumatic	Dump Valve and Pulsafeeder
14	Temp-Reflector	T.C. IC (Brown)	0-300°C	RC	Proportional and Reset Pneumatic	Boiler Feed H ₂ O Cooling H ₂ O to Cooler
15	Level Soup Dump	Weighing		I		

TABLE II (Cont'd) 47

No.		MEASURING ELEMENT AND VENDOR	RANGE	RECEIVER TYPE	CONTROL TYPE	CONTROLLED VARIABLE
16	Level Reflector Dump	Weighing		I		
17	Temp Motor (Soup)	T.C. IC	0-260°C	I (Meter)		Alarm
18	Temp. Out-Oil Soup Pump	T.C. IC	0-300°C	PI		
19	Temp. In-Oil Soup Pump	T.C. IC	0-300°C	PI		
20	Press In-Oil Soup Pump	Press Switch M-H Model L404 A	0-50 psi			Alarm
21	Level-Oil Tank (Soup)	Low Level Switch M-H No. C627A				Alarm
22	Flow-H ₂ O to Oil Cooler	Press Switch M-H P404A	0-10 psi			Alarm
23	Power Soup Pump	Ammeter		I		Scram
24	Temp-Cooling H ₂ O In (For all Coolers)	3 T.C. IC(Averaging)	0-300°C	PI		
25	Temp-Cooling H ₂ O Out Soup Dump Tank	T.C. IC	0-300°C	PI		
26	Temp-Cooling H ₂ O Out Condensate Condenser	T.C. IC	0-300°C	PI		
27	Flow Cond. Condenser Cooling H ₂ O to	Roto	5-10 gpm			
28	Temp.-Condensate	T.C. IC	0-300°C	PI		
29	Temp. Cooling H ₂ O to Pulsafeeder Cooler	T.C. IC	0-300°C	PI		
30	Flow-Cooling H ₂ O Pulsafeeder Cooler	Roto				
31	Temp. Soup In to Pulsafeeder Cooler	T.C. IC	0-300°C	PI		

TABLE II (Cont'd) 48

No		MEASURING ELEMENT AND VENDOR	RANGE	RECEIVER TYPE	CONTROL TYPE	CONTROLLED VARIABLE
32	Temp. Soup out of Pulsafeeder Cooler	T.C. IC	0-300°C	PI		
33	Flow Dump Circulating Steam in Soup	Pressure Gauge				
34	Temp. D ₂ O in Exchanger	T.C. IC	0-300°C	PI		
35	Temp. D ₂ O Out Exchanger	T.C. IC	0-300°C	PI		
36	Cooling H ₂ O Temp. -D ₂ O Exchanger	T.C. IC	0-300°C	PI		
37	Cooling H ₂ O Flow-D ₂ O Exchanger	Roto				
38	Temp-Motor (D ₂ O)	T.C. IC	0-260°C	Ass'y Products I = (Meter)		Alarm
39	Oil in Temp. -D ₂ O Pump	T.C. IC	0-300°C	PI		
40	Oil Out Temp-D ₂ O Pump	T.C. IC	0-300°C	PI		
41	Power D ₂ O Pump	Ammeter		I		
42	Oil in Press. D ₂ O Pump	Press Switch M-H No. L404A	0-50 psi			Alarm
43	Oil in Tank Level D ₂ O Pump	Low Level Switch M-H No. 627A				Alarm
44	H ₂ O to Oil Cooler Flow D ₂ O Pump	Press Switch M-H No. P-404A	0-10 psi			Alarm
45	Press Gas Supply	Press Gage and Switch	0-1500 psi			Alarm
46	Reflector Shell Temp 6 Points	6 T.C. IC	0-300°C	PI		
47	Temp D ₂ O Dump Tank	T.C. IC	0-300°C	PI		
48	Press = D ₂ O Dump Tank	Press Gauge				

TABLE II (Cont'd) 49

No.		MEASURING ELEMENT AND VENDOR	RANGE	RECEIVER TYPE	CONTROL TYPE	CONTROLLED VARIABLE
49	Cooling H ₂ O Temp = D ₂ O Dump Tank	T.C. IC	0-300°C	PI		Cooling H ₂ O Flow
50	Cooling H ₂ O Temp = D ₂ O Condenser	Self Energizing Valve (Taylor)	15-90°C			
51	Regulator Press Dump System					
52	Regulator Press Dump System					

SIMULATOR

In order to check and extend the calculation of reactor kinetics and to test any control systems before the reactor is actually operated, a simulator is being constructed by the Instrument Department. It was first proposed to modify the MTR simulator to provide for the temperature coefficient of reactivity, the circulation of core fluid, and the gas coefficient. Possible schemes considered were servo operation of the k potentiometer in response to a temperature determined by integration of the power level, and a "memory" unit consisting of magnetic recording tapes to represent circulation of fluid.

The servo-driven k pot would be, in effect, a multiplier which obtains the product of temperature (relative to some reference level) and flux and supplies a current proportional to this product to the neutron-adding bus. With the rate of change in power level and temperature expected during a surge, however, the fastest servos were too slow for accurate simulation. An electronic multiplier thus became necessary. With this modification, the block diagram of the simulator (Fig. 16) includes the following sections:

1. An integrator to yield the neutron flux or power level (n integrator);
2. Delayed neutron circuits (RC networks and cathode followers similar to those in the MTR simulator, for four or five delay groups);
3. Manual k potentiometer and associated resistors to provide various magnitudes of positive and negative step changes in excess reactivity;
4. An integrator to obtain temperature from power level (T integrator);
5. A multiplier to provide the product of $T \times n$ which is fed into the neutron-adding bus for temperature coefficient;
6. A memory unit to incorporate the effect of external circulation and cooling on the effective reactor temperature;
7. A similar memory unit to incorporate the effect of circulation or delayed neutron emitter concentration in the one group (possibly two) whose period is near the two-second interval the soup spends out of the core;
8. Auxiliaries: power supplies, recorders, etc.

BLOCK DIAGRAM OF SIMULATOR
FIG. 16

The first electronic multiplier extensively explored was the "crossed-field electron-beam multiplier" developed by A. B. Macnee for the MIT electronic differential analyzer. Since applicable information on this device was not available, a model of this multiplier was built with a 2BP11 cathode ray tube, which on testing proved accurate over a product range of about 30 to 1. Since the desired range was 1000 to 1 (two decades in flux and one in temperature), this was discouraging. Probable causes of the range limitation were small inaccuracies in positioning the tube, mask, and deflection coil, and defocussing of the cathode-ray spot (along with non-uniformity of the defocussed spot) under strong deflecting fields. Reduction of errors to tolerable value for three decades of product range was deemed impractical without very extensive development, and attention was turned to other multipliers, notably one based on the logarithmic characteristics of diodes.

The use of diodes as logarithm and antilogarithm generators over a range of several decades is well known, but for use down to zero frequency the heater supply must be carefully stabilized and the tubes protected from vibration and temperature changes. With these precautions, log diodes should provide a multiplier which is both fast and accurate. Three diode units—two logarithm generators and one antilog generator—have been constructed and will shortly be tested, with every expectation of three decades or more of product range. Each unit consists of diode, shock mounted in a temperature stabilizing box, and a d-c amplifier to complete the feedback loop.

A third type of multiplier has received some attention as an alternate device. It depends on the Hall effect in a semi-conductor (germanium), by which a transverse voltage is developed proportional to the cross-product of longitudinal current and transverse magnetic field. Some experimental evidence indicates that this effect can, if necessary, be made the basis of a good fast multiplier without extensive further development.

Both the multiplier and the two integrators require d-c amplifiers of higher performance than the one employed by Bell and Straus in the MTR simulator. Accordingly, a d-c amplifier has been developed with a gain of 50,000 low noise and drift, and accurate balancing of both input and output with respect to ground. Balance may be further improved by a factor of two by the use of a chopper-type centering device, if it is ever necessary.

Power supplies have been constructed for these portions of the simulator. One, for the d-c amplifiers and delayed neutron circuitry, is a conventional

well-stabilized dual unit. The second, for diode heaters, is unique in that it holds its output voltage constant to one part in ten thousand over several days of operation. It employs three cascaded series regulator stages, the final one taking its reference voltage from a standard cell and using a chopper-type amplifier for extreme stability.

Construction of the sections described is nearly complete, and assembly is well advanced on a simulator which will represent reactor behavior for the first two seconds after an upset (before the concentration and temperature of the cold soup returning from the external loop is affected by the surge). Testing of the simulator at this stage (Phase I) and runs on the first two seconds should be in progress by the first of September. A multichannel photographic recorder has been procured, and several long-persistence oscilloscopes are in order for data presentation and recording.

Preliminary design work has been completed on two memory devices based on banks of capacitors "circulated" with stepping switches to simulate the effect of recirculation on soup temperature and delayed emitter concentration. The first of these, which will be incorporated in Phase II of the simulator and will permit representation of times up to approximately 10 seconds, considers flow in the core as completely turbulent. The corollary assumption that temperature and concentrations are uniform throughout the core makes the progression from Phase I to Phase II a relatively simple one, and runs with the Phase II memory should follow the Phase I runs within a short time.

Phase III, simulation of the reactor with slug flow or variable mixing in the core, involves a decidedly more elaborate capacitor-type memory. Preliminary design work has been carried out on this phase, but no construction has occurred. This third phase may involve incorporation of a gas coefficient independent of temperature coefficient, but on Phase I and possibly Phase II, the effect of gas evolution will be included as an increase of temperature coefficient, since a linear gas coefficient with no delay in bubble evolution would follow the same equations as a linear temperature coefficient.

Design of the simulator has been kept as flexible as possible, in order to facilitate its use for other cases than the HRE. A wide range of temperature coefficients will be available, and recirculation conditions can be changed without undue difficulty. The final simulator should then, if handled with sufficient care, prove quite useful as a flexible and precise general simulator.

V. REACTOR PHYSICS

SHIELDING

The problem of shielding the HRE differs from that of shielding a heterogeneous reactor in that there are sources of neutrons other than in the reactor proper. These extra neutrons come from the fission fragments which are carried outside of the core and into the external circulating system. As a result of this, care must be exercised in the placement of the external piping, heat exchanger, and soup circulating pump.

A second consideration necessary in the shielding of the HRE is a result of the experimental nature of the project and is embodied in the necessary accessibility of components for possible changes. This accessibility requirement attaches importance to the induced activity of the external hydraulic system and of the shield itself. Due to the possibility of breakdown of the external circulating system it would be desirable and convenient if the activity after shutdown could be of a sufficiently low level to permit human access.

From these considerations it is obvious that the external soup system components will have to be placed in a compromise position which is far enough from the outside of the shield to attenuate the radiations to a tolerable level when operating, and far enough from the reactor itself so that the induced activity resulting from thermal shield flux is at a safe value.

In attacking these problems, three different approaches were investigated:

1. Solutions of neutron and gamma transport equations,
2. Empirical design with the aid of bulk shielding experiments, and
3. Comparison of the HRE with the X-10 pile.

The first approach led to insurmountable mathematical difficulty and has been abandoned for the present.

The second approach depends upon the interpretation of bulk shielding experiments, which up to the present have been essentially measurements of thermal flux in samples of shielding material which are exposed to a fission source. The interpretive process consists of predicting the fast flux as a

function of the slow flux and obtaining fast flux attenuation data. The fast flux, which includes all neutrons from 9 Mev down to the thermal region, is assumed directly proportional to the slow flux with a proportionality factor obtained from age theory applied to a single exponential approximation of the thermal flux measurements. Recent incomplete data of fast flux measurements show poor agreement with these calculations. This discrepancy can result in a factor of 100 in the ratio of fast flux to secondary gamma flux, both of which may be a major factor in the biological dosage. When shielding data is obtained by measurements of neutron spectra at various positions through the sample, this large uncertainty will cease to exist.

The third approach is attractive because of the considerable data which is available and the long record of safe operation. It has been roughly estimated that about seven feet of barytes concrete would be adequate. In what follows, it will be shown that with minor modifications this is true.

The X-10 pile radiations at the outside of the shield have been measured a number of times. Reasonable values based on these measurements are:

Fast neutrons ~ 1 neutron/cm² sec,⁽¹⁾

Gamma flux ~ 1 mr/hr. ⁽²⁾

The shield of the X-10 pile consists of five feet of haydite-barytes concrete sandwiched between two one-foot slabs of ordinary concrete. The haydite-barytes concrete contains about 1% hydrogen and 31% barium by weight and has an average density of 2.18.

The input to the shield has been measured for both gammas and neutrons with the following results:

Fast neutrons 1 Mev 0.12×10^5 neutrons/cm² sec watt ⁽³⁾

Cd 1 Mev 1.8×10^5 neutrons/cm² sec watt ⁽⁴⁾

Gamma flux or 10^4 roentgens/hr ⁽⁵⁾

Thermal neutrons 10^{10} neutrons/cm² sec @ 3500 kw ⁽⁶⁾

A 12 group calculation has been performed to determine the modification of the fission spectrum by the core and reflector of the HRE.

(1) Clark, Ramsey.

(2) Clark, R. L., Martin, P. O., *Gamma Isodosage Contours from the X-10 Pile*, ORNL 737 (June 19, 1950).

(3) Bopp, C. D. and Sisman, O., *The Neutron Flux Spectrum and Fast and Epithermal Flux in Hole 19 of the ORNL Reactor*, ORNL 525 (July 28, 1950).

(4) Ibid.

(5) Rockwell, Theodore III, *Physical Tests on Core Drillings from the ORNL Graphite Reactor Shield*, ORNL 241 (Feb. 28, 1949).

(6) Ibid.

Fast neutron current input to shield:

X-10 pile -- 1.8×10^{11} neutrons/cm² sec

HRE -- 2.0×10^{11} neutrons/cm² sec

The fast current above 1 Mev is higher in the HRE by a factor of about five; however, there is a definite advantage in the spherical geometry of the HRE since comparing it with the slab characteristics of the X-10 pile shield we have an additional attenuation by a factor of $(261/48)^2 = 29.6$, where 48 is the radius of the reactor and 261 that of the equivalent spherical shield (both figures in cm). Even if we attribute the effectiveness to be due only to neutrons of energy above 1 Mev we have for the same material around the HRE a biological dose $.1 \text{ mr/hr} \times 5/29.6 \approx .02 \text{ mr/hr}$.

The secondary gammas generated in the X-10 pile shield are due to the diffusion of thermal neutrons ($10^{10} \text{ n/cm}^2 \text{ sec}$) into the shield and the thermalization of the 1.8×10^{11} fast neutron current. Since the seven feet of concrete has reduced these gammas and the primary gammas (10^4 R/hr) to a level of 1 mr/hr we can say with conservatism that the same shield wrapped around the HRE will limit the effect of secondary gammas to 1 mr/hr.

The primary augmentation of the X-10 pile shield material is then dependent only on a comparison of the primary gamma sources, which in the X-10 pile (shield input) is 10^4 R/hr . The HRE reactor as a source of gammas must include the heavy pressure vessel which contributes to both the self shielding and secondary gammas. The following tabulations indicate the magnitude of the primary gamma current.

HRE as a Source of Gammas

Power 1000 kw

Fissions/sec 3×10^{16}

Gammas generated in the core:

ENERGY (Mev)

1	15×10^{16} photons/sec (fission)	
2	1.2×10^{16} photons/sec (H_2O capture)	Combine call 2 Mev 7.2×10^{16} photons/sec
2.5	6×10^{16} photons/sec (fission products)	
6	$.6 \times 10^{16}$ photons/sec (U^{235} capture)	

	1 Mev	2 Mev	6 Mev	8 Mev
Fission and capture source photons/sec	15×10^{16}	7.2×10^{16}	$.6 \times 10^{16}$	-
Current interface core-reflector photons/cm ² sec	1×10^{13}	$.6 \times 10^{13}$	$.6 \times 10^{12}$	-
Current interface reflector-pressure vessel photons/cm ² sec	4×10^{11}	4×10^{11}	7×10^{10}	-
Current interface pressure vessel shield photons/cm ²	1.3×10^{10}	3.4×10^{10}	1.3×10^{10}	-
Current secondary gamma pressure vessel photons/cm ²	-	-	-	7.3×10^{10}
Input to shield Mev/cm ² sec	1.3×10^{10}	6.8×10^{10}	7.8×10^{10}	58.5×10^{10}
Total Mev/cm ² sec = 7.4×10^{11}				
Input to shield R/hr	2.5×10^4	1.3×10^5	1.5×10^5	1.1×10^6
Total R/hr = 1.4×10^6				

The total R/hr is seen to be 140 times that of the X-10 pile. This, however, does not represent the difference in biological effect at the outside of the shield since the energy of the gammas are different, and the difference in geometry favors the HRE. The following table illustrates this point:

	Gamma Energy	1 Mev	2 Mev	6 Mev	8 Mev
X-10	Input to shield R/hr	820	4280	4900	-
	Attenuation factor	1.4×10^{10}	2.1×10^8	3.0×10^6	-
	Output of shield R/hr	5.9×10^{-8}	2×10^{-5}	1.6×10^{-3}	-
Total biological dose -- 1.6 mr/hr					
HRE	Input to shield R/hr	2.5×10^4	1.3×10^5	1.5×10^5	1.1×10^6
	Attenuation factor	4.2×10^{11}	6.3×10^9	8.7×10^7	3×10^7
	Output of shield R/hr	6×10^{-8}	2×10^{-5}	1.7×10^{-3}	37×10^{-3}
Total biological dose -- 38.7 mr/hr					

The assumed attenuation of ordinary concrete is justified by the calculated value of 1.6 mr/hr of primary gamma compared with 1 mr/hr gross gamma measured. In the case of the HRE the primary gamma effect is due almost completely to the 8 Mev radiation from the steel pressure vessel. The 38.7 mr/hr compared with a permissible 7.5 mr/hr makes it imperative to use concrete of greater density than that of the haydite-barytes concrete used in the X-10 pile (ρ 2.2).

If we are to limit this primary gamma radiation to the X-10 pile levels it is necessary to use a concrete of density 2.6 or 18% higher. Without an external soup system it would be only necessary to increase the density of the concrete to this value to limit the gross biological dose outside the shield to a value of 2.7 mr/hr, or about 1/3 tolerance. However, the additional source of neutrons and gammas from the external soup system must be taken into consideration. These considerations outlined below cause density to be raised, automatically reducing the dose for reactor gammas to insignificant levels.

On the basis of a holdup of 20% in the circulating system, we may express these sources in the following manner:

Fast neutrons - 0.1% of core source (delayed neutrons);

Gammas (2.5 Mev) - 20% of core source (fission products)

On the basis of piping of 11.4 cm² cross sectional area and a total external piping volume of 10 liters, these sources have the value shown in the table:

	CORE STRENGTH	STRENGTH PER CM OF PIPE
Neutrons	7.5×10^{16} n/sec	8.55×10^{10} n/sec
Gammas	6×10^{16} photons/sec	1.37×10^{13} photons/sec

Considering first the neutrons and the source may be expressed as 7.1×10^9 neutrons/cm² sec directed radially from a cylindrical source of 1.9 cm radius. Using the same attenuation as measured in the X-10 pile shield, i.e., 40 per foot, the necessary neutron shielding for the piping is as follows:

SHIELD THICKNESS (ft)	DOSE (mr/hr)
4	4.7
4.5	.66
5	.1

To place the piping any closer to the edge of the shield than four feet would lead to an excessive neutron dose.

The gamma source on the same basis could be considered as having a strength 1.4×10^{12} photons/cm²/sec or 5.4×10^6 R/hr.

SHIELD THICKNESS (ft)	HAYDITE-BARYTES SHIELD DOSE (mr/hr)	DENSITY REQUIRED FOR 1 mr/hr
4.0	2800	3.9
4.5	685	3.44
5.0	170	3.1
5.5	42	2.8

From these considerations it appears that a concrete of 3.1 density would make it permissible to place the external soup system at an average distance of five inside the shield edge. The total biological dose would then be:

	mr/hr
Fast neutrons from reactor	0.1
Gammas from reactor	Negligible
Secondary gammas from shield	1.0
Fast neutrons from soup circulating system	0.1
Gamma from soup circulating system	1.0
Total	2.2 mr/hr

The concrete used in this shield should be properly balanced with respect to water content and density. Analysis of the haydite-barytes concrete used in the X-10 pile indicates an average water content of about 9%. Original specifications for this material is 10%, and a density of 2.5. If it is not feasible to manufacture concrete blocks with density 3.1 and a water content of 7%, it is suggested that an extra foot of high water content concrete be added to the shield preferably around the reactor pressure vessel.

INDUCED ACTIVITY

Being an experimental reactor, the HRE is to be constructed in such a way as to permit access to the external piping, pumps, etc. In order to make

this possible and practical, the induced activity should be reasonable after a power-on run of one month's duration. The cooling time should be less than a week, preferably one day.

The multitude of components in which activity is induced and the large area over which they are placed makes it of prime importance to know the thermal flux density throughout the shield. The results of a computation by two-group theory normalized to data outlined under shielding is shown in Fig. 17.

The induced activity in the concrete itself has been calculated on the basis of experimental data recently obtained on in-pile exposure of samples of barytes concrete. One sample was exposed for 672 hours in the X-10 pile and decay curves plotted. An analysis of these curves shows that the predominant constituent after one day cooling time is 12 day barium with an average gamma energy of 1 Mev and total gamma energy of 2 Mev.

For a maximum tolerance in a cavity in the shield of 7.5 mr/hr, one day after pile shut-down, the thermal flux during operation at the point in question should not exceed 10^6 neutrons/cm² sec. Referring to Fig. 1, this condition is satisfied only at positions within 3.5 ft from the outside of the shield. Since the position for the external soup system, on the basis of shielding considerations has been selected as five feet from the outside of the shield, the conditions are incompatible and indicate measures to reduce the induced activity. One possible solution is the inclusion of boron (~ 1%) in the shield concrete to greatly depress the thermal flux and hence the induced activity of the concrete. Another is an increase in shield thickness such that the conditions will coincide. This would require an extra 1.5 ft of concrete, which should be placed between the reactor and the external soup system.

Calculations made on the induced activity in the metal parts of the external soup system are reported in the Engineering Section of this report. A preliminary investigation of the assumptions made in these calculations indicates extremely pessimistic results with respect to the heat exchanger, pump, and piping. A re-evaluation of these will be made when the composition of the concrete has been determined. The inclusion of 1% boron in the shield material should reduce the induced activity by a factor of about 10^3 , or to negligible amounts.

62

Summarizing the above considerations leads to a recommended shield arrangement of special concrete of 3.1 density containing 7% water, 1% boron to be seven feet thick with the external soup system at a position five feet from the outside of the shield.

VI. RECOMBINATION OF HYDROGEN AND OXYGEN

INTRODUCTION

In operation of a homogeneous reactor in which an aqueous solution of a uranium salt serves as the fuel, decomposition of water into hydrogen and oxygen will occur primarily through the influence of fission fragment recoils. The rate of decomposition has been assumed to be a linear function of the power level of the reactor, and the production of this stoichiometric mixture of these gases will fluctuate within narrow limits during normal operation and between wide limits during startup and shutdown of the reactor. The gas mixture will, as produced, be diluted with the steam generated in the reactor core and will contain small quantities of fission product gases along with small quantities of uranyl sulfate as fog or entrained spray. The obvious method for handling this gas production problem is to cause recombination of the hydrogen and oxygen within the closed reactor system and to return the water produced to the cycle to maintain the desired concentration of uranyl sulfate in the fuel solution.

At present it is anticipated that the hydrogen and oxygen, admixed with steam and fission product gases, will be bled through a throttling valve from the high pressure fuel system so that the recombiner system may be operated essentially at atmospheric pressure. The HRE when operating at a power level of 1000 kw is expected to produce 16 cubic feet per minute of hydrogen-oxygen mixture. Present plans include recombination of most of this volume in an enclosed burner with the container cooled by water or steam. Prevention of flashbacks at low flow rates of gas will require continuous introduction of steam into the gas stream. The mixture issuing from the burner nozzle will not burn when the hydrogen and oxygen production rate falls below a certain figure. The gas produced at these low rates and the gas which fails at high rates to combine in the burner must be handled by an auxiliary recombiner. The auxiliary recombiner may be either of the thermal or catalytic type.

Gas production in the reflector system must also be dealt with although the smaller production, lack of fission products, and freedom from entrained fuel, make this problem somewhat more simple than its fuel system counterpart. However, the fact that the reflector system is to be pressurized with helium makes it inexpedient to conduct the recombination at atmospheric pressure. It is anticipated that this recombination can be readily effected by use of a catalyst mass.

COMPOSITION LIMITS FOR EXPLOSIONS IN HYDROGEN-OXYGEN-STEAM MIXTURES

Before design of flow systems for trouble-free recombination of hydrogen and oxygen with fuel system could be approached it was necessary to define the composition limits for explosive mixtures of the stoichiometric mixture of hydrogen and oxygen in the presence of steam. A similar study of the explosive limits of hydrogen and oxygen in mixture with helium is required for the reflector cycle.

The experimental method which was used involved introduction of the hydrogen-oxygen mixture into a stainless steel bomb partially filled with water and maintained at the desired temperature. The partial pressure of steam was therefore fixed at the vapor pressure of water at the temperature of the bomb. The hydrogen and oxygen were generated by electrolysis of water; the resulting stoichiometric mixture is referred to in subsequent discussions as electrolytic gas. Ignition of the mixture was achieved by exposure to a hot wire.

Results of the initial investigation, as previously reported,⁽¹⁾ showed that at temperatures below 120°C and above about 200°C, at total pressures below 40 and above 400 psia, respectively, mixtures containing more than 30% of the stoichiometric mixture were explosive. Between these limits, however, the fraction of electrolytic gas necessary for explosion appeared to reach a maximum of about 40% near 165°C and a total pressure of 180 psia. More recent data obtained with the same 65-ml stainless steel bomb but with more careful control of experimental conditions have cast considerable doubt on the existence of this maximum. As the data shown in Table I indicates, the explosion limit is very close to 30% electrolytic gas over the entire range of pressures and temperatures studied.

A similar but larger apparatus has been assembled and is currently being used to ascertain the explosion limits for mixtures of hydrogen and oxygen with helium. Since the stoichiometric gas mixture is generated by electrolysis of aqueous sodium hydroxide solution the gas mixture contains a small amount (20 to 25 mm Hg) of water vapor. Results of the few experiments performed to date indicate that in the range studied (230 to 550 psia total pressure) mixtures containing more than 25% of electrolytic gas are explosive.

(1) Progress Report, *Materials Chemistry Division*, April 1, 1950 to June 30, 1950, C&CCD-Y-12, Y-635 (August 1, 1950).

TABLE I

**Explosion Limits for Mixtures of Hydrogen, Oxygen, and
Steam in Equilibrium with Liquid Water**

TEMPERATURE (°C)	TOTAL PRESSURE (psia)	PARTIAL PRESSURES (psia)			EXPLOSION LIMIT* [% (2H ₂ + O ₂)]
		H ₂	O ₂	STEAM	
105	25.7	5.3	2.6	17.8	31
121	44	9.3	4.7	30	32
146		17	8.	60	29
154	108	22	12	74	31
165	140	29	14	97	30
169	170	38	19	113	33
197	316	67	33	216	32
212	415	87	43	285	31
224	515	103	52	360	30
238	670	133	67	470	30
250	830	170	80	580	30
261	985	197	98	690	30

* Mixtures containing percentages of hydrogen-oxygen lower than this limit are non-explosive.

Some information as to the order of magnitude of pressure developed during explosion of electrolytic gas mixture has been obtained. A 6-in. bomb of 3-in. diameter iron pipe was capped at one end and fitted with a rupture disc at the other. Hydrostatic tests were used to ascertain the rupture pressure of typical specimens of various types of rupture discs. Mixtures of electrolytic gas at known pressures were then exploded in the bomb sealed with a suitable disc. By this procedure it was indicated that peak pressure during explosion was of the order of 20 times the initial pressure at low (> 30 psia) initial pressures.

PILOT TESTS OF PRIMARY RECOMBINER

The primary recombiner for the fuel circuit of the reactor must be designed to handle, with an appreciable factor of safety, the peak expected production of gas from the fuel system. Since the gas production will increase from zero to 16 cfm it is essential that the recombiner be adaptable to a wide range of flow rates. Maintenance and repair of this equipment in the intensely radioactive zone would be difficult if not impossible; it is necessary that the system be designed so simply as to assure trouble free service. For safety, and to remove the possibility of shutdowns from this source, the system should be free from the possibility of flashbacks.

At present it appears that these general specifications will best be met by a single burner of the multiple orifice type designed to operate over as wide a flow rate range as possible. Since high flow rate of gas at the burner nozzle appears to be the only available means of avoiding flashbacks through the nozzle it will be necessary to introduce sufficient steam into the gas stream to exceed the flashback velocity and extinguish the flame with low flows of hydrogen and oxygen. It presently appears that the problem of maintaining an ignition source near the burner will be solved by use of a spark gap set in the water-cooled walls of the envelope.

During the current period, work on the recombiner has been confined to experimental testing of burner orifices to select one capable of handling the range up to 18 cfm of hydrogen and oxygen and design of the combination chamber and auxiliary equipment to permit testing and evaluation of burner efficiency in a closed system.

PRELIMINARY BURNER TESTS

Preliminary calculation indicated that the desired orifice diameter was about .25 in. and that dilution of the gas ($H_2 + \frac{1}{2}O_2$) with steam to increase the velocity through the burner orifice would permit burning at lower gas flow rates than would be possible without steam. Consequently tests were carried out employing a multihole nozzle with an equivalent diameter of 0.25 in. in which the minimum gas flow for sustained combustion was determined with steam flow rates varying from about .1 to 1 cfm. The results as shown in Table II indicate that combustion is sustained with as little as 0.09 cfm of combustible gas with flow rates of 0.13 cfm steam. At a fixed flow of .09 cfm of gas, a slight reduction below .13 cfm of steam caused a flashback. Since a steam flow rate of 0.54 cfm with no gas flow corresponded to a velocity of 33 FPS, which was well above the flashback velocity of about 13 FPS, it was decided to select this value as the fixed flow rate of steam for pilot plant operation.

TABLE II

Minimum Gas Flow Rates ($H_2 + \frac{1}{2}O_2$) with Varying Steam Flows Through Multihole Nozzle with Equivalent Diameter of .25 Inches*

FLOW RATES (cfm at 70°F and 1 Atm)			Cfm AT 212°F AND 1 Atm	GAS VELOCITY (FPS)	GAS COMPOSITION VOLUME (%)		
$H_2 + \frac{1}{2}O_2$	STEAM	COMB.			O ₂	H ₂	H ₂ O
.45	1.00	1.45	1.84	88	10.3	20.7	69.0
.23	.54	.77	.98	47	10.0	19.9	70.1
.09	.13	.22	.28	13	13.6	27.3	59.1

* Nozzle contained 65 openings, each 1/32 in. diameter.

Note: Flames were sustained continuously for five minutes without flashback.

To permit selection of a burner orifice capable of maintaining sustained combustion over the desired range, additional tests were carried out employing three different burner orifices to determine (a) the minimum gas flow for sustained combustion with a fixed flow of steam of .54 cfm, (b) the minimum gas flow with a fixed flow of steam of .54 cfm that would support combustion

in contact with a spark; (c) the minimum steam flow without flashback with the gas flow held constant at the value obtained in (a), and (d) the maximum limit of total gas flow through the burner (during combustion).

Three burner nozzles were employed in these tests. One of these was a commercial spray nozzle with a single 0.22 in. diameter opening (Fulljet 1/2 HHSS25, Spraying Systems Company, Chicago) while the other two were multi-hole nozzles containing 49 and 65 holes, each 1/32 inch in diameter and with equivalent orifice diameter of 0.22 and 0.25 inches, respectively.

The results of these tests are shown in Table III. It will be observed that with the fixed flow of steam the 49-hole nozzle sustained combustion, with and without the spark, at slightly lower gas flow than did the other nozzles. The gas flow required to blow out the flame (maximum capacity) was significantly higher for the 65-hole orifice.

The multihole nozzles were shown to be superior to the single-jet orifice by maintaining the gas flow at the lowest rate which would burn with 0.54 cfm of steam and dropping the steam flow until flashback occurred. The ratio 0.54 cfm/steam flow in cfm required to prevent flashback for each burner has arbitrarily been defined as the Factor of Safety for the burner. As Table III indicates, the 49-hole burner was shown to be slightly better than the 65-hole model and very much better than the single jet burner in this regard. However, the pressure drop across the 65-hole orifice is only a little more than half that across the 49-hole model. Since it was desirable to operate with a small pressure drop as well as to obtain freedom from flashbacks it was decided to employ the 65-hole nozzle in the enclosed burner pilot plant.

PILOT PLANT LAYOUT

The initial pilot plant installation consisted of a burner chamber, condensate pot, and a condensate receiver together with equipment for metering H_2 , O_2 , and steam, and for measuring and recording temperatures and pressures. The desired quantities of stoichiometric hydrogen-oxygen mixture and steam passed through preheaters to prevent condensation of the steam and entered the burner chamber through an orifice where they were burned in contact with a spark. The water cooled burner chamber (designed to condense up to 30 pounds steam per hour) was placed in a vertical position and was connected to the

TABLE III

Summary of Burner Test Data

NOZZLE	FLOW RATES (cfm at 70°F, 1 atm)		COMBINED FLOW RATE AT 212°F AND 1 atm	GAS VELOCITY (FPS)	FACTOR OF SAFETY	ITEM
	GAS	STEAM				
49 MH	.21	.54	.95	60.4	6.8	A
	< .21	.54	.95	60.4		B
	.30	.09	.49	30.6		C
	.30	< .09	< .49	< 30.6		D
	17.9	.54	23.3	-		E
65 MH	.23	.54	.97	46.3	5.7	A
	.21	.54	.95	45.5		B
	.23	.11	.43	20.4		C
	.23	.10	.41	19.4		D
	19.1	.54	25.0	-		E
1/2 HHSS25	.30	.54	1.08	67.4	2.2	A
	.21	.54	.95	28.6		B
	.33	.30	.80	50.9		C
	.33	.24	.73	46.4		D
	17.1	.54	22.4	-		E

A - Minimum gas flow for sustained combustion with .54 cfm steam.

B - Minimum gas flow for combustion in contact with spark.

C - Minimum steam, with gas flow rate same as in A, without flashback.

D - Approximate flashback conditions.

E - Maximum capacity of burner orifice (approximately).

condensate pot by means of a 2-in. pipe which extends 2 in. above the bottom of the burner chamber to maintain a constant level of condensate at this point. The condensate pot contained an overflow outlet 4 in. above the bottom and was heated to control the atmosphere in the burner chamber. Leaving the pot, condensate overflowed into a receiver from where it was siphoned at intervals for weighing.

OPERATION OF PILOT LAYOUT

Initial operation of this equipment was attended by a number of difficulties. The enclosed burner proved easy to light at moderate flow rates but flashbacks were encountered under a variety of operating conditions and the multihole nozzle plugged tightly after several minutes of operation. Inspection of the dismantled equipment showed that a flashback had occurred and had caused overheating and considerable oxidation in the line behind the burner. The burner had been plugged by the loose scale so formed.

Subsequent tests with the burner in the open disclosed that some condensation of steam was occurring. The slugs of water so obtained were, on passage through the zone of flame, leading to uncontrollable pressure surges in the system and producing the flashbacks. Additional heat transfer surfaces have been introduced into the lines preceding the burner system to eliminate difficulty from this source. In addition, merely as a precaution to prevent injury to equipment by flashbacks, a flashback arrestor from an acetylene welding system has been placed in the line before the burner. It is intended to operate without this precaution as soon as sufficient experience is gained.

With these changes the system has been operated for short intervals without serious difficulty. The combustion chamber design seems satisfactory for the purpose, although the burner has not been operated at high flow rates for an interval sufficient to test this point thoroughly. The spark ignition system has performed well to date and no serious difficulty from this part of the assembly is anticipated.

Some difficulty in adjusting the gas flows to yield a stoichiometric mixture of hydrogen and oxygen is still encountered. Recent modifications of the metering system and subsequent recalibration of the equipment in place have minimized but not completely eliminated difficulties from this source. Continued studies should, in the near future, permit accurate valuation of the burner under all flow conditions.

THERMAL RECOMBINATION OF HYDROGEN AND OXYGEN

If the steam flow to the burner is maintained at a constant value then the stoichiometric mixture produced at low power levels will be fed to the burner in a non-combustible mixture. In addition the large flame burner will probably not be perfectly efficient at the high flow rates. A small secondary recombiner will therefore be required in the fuel system. The magnitude of the gases passing the combustion chamber unburned must remain unknown until actual valuation of the burner in the closed system can be made. Present evidence indicates, however, that flow rates below 0.2 cfm will yield mixtures incapable of ignition at the burner nozzle. Thermal, or catalytic, recombination of this material will be required.

To date thermal recombination has been tested only in small scale low pressure equipment. For these studies the hydrogen and oxygen has been supplied from an electrolytic generator which was calibrated so that the current passed was a measure of stoichiometric mixture introduced. This gas was admixed with steam so that the combination was considerably below the explosion limit. Steam flow was calibrated by measurement of water condensed at the exit end of the reactor. Reaction efficiency was calculated after measurement of the volume of uncombined gas.

Initial experiments with an unpacked stainless steel tube 1/2 in. in diameter and 12 in. long have covered the range from 600 to 780°C. Flow rates from 0.5 to 4.0 liters per minute with the mixture containing 11 to 0.5% electrolytic gas were used. In this apparatus virtually no reaction occurs below 600°C, but the combination is practically complete at 700°C when low flow rates are used. The experiments show a sharp dependence of reaction completeness on residence time in the chamber. The reaction efficiency is improved somewhat with increasing richness of the gas mixture.

These experiments have been extended in the direction of higher flow rates and richer mixtures by use of a larger generator and with a larger converter. The reaction chamber is a 5-in. length of 4 1/4-in. diameter stainless steel pipe with a preheater consisting of a 12-in. length of 1 1/4-in. pipe packed with stainless steel sponge.

Variation of reaction efficiency at 700°C with 1% electrolytic gas mixture as a function of flow rate with this equipment is shown in Fig. 18 below. It

74

FIG 16
THERMAL RECOMBINATION
AS A FUNCTION
OF FLOW RATE
TEMPERATURE 700°C
1% ELECTROLYTIC GAS IN STEAM

Extent of Reaction (%)

- - With no packing
- - Packed with Al_2O_3
- ◐ - Packed with stainless steel

Flow Rate (liters/minute)

is interesting to note that packing the reactor with stainless steel sponge results in a decrease in efficiency of this apparatus. However, packing the assembly with 8-mesh activated alumina serve to increase the efficiency. These phenomena may be qualitatively understood if one assumes the reaction in the empty chamber to be due to chains which are deactivated at the walls. The stainless packing serves to decrease the rate by this mechanism. The alumina packing with the enormous surface probably supresses the homogeneous reaction completely but substitutes a surface reaction whose rate under these conditions is comparable.

The difference on these reactions is borne out by the fact that efficiency of the apparatus containing alumina is independent of gas composition at least up to 10% electrolytic gas. The empty chamber or the stainless packed chamber become increasingly efficient as the gas becomes richer.

CATALYTIC RECOMBINATION OF HYDROGEN AND OXYGEN

Two factors, the problem of removal of the heat produced and the possibility of poisoning by traces of fission products, seem to restrict the ultimate usefulness of a catalytic bed as the primary recombiner for the fuel circuit. There is, at present, no direct evidence that these factors lead to problems which are insolvable.

Studies of catalytic recombination have been restricted to tests of a single agent (Product 43, a carbon-base platinum catalyst) at relatively low flowrates and with electrolytic gas-steam mixtures considerably below the explosive limit. These experiments, which used a catalyst bed in the small thermal recombination apparatus described above, have shown that the reaction efficiency at a given flow rate is virtually independent of the gas composition. At 150°C the uncombined gases amounted to less than 1% of the total when flow rates of 1 liter per minute were used. At 250°C more than 90% of the gas was combined at flow rates of as much as 50 liters per minute. Simple tests have established that the catalyst is not poisoned by moderate quantities of bromine or iodine.

Tests to provide additional data for design of a small pilot scale low pressure catalytic recombiner are planned for the immediate future. Equipment for study of the catalyst in a high pressure system containing helium has been

designed and should soon be available for testing. In addition, in-pile tests of poisoning of the catalyst mass by fission products are presently being designed.

VII. CHEMICAL STUDIES

SOLUBILITIES OF FISSION PRODUCT SULFATES

During the operation of a homogeneous solution reactor the fission products will "grow into" the reactor solution. Eventually the solubility products of some of the fission product salts may be exceeded, resulting in the precipitation of solid material in the solution. The amount of precipitate may be quite significant, especially in the operation of homogeneous reactors of high power ratings and may have to be considered both during the operation of homogeneous reactors and in the solution decontamination process. Hence it is of interest to determine the solubilities of the various fission product sulfates under the conditions existing in the reactor. Since contemplated homogeneous reactors will operate at high temperatures and pressures, it is necessary to determine the solubilities of the fission product salts at elevated temperatures and pressures. In the experiment planned the solubilities of the fission product sulfates will be measured since a sulfate solution will be used in the X-10 homogeneous reactor experiment. No attempt will be made to regulate the pressure on the solution. It will be assumed that the pressure coefficient of solubility of the fission product sulfates will be small.

Two general experimental methods are being used for determining the solubilities at these temperatures and pressures. In the first method a thick-walled quartz tube containing a known concentration of solution is heated to the point of appearance or disappearance of a solid phase, thus indicating the limit of solubility at a given concentration. This method has to date proved of limited value due to the comparatively low solubilities and to the overlap of metastable states in so many of the fission products which are of interest. It is, however, being used for exploratory work and as a guide for further investigations.

The second method involves the physical separation of phases equilibrated at a known temperature and the later analysis of these phases to determine the concentration. This method has the advantage of permitting the study of highly insoluble materials through the use of larger volumes and of tracer techniques.

Since the temperature involved (200 - 370°C) result in pressures of 2000 to 3000 psi, steel bombs are used. The phase separation is performed within

the bomb either by decantation through a valve or by filtration through a stainless steel filter disk. At the present time the latter method is being used since it appears to be more trouble-free. A small #347 stainless steel bomb is placed in a heating jacket, shaken in a mechanical shaker and equilibrated at a given temperature. The bomb is then inverted and the solution separated from the solid phase by permitting the liquid to flow into the collection chamber through a filter. After cooling to room temperature the solution is analyzed either by radiochemical methods in which case the starting material has a known specific activity or by conventional analytical methods. A rough correction will suffice for the amount of water vapor condensed with the liquid phase during the cooling operation. The solid phase in equilibrium or the wet residue may also be analyzed for composition.

Work is now in progress on the rare earth sulfate solubilities using the above mentioned bomb method. Concurrently exploratory work on other fission products is being carried out by means of the quartz tube method.

CHEMICAL CONTROL

The problem of chemical control of the "soup" solution of the experimental homogeneous reactor includes the separate problems of the determination of total uranium, reduced uranium, acidity, suspended particles and their nature, and oxidizing power. The presence of the following factors further complicates these determinations.

- (1) *Temperature.* An experimental operating range of 200-250°C is achieved by the initial application of external heat to the system.

An internal heat of 250°C within the system due to the resultant power of the reactor and the constant heat is released from the radioactive decay of the fission products.

- (2) *Pressure.* Any apparatus used in measuring any of the desired properties of the "soup" must be capable of withstanding sudden pressure changes from 1000 psi to 10 psi. The system will be under a total operating pressure of 1000 psi of which 580 psi will be contributed by water at 250°C and the balance by a pressurizer operating at 285°C.

- (3) *Radioactivity.* The radioactive level of the "soup" has been calculated to be about 30 curies per ml as fission products at 1000 kw.

Severe limitations in the type of apparatus to be used in the measurement of any of the properties of the "soup" are imposed by the requirements inherent in the construction, design, and fabrication materials of the experimental homogeneous reactor as well as the resultant high level of radiation of the solution. In general, all optical methods are inoperative for routine control. Remote control is mandatory for any conceivable method of making any determinations.

Three methods by which chemical control would be possible have been investigated and are discussed below.

DETERMINATION OF URANIUM CONCENTRATION

The total uranium content of the "soup" appears to be the most important analytical determination to be made. The accuracy desired is 0.1 g U/liter.⁽¹⁾

(1) Winters, C. E. to Secoy, C. H., private communication, May 16, 1950.

Direct Methods.

(1) *X-ray*: The possibility of using a modification of the General Electric X-Ray Photometer was considered. It was found that absolute errors in excess of 0.1 g U/liter occur in the calibration of the instrument.⁽²⁾ The following factors were also to be noted:

- (a) Using the usual X-ray targets, it is impossible to operate at the K-edge for uranium, where the greatest "jump" in absorption is observed.
- (b) The presence of foreign elements of atomic number up to element 42 and above element 53 in concentrations as low as 1% would rapidly increase the apparent uranium content of the "soup."
- (c) It would be necessary to have a sample container of low absorption characteristic which would provide a sufficiently thin wall thickness to effectively transmit the X rays and at the same time withstand the changes of pressure before noted.

The possibility of measuring with a discriminator pulse analyzer and a proportional beta counter the energy of a photon ejected by an X ray emanating from uranium induced by an external gamma source or other means was also eliminated. Mr. Borkowski⁽³⁾ stated that even with the use of a pulse technique of introducing gamma rays, the method would not have sufficient sensitivity due to the high level of gamma and X-ray background.

(2) *Nuclear Induction*: It is possible that a specific method for the determination of U^{235} concentration may be found in the measurement of the nuclear inductance of the solution. Mr. Walchli and Mr. Zimmerman of Y-12 are attempting to find a resonance peak for U^{235} . It appears that if such a peak is found, the application of this measurement to the accurate determination of the U^{235} concentration will still remain a major problem.

(3) *Conventional Chemical Methods*: In general, the use of standard chemical methods are highly undesirable because of the problem of sample removal and fission product separation before analysis.

Indirect Methods.

(1) *Conductivity*: Indication of changes of the uranium concentration in the reactor solution could be obtained by following the conductivity of the

(2) Bartlett, T. W.; *The General Electric X-Ray Photometer and Its Application to the Determination of Uranium. II. Determination of Uranium in Solutions*, AECD-2766 (Oct., 28, 1949).

(3) Borkowski, C. J., private communication, May 18, 1950.

solution. If the contribution of the other ions in the solution to the total conductivity is known, then a direct measure of the uranium concentration is available

The simplest means of measuring conductivity would be to insert two electrodes (probably platinum) of known area into the solution at a known distance apart and measure either the resistance or the conductance of the solution between the electrodes.

This method is not readily adaptable to the homogeneous reactor system since the conditions require that at least one lead be insulated from the steel pipe and that both the insulating material and the electrodes be stable to radiation and pressure. The Instrument Department has been giving consideration to this phase of the problem and may be able to develop suitable insulators and electrodes.

K. Kline of the Instrument Department is working on another method for measuring conductivity which might be adapted to the reactor problem. It consists of placing a coil inside the pipe, applying a predetermined frequency on the coil and measuring the conductivity in terms of the change in Q of the coil.

Early results do indicate a dependence of Q upon the uranium concentration. The method, however, is in the early stages of development and no conclusive results have been obtained.

(2) *Density*: Density is another property of the reactor solution which is affected by uranium concentration. The accurate determination of density within the system itself is difficult but one method which appears feasible makes use of an electromagnetic densitometer.

The measurement of density in this way has been reported by Lamb and Lee⁽⁴⁾ and by Richards.⁽⁵⁾ In principle, a submerged float containing an iron core is moved through a liquid by the effect of the magnetic field of a d-c or a-c coil exterior to the liquid. The force produced in the coil which is necessary to move the float to or from a given position is proportional to the

(4) Lamb, A. E., and Lee, R. E., "The Densities of Certain Dilute Aqueous Solutions by a New and Precise Method," *Am. Chem. Soc. J.* 35, 1666 (1913).

(5) Richards, A. R., "An Electromagnetic Densitometer," *Ind. and Eng. Chem., Anal. Ed.* 14, 595 (1942).

100 081
~~313 006~~

density of the liquid. The force is measured in milliamperes passing through the coil. Since density is dependent upon temperature, changes in temperature must be either controlled or known. Under favorable conditions the method can be extremely accurate. The sensitivity, however, decreases as the range is increased.

Here again the development of this method for use in the homogeneous reactor is in the early stages. Aspects to be investigated include (a) the dimensions of the float and coil required, (b) the material to be used for the float which of necessity must be thin-walled and yet be able to withstand pressure and corrosion, (c) a method for the precise automatic recording of the float movement, (d) the effect of high temperature and pressure, and (e) the control of the temperature.

(3) *Density and/or Adiabatic Compressibility by Sonic Interferometer:* Falkenhagen and Bachem⁽⁶⁾ have shown that the velocity of sound is dependent on the concentration (over the range of 0.1 M to 0.6 M) of KBr, BaCl₂, NaCl, MgSO₄, K₃[Fe(CN)₆], Na₂CO₃, and K₄[Fe(CN)₆] in aqueous media. Since the velocity, v , equals $1/\rho B_{ad}$, it seems that a means might be devised to measure ρ , the density, or at least the product of the density and B_{ad} , the adiabatic compressibility as per the above relationship.

The major problems are as follows:

- (1) Accurately measuring the temperature of the "soup" or controlling the temperature of the "soup" by a bath thermostated to the small temperature variation permissible. It is to be remembered that the "soup" heats itself by virtue of its own radiation about 30 calories/ml/hr.
- (2) Possible radiation damage to the source of the sound generator, the piezoquartz or the magnetostriction material
- (3) Probable presence of gas bubbles which cannot be tolerated in a sonic interferometer.

DETERMINATION OF OXIDIZING POWER

If chromic acid is used as holding oxidant in the reactor solution, it is expected that some reduction of chromium will take place. If this reduction

(6) Falkenhagen, H. H. and Bachem, Ch., "Zur Kompressibilität Starker Elektrolyte," *Z. Elektrochem* 41, 570 (1935).

is appreciable more chromic acid would be required. Rather than attempt to determine the rate of reduction, it seemed a better idea to regenerate the chromic acid continuously if possible. This would also prevent the build-up of chromium in solution.

It was found that on a laboratory scale [1.5 liters of 0.005 M $\text{Cr}_2(\text{SO}_4)_3$ and 0.01 M CrO_3] chromic acid could be regenerated electrolytically. In order to demonstrate this, the chromic acid solution was circulated (using a circulating pump) at a rate of 1½ gals/min past two platinum electrodes sealed in a glass tube. The anode was a platinum gauze cylinder 5 cm long and 1.3 cm in diameter. The cathode was much smaller being a platinum wire 1 mm in diameter and 3 mm long. This arrangement favored the oxidation reaction at the anode.

Samples were taken periodically and analyzed colorimetrically for Cr^{+6} and Cr^{+3} . The pH and temperature were also determined.

As a result of four laboratory runs the following results were obtained:

1. Essentially all of a 0.005 M chromic sulfate solution can be re-oxidized at room temperature with an average current efficiency of 24%.
2. If the anode is first plated with lead dioxide the current efficiency is increased to 35%.
3. Heating the solution to 95°C results in an increase in current but a decrease in current efficiency. The net effect is a slight increase in the rate of oxidation.

On the basis of the tests conducted on a laboratory scale, the electrolytic regenerator of chromic acid in the homogeneous reactor solution seems possible, providing the required rate of oxidation is not too high. Using the laboratory results as a guide, a reasonable estimate of the time required to re-oxidize completely 50 liters of 0.001 M Cr^{+3} would be three to four hours.

No further work on the regeneration of chromic acid is contemplated unless the need for such regeneration becomes more apparent.

DETERMINATION OF OTHER PROPERTIES

Very little consideration has as yet been given to the determination of other properties of the reactor solution such as reduced uranium, acidity,

etc The determination of total uranium appears to be by far the most valuable information on "soup" that can be obtained by analytical means. Accordingly, most of the effort to date has been directed along these lines.

EXPERIMENTAL AND DEVELOPMENTAL--AN ELECTROMAGNETIC DENSITOMETER

It is planned to construct a complete unit capable of withstanding the temperature, pressure, and radiation conditions of the reactor. This unit will have an intake and output pipe so that it can be incorporated into the reactor system after first being calibrated and tested in the laboratory. While operating, the fluid will be static and the unit will be protected against sudden pressure changes such as result from dumping.

As a starting point, certain specifications have been decided upon. Those regarding overall size are arbitrary and may be changed if necessary. Specifications as to float or sinker material, coil strength, armature size, etc., are dictated by the conditions of the solutions and by the magnetic field strength required. The design of all parts of the densitometer meets the requirement that it will be undesirable or may be impossible to introduce insulated electrical leads into the high pressure system. The instrument will also be designed to permit recalibration without removal.

Temperature Control. The temperature effect upon density measurement will be critical. It is expected that changes in temperature greater than 0.2°C could not be tolerated unless the proper corrections are applied. The control or measurement of temperature with this degree of accuracy would be quite difficult due to the continuous internal heating of the solution and to the problem of obtaining a suitable thermometer.

It is believed that the problem of temperature control may be circumvented by using two densitometers both pressurized to the condition of the reactor. One of these will contain a solution of U^{238} of known concentration, and the other will contain the unknown soup solution. Both solutions will be thermostated by the soup solution itself. The densitometer containing the known U^{238} will then become in effect a thermometer, in that changes in temperature will be reflected in the coil current readings.

The current in the unknown densitometer coil will be governed by changes in the temperature and concentration of the soup solution. When calibrated,

the difference in the two current readings should be independent of temperature. Since this is still theory, no definite problems have been encountered but it is anticipated that there may still be the problem of temperature gradients even though the solutions are thermostated.

Sinker. Either a sinker or a float could be used. If a sinker is used, its density must be slightly greater than the highest density solution in the range to be studied. Then the coil current required to hold the sinker up is observed. If a float is used, its density must be slightly less than the solution of lowest density in the range to be studied. In this case, the coil current required to overcome the bouyancy force and hold the float down is determined. A sinker was selected for our preliminary densitometer mainly because this best fitted into our plans for a position detection device (to be described later). A sinker also gives the advantage that additional mass may be used in the construction of a given volume. This gives a more rugged float and facilitates the machining operation.

Since the sensitivity increases as the difference between the float or sinker and the solution decreases, it may be necessary to go to a float to measure densities in the lower density range.

The sinker material is to be stainless steel. Other metals and alloys such as platinum and gold were considered but were eliminated on one or more of three counts:

1. Not corrosion resistant
2. Not pressure stable
3. Too high a density

The float has been designed in the shape of a cylinder with rounded ends. The cylinder is 1.6 cm O.D. and 4 cm long. A soft iron core enclosed in stainless steel will extend from the top and a permanent alnico magnet will extend from the bottom. The weight at the magnet end will be the greater so that the sinker will position itself with the iron core end up.

The machining of the sinker has proven to be a research problem in itself and of necessity has been a time-consuming operation for the Research Shops. When the job is completed, the sinker will be hydraulically pressure tested for pressures up to 5000 psi. It will also ultimately be passivated using the same oxidant employed in the reactor.

Detection Device. The number of techniques which may be used to detect the position of the sinker become quite limited if it is assumed that no electrical leads inside the pipe are to be used.

Of the few remaining devices which seemed at all feasible it was decided to use a magnetically operated switch placed on the outside of the densitometer. Other methods which were considered were based on the change produced by the position of the sinker on the measurement of an X-ray, Sonar, or Radiation (from "soup") beam.

None of these seemed sufficiently stable to changes in physical properties of the soup and pipe to warrant further investigation.

The magnetic switch is controlled by the position of the magnet attached to the sinker. When the sinker is in the down position, the field of the alnico magnet is strong enough to actuate the switch which also has an alnico magnet attached to it. This closes one circuit. When the sinker is pulled up by the coil the field of the alnico magnet is removed and the switch falls by gravity breaking the first circuit and closing the second.

This method enables one to tell whether the float is up or down but does not indicate the movement in between. It is hoped that the operation of the switch by the up and down positions will be reproducible for a given density and therefore sufficient. The effect of temperature and radiation upon the magnetic strength of the permanent magnets has been considered and is being investigated in pile experiments. It may be desirable to substitute an iron core for the sinker magnet. Preliminary pile experiments have indicated no detectable change in an alnico magnet exposed to 75% of the maximum flux in the X-10 pile at 152°C for the first three weeks.

Coil. A direct current coil will be used. This coil will be required to move a maximum mass of 2.5 g a distance of 1 cm to the point just outside the coil. The number of turns and diameter will be chosen to give a current range of 0 - 1 amp. The winding of the coil will be done by Toucey's Instrument Group and since this is partly a trial and error operation, the winding of the coil will be held up until the sinker has been prepared.

Electrical Circuit. It is proposed that the current in the magnetic coil be controlled by a motor driven potentiometer, so that the current can be increased or decreased at a constant rate. When the sinker is in the down

position the circuit through the magnetic switch will include a Brown Recorder (for coil current) and the motor driven potentiometer operating so as to increase the current in the coil. When the sinker is up the circuit through the switch will drive the potentiometer in a reducing current direction.

Both the thermometer sinker and the sinker in the soup solution will be released by their respective electromagnetic coils at the same instant to avoid temperature differences due to time lag between the soup solution and the U²³⁵ thermometer solution.

PHASE RULE STUDIES

INTRODUCTION

A phase study of the system, uranyl fluoride - water has been completed up to the critical temperature except that the identities of the solid phases have not been established with surety.

No solubility data for this system is in the open literature. In fact, very little was known concerning uranyl fluoride solutions prior to 1941. A few solubility values in the temperature range from 0° to 100° have been reported in the project literature.^(1,2) These data do not agree, and, consequently, it seemed advisable to repeat measurements in this region as well as to extend the study to higher and lower temperatures.

The ice curve has been determined from 0° to the eutectic point at -13° and 64.25% UO_2F_2 . The solubility curve for the solid has been determined all the way to the critical temperature of the saturated solution, 377°. A solid phase transition (an incongruent melting point) occurs at 150° and a second transition occurs at 240°. At 347° an invariant system is found consisting of the four phases, solid - liquid I - liquid II - vapor. At temperatures below 347° and in solutions not saturated with respect to the solid, a two liquid phase region occurs. This two liquid phase region is similar to that found by Secoy⁽³⁾ for the uranyl sulfate - water system except that its upper limit is the temperature of solidification of the salt-rich liquid phase rather than the critical temperature of the water-rich liquid phase.

EXPERIMENTAL

Anhydrous uranyl fluoride obtained from the Harshaw Chemical Company was used in these experiments. A spectrographic analysis of the Harshaw material showed no impurities other than faint traces of a few metals. Analysis by

(1) Dean, G. R., *Properties of Uranyl Fluoride*, CC-2092 (Sept., 1944).

(2) Kunin, R., *The System $\text{UO}_2\text{F}_2\text{-HF-H}_2\text{O}$* , A-3255 (May, 1945).

(3) Secoy, C. H., *The System Uranyl Sulfate - Water*, ORNL 98 (July 7, 1948).

direct oxidation at 900° to U_3O_8 gave 99.5% UO_2F_2 . By potentiometric analysis, this value was 99.3%. Fluoride was determined by conversion to SiF_4 gas and subsequent titration with standard $Th(NO_3)_4$ to give 11.8% fluorine (theoretical = 12.07) which is in the range of experimental accuracy for this method. Direct measurement of pH and titration curve determinations⁽⁴⁾ indicated no detectable amount of excess uranium trioxide (i.e., as UO_2^{++} in solution); therefore, the low determination by conversion to U_3O_8 might be due to a slight amount of moisture.

Solubility data for the phase study were obtained by four different methods depending on the particular region of the system.

All solubility points below 0° were obtained by standard methods of cooling and warming curve determinations. A copper-constantin thermocouple was used for temperature measurements. Analytical solubility determinations were made from 0° to 90°. The solutions were stirred in a thermostat from four to twenty-four hours. Samples taken after four hours stirring time agreed in most cases with later samples. These samples were analyzed by direct ignition at 900° to U_3O_8 , the precision of duplicates being within ± 0.10 percent.

All work above 100° was done in sealed quartz capillary tubes as described by Secoy.⁽⁵⁾ An aluminum cylinder containing a thermocouple well and observation slit was substituted for the stainless steel cylinder used previously. Four and five millimeter inside diameter quartz tubing was used from 100° to 250°; however, above 250° two millimeter capillary tubing was required. With the exception of data between 150° and 240°, points were obtained by slowly heating the cylindrical block (wrapped with nichrome resistance tape and rocked in a special mechanism) containing a known solution in the quartz tube and observing through a slit any phenomena occurring. These solubility points were checked to ± 1° or better by raising and lowering the tube temperature. Owing to the rather vertical portion of the curve in the range 150° to 240° this latter synthetic method was not effective. Therefore an analytical approach was tried in which a saturated solution and excess solid were rocked

(4) Marshall, W. L., and Gill, J. S., "The Uranyl Fluoride - Water System" *Chemistry Division Quarterly Report for Period Ending March 31, 1950. Part I. Chemical Research*, ORNL 685, p. 34 (June 16, 1950).

(5) Secoy, C. H., *op. cit.*

in the aluminum cylinder for 24 to 48 hours at a constant temperature, the variation in temperature being of the order of $\pm 1^\circ$. The rocker was then stopped and the tube allowed to cool about an hour before analysis. Above 150° the saturated solution is very viscous but will still flow in 5 mm (I.D.) tubing; whereas, below this temperature, if it is not shaken on cooling, the solution forms a translucent gel. It appears unlikely that the solubility equilibrium is changed to any extent. After cooling, the tube was broken and the gel-solid and crystalline-solid separately analyzed for uranium.

The pH measurements were made on prepared solutions using a Beckman pH meter. No effect on the glass electrode was noted.

THE DATA AND DISCUSSION

The data are given in Tables I and II and are shown graphically in Figs. 19, 20 and 21.

Table I and Figs. 19 and 20 show the variation of density and pH with concentration at room temperature. The condensed phase diagram for the system is shown in Fig. 21, the data being given in Table II.

TABLE I

The Density and pH of Aqueous Uranyl Fluoride Solutions at 25°C

WEIGHT (Percent UO_2F_2)	DENSITY	pH
2.112	1.0136	3.70
7.565	1.0699	3.18
13.86	1.1349	2.86
19.39	1.2005	2.69
26.75	1.3016	2.50
34.76	1.4411	2.25
40.98	1.5754	2.13
49.24	1.7511	2.05
55.13	1.9212	1.76
61.98	2.1764	1.52

TABLE II

The Solubility of Uranyl Fluoride in Water

WEIGHT (Percent UO_2F_2)	TEMPERATURE (°C)	PHASE DISAPPEARING OR APPEARING	SOLIDIFICATION POINT - UO_2F_2 IN LIQUID PHASE	CRITICAL POINT (°C)
44.23	-4.2	Ice		
47.72	-5.0	Ice		
50.76	-5.9	Ice		
55.49	-7.8	Ice		
57.28	-8.1	Ice		
58.54	-9.2	Ice		
61.20	-10.9	Ice		
62.58	-11.9	Ice		
(64.25	-13.)	Ice + $\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
64.28	-10.7	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
64.30	0.0	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
64.40	10.1	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
66.09	19.7	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
66.50	30.5	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
67.78	39.8	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
67.25	51.2	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
68.45	54.3	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
68.42	60.1	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
69.37	65.8	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
71.73	75.0	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
73.02	89.8	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
76.98	125	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$		
81.72	150	$\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O} + \text{UO}_2\text{F}_2 \cdot \text{YH}_2\text{O}$		
81.40	195	$\text{UO}_2\text{F}_2 \cdot \text{YH}_2\text{O}$		
82.61	219	$\text{UO}_2\text{F}_2 \cdot \text{YH}_2\text{O}$		
-	240	$\text{UO}_2\text{F}_2 \cdot \text{YH}_2\text{O} + \text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$		
82.53	243	$\text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$		
81.22	252	$\text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$		
77.05	283	$\text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$		
72.31	322	$\text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$		
70.5 (ex- trapolated)	347	$\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O} + \text{liquid salt} + \text{aqueous}$		
66.46	324	Aqueous	344	
61.98	320	Aqueous		
55.13	314	Aqueous	347	
49.24	314	Liquid Salt	347	
40.98	313	Liquid Salt	347	
36.1				376 (prelim. data)
34.76	313	Liquid Salt	347	
26.75	313	Liquid Salt	344	
23.				(prelim. 378)
19.36	314	Liquid Salt	325(?)	
13.86	313	Liquid Salt (Immediately crystallizes metastable)		
13.86	298	solid W (Reaction with container)		
10.85				(prelim. 377)
7.56	277	solid W (Reaction with container)		
2.11	215	solid W (Reaction with container)

FIG. 19
THE pH OF AQUEOUS URANYL FLUORIDE AT 25°C

FIG. 20
THE DENSITY OF AQUEOUS URANYL FLUORIDE AT 25°C

FIG. 21
THE SYSTEM, URANYL FLUORIDE - WATER

Region J of Fig 21 represents complete solution for the system uranyl fluoride-water. The ice curve is represented by line AB down to the eutectic point B. Any mixture of the two components in region ABK will consist of ice and saturated solution represented on the ice curve. Below line KBL there will be two solid phases, ice and $\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$. Line BC corresponds to the $\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$ solubility concentration in contact with solid $\text{UO}_2\text{F}_2 \cdot \text{XH}_2\text{O}$. This hydrate is probably $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$, based on analytical determinations of the solid phase; however, more work must be done to fix precisely the hydrate composition.

Point C corresponds to either a hydrate or allotropic transition to $\text{UO}_2\text{F}_2 \cdot \text{YH}_2\text{O}$ in which Y may or may not equal X. A preliminary analysis of the solid phase at 195° gave 98.5% and 101.5% $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ uranyl fluoride dihydrate (theoretical 100% if correct hydrate). The solid phase below 150° appears as very fine, silky needles which mix throughout the solution, whereas in the region $150\text{--}240^\circ$ the solid phase is more well defined and of a definite crystal structure. An attempt was made to determine the structural system of the crystals formed in the $150\text{--}240^\circ$ temperature range. No success was attained using a polarizing microscope. It appeared that the individual crystal units (metastable at room temperatures) had rearranged within the macro-crystal system to produce a pseudomorphic form. By visual observation the crystal structure is probably either in the hexagonal or cubic system.

At 240° another transition occurs to give $\text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$ (where Z may or may not equal Y) and also to give a negative solubility-temperature relationship. Points along line DE were rather difficult to obtain because of tube explosions upon reaching the solid phase temperature. In the few runs that were successful, the solid phase appeared to liberate bubbles, possibly due to the liberation of water vapor. Analysis of the solid phase at 295° and 322° gave 100.3% and 99.7% $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$, respectively. Reliance on the few analyses indicate allotropic forms of the dihydrate for the three UO_2F_2 solid phases. Point E represents an invariant point at which temperature and composition, a solid ($\text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$), and two liquid phases are in equilibrium in the condensed system. Seven attempts to get a point near the apex met with failure due to tube explosion just before the apex temperature (347°) was reached.

The invariant point temperature was fixed by the solidification points for the uranyl fluoride rich liquid phase, at which temperature this liquid loses water to the water-rich liquid phase and solid $\text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$ is deposited.

Area *GFE* represents a two-liquid phase region. The minimum critical point lies between 49.24 and 55.13 percent uranyl fluoride and at 313°. In the region above *GE* and below *HI*, there are two phases in the condensed system, water-rich liquid and solid $\text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$. The critical temperature of the saturated solution is represented along line *HI*. Above this line, there is a gaseous phase and the $\text{UO}_2\text{F}_2 \cdot \text{ZH}_2\text{O}$ solid. The critical point for pure water (374.4°) does not appear to have been elevated more than three or four degrees, thus indicating that the solubility of the *Z* solid has reached a low value.

Along *FM* a crystal formation appeared due to reaction of the fluoride solution with the quartz tube. These crystals have been isolated and identified by chemical analysis and spectroscopic data as silica and a yellow uranium-silicon compound. The phenomenon is strictly a corrosion problem involving the quartz container. This corrosion evidently is caused by free hydrogen fluoride formed by a forward shift of the equilibrium, $\text{UO}_2\text{F}_2 + \text{H}_2\text{O} \leftrightarrow \text{UO}_3 + 2\text{HF}$, with temperature.

The solubility curve, then, probably follows curve *FGH* to the critical temperature of the solution; however, attempts to get experimental points were not successful because of the crystal formations. This corrosion effect is also observed to a much smaller extent above 300° in the more concentrated region.

There is no reason to believe that at 250° the system is not stable at all concentrations up to saturation (81% UO_2F_2) if the corrosion problem is solved. However, the system is not hydrolytically stable but must surely have a partial hydrogen fluoride vapor pressure at 250°.

FUTURE WORK

Pressure bombs are being constructed containing a closed gold liner to further verify the thermal stability of the solutions. Also, experiments are planned to study the hydrolytic behavior in the upper temperature range.

SUMMARY

(1) The uranyl fluoride - water system has been studied from the ice eutectic to the critical temperature. Density and pH data are given at 25°C.

(2) The system appears thermally stable at 250°C and at all concentrations if the corrosion problem of the container is solved. However, the system is hydrolytically unstable and probably exhibits a partial hydrogen fluoride vapor pressure at 250°C.

(3) Future study on the partial hydrogen fluoride pressure in the 100 - 300°C range is planned.

SLURRY PROBLEMS

During the past quarter the preparation of slurries suitable for use in a homogeneous reactor was further investigated.

These slurries contain 40 grams of uranium per liter and they should be stable with respect to sedimentation upon shutdown of the slurry circulating system. The operating conditions are 250°C and 1000 lbs/sq in. pressure.

It has been shown that slurries prepared from uranium trioxide and water sedimented very rapidly after being heated at 250°C for one hour. Further work indicated that these slurries could be stabilized by the addition of bentonite, a naturally occurring colloidal alumino-silicate clay. Bentonite was employed most effectively when present in particle sizes below 25 millimicrons. The fractionation of the clay was accomplished in Sharples super-centrifuge.

It was also found that the presence of phosphate, incorporated as uranyl phosphate, was necessary to complex the iron and other exchangeable cations liberated from bentonite, which has cation exchange properties, since the presence of these cations adversely affected the stabilizing properties of bentonite.

Determination of the stability of the slurries heated at 250°C for 21 hours as a function of the viscosity of the bentonite suspension indicated that a slurry of the following composition gave the best results for a minimum bentonite concentration.

Uranium - 40 grams	65% uranium trioxide
	35% uranyl phosphate
	11 gms bentonite avg.
Bentonite suspension-	particle size - below
1000 ml	25 millimicrons
	Viscosity - 280 C.P.
	(Brookfield)

Using this slurry composition as a point of departure, the work of this quarter was devoted to methods of decreasing the amount of bentonite or improving the suspending characteristics of the slurry as well as the effect of longer heating periods on slurry stability.

The use of electrodialysed bentonite, sodium bentonite, and the addition of magnesium oxide to both natural and electrodialysed bentonite as variables affecting the bentonite suspension were observed (Table I).

It can be seen from these results that slurry prepared using electro-dialysed containing magnesium oxide gave the best results. No separation of the solid phase was noticed until after three days of standing. However, the uranium concentration in this experiment was low and it was also found that the head of bomb had been corroded during the course of the heating which resulted in an increase in the iron content of heated slurry over the unheated one.

For these reasons as well as to furnish a check, the experiment was repeated using a corrosion-resistant head on the stainless bomb. It was not possible to duplicate the previous results which suggests that the stability of the first slurry may be related in some manner to the presence of the iron.

When natural bentonite is electrodialysed all the exchangeable cations are replaced yielding a hydrogen bentonite which has acidic properties. The bentonite is also focculated in this process leading to an increase in the viscosity of the suspension. The sodium bentonite is formed by neutralization with sodium hydroxide. Magnesium oxide is known to increase the viscosity of natural bentonite suspensions and probably forms a magnesium bentonite with the electrodialysed clay.

Examination of the electrodes and membranes of electro dialysis apparatus showed that iron had been accumulated in the cathode compartment. This suggested the possibility that the interfering cations might have been removed sufficiently to eliminate the need for phosphate.

This was tested by preparing a slurry of uranium trioxide in suspension of electrodialysed bentonite and subjecting it to extended heating periods.

The results obtained after 66 hours were sufficiently promising to warrant extending the heating period to a total of 330 hours (13-3/4 days) (Table II).

A sample of the 330 hour slurry was observed for rate of sedimentation (Table III). At the end of 43.5 hours the slurry solids occupied 68.5% of the total volume with a fairly uniform distribution of uranium in the solids volume. From the rate of settling it appeared that further settling would be very small.

No difficulty was experienced in repeating these results. The data in Table II are a composite of three different preparations of the slurry.

This slurry, by elimination of the phosphate, represents an improvement from the standpoint of neutron economy as well as chemical reprocessing of the uranium.

A scouting experiment to determine the solubility of uranium hydroxide in concentrated phosphoric acid (85%), showed that at room temperature the solution contained 0.7 - 0.8 grams/cc of uranium. The hydroxide was dissolved by heating it in the acid and on cooling to room temperature a very viscous clear green liquid was obtained.

TABLE I 10/

The Effect of Some Bentonite Variables on the Stability of the Heated Slurry

Slurry Composition:

40 grams - Uranium (65% uranium trioxide; 35% uranyl phosphate)

1000 ml - Bentonite suspension (avg. particle size below 25 millimicrons)

Heating Conditions: 250°C for 21 hours in a stainless steel bomb.

101

	URANIUM CONCENTRATION (grams/liter)				
	BENTONITE 11 gms/li Viscosity-280 C.P. (Brookfield)	BENTONITE 12 gms/li MAGNESIUM OXIDE 192 gms Viscosity-140 C.P. (Brookfield)	ELECTRODIALYSED BENTONITE 12 gms/li pH 196 Viscosity-210 C.P. (Brookfield)	ELECTRODIALYSED BENTONITE 11 gms/li Adjusted to pH 5.7 with NaOH	ELECTRODIALYSED BENTONITE 11 gms/li MAGNESIUM OXIDE 231 gms Viscosity-1560 C.P. (Brookfield)
SEDIMENTATION TIME SAMPLING LEVEL	6 days	7 days	6 days	2 days	3 days
1	32	12.2	.75	22.2	27.9
2	39.1	54.0	32.8	25.1	29.6
3	39.1	54.0	47.6	26.0	29.2
4	42.0	54.0	48.3	26.8	30.4
5	44.0	57.1	47.6	28.8	30.0
6		54.5		60.9	35.6

10

100

013 025

TABLE II

The Sedimentation Behavior of Slurries Over Long Heating Periods

Slurry Composition -

Uranium - 40 grams (as anhydrous UO_3)

Bentonite Suspension - 1000 ml 12 grams electrolysed bentonite solids; average particle size below 25 millimicrons; viscosity - 210 C.P. (Brookfield)

Heating Conditions - 250°C in a stainless steel bomb

HEATING TIME	4 HOURS	66 HOURS	100 HOURS	189 HOURS	330 HOURS
SEDIMENTATION TIME	5 DAYS	1.5 DAYS	18 HOURS	88 HOURS	43.5 HOURS
SAMPLING LEVEL	URANIUM CONCENTRATION (grams/liter)				
1	14.1	17.8	10.3	8.8	1.2
2	30.1	33.5	39.3	36.3	1.6
3	32.8	35.7	39.3	39.2	40
4	32.8	34.0	40.0	40.7	50.7
5	34.0	35.0	40.0	41.9	52.7
6	37.7	38.0	41.3	44.2	55.7
Volume ratio Settled solids Total solids	.90	.88	.90	.88	.685

TABLE III

Rate of Sedimentation of a Slurry Heated for 330 Hours

Slurry Composition

Uranium - 40 grams (as anhydrous UO_3)

Bentonite Suspension - 12.5 grams/liter electro-dialysed bentonite solids; average particle size below 25 millimicrons; viscosity 210 C.P.; (Brookfield)

SETTLING TIME (Hours)	0	2	18.5	20.5	23.0	25.5	43.5
<u>SLURRY SOLIDS VOLUME</u> TOTAL VOLUME	1	.97	76	73.5	70.5	70.0	68.5

RADIATION CHEMISTRY

Sixteen in-pile experiments have been completed during the period of this report. They show that suitably pretreated stainless steel (type 347) will withstand aqueous uranyl sulfate (40 g U^{235} /liter) at 250°C for as long as 14 days in a flux of about 5×10^{11} neutrons/cm² sec. Failures have been observed under special conditions and the detailed reasons for the failures remain unknown. Until they are elucidated the exact details for successful operation cannot be given, but there is only a small probability that the system will not work.

The criteria used at present in evaluating the results are the behavior of pressure with time, and the appearance of the solution after the irradiation. A normal pressure-time curve rises quite rapidly on exposure to the neutrons and then falls off more or less asymptotically to a pressure around 3000-5000 lb/in.² A quick drop in pressure has been observed to accompany precipitation of the uranium, and is the first indication of failure. The solutions from bombs showing this behavior have always been free of uranium (i.e., colorless) and have been accompanied by precipitates.

Tables I, II and III summarize the data which have been obtained.

TABLE I

Gross Results of In-Pile Corrosion Tests

40 g U^{235} /liter, Flux = 5×10^{11} , Temperature = 250-290°C
Stainless steel Type 347

PRETREATMENT OF BOMB	NUMBER OF RUNS SHOWING		
	NORMAL BEHAVIOR	FAILURE	ACCIDENTAL LOSS OF RUN
None	1	1	0
Nitrate	4	3	0
Chromate	6	0	1
Total	11	4	1

TABLE II

Durations of Successful In-Pile Corrosion Tests

Days operation without failure for given pretreatment
(no failure before stopping; tests stopped arbitrarily
or for other reasons than failure)

UNTREATED	NITRATE	CHROMATE
7	9	11
	12	12
	3	3
	3	6
		14
		14

TABLE III

Details of Unsuccessful Experiments

Untreated bomb - 1 failure - O_2 was added before start of irradiation.

Nitrate treated bomb - 2 failures - bombs used in a successful
3 day test at $250^\circ C$ were emptied, refilled,
and brought to $290^\circ C$. The failure appeared
at once on further irradiation.

Nitrate treated bomb - 1 failure - solution accidentally cooled to
low temperature in pile.

VIII. CORROSION

106

~~013 030~~

105

SUMMARY

Much corrosion work has been completed and is being continued for the Homogeneous Reactor Experiment. Numerous protective treatments have been attempted on stainless steels to eliminate reduction of the uranyl ion in uranyl sulfate at 250°C. [Marked] success has been obtained with pretreatments in 1% ^{HNO₃} nitric acid and in 2% chromic acid at 250°C. The most effective time for the pretreating operation with nitric acid appears to be four to 24 hours. Periodic pretreatment of stainless steel surfaces with nitric or chromic acids at intervals of one to four weeks appears successful for preventing solution deterioration. The feasibility of pretreating stainless steel surfaces with nitric acid in a large scale dynamic test unit has successfully been demonstrated. This unit has operated 425 hours thus far without indication of solution reduction. The presence of old, heavy film accumulations on stainless steel surfaces renders the ^{HNO₃} nitric acid pretreatment ineffective and solution reduction occurs at 250°C. The use of 100-300 psi partial pressures of oxygen will prevent deterioration of uranyl sulfate in a stainless steel system at 250°C. The corrosion resistance of various stainless steels in uranyl sulfate containing 1% ^{HNO₃} nitric acid at 250°C has remained excellent after 2350 hours. Corrosion rates of 0.15 mil/year and less have been obtained. The corrosion resistance of crystal bar zirconium in uranyl sulfate at 250°C remains excellent. Recent Bureau of Mines zirconium has shown fine resistance in uranyl sulfate after 1848 hours. Etching zirconium in hydrofluoric acid, in general, has resulted in improved corrosion resistance. Initial irradiation-corrosion tests have shown erratic results but nitric and chromic acid pretreatments on stainless steel appear to be successful. The corrosion resistance of various materials considered for use as bearings and valve seats was investigated. [A study was started to determine the corrosion resistance of reflector materials in water at 100-200°C.] The presence of sodium dichromate or chromate effectively reduces the magnitude of corrosion damage on carbon steel and aluminum even in the presence of hydrogen peroxide. A summary of the service corrosion projects in progress is presented. 1/15/51

INTRODUCTION

Test facilities to accommodate the large volume of work under way for the Homogeneous Reactor Experiment have been expanded. A total of 64 small 225 ml capacity autoclaves and four 1000-2000 ml capacity autoclaves are now available. Electrically heated ovens maintained at 250°C are used to heat the smaller autoclaves. The larger test units have individual electrical systems for heating.

The corrosion work on the Homogeneous Reactor will be divided into seven sections for discussion in this report. The subject headings are:

- (1) Protective Treatments on Stainless Steels
- (2) Corrosion Resistance of Stainless Steels
- (3) Corrosion Resistance of Zirconium
- (4) Irradiation-Corrosion Tests
- (5) Corrosion Resistance of Bearing Materials
- (6) Corrosion Resistance of Reflector Materials
- (7) Miscellaneous Corrosion Tests
- (8) Service Corrosion Tests

PROTECTIVE TREATMENTS ON STAINLESS STEELS

A general discussion on the suitability of stainless steels in a uranyl sulfate system operating at 250°C and 1000 psi pressure was included in the *Homogeneous Reactor Feasibility Report*, July, 1950 (ORNL 730). Unless precautionary measures are taken, the ordinary use of stainless steel to contain the sulfate medium at elevated temperatures does not appear practical. The impracticability of such use is clearly evidenced by reduction of the uranyl ion to oxides of uranium. Such reduction is accompanied by a heavy formation uranium oxide film on the surfaces of the stainless steels. Exclusive of irradiation effects, this reduction of the solution may be attributed to corrosion reactions taking place on the metal surfaces at elevated temperature in the acid sulfate solution.

The approach to overcome the difficulty of solution deterioration has been to employ oxidizing agents in the sulfate solution or to pretreat the stainless steel surfaces by a suitable treatment prior to introduction of the sulfate into the metal system. Marked degrees of success have been obtained with both treatments. Conclusive corrosion tests have been completed using small concentrations of nitric or chromic acid, or using 100-300 psi partial pressure of oxygen, to show that solution decomposition can be prevented. These oxidants are sufficient to maintain the solution in an oxidized state which is a major requirement for the successful use of stainless steels in corrosive media. Irradiation tests with sulfate solution containing nitric or chromic acid as an oxidant have indicated that the nitric acid addition might be more satisfactory than the chromic acid since the latter is reduced to an insoluble precipitate of a reduced chromium oxide. No reduction of the uranyl ion takes place during the chromate decomposition.

The second remedy to the solution decomposition problem centered around the use of a protective pretreatment of the metal surfaces before contact was made with the uranyl sulfate. The purpose of such treatment was to obtain a chemically inactive surface condition which, at operating temperature, 250°C, would not promote reduction or deterioration of the solution. Numerous treatments were attempted and again treatments involving the use of either nitric or chromic acid were successful. The generally accepted theory by which these

materials make a surface chemically inactive is based on the changing or formation of the protective oxide film or other type of compound surface layer. The nitrate and chromate ions either share or absorb electrons from the surface metal atoms whether or not a natural oxide layer is already existent. The subsequent electron rearrangement reduces the tendency for hydrogen atoms, produced from a corrosion reaction in an acid system, to enter the metal lattice and destroy its passivity. The nitrate and chromate ions are probably adsorbed also on the metal surface and reduce the reactivity of the surface metal atoms in similar fashion as adsorbed oxygen reduces the reactivity of stainless steel exposed to air. The present day belief is that passivation effects do not hold at elevated temperatures. However, whether or not the passivation mechanism is involved, test results have definitely shown that some phenomenon exists which will satisfactorily act to prevent decomposition of uranyl sulfate in contact with stainless steels. This action may be attributed to the electron rearrangement theory or to the formation of an insoluble, tightly adhering film of oxide or corrosion products. An interesting development along the pretreatment of surfaces with nitric acid appeared. If a heavy, old film of oxide or scale is originally present on the surface of the stainless steel to be pretreated, the pretreatment is of no value. Decomposition of solution has taken place in every instance of treatment under these conditions. In other words, for a surface to be successfully pretreated with nitric acid, it is imperative that it be free from old films or scales. This can be accomplished by the use of chemical etchants.

A resumé of the various pretreatments attempted and the final results is presented. In every case, the treatment was conducted in Type 347 stainless steel autoclaves which had been newly machined. Corrosion specimens, where used, were prepared by polishing to remove old films. After the pretreatments, the autoclaves were partially filled with 0.17 M uranyl sulfate solution and operated at 250°C for a period of one week. The initial pH of the sulfate solution ranged from 2.1 - 2.6.

Treatment 1

Test bomb treated 0.5 hour in 30% nitric acid at 70°C. Decomposition of sulfate solution was evident after exposure of one week. Treatment ineffective.

Treatment 2

Test bomb and samples treated in 1% nitric acid for 12 hours at 100°C. Solution decomposition occurred when exposed to sulfate solution for one week at 250°C. Treatment ineffective.

Corrosion data on 347 stainless steel: Pretreatment, 1.2 mpy;
Uranyl sulfate run, +42.4 mdd.

Treatment 3

Test bomb and samples treated in 1% nitric acid for 12 hours at 150°C. Uranyl sulfate solution was decomposed at 250°C. Treatment ineffective.

Corrosion data on 347 stainless steel: Pretreatment, 2.9 mpy;
Uranyl sulfate run, 2.9 mpy.

Treatment 4

Test bomb and samples treated in 3% nitric acid for 12 hours at 150°C. Decomposition of the sulfate solution occurred at 250°C. Treatment ineffective.

Corrosion data on 347 stainless steel: Pretreatment, 2.1 mpy;
Uranyl sulfate run, +85.7 mdd.

Treatment 5

Test bomb and samples treated in 1% nitric acid for 12 hours at 200°C. Uranyl sulfate solution decomposed at 250°C. Treatment ineffective.

Corrosion data on 347 stainless steel: Pretreatment, +55.2 mdd;
Uranyl sulfate run, 0.1 mpy.

Treatment 6

Test bomb and specimens treated in 1% nitric acid for 12 hours at 250°C. No decomposition of uranyl sulfate evident after 168 hours at 250°C. Treatment effective.

Corrosion data on 347 stainless steel: Pretreatment, +0.1 mdd;
Uranyl sulfate run, 0.1 mpy.

Treatment 7

Test bomb treated with 20% chromic acid anhydride for 0.5 hour at 70°C. Uranyl sulfate solution decomposed at 250°C. Treatment ineffective.

Treatment 8

Test bomb and samples treated in 2% chromic acid anhydride for 12 hours at 100°C. Decomposition of uranyl sulfate occurred at 250°C. Treatment ineffective.

Treatment 9

Test bomb and samples treated in 0.5% chromic acid anhydride at 150°C for 12 hours. Uranyl sulfate solution decomposed during test. Treatment ineffective.

Corrosion data on 347 stainless steel: Pretreatment, 0.7 mpy;
Uranyl sulfate run, 4.8 mpy.

Treatment 10

Test bomb and samples treated in 2% chromic acid anhydride at 150°C for 12 hours. Decomposition of uranyl sulfate occurred during test. Treatment ineffective.

Corrosion data on 347 stainless steel: Pretreatment, 7.9 mpy;
Uranyl sulfate run, +137.4 mdd.

Treatment 11

Test bomb and samples treated in 2% chromic acid anhydride for 12 hours at 200°C. Uranyl sulfate solution decomposed at 250°C. Treatment ineffective.

Corrosion data on 347 stainless steel: Pretreatment, +16 mdd;
Uranyl sulfate run, +84.4 mdd.

Treatment 12

Test bomb and samples treated in 2% chromic acid anhydride at 250°C for 12 hours. No solution decomposition evident in uranyl sulfate after one week at 250°C. Treatment effective.

Corrosion data on 347 stainless steel: Pretreatment, +5.2
Uranyl sulfate run, +19.2 mdd

Treatment 13

Test bomb treated in 2% chromic acid and 5% phosphoric acid for 0.5 hour at 70°C. Uranyl sulfate solution decomposed at 250°C. Treatment ineffective.

Treatment 14

Test bomb assembly plated with 0.2 - 0.5 mils of chromium. Solution of uranyl sulfate decomposed during run of one week at 250°C. Treatment ineffective.

Treatment 15

Test bomb assembly electropolished in mixture of sulfuric acid and glycol. Decomposition of uranyl sulfate occurred during run of one week at 250°C. Treatment ineffective.

Treatment 16

Test bomb assembly passivated in boiling 10% by volume sulfuric acid for three minutes. Decomposition of sulfate medium occurred during test at 250°C. Treatment ineffective.

Treatment 17

Test bomb assembly heated for one hour at 500°C in normal atmosphere to develop thick oxide coating. The heavy film did not prevent sulfate medium from decomposing at 250°C. Treatment ineffective.

Treatment 18

Test bomb assembly subjected to molten sodium dichromate protective treatment of Research Laboratory at Rustless Stainless Steel Division. Uranyl sulfate decomposition at 250°C was not prevented. Treatment ineffective.

Treatment 19

Test bomb and samples treated in 2.5% phosphoric acid for 12 hours at 250°C. Decomposition of uranyl sulfate occurred during run of one week at 250°C. Treatment ineffective.

Corrosion data on 347 stainless steel: Uranyl sulfate run, +19.8 mdd.

Treatment 20

Test specimens subjected to Permaglax protective treatment by Holden Co. Treatment consisted of immersion in blacking compound for six minutes at 250°F. Uranyl sulfate solution contained in silica test tube was decomposed by test specimen at 250°C. Treatment ineffective.

Corrosion data on 347 stainless steel: Uranyl sulfate run, 21.6 mpy.

Treatment 21

Test bomb and samples treated in 10% sodium silicate for 24 hours at 250°C. Decomposition of uranyl sulfate occurred in bomb at 250°C. Treatment ineffective.

Corrosion data on 347 stainless steel: Pretreatment, +777.2 mdd;
Uranyl sulfate run, +11.2 mdd.

Treatment 22

It was previously observed that uranyl sulfate solution in a 347 stainless steel system is not decomposed at temperatures of 100°C. A test bomb was presoaked for 95 hours in 0.17 M uranyl sulfate at 100°C and then operated at 250°C for one week. Decomposition of the sulfate occurred during the run. Treatment ineffective.

Treatment 23

Test bomb etched 20 minutes at room temperature in 3.4% mercurous nitrate, 48% hydrochloric acid mixture, washed thoroughly, and soaked three hours in 50% nitric acid. Uranyl sulfate decomposed in the bomb during a run at 250°C. Treatment ineffective.

Treatment 24

The use of hydrogen peroxide as an oxidant to prevent decomposition of uranyl sulfate in stainless steel systems at 250°C was investigated. It has been established that the presence of hydrogen peroxide in sufficient concentration will precipitate uranyl peroxide from uranyl sulfate solution. A series of tests was conducted to determine the amount of peroxide that could be added to uranyl sulfate solution without causing peroxide precipitation. Various dilutions of standard 3% hydrogen peroxide-water mixtures were added to 50 ml samples of 0.17 M uranyl sulfate at room temperature. The solutions were allowed to stand 60 hours before observations were made for the presence of a uranyl peroxide precipitate. It was observed that a dilution of 1 ml of 3% hydrogen peroxide in 19 ml of distilled water was the first ratio that did not cause any precipitation in the uranyl sulfate solution. One ml of this solution was used which was equivalent to a molarity of 0.0009 hydrogen peroxide. A clean stainless steel test bomb was prepared and was partially filled with 0.17 M uranyl sulfate containing 0.0009 M hydrogen peroxide. The bomb was operated at 250°C for three days. When dismantled, the solution had decomposed. The use of hydrogen peroxide therefore under the conditions of the test was not effective to prevent solution deterioration.

Treatment 25

The use of water at 250°C for pretreating stainless steel surfaces was investigated. It was hoped that similar surface phenomena and reactions might be obtained with distilled water as with dilute nitric acid at elevated temperatures. Clean stainless steel test bombs were pretreated for 24, 48, and 72 hour periods at 250°C using high purity water. In all subsequent tests with uranyl sulfate at 250°C, solution decomposition occurred in each instance during a run of one week. Treatments ineffective.

Corrosion data on 347 stainless steel:

24 hour treatment	Pretreatment, 0.7 mpy, Uranyl sulfate run, 0.5 mpy.
48 hour treatment	Pretreatment, 3.5 mpy, Uranyl sulfate run, 28.9 mpy.
78 hour treatment	Pretreatment, 0.6 mpy, Uranyl sulfate run, +9.8 mdd.

Two treatments were found successful in the entire group of 25 different methods. These were Treatments 6 and 12 involving the use of 1% nitric acid and 2% chromic acid anhydride at 250°C. The remaining 23 treatments proved completely ineffective, and for this obvious reason, efforts were directed into the use and development of the two satisfactory pretreating methods.

Treatment of stainless steel surfaces with 1% nitric acid at 250°C shall be considered first. Numerous tests have been completed and are in progress in order to obtain a complete evaluation and the limitations of this treatment. Attempts have been made to determine the most efficient treating time, the expectant life of single treatments, the effect of cyclic treatments, the effect of early removal of nitric oxide vapors, and other pertinent factors. These important criteria are considered individually.

NITRIC ACID PRETREATMENTS

The Effect of Nitric Acid Pretreatment on Corrosion Resistance. Before conducting the above phases of the nitric acid treatment, it was desired that its effect on the corrosion resistance of stainless steel be determined. Since the use of 347 stainless steel for the major portion of the reactor appears certain, this material was selected for the initial tests. Specimens used for the tests averaged 20.2 cm² in area, and were polished and degreased prior to exposure. The results of four tests of different exposure times are shown below. Duplicate specimens were used.

TEST NO.	EXPOSURE TIME (hr)	CORROSION RATE	SAMPLE CONDITION
1	12	+0.1 mdd*	Shiny brown
2	12	0.9 mpy**	Interference colors
3	24	0.7 mpy	Slight brown tarnish
4	100	+0.4 mdd	Shiny black

*mg/dm²/day
**mils/year

These results are very favorable, and show the excellent corrosion resistance of 347 stainless steel to the nitric acid treatment. Results indicate that as the time of treatment is increased, the progression of corrosion is from a slight, actual penetration or thickness loss to the formation of a protective film on the metal surface.

A number of specimens were treated in 1% nitric acid at 250°C for 24 hours for irradiation tests conducted by the Chemistry Division at X-10. The results of these tests were rather erratic. Sample sizes were small, approximately 2.0 cm² in area, and, due to the method used for treatment, may not be too representative of the nitric acid exposure. Results of the tests with 347 stainless steel specimens are as follows:

BOMB NO.	CORROSION RATE
--	+36.3 mdd
288	4.7 mpy
290	16.7 mpy
291	24.3 mpy
296	+20.7 mdd
297	0.9 mpy

The sample prepared for Bomb 297 is the only one which approaches the magnitude of results obtained on larger size 347 stainless steel specimens.

Effect of Exposure Time on Life of Nitric Acid pretreatment. Tests were conducted to correlate the time of a nitric acid pretreatment with its subsequent life in a stainless steel autoclave containing uranyl sulfate solution at 250°C. The life of the treatment was determined by the time required for

decomposition of the sulfate solution. Clean stainless steel bombs were used for the tests and 1% nitric acid at 250°C was used for pretreating. The time of pretreatment was varied. The test bombs were treated for periods of 1, 4, 8, 12, 24, and 96 hours. At the end of these treatments, 0.17 M uranyl sulfate was placed in the bombs and operated at 250°C until signs of solution decomposition were apparent. Results of these tests follow and include data for 347 stainless steel specimens which were treated in similar fashion as the test bombs.

1 Hour Pretreatment

Solution decomposition was nearly complete at the end of 168 hours. Samples showed a deposition of black uranium oxides corresponding to a weight gain rate of +18.1 mdd.

4 Hour Pretreatment

Test has operated thus far for 840 hours (five weeks) without indications of solution deterioration. Corrosion rate on samples is 0.02 mpy. The test is being continued.

8 Hour Pretreatment

Test has operated thus far for 840 hours; no indications of solution decomposition have appeared. Corrosion rate on samples is 0.01 mpy. The test is being continued.

12 Hour Pretreatment

Test has operated 840 hours to date and is being continued. No signs of solution decomposition are apparent. The corrosion rate on the samples is 0.005 mpy.

24 Hour Pretreatment

Test has operated 840 hours to date. Solution decomposition has not occurred. The test samples exhibited a slight weight increase of 0.8 mdd. The test is being continued.

96 Hour Pretreatment

Test has operated 1344 hours (eight weeks) with no indications of solution decomposition. Unfortunately, corrosion specimens were not included in this run. The test is being continued.

No definite conclusions can be made at this time concerning the expectant life of various pretreating times. These results will not be available until decomposition of the uranyl sulfate in the bombs takes place. One observation is certain, however, and that is that a pretreatment time of one hour is not effective. The minimum time for a suitable treatment appears to be established at four hours. At this point in the tests, there is no difference between a four hour and a 96 hour pretreating time as far as life of the treatment is concerned.

It was observed that subsequent corrosion attack on the stainless steel specimens was greatly effected by the length of the pretreating operation. Decreasing corrosion attack on the specimens in uranyl sulfate solution was noted as treating time increased from four to 12 hours. At 24 hours pretreating time, corrosion on the samples was manifested by a slight increase in weight equivalent to a weight gain rate of $0.8 \text{ mg/dm}^2/\text{day}$. Uranium analyses of the test solution showed that this increase was not due to any deposition of uranium oxides on the metal surfaces as a result of solution decomposition. Corrosion data on the 96 hour pretreating treatment were not available to complete the overall effects of pretreating time on corrosion.

Effect of Cyclic Nitric Acid Pretreatments. Periodic pretreatments with 1% nitric acid for 12-24 hours have been made in stainless steel test bombs. These treatments were made at one, two, three and four week intervals. The bombs were then operated with 0.17 M uranyl sulfate at 250°C in the interim periods. Tests of this nature have operated successfully for periods of 13 weeks (2184 hours) without evidence of solution decomposition. It is felt that such cyclic pretreatment would be highly successful for operation of an uranyl sulfate reactor, but would present a handicap inasmuch as the system would have to be drained of sulfate solution to allow for the pretreating operation. A shutdown every week or two for pretreating would not be a desirable condition, once every four or six weeks might be practical, however. A more direct and satisfactory approach would be the injection of small amounts of nitric acid every week or so during operation of the reactor. This would afford additional assurance for prolonging the life of the initial nitric acid pretreatment.

Effect of Nitric Oxide Removal on pretreatment Life. In conjunction with the tests to determine the effect of nitric acid contact time on the life of the treatment, a test was operated to ascertain the effect of early removal of the nitric oxide vapors from uranyl sulfate in a bomb operated at 250°C . The

uranyl sulfate solution was made 0.11 M (1%) with nitric acid and placed in a stainless steel bomb with 347 stainless steel corrosion specimens. The bomb assembly was heated at 250°C for 24 hours. At the end of this time, the volatile nitric acid vapors were released and the test was continued. Weekly inspections were made and the original uranyl sulfate solution was used throughout the test. To date, the test has operated 1680 hours (10 weeks) without signs of solution deterioration. The corrosion rate on the samples is 0.05 mil/year. This type of test will be repeated, using shorter periods for the time of draw-off of the nitric acid fumes since, if nitric acid is injected into an operating homogeneous reactor to prevent solution decomposition, the residence time of the nitric acid vapors in the system will establish the effectiveness of the treatment.

Pretreatment of Dynamic Uranyl Sulfate System. The worthiness of the nitric acid pretreatment was first tried on a large scale operation with a dynamic unit operated by C. Savage. This unit consists of a stainless steel pressurizer and heater, a Westinghouse totally enclosed pump, an orifice, test loop, and various valves. The purpose of the unit is to determine the operating characteristics of the Westinghouse pump. The total volume of uranyl sulfate required for operation of the system is eight liters and prior to putting the sulfate into the stainless steel system at 250°C, it was necessary to pretreat the unit to prevent solution decomposition. Before such treatment was possible, the effects of the nitric acid treatment on the corrosion resistance of various materials in the test unit had to be determined. These materials were 410 stainless steel, 347 stainless steel, tantalum, Inconel and graphitar. As an extreme condition, these materials were tested in 1% nitric acid at 250°C for four days. Results follow.

MATERIAL	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)	MATERIAL CONDITION
410 SS	-1.0	0.2	Blue gray color
347 SS	+0.4	--	Light brown tarnish
Inconel	-145.4	24.6	Dull black color
Graphitar	-719.8	333.4	Flaky surfaces
Tantalum	+2.9	--	Original luster

The graphitar suffered badly from this harsh treatment, and the Inconel also underwent heavy corrosion attack. The remaining materials showed excellent corrosion resistance. The graphitar and Inconel are materials used in the interior of the pump and are located at points where temperatures do not exceed 125-130°C. It was believed that with this condition and an exposure time of eight to 12 hours in the nitric acid at 250°C, the corrosion resistance to the two materials would be suitable.

The entire system was pretreated with 1% nitric acid at 250°C for 12 hours. Chemical analyses of the final solution showed no indication of more than a very mild corrosion attack. Uranyl sulfate was placed into the unit and operated at 250°C. Solution decomposition occurred in less than eight hours. This incident necessitated a cleaning operation with nitric acid to remove precipitated uranium oxides. During this period other experimental corrosion data disclosed that when an old and heavy film of oxide or scale was present on stainless steel surfaces, the nitric acid pretreatment was not effective. For this reason, and the fact that no previous cleaning of the stainless steel used for construction of the dynamic test unit had been performed, it was decided to etch the entire system. This was accomplished with the use of a chemical etchant consisting of 3.4% mercurous nitrate and 48% hydrochloric acid in water. The procedure was conducted at room temperature for 10-15 minutes. After removing this liquid, the unit was given an alkaline rinse and then thoroughly flushed with hot water. As a final measure, the unit was operated at 150°C with water to remove all residual traces of the etching solution. This method of cleaning and washing cannot be overemphasized since the presence of small traces of chloride ions could be sufficient to destroy passivity effects from the nitric acid treatment.

The unit was then pretreated with 1% nitric acid at 250°C for 12 hours. Fresh 0.17 M uranyl sulfate (eight liters volume) was added and the apparatus operated at 250°C. A total of 425 hours has been accumulated on the system with intermittent operation and there has been no evidences of solution deterioration. This test has successfully demonstrated the feasibility of nitric acid pretreatment on a large scale stainless steel system operating with uranyl sulfate at 250°C.

Effect of Old Films on Nitric Acid Pretreatment. Tests were conducted to determine the effect of nitric acid on unpolished stainless steel surfaces. All studies conducted previously were made on polished surfaces, an operation

necessary to remove old surface films, scales, and defects in order that more accurate measurements of corrosion damage could be obtained. For the effect of films study, Types 317 ELC (extra low carbon), 410, and 347 stainless steels were used. Samples were selected that possessed an exceptionally heavy accumulation of film and scale from long exposure in material storage racks. Samples were freed of grease and oil by solvent cleaning, and were then subjected to 1% nitric acid pretreatments at 250°C for various times. Uranyl sulfate solution was placed into bombs containing the specimens and operated at 250°C for one week. Results are tabulated below and are based on corrosion damage after the uranyl sulfate run.

MATERIAL	NITRIC ACID TREATMENT (hours)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)	SOLUTION CONDITION
317 ELC	24	-37.7	6.8	Decomposed
347*	24	+144.0	--	Decomposed
410	24	-139.7	26.1	Decomposed
347	100	+ 20.2	--	Decomposed
410	100	-195.7	36.6	Decomposed

* Helarc welded sample.

In every test, solution decomposition was evident and the samples showed heavy accumulation of uranium oxides on the surfaces. The severe nature of the corrosiveness of the solution in a reduced state is evidenced by the heavy corrosion attack on three of the stainless steels in spite of the presence of uranium oxide deposition on the metal surfaces. Experimental evidences indicate that the phenomenon of solution decomposition is a direct result of the condition of the metal specimens since the bombs were treated in similar manner as other bombs which have operated for long periods of time without causing precipitation of the uranyl sulfate. The reason for the breakdown of the protective influence normally existed by the nitric acid treatment is uncertain. One possibility might be that the original surface layer on the sample was of sufficient thickness to create a barrier which prevented the nitric acid from contacting the metal surface beneath the film to share or absorb metal electrons. In line with the general theory of passivity, if sharing or absorbing metal electrons is not accomplished by the passivation treatment, the metal lattice is made susceptible to the entrance of hydrogen from the corrosion reaction which would destroy passivity.

Miscellaneous Nitric Acid Pretreatments. Additional tests using nitric acid pretreatments on stainless steel bombs are in progress. These tests have been in operation for a period of eight to 11 weeks with no solution decomposition occurring. All tests were given one initial treatment with one percent nitric acid at 250°C for 24 hours. The tests are being continued.

CHROMIC ACID PRETREATMENTS

The second treatment which was found successful for treating stainless steel surfaces to prevent decomposition of uranyl sulfate solution at 250°C involves the use of 2% chromic acid anhydride (CrO_3) at 250°C. Work has been conducted to investigate the feasibility of this type of treatment and to compare its effectiveness with the nitric acid pretreatment.

Effect of Chromic Acid Treatment on Corrosion Resistance. In general, the effect of the chromic acid treatment on 347 stainless steel has been to show a weight gain rate. With samples averaging 20.0 cm^2 in area, the average weight gain rate has been +10.3 $\text{mg}/\text{dm}^2/\text{day}$ for an exposure of 24 hours at 250°C in a 2% chromic acid solution. Variations in the magnitude of the corrosion on 347 stainless steel surfaces is evidenced from the results of treatments on specimens averaging 2.0 cm^2 which were used for irradiation studies. These specimens were treated for 24 hours at 250°C in 2% chromic acid.

BOMB NO.	CORROSION RATE
287	Negative
289	+502.5 mdd
292	3.7 mpy
293	+5.2 mdd
294	+103.6 mdd
295	+134.7 mdd

With two exceptions, Bombs 287 and 292, all specimens exhibited a weight increase probably due to the formation of a chromic oxide film on the metal surfaces.

Effect of Cyclic Chromic Acid Treatments. Periodic treatments, 24 hours at 250°C, have been made on stainless steel bombs at one, two, three and four week intervals with the 2% aqueous chromic acid. These tests have been operated successfully in 0.17 M uranyl sulfate solution at 250°C for a period of 11 weeks with one exception. This exception occurred in the bomb that was pretreated over every four weeks. At the end of the eleventh week, the uranyl sulfate solution decomposed. The other tests are being continued.

THE USE OF OXYGEN PARTIAL PRESSURES

Another method under consideration for the prevention of uranyl sulfate decomposition in stainless steel systems at 250°C is the use of partial pressures of molecular oxygen. A test was made using a one liter capacity electrically heated stainless steel autoclave. Uranyl sulfate solution was added to the autoclave, and the unit was connected with a cylinder of oxygen. A partial pressure of 300 psi of oxygen above the saturation pressure of water was maintained at all times. The total pressure on the system during the run at 250°C was 860 psi. At the end of 336 hours, the uranyl sulfate solution showed no sign of decomposition and the corrosion rate on the 347 stainless steel was 0.2 mil/year. The test was repeated using 100 psi partial pressure of oxygen for 270 hours and again the uranyl sulfate showed no precipitation. The corrosion rate on the stainless steel was 0.08 mil/year.

This test will be repeated using lower and lower partial pressures of oxygen until a minimum pressure that will still prevent solution decomposition is obtained. It is planned also to operate tests using various mol ratios of oxygen and hydrogen gases to determine their effect on solution stability and corrosion resistance of various materials.

Summarizing the effects of the pretreatment data in the foregoing paragraphs, it may be stated that:

1. General passivation and protective treatments conducted at temperatures of 200°C and less are not effective for preventing decomposition of uranyl sulfate in stainless steel systems operating at 250°C.
2. The use of 1% nitric acid or 2% chromic acid for pretreatments at 250°C have been found successful for preventing decomposition of uranyl sulfate in stainless steel systems.

3. The presence of an old, heavy surface film on stainless steel surfaces nullifies the effect of the nitric acid pretreatment and uranyl sulfate decomposition is promoted. It is imperative that stainless steel surfaces are chemically clean prior to the nitric acid treatment.
4. The minimum exposure time for a nitric acid pretreatment appears to be four hours and is desired to be at least eight to 12 hours maximum protection.
5. The use of 100 psi partial pressure of oxygen is successful for preventing decomposition of uranyl sulfate in stainless steel system at 250°C. Resultant corrosion attack on the stainless steel is very slight.
6. The feasibility of using a nitric acid pretreatment on a large scale dynamic stainless steel test loop using uranyl sulfate at 250°C has been successfully demonstrated. Such a unit has operated 425 hours to date without signs of solution decomposition.

CORROSION RESISTANCE OF STAINLESS STEELS

Numerous corrosion data on 347 stainless steel have already been mentioned to warrant its selection as a construction material for a homogeneous reactor. In systems which were pretreated with 1% nitric acid, the corrosion rate has ranged from 0.005 - 0.05 mil/year for exposures of eight to 11 weeks.

Other tests have been conducted in which the uranyl sulfate contained 1% nitric acid. This solution was used fresh each week and operated at 250°C. The addition of nitric acid to the sulfate solution at weekly intervals has completely eliminated the danger of solution decomposition. The results of a series of tests with various stainless steels appears in Table I.

TABLE I

The Corrosion of Stainless Steels in 0.17 M Uranyl
Sulfate Containing 1% Nitric Acid at 250°C

MATERIAL	EXPOSURE (hr)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)	APPEARANCE
309	2352	-0.80	0.14	Shiny black
316 ELC	2352	-0.13	0.02	Shiny black
347	2352	-0.34	0.06	Dull tarnish
410	1965	+0.59	-	Black film
Carpenter 20	1848	-0.64	0.12	Dull black

Tests were completed with a group of stainless steels exposed to uranyl sulfate containing 2% chromic acid. Fresh sulfate solution was used weekly and the tests were operated at 250°C. The use of chromic acid in the uranyl sulfate solution was found to eliminate the solution reduction problem also, but this type of application does not seem practical since irradiation test results on uranyl sulfate-chromic acid systems disclosed that the chromic acid is reduced to an insoluble form of chromic acid. The presence of such a precipitate in a homogeneous reactor system would present additional and undesirable problems. The results of the corrosion tests are included in Table II.

TABLE II

The Corrosion of Stainless Steels in 0.17 M Uranyl Sulfate
Containing 2% Chromic Acid at 250°C

MATERIAL	EXPOSURE (hr)	WEIGHT CHANGE (mdd)	APPEARANCE
309	1974	+5.9	Black flaky surface
316 ELC	1974	+6.4	Black flaky surface
347	1974	+5.9	Black flaky surface
410	1974	+7.2	Black flaky surface
Carpenter 20	1974	+2.7	Black flaky surface

These samples all reacted in like manner in the test solutions, i.e., all exhibited weight gains. From following the progress of the tests through weekly inspections, it was apparent that after a period of 1000-1200 hours an optimum film thickness was reached at which point it started to flake from the samples. Once the base metal was exposed, the film renewed itself and the process continued throughout the course of the tests. There were no occasions where decomposition of the uranyl sulfate took place.

CORROSION RESISTANCE OF ZIRCONIUM

Zirconium is of great interest for a construction material in a homogeneous reactor due to its low cross section and its good corrosion resistance. Much work has been completed and is being conducted on various types of zirconium in uranyl sulfate at 250°C. Corrosion studies with crystal bar zirconium and Bureau of Mines zirconium are included in the following sections.

CORROSION OF CRYSTAL BAR ZIRCONIUM

Samples of crystal bar zirconium made by the iodide process were received from MIT. The major portion of the chemical analyses included in this zirconium section were conducted by the Chemistry Division of ORNL. Analyses of the bars tested appear in Table III.

TABLE III

Chemical Analyses of Crystal Bar Zirconium

MATERIAL DESIGNATION	AP	Ca	Fe	Mg	Ti	C	N
CB1	~0.02	0.026	0.05	<0.002	0.09	0.18	0.004
CB2	~0.02	<0.004	0.03	<0.002	0.07	0.15	0.003
CB3	~0.02	0.081	0.04	0.012	0.09	0.14	<0.001
CB4	~0.02	<0.004	0.05	0.003	0.09	0.19	0.002
CB5	~0.02	<0.004	0.07	0.015	0.07	0.15	0.005
CB6	~0.02	<0.004	0.07	<0.002	0.07	0.16	<0.001
CB7	~0.02	<0.004	0.03	0.005	0.05	0.10	<0.001
CB109-C	0.01	<0.002	0.07	<0.001	0.03	0.10	0.002

In order to operate the zirconium corrosion tests in stainless steel bombs without incurring solution precipitation, it was necessary to use a quartz or fused silica test tube as a liner to contain the uranyl sulfate and the zirconium sample. All tests with zirconium were conducted in this manner unless otherwise stated. The results of the crystal bar zirconium tests appear in Table IV.

TABLE IV

**The Corrosion of Crystal Bar Zirconium
in 0.17 M Uranyl Sulfate at 250°C**

MATERIAL DESIGNATION	EXPOSURE (hr)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)	SAMPLE APPEARANCE
CB1	1499	-0.7	0.2	Pink shiny film
CB2	1331	-2.0	0.5	Light gray film
CB3	1803	-0.07	0.01	Purple colored film
CB4	3180	+0.3	--	Dark gray film
CB5	2815	Neg.	Neg.	Reddish gray film
CB6	2816	-0.04	<0.01	Red colored film
CB7	1008	-0.07	0.2	Shiny metallic film
CB109-1C	2520	+0.2	--	Gray streaked film

These samples all showed excellent corrosion resistance and did not exhibit any tendency to reduce the uranyl sulfate solution in the silica tubes during the tests. The unavailability of suitably large ingots and corresponding high cost greatly restrict the use of crystal bar zirconium for component parts of a homogeneous reactor system. Tubing is available, however, in $\frac{1}{4}$ -in. O.D. dimensions.

CORROSION OF BUREAU OF MINES ZIRCONIUM

The major portion of the zirconium corrosion program has been conducted with various types of Bureau of Mines material. Development of production techniques for high purity metal and fabricating techniques during the past several years has been rapid. These factors plus relatively low cost make the use of Bureau of Mines zirconium a more desirable choice for use in a homogeneous reactor than crystal bar zirconium. Numerous data have been reported in previous reports and the following results are a continuation of these tests in addition to results on new types of zirconium recently received. Corrosion tests were conducted in uranyl sulfate contained in quartz tubes and also in uranyl sulfate containing 1% nitric acid. Tests were inspected weekly for measurement of corrosion damage.

A. BM:1-F-7

Material

Produced from sponge metal; arc melted in water cooled copper crucible using a tungsten electrode; material received in ingot form.

Analysis

Carbon	0.06%
Tungsten	0.40%
Aluminum	0.20%
Calcium	0.035%
Nitrogen	0.042%
Iron	0.24%
Hafnium	1.3%
Magnesium	0.004%
Titanium	0.18%

Corrosion Data

Operated in 0.17 M uranyl sulfate for 1499 hours at 250°C

Weight change -8.3 mdd

Corrosion rate 1.9 mpy

The sample was light gray in color and showed a few tiny black specks which may be uranium oxide from decomposition of the uranyl sulfate solution. The test is being continued.

B. BM:1-H-7

Material

Produced from sponge metal; melted in graphite crucible in vacuum resistance furnace; ingot cast in graphite mold; material received as an as cast ingot.

Analysis

Carbon	0.24%
Iron	0.011%
Aluminum	0.02%
Calcium	<0.005%
Magnesium	<0.001%
Titanium	0.029%
Tungsten	<0.01%
Chloride	<0.002
Nitrogen	0.003

Corrosion Data

Operated for 1056 hours in 0.17 M uranyl sulfate containing 1% nitric acid at 250°C.

Weight change -0.024 mdd
Corrosion rate 0.005 mpy

The sample exhibited a uniform light gray film. The test is being continued.

C. BM:1-I-7

Material

Produced from sponge metal; graphite melted; ingot sheathed in mild steel and forged at 850°C; hot rolled; sheath removed and zirconium sheet pickled; hot rolled in air at 650°C; sandblasted and pickled; final thickness, 0.250 in.

Analysis

Aluminum	0.28%
Calcium	0.06%
Carbon	0.14%
Iron	0.03%
Hafnium	1.2%
Nitrogen	0.004%
Magnesium	0.001%
Titanium	0.066%

Corrosion Data

(1) Sample exposed to 0.17 M uranyl sulfate in stainless steel system at 250°C using 300 and 100 psi partial pressure of oxygen. No quartz liner present. A light gray film appeared on the specimen

Weight change -7.8 mdd
Corrosion rate 1.8 mpy

(2) Sample exposed to 0.17 M uranyl sulfate in a stainless steel system at 250°C using 300 and 100 psi partial pressure of oxygen. A light gray film was present on the sample at the end of the test.

Weight change +4.6 mdd at 300 psi-336 hr
+3.3 mdd at 100 psi-270 hr

D. BM:1-J-7

Material

Produced from sponge metal; graphite melted; sheathed in mild steel and forged at 850°C; hot rolled; sheath removed; zirconium sheet pickled; cold rolled to 15% reduction; 0.250 in. final thickness.

Analysis

Aluminum	0.01%
Carbon	0.19%
Calcium	0.003%
Iron	0.025%
Hafnium	1.2%
Nitrogen	0.005%
Magnesium	0.001%
Titanium	0.038%

Corrosion Data

Sample exposed to 0.17 M uranyl sulfate containing 1% nitric acid at 250°C for 1098 hours. Specimen exhibited a light gray appearance with three prominent red colored spots; a few minute black specks were also observed on the surface. The test is continuing.

Weight Change -3.1 mdd
Corrosion rate 0.7 mpy

E. BM:1-K-7

Material

Produced from sponge metal; graphite melted; sheathed in mild steel and forged at 850°C; hot rolled at 850°C; sheath removed and zirconium sheet pickled; swaged in air at 650°C; cleaned; cold swaged with annealing between passes to 0.210 in. diameter; sandblasted and pickled.

Analysis

Aluminum	0.68%
Calcium	0.13%
Carbon	0.19%
Iron	0.036%
Hafnium	1.1%
Nitrogen	0.014%
Magnesium	0.001%
Titanium	0.063%

Corrosion Data

(1) Exposed to 0.17 M uranyl sulfate in silica tube at 250°C. The samples showed gray streaked uniform films after test; no indications of solution deterioration. The tests are continuing.

NO.	EXPOSURE (hr)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)
1	1008	-12.4	2.8
2	1003	- 7.3	1.6

(2) A test was conducted in uranyl sulfate containing 1% nitric acid at 250°C. This test has operated 2644 hours and is continuing. The sample appearance is reddish-gray streaked in color

Weight change -6.0 mdd
Corrosion rate 1.4 mpy

(3) Tests were conducted with uranyl sulfate contained in a stainless steel system at 250°C under 300 and 100 psi partial pressure of oxygen; no silica liner was present. The sample showed a gray-black film at the end of the test.

Weight change +5.5 mdd at 300 psi-336 hr
+3.6 mdd at 100 psi-270 hr

(4) A sample was etched in 5% hydrofluoric acid for five minutes and run in uranyl sulfate contained in a silica tube at 250°C in an attempt to determine the effect of surface condition on corrosion resistance. The etched sample was darker in color than the original and has remained so during this test which is being continued.

EXPOSURE (hr)	WEIGHT LOSS (mg)	WEIGHT LOSS (mdd)	CORROSION RATE (mpy)
336	1.0	1.2	0.27
672	3.4	2.7	0.60
1008	14.1	7.5	1.70

Corrosion attack appeared to be progressing almost linearly with time on the specimen.

F. BM: Hoover

Material

Cast ingot forged and swaged at 750°C, cleaned; hot swaged at 700°C, annealed at 800°C and cooled in air, cold swaged to 0.280 in., annealed, cleaned and cold swaged to finished size.

Analysis

Aluminum	0.01%
Calcium	0.002%
Iron	0.014%
Magnesium	0.001%
Titanium	0.034%
Carbon	0.12%
Nitrogen	0.005%

Corrosion Data

(1) A specimen was etched for 10 minutes in 10% hydrofluoric acid to remove surface scale and then run in uranyl sulfate contained in a silica tube at 250°C for 1848 hours. The test was stopped at this point because a heavy black precipitate (probably uranium oxide) formed on the sample. The data below indicate this phenomenon.

EXPOSURE (hr)	WEIGHT GAIN (mdd)
168	25.2
336	22.8
504	2.9
672	1.4
840	0.8
1008	2.4
1176	2.2
1344	2.5
1512	3.1
1848	31.8 (solid precipitated)

(2) A specimen was placed in uranyl sulfate (silica tube) and run for 672 hours at 250°C before black specks were observed on the surfaces. The test was stopped at this point.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)
168	+0.3
336	+0.4
504	-0.2
672	+0.7 (solid precipitated)

Prior to the formation of black specks on the surface, the sample exhibited a speckled gray film.

G. BM: S-831

Material

Produced from oxide made at Y-12; cast ingot welded in mild steel sheath; hot forged at 850°C; hot rolled in 850°C; sheath removed; zirconium sheet cold rolled to 0.256 in.; machined to desired size.

Analysis

Aluminum	0.02%
Calcium	0.05%
Iron	0.17%
Magnesium	0.005%
Titanium	0.005%
Carbon	0.19%

Corrosion Data

This specimen was exposed to 0.17 M uranyl sulfate containing 1% nitric acid at 250°C. The sample had exhibited a reddish-gray colored film until 1098 hours when a few black spots were observed. The test is being continued.

EXPOSURE (hr)	WEIGHT GAIN (mdd)
121	7.5
292	3.8
460	2.8
628	1.5
796	1.5
964	1.2
1098	0.8

H. BM:8948

Material

Arc melted with consumable electrode in inert atmosphere; magnesium reduction; material received in cast condition as machined from ingot; also received in hot rolled condition (rolled at 650°C to 0.50 in. slab; oxide coating machined off).

Analysis

	CAST	HOT ROLLED
Aluminum	0.015%	0.014%
Calcium	<0.002%	<0.002%
Iron	0.069%	0.09%
Magnesium	<0.001%	<0.001%
Titanium	0.032%	0.036%
Carbon	0.11%	0.13%
Nitrogen	0.01	0.009

Corrosion Data

(1) A cast specimen was exposed to uranyl sulfate (silica liner) at 250°C for 2488 hours. At the end of this time, a black precipitate of uranium oxide was observed on the sample and the test was stopped.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)
168	-11.5	2.6
336	-9.4	2.1
504	-6.1	1.4
672	-0.8	0.2
840	+0.5	-
1174	+0.3	-
1480	-0.02	0.004
1816	-1.1	0.24
2152	+0.7	-
2488	+15.6	-

(2) Samples of cast and hot rolled material were etched for five minutes in 5% hydrofluoric acid to remove surface films. The specimens were run in uranyl sulfate (silica liner) at 250°C for 2488 hours. Both samples exhibited peach colored films during test. The cast specimen showed black deposits of uranium oxide after 2488 hours and the test was stopped; the hot rolled specimen is containing in test; no signs of precipitation are apparent on it.

EXPOSURE (hr)	WEIGHT CHANGE(mdd)	
	CAST	HOT ROLLED
168	+1.0	+0.4
336	+1.0	+1.1
504	+1.1	+1.1
672	+1.1	+1.3
840	+1.3	+1.3
1174	+2.6	+1.0
1480	-0.5	+0.8
1816	-1.0	+1.8
2152	-0.7	+1.0
2488	+10.6	+0.2

These results indicate that the hot rolled material in an etched condition has superior corrosion resistance to etched and unetched cast zirconium.

I. BM: S945

Material

Arc melted with consumable electrode under inert atmosphere; slab was hot rolled in air at 650°C to 0.500 in. thickness; the oxide layer was machined off.

Analysis

Aluminum	0.022%
Calcium	0.002%
Iron	0.11%
Magnesium	0.001%
Titanium	0.44%
Carbon	0.11%
Nitrogen	0.004%

Corrosion Data

The sample was polished and etched five minutes in 5% hydrofluoric acid to remove the surface layer. The test was conducted in uranyl sulfate (silica liner) at 250°C for 2488 hours. During this time, the sample condition was good showing a peach colored film. At the end of 2488 hours, however, a black precipitate of uranium oxide appeared on the surfaces.

EXPOSURE (hr)	WEIGHT GAIN (mdd)
168	1.7
336	1.9
504	1.9
672	2.0
840	2.4
1174	2.1
1480	1.5
1816	0.9
2152	0.7
2488	9.1 (solid precipitated)

J. BM: IV-D

Material

Recent Bureau of Mines zirconium produced from zirconium oxide prepared by salicylic acid purification at Y-12; the oxide was converted to sponge by Bureau of Mines; resistance melted in graphite.

Analysis

Aluminum	0.01%
Calcium	0.002%
Iron	0.12%
Magnesium	0.001%
Titanium	0.034%

Corrosion Data

(1) Two samples in a roughly machined condition were tested in uranyl sulfate (silica liner) at 250°C. One sample was coated with uranium oxides after 168 hours; the second sample was coated in similar fashion at the end of 336 hours.

EXPOSURE (hr)	WEIGHT GAIN (mdd)	
	No. 1	No. 2
168	164.1	0.1
336	--	56.6

(2) Two samples were polished on No. 80 and 120 emery paper and exposed to uranyl sulfate (silica liner) at 250°C. Both samples continue to show excellent condition after 1848 hours and are pink to red in color.

SAMPLE No.	EXPOSURE (hr)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)
1	168	-2.2	0.5
	336	-1.4	0.5
	504	-0.8	0.2
	840	-0.5	0.1
	1176	-0.3	0.07
	1512	-0.4	0.09
	1848	-0.4	0.09
2	168	-2.5	0.6
	502	-0.6	0.14
	808	-0.4	0.09
	1144	-0.3	0.07
	1480	-0.3	0.07
	1816	+0.3	-

(3) A sample was polished and etched for five minutes in 5% hydrofluoric acid to remove the surface layer. It was then run in uranyl sulfate contained in a silica liner at 250°C. After 1848 hours, the condition of the specimen is excellent, exhibiting a uniform pinkish-gray film.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)
168	Neg.	Neg.
336	-0.17	0.04
504	-0.29	0.06
840	+0.26	--
1176	+0.37	--
1512	-0.2	0.05
1848	+1.8	--

Thus far, the corrosion resistance of the etched specimen appears to be superior to that of the polished sample.

(4) A sample was polished on No. 80 and 120 paper and then pretreated for 12 hours at 250°C in 1% nitric acid. The corrosion rate on the specimen by this treatment was 4.7 mil/year. The sample was then placed in a treated stainless steel bomb containing 0.17 M uranyl sulfate and operated to date for 840 hours. The condition of the specimen is excellent and corrosion attack has been nearly negligible.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)
168	1.5	0.34
336	1.0	0.23
504	0.3	0.07
672	0.2	0.05
840	0.07	0.02

From these results, it is indicated that the nitric acid pretreatment to prevent uranyl sulfate decomposition is as effective for this type of zirconium as it is for stainless steels. If this is true, it would mean that suitable Bureau of Mines zirconium could be used completely in the construction of a homogeneous reactor or intermixed with stainless steel component parts.

(5) Polished and unpolished samples were pretreated in 2% chromic acid at 250°C for 24 hours. Both samples showed a weight gain from this treatment, 21.2 mdd on the unpolished specimen and 6.9 mdd on the polished sample. The specimens were placed in uranyl sulfate (silica liner) and have operated 168 hours at 250°C to date. The unpolished specimen showed a weight gain of 38.5 mg/dm²/day at the end of this period and black deposition or specks of uranium oxide were observed. The polished specimen gained 14.6 mg/dm²/day during this period and its condition remains good. This test is being continued.

(6) Polished and polished-etched specimens were exposed to 300 and 100 psi partial pressure of oxygen in uranyl sulfate contained in a stainless steel system at 250°C. The etched specimen was treated five minutes in 5% hydrofluoric acid at room temperature. The samples were in excellent condition at the end of the tests.

EXPOSURE (hr)	OXYGEN PARTIAL PRESSURE (psi)	WEIGHT CHANGE (mdd)	
		POLISHED	POLISHED-ETCHED
336	350	-1.9	+0.7
270	150	+0.4	+0.8

K. BM: S980-S982-S983

Material

Bureau of Mines zirconium containing various tantalum additions; arc melted with consumable electrode containing a tantalum center; hot rolled at 600°C; cold rolled to 0.062 in.

Analysis

	S980	S982	S983
Aluminum	0.046%	0.05%	0.036%
Iron	0.16%	0.22%	0.14%
Titanium	0.15%	0.17%	0.16%
Tantalum	0.80%	0.30%	0.095%

Corrosion Data

The samples have been operated 2520 hours to date in uranyl sulfate contained in a silica tube at 250°C. The condition of the specimens has remained very good. The general appearance is a dull gray film with pink and white striations.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)		
	S980	S982	S983
168	+0.4	+0.8	+2.9
336	-0.6	-0.2	+2.2
504	+0.3	+0.05	+3.1
672	-0.05	-0.1	+2.3
840	-0.1	Neg.	+2.9
1008	-0.3	-0.3	+2.2
1176	-0.1	Neg.	+2.1
1512	Neg.	Neg.	+2.1
1848	+0.1	+0.2	+1.9
2184	+0.1	+0.1	+1.9
2520	+0.6	+0.7	+2.5

The presence of 0.3-0.8 percent tantalum appears to be the desirable range for most satisfactory corrosion behavior.

L. Zirconium-Titanium Welded Specimens

Material

BM zirconium in sheet form was welded to titanium sheet by a fusion butt method.

Corrosion Data

One sample was polished on all sides and one was polished on a single flat area only. The specimens were placed in silica tubes containing 0.17 M uranyl sulfate and operated at 250°C. After 1176 hours, the sample condition appears fairly good. In both cases, the titanium has become covered with a shiny brown film which is more adherent on the polished specimen than on the unpolished one. The titanium metal is black at the weld area. The zirconium in both cases has shown a pinkish white film with white film at the weld area. The tests are being continued.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)	
	POLISHED	PARTIALLY POLISHED
168	-0.7	-1.1
336	-0.6	-1.8
504	-0.8	-2.4
672	-0.9	-2.0
840	-1.2	-2.6
1176	+0.7	-0.1

ZIRCONIUM WELDING

The experiments on welding thick plates of zirconium which Battelle Memorial Institute was conducting for the Laboratory were completed satisfactorily on July 1, 1950. A topical report on these experiments should be available about September 1.

The results indicate that inert atmosphere welding under closely controlled conditions will yield welds of satisfactory corrosion resistance and physical characteristics.

IRRADIATION-CORROSION TESTS

Since February, 1950, the Corrosion Group in conjunction with Chemistry Division personnel, has been studying the effects of irradiation on the corrosion resistance of Type 347 stainless steel and Bureau of Mines zirconium. These materials are exposed to enriched uranyl sulfate solutions at temperatures of 250°C. Preliminary results are now available and are included in this report. Results are reported by Run No. to permit comparison with liquid-gas result measurements. A few of the test results have already been reported in ORNL 730.⁽¹⁾

Run 284

A small tensile specimen of zirconium was exposed in 10 ml of 42.8 mg "25"/ml UO_2SO_4 solution. The temperature of the test ranged from 250 - 260°C for 336 hours and the total irradiation exposure was 928 megawatt hours. The weight change on the sample was +7.06 mg/dm²/day. A similar but non-irradiated test with a zirconium tensile specimen in 0.17 M uranyl sulfate at 250°C for 672 hours gave a weight gain of 1.31 mdd. The irradiated specimen exhibited a brassy color; the non-irradiated specimen was coated with an adherent gray-white oxide film. Both samples were then pulled on a tensile machine. The ultimate strength of the irradiated specimen was 89,990 psi compared to 90,500 psi for the non-irradiated specimen. These results check very closely with the known ultimate tensile strength of 90,000 psi for Bureau of Mines zirconium.

Run 285

An untreated stainless steel specimen was placed in a bomb to which a partial pressure of 300 psi of oxygen was added before the start of the test. At the completion of the run, solution decomposition had occurred and the sample appeared badly corroded.

A group of tests was completed in which 347 stainless steel specimens and bombs were pretreated with either 1% nitric acid or 2% chromic acid for 24 hours at 250°C in order to determine the effect of irradiation on the expectant life of such treatments. The irradiation-corrosion tests were conducted at 260°C. Results are tabulated below:

(1) Winters, C. E., *Homogeneous Reactor Experiment Feasibility Report*, ORNL 730 (July 6, 1950)

RUN NO.	PRETREATMENT	EXPOSURE (hr)	EXPOSURE HOLE	EXPOSURE (MWH)	WEIGHT CHANGE (mdd)	SAMPLE DESCRIPTION
286	HNO ₃	216	12	609	+4.6	Heavy black scale
287	CrO ₃	288	12	747	+7.3	Original black scale
288	HNO ₃	288	12	809	+6.5	Heavy black scale, brown ring near one end
289	CrO ₃	288	12	809	+3.5	No apparent change

These samples will be returned for a continuation of the irradiation tests for a total period of at least nine weeks. The tests will be inspected at various intervals during this time for measurement of corrosion damage and irradiation effects. At the first sign of excessive corrosion or solution damage, the tests will be stopped. Additional tests with stainless steels and zirconium will be started when additional experimental facilities become available.

From an inspection of the preliminary test results listed above, it appears that the chromic acid pretreatment is superior to the nitric acid treatment. This assumption is based mainly upon a visual observation of the specimens. There were no indications of any reduction of the uranyl ion during the course of these tests.

CORROSION OF BEARING MATERIALS

Numerous tests have been completed or are in progress to determine the corrosion characteristics of various metals which could be used as bearing or valve seat materials exposed to uranyl sulfate systems operating at 150 - 250°C. The selection of suitable materials in addition to a required hardness will be governed by its resistance to uranyl sulfate solution as well as its resistance to either the nitric or chromic acid pretreatments. The latter requirement is especially true for valve seat materials. In the case of bearings located in the pumps the temperature of operation seldom exceeds 150°C, and corrosion requirements are not as critical. A discussion of the results with various metals and alloys follows.

STELLITE ALLOYS

Five Stellite alloys considered for use in the fabrication of valve seats were tested. These were Stellite 6, 19, 21, 25-1 and L605. These materials are cobalt-chromium-tungsten base alloys noted for their hardenability and resistance to abrasion.

The corrosion resistance of these materials in 1% nitric acid at 250°C for 24 hours was very poor and would rule out their use in a system which required periodic nitric acid treatments under these conditions. Corrosion attack on the materials by 2% chromic acid at 250°C for 24 hours was also intense as evidenced by the following figures.

MATERIAL	INITIAL HARDNESS	CORROSION RATE (MPY)	SAMPLE DESCRIPTION
Stellite 6	51 Rc	20.5	Adherent black scale
Stellite 19	51	51.3	Adherent black scale
Stellite 21	43	31.8	Adherent black scale
Stellite 25-1	34	10.0	Adherent black scale
Stellite L605	21	18.2	Adherent black scale

A series of tests was run with the above Stellite alloys exposed to 0.17 M uranyl sulfate at 250°C in a pretreated stainless steel bomb. These data are included in the tabulation below. The test was operated for 168 hours.

MATERIAL	WEIGHT CHANGE (mdd)	SAMPLE DESCRIPTION
Stellite 6	+354.5	Heavy black film
Stellite 19	+303.1	Heavy black film
Stellite 21	+165.8	Heavy black film
Stellite 25-1	-313.7	Metallic luster
Stellite L605	+ 55.9	Black film

The behavior and condition of the samples at the end of the test was such that the use of these materials in the test medium at 250°C is not recommended. Chemical analyses disclosed no sign of solution decomposition during test.

Tests were also conducted with the five Stellite alloys in 0.17 M uranyl sulfate at a temperature of 150°C. These samples were not pretreated prior to the test. The test was operated for 1176 hours with weekly inspections.

HOURS	WEIGHT CHANGE (mdd)				
	No. 6	No. 19	No. 21	No. 25-1	No. L605
168	+57.6	+45.8	+62.9	+36.4	+38.9
336	+ 5.9	+57.1	+33.2	-12.5	-11.2
504	+12.4	+78.2	+58.1	- 7.9	- 3.5
672	-11.9	- 2.8	-11.2	-15.2	-19.5
840	+11.3	+32.9	+ 6.1	- 4.7	- 1.2
1008	+26.3	+43.7	+ 2.1	-12.2	- 0.7
1176	+42.0	+58.3	- 2.7	-10.9	+ 9.0

These results are somewhat erratic but illustrate how film formation and dissolution occurred during the course of the test. The most suitable Stellite alloy at this temperature was No. 21. At the end of the test, it had regained its original metallic luster although it possessed an adherent black film during the first 504 hours of the test. Chemical analyses of the uranyl sulfate test solution showed that the Stellite alloys in an untreated condition had no tendency to reduce the uranyl ion at 150°C.

TITANIUM CARBIDE

Samples of titanium carbide were tested at 150°C and 250°C in 0.17 M uranyl sulfate. The sample tested at 250°C was first given a pretreatment in 2% chromic acid, at 250°C for 24 hours. The resulting weight gain on this specimen in the uranyl sulfate was extremely high, 1781.7 mg/dm²/day, and the sample appeared distorted in shape. The specimen tested at 150°C was in an untreated condition.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)	
	150°C	250°C
168	+366.6	+347.9
336	+230.8	-

Both specimens showed heavy weight gain rates even though corrosion attack was evident, such as rounded edges, distortion and swelling. This material therefore is not recommended for use under the conditions of the test.

HASTELLOY C

The possibility of using Hastelloy C was investigated and tests were operated at 100°, 150°, and 250°C in 0.17 M uranyl sulfate solution. Tests at the latter two temperatures were conducted in silica tubes. None of the samples were pretreated prior to test. The results of the tests appear below.

TEMPERATURE (°C)	EXPOSURE (hr)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)	SAMPLE DESCRIPTION
100	1344	- 2.3	0.37	Bright metallic surface
150	336	+ 36.7	-	Black flaky scale
250	96	-112.2	18.1	Black loose scale

The use of untreated Hastelloy C for bearing surfaces at temperatures above 100°C in uranyl sulfate is not satisfactory. In both tests at 150° and 250°C, chemical analyses of the uranyl sulfate solution before and after test showed reduction of the uranyl ion by contact with the test specimen. The effectiveness of nitric acid and chromic acid pretreatments on Hastelloy C to prevent solution reduction will be investigated.

DURHY

A sample of Durhy (silicon carbide) was provided from Wright Field in Dayton, Ohio. This material is used for turbine blades because of its high resistance to thermal shock. The material contains 36-44% silicon carbide, 44-55% silicon, and 6.4-8.9% carbon. Its modulus of rupture at 1350°C is 12,000 - 14,000 psi. Its use as a possible bearing material was suggested and tests have been conducted at 100° and 150°C in uranyl sulfate solution.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)		SAMPLE DESCRIPTION
	100°C	150°C	
168	-6.5	-13.9	Original gray color
336	-4.0	- 8.1	Original gray color
504	-2.9		Original gray color
672	-2.3		Original gray color
840	-1.9		Original gray color

A slight increase in corrosion attack was noted as the temperature was increased from 100° to 150°C. The condition of the sample has remained unchanged during the tests and there has been no indication of solution deterioration. The tests are being continued.

CARBOLOY 44A

A sample of Carboloy 44A, a sintered tungsten carbide and cobalt base alloy, has been tested in 0.17 M uranyl sulfate at 100° and 150°C. These tests, using untreated specimens, were made in silica glassware. Results appear below.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)	
	100°C	150°C
168	-215.8	-734.6
336	-	-393.1

Excessive corrosion damage was apparent on the specimens at both temperatures. At 150°C, a black spotty film appeared on the metal which resembled uranium oxides. This material is deemed unsuitable as a bearing alloy in uranyl sulfate solution.

GRAPHITAR

Graphitar bearings are used in the totally enclosed Westinghouse pump undergoing test in a uranyl sulfate system at 250°C, and have shown only mild signs of wear. These bearings also seem to exhibit satisfactory corrosion resistance to the sulfate medium which is at a temperature of approximately 150°C or less in the pump housing. In order to more closely follow the corrosion resistance of the Graphitar, a test has been operated in 0.17 M uranyl sulfate at 100°C for 1512 hours.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)
336	+91.9
672	+57.2
1008	+42.8
1344	+37.8
1512	+34.0

Although a large weight gain was initially recorded, this rate is decreasing with increased exposure time. The gain may be due to porosity of the material which permits the entry of uranyl sulfate solution into the Graphitar, where it remains occluded. The condition of the samples has remained excellent throughout the course of the test.

DURIMET 20

Durimet 20, a 29Ni-19Cr-3Mo-4Cu-1Si wrought or cast alloy, was included in the tests for valve seats although its hardness is relatively soft, 90 RB in the wrought form. Its use, however, may be possible in connection with a suitable hard-faced material to eliminate galling problems. Tests have been conducted at 100°, 150°, and 250°C in 0.17 M uranyl sulfate solutions. The samples were untreated and the 150° and 250°C tests were run in silica tubes.

TEMPERATURE (°C)	EXPOSURE (hr)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)	SAMPLE DESCRIPTION
100.	1344	- 0.05	0.001	Clean bright surface
150	336	- 0.44	0.08	Clean bright surface
250	47	-348.0	62.9	Dull black coating

The use of Durimet 20 at temperatures of 150°C and less appears perfectly satisfactory. There were no indications that reduction of the uranyl ion was caused by the material. At 250°C, however, it was apparent that solution reduction had occurred and corrosion attack on the specimen was very intense.

TYPE 410 STAINLESS STEEL

This hardenable straight chromium steel has been successfully used as bearing and valve seat material in industry. Much work on its corrosion resistance at 250°C has been conducted and it was found to be completely satisfactory, if nitric acid was present in the uranyl sulfate solution or if the specimens were first pretreated in nitric acid at 250°C. Little was known about its resistance to corrosion at 150°C.

A sample of cold rolled and polished 410 stainless steel (hardness, 86 RB), was tested in uranyl sulfate contained in a silica liner at 150°C. The test was operated for 336 hours. Corrosion attack on the specimen was 45.8 mils/year and it was coated with a non-uniform black film. In this form the material is unsuitable.

Samples were heat treated at 1850°F for 15 minutes, cooled in air, pickled and polished. The hardness obtained was 41 RC. One specimen was pretreated in 1% nitric acid for 24 hours at 250°C; the other specimen was not treated. The two samples were run in 0.17 M uranyl sulfate (silica liner) at 150°C. At the end of 336 hours, the untreated specimen gained in weight at the rate of 241.0 mg/dm²/day. The sample was coated with a heavy black flaky scale and the solution had decomposed. The treated sample for the same length of time showed a weight gain of 2.1 mg/dm²/day and was in excellent condition. There was no solution decomposition.

Type 410 stainless steel may be hardened to 40-50 RC by suitable heat treatment and may successfully be used in the hardened condition in uranyl sulfate at 150°C if it is first pretreated in 1% nitric acid at 250°C for 24 hours.

REXALLOY

A sample of Rexalloy, a high speed cutting tool material, has been exposed to 0.17 M uranyl sulfate at 100°C for 672 hours.

EXPOSURE (hr)	WEIGHT LOSS (mg)
168	0.8
336	1.2
504	1.6
672	1.1

This specimen has showed very little corrosion attack and has retained its original metallic luster. The test is being continued and a test will be conducted at 150°C.

CORROSION RESISTANCE OF REFLECTOR MATERIALS

A corrosion program was started to determine the resistance of materials to be used in the D₂O cooled reflector system. The reflector pressure shell is to be forged from ASTM A-105-46, Grade 1 steel. Boral is contemplated for use as the neutron absorbing plates for the shim controls.

The present corrosion tests have been conducted in high purity water at temperatures of 100 and 200°C. Actual operating temperatures of the reflector cooling system is expected to fall within this range. The carbon steel used for test purposes was SAE 1030, similar in composition to the ASTM grade specified for the reflector shell. 2S aluminum was included in the studies to determine the effect of dissimilar metal on corrosion resistance. Small amounts of hydrogen peroxide were added to the water to simulate decomposition of the water by irradiation effects.

The first phase of the investigation was conducted at 100°C to act as a sorting program to determine the effects of peroxide concentration, pH, inorganic inhibitors, and dissimilar metal contact on the corrosion resistance of the carbon steel. These results are included in the following sections.

EFFECT OF WATER pH ON CORROSION RESISTANCE OF SAE 1030

Tests were operated for 2012 hours (three months) under stagnant conditions at 100°C in peroxide-free water to determine the effect of pH on the corrosion resistance of SAE 1030 carbon steel. No attempt was made to control or adjust the pH during the course of the test. Duplicate polished specimens were used.

INITIAL pH	FINAL pH	WEIGHT LOSS (mdm)	CORROSION RATE (mpy)	SAMPLE DESCRIPTION
5.7	5.9	472.9	2.9	Uniform brown film; no pits
7.9	8.1	33.7	0.2	Dull black coating; no pits
9.8	9.0	11.0	0.07	Few spots; bright surfaces

These results show the corrosion resistance to be a direct function of water pH in relatively oxygen-free water at 100°C. As the pH was increased, the resistance of the carbon steel increased proportionately. A pH range of approximately 10 proved most effective for minimizing attack and the specimens remained bright and metallic in appearance.

EFFECT OF HYDROGEN PEROXIDE ON CORROSION RESISTANCE OF SAE 1030

Tests solutions were maintained at approximately 0.005 M in hydrogen peroxide by regular additions during the entire exposure time. This concentration was arbitrarily selected to represent the maximum concentration of peroxide that could exist in the reflector system as a result of water decomposition by irradiation. The pH ranges of the stagnant test solutions were the same as previously mentioned and the tests were operated at 100°C for 2012 hours (three months). The pH was not controlled during the tests. Duplicate specimens were used.

INITIAL pH	FINAL pH	WEIGHT LOSS (mdm)	CORROSION RATE (mpy)	SAMPLE DESCRIPTION
6.2	6.4	1970.0	12.0	Heavy rust deposition
7.9	6.7	2277.5	14.4	Thick rust deposits
9.8	6.9	1796.6	10.8	Uniform rust film

The presence of hydrogen peroxide was observed to have a pronounced adverse effect on the corrosion resistance of the carbon steel. Heavy accumulations of rust were visible on all specimens, and the previously mentioned beneficial effect of increased initial pH was only of slight significance in these tests, probably because of the drop in pH during the test. A similar test is in progress where the pH is controlled to the initial value throughout the experiment. Pit depths of eight to 12 mils were recorded on the samples after cleaning. Thus, with hydrogen peroxide present in the water, the corrosion of 1030 carbon steel is markedly increased with the accumulation of voluminous quantities of corrosion products.

EFFECT OF SODIUM DICHROMATE ON CORROSION RESISTANCE OF CARBON STEEL

In an attempt to eliminate the adverse effect of hydrogen peroxide on the corrosion resistance of the carbon steel, various concentrations of sodium dichromate were added to the test medium. The pH was also varied. Tests were operated at 100°C for 2012 hours with duplicate specimens. The solution pH was not adjusted, but a concentration of 0.005 M hydrogen peroxide was maintained.

INITIAL pH	FINAL pH	Na ₂ Cr ₂ O ₇ (ppm)	WEIGHT LOSS (mg)	CORROSION RATE (mpy)	SAMPLE DESCRIPTION
7.8	4.5	100	36.2	0.23	Uniform dull yellow film
6.6	4.5	500	11.4	0.07	Bright metallic color
10.0	5.2	100	199.3	1.20	Few spots; bright color
9.7	4.2	300	21.0	0.13	Uniform green film
9.9	3.9	500	1.5	0.007	Bright metallic color

The effectiveness of sodium dichromate as a corrosion inhibitor in water containing hydrogen peroxide is clearly illustrated. Concentrations of 500 ppm were most effective at both pH ranges, although at an initial water pH of 10, its effect was 10 times better than at an initial pH of 7.7. Extremely mild corrosion attack on the carbon steel specimens was evident at 500 ppm concentrations. The samples retained their original metallic luster and there was no indication or sign of localized corrosion attack. Corrosion attack with 300 and 100 ppm, respectively, was only very slightly more intense. All three concentrations offered satisfactory results.

EFFECTS OF SODIUM CHROMATE ON CORROSION RESISTANCE OF CARBON STEEL

Similar tests were conducted using sodium chromate in place of sodium dichromate. These tests were operated for 2012 hours at 100°C in water with and without 0.005 M hydrogen peroxide. Various concentrations of sodium chromate were employed. The pH range for all tests was 5.5 - 6.5.

FINAL pH	HYDROGEN PEROXIDE M	Na ₂ CrO ₄ (ppm)	WEIGHT LOSS (mdm)	CORROSION RATE (mpy)	SAMPLE DESCRIPTION
6.8	None	125	3.7	0.03	Bright metallic color
3.9	0.005	100	68.5	0.42	Dull green film
3.6	0.005	300	25.2	0.16	Dull green film
3.8	0.005	500	16.6	0.10	Bright metallic color

Sodium chromate also proved effective for reducing corrosion attack on the carbon steel in the presence of hydrogen peroxide. It compared in similar manner to the results obtained with sodium dichromate. As the concentration was increased from 100 to 500 ppm, corrosion attack on the specimens decreased noticeably.

EFFECT OF 2S ALUMINUM ON CONTACT CORROSION OF CARBON STEEL

A study was made on the effect of water pH, hydrogen peroxide, and the use of inhibitors on the corrosion resistance of 1030 carbon steel in contact with 2S aluminum.

Tests were run for 2012 hours at 100°C. The test couples were made by means of 2S aluminum nuts and bolts.

INITIAL pH	HYDROGEN PEROXIDE	INHIBITOR (ppm)	MATERIAL	WEIGHT CHANGE (mdm)	CORROSION RATE (mpy)
5.8	None	None	1030	-24.7	0.15
			2S	+ 8.6	-
7.9	None	None	1030	-18.4	0.11
			2S	-25.1	0.44
9.9	None	None	1030	-11.5	0.07
			2S	-109.9	1.93
5.7	0.005 M	None	1030	-2033.3	12.26
			2S	-15.3	0.27
7.8	0.005 M	None	1030	-2088.7	12.6
			2S	-119.3	2.1
7.8	0.005 M	100	1030	-125.7	0.77
		Na ₂ Cr ₂ O ₇	2S	-29.7	0.52
7.8	0.005 M	500	1030	+ 2.4	-
		Na ₂ Cr ₂ O ₇	2S	-44.0	0.74
5.8	0.005 M	100	1030	-157.8	0.96
		Na ₂ CrO ₄	2S	+ 9.0	-
5.8	0.005 M	500	1030	- 4.1	0.03
		Na ₂ CrO ₄	2S	-20.9	0.37

The effect of increasing the pH of the water was beneficial to the corrosion resistance of the carbon steel, but at the same time it increased corrosion attack on the 2S aluminum. The corrosion rate on this material increased to nearly 2 mils/year as the pH was increased from 5.8 to 9.7. Corrosion attack on the carbon steel was 0.07 mils/year at this pH. The steel specimens were covered with a dull black film in these tests; the aluminum reacted similarly except around the contact area where it retained its original gray color. No signs of localized corrosion attack on any of the specimens were observed. In the pH range of 5.8, the steel was anodic to the aluminum; at a pH range of 7.9 - 9.9, the aluminum was anodic to the carbon steel.

The addition of 0.005 M hydrogen peroxide to the test solutions at a pH of 5.7 to 7.8 greatly increased the magnitude of corrosion attack on the carbon steel resulting in an average rate of 12.5 mils/year. Bulky rust depositions were very pronounced and pit depths of eight to 12 mils were recorded. The 2S aluminum specimens showed signs of corrosion attack and the surface areas, exclusive of the immediate contact area, were coated with a heavy brown colored film. The contact areas remained gray in color with spotty black markings. There were no indications of excessive pitting attack.

The addition of 100 - 500 ppm of sodium dichromate or sodium chromate to the test solutions containing 0.005 M hydrogen peroxide was definitely beneficial. Best results were obtained with 500 ppm of sodium chromate as evidenced by the corrosion rates on the carbon steel and 2S aluminum, 0.03 and 0.37 mil/year, respectively. In this case, both samples exhibited dull brown and black films but there were no formulations of voluminous corrosion products. Pitting attack was negligible. Favorable results were also obtained with additions of 100 ppm of either sodium chromate or sodium dichromate. The second phase of the reflector materials corrosion program was conducted at 200°C in clean stainless steel bombs. Specimens were insulated from the bomb by means of silica glass hooks. The tests were inspected weekly and new solutions were placed into the bombs before putting back into operation. The results of these tests appear in Table V.

TABLE V

The Corrosion of Reflector Materials in Water at 200°C

MATERIAL	EXPOSURE (hr)	INITIAL pH	HYDROGEN PEROXIDE	INHIBITOR (ppm)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)
1030	336	5.1	None	None	- 9.5	1.7
1030	336	5.1	0.005 M	None	-23.9	4.4
1030	336	5.6	None	None	-11.1	2.0
2S Al					+ 4.4	-
1030	336	5.7	0.005 M	None	- 6.2	1.1
2S Al					- 9.3	4.9
1030	336	5.8	None	125	+ 3.3	-
2S Al				Na ₂ CrO ₄	- 3.6	1.9
1030	336	5.5	0.005 M	125	+ 2.7	-
2S Al				Na ₂ CrO ₄	+ 4.6	-
Zr	1512	5.7	None	None	+ 0.4	-
2S Al					+ 0.7	-

The results with 1030 carbon steel show the detrimental effect of the presence of hydrogen peroxide at 200°C. Corrosion attack was increased by a factor of two and one-half when peroxide was present in the water. The samples in both cases and especially in the test containing peroxide were irregularly spotted with depositions of corrosion products. Evidences of localized corrosion attack were apparent on both specimens. This study is being continued to investigate the use of sodium chromate and dichromate inhibitors at 200°C.

Best results on the 1030 steel:- 2S aluminum couple tests were obtained with 125 ppm sodium chromate present in the solution containing 0.005 M hydrogen peroxide. The samples exhibited weight gains of 4.6 mdd and 2.7 mdd for the aluminum and carbon steel, respectively. Both specimens showed dull colored films, but there were no voluminous corrosion products or signs of localized corrosion attack. The presence of 125 ppm sodium chromate in the absence of the peroxide was also beneficial although a mild corrosion attack on the 2S aluminum was reported. The most prominent corrosion attack was

observed on the specimens exposed to the solution containing 0.005 M hydrogen peroxide and no inhibitor. Both samples were pitted and had rather intensive scale formation.

The BM zirconium - 2S aluminum couple appears in excellent condition after 1512 hours in water at 200°C. Weight gains of 0.4 and 0.7 mg/dm²/day were reported for the zirconium and the aluminum, respectively.* No pitting attack has been found on these samples.

CORROSION RESISTANCE OF BORAL IN WATER

Tests have been started to determine the corrosion resistance of Boral in water at 100°C and at 200°C. Information at the latter temperature is not available at present. Tests have been conducted in water with and without 0.005 M hydrogen peroxide at 100°C for 672 hours to date. These results appear below.

EXPOSURE	INITIAL pH	WEIGHT GAIN (mdd)	
		NO PEROXIDE	0.005 M PEROXIDE
168	6.3	31.9	33.9
336	6.3	20.6	21.6
504	6.3	16.5	18.3
672	6.3	13.3	15.0

A slightly higher weight gain rate was observed on the specimen exposed to the peroxide solution indicating a heavier rate of film formation due to the availability of excess oxygen. Both samples appear in excellent condition with no signs of bulky film build-up or pitting type of corrosion.

MISCELLANEOUS CORROSION TESTS

TANTALUM

A piece of sheet tantalum has been exposed to 0.17 M uranyl sulfate contained in a silica tube at 250°C for 1344 hours (eight weeks). The sample was inspected weekly for measurement of corrosion attack. Results appear below.

EXPOSURE (hr)	WEIGHT GAIN (mdd)
168	2.9
336	2.1
504	1.0
672	0.8
840	0.7
1008	0.8
1176	1.4
1344	1.0

The sample has exhibited a dull brown film during the test with no indication of any corrosion damage. At the end of 1344 hours a slight yellow precipitate, identity as yet unknown, appeared in the silica liner containing the uranyl sulfate. This precipitate did not resemble the usual black residue formed when the uranyl ion was reduced by contact with certain materials. The test is being continued.

TITANIUM

A titanium sample was exposed to 0.17 M uranyl sulfate at 250°C in a silica tube. This test has operated 1344 hours to date. The sample was inspected weekly and results are listed below.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)
168	+0.3
336	+1.3
504	+0.5
672	+0.3
840	+0.3
1008	+0.3
1176	+0.8
1344	-0.07

Not until the last week of exposure was there any indication of corrosion attack. The sample was reddish-brown in color with a few dark spots. A slight yellow precipitate, similar to that observed with the tantalum specimen, was found in the silica liner but there were no signs of the usual solution reduction phenomenon. This test is being continued.

These results show the corrosion resistance to be a direct function of water pH in relatively oxygen-free water at 100°C. As the pH was increased, the resistance of the carbon steel increased proportionately. A pH range of approximately 10 proved most effective for minimizing attack and the specimens remained bright and metallic in appearance.

EFFECT OF HYDROGEN PEROXIDE ON CORROSION RESISTANCE OF SAE 1030

Tests solutions were maintained at approximately 0.005 M in hydrogen peroxide by regular additions during the entire exposure time. This concentration was arbitrarily selected to represent the maximum concentration of peroxide that could exist in the reflector system as a result of water decomposition by irradiation. The pH ranges of the stagnant test solutions were the same as previously mentioned and the tests were operated at 100°C for 2012 hours (three months). The pH was not controlled during the tests. Duplicate specimens were used.

INITIAL pH	FINAL pH	WEIGHT LOSS (mdm)	CORROSION RATE (mpy)	SAMPLE DESCRIPTION
6.2	6.4	1970.0	12.0	Heavy rust deposition
7.9	6.7	2277.5	14.4	Thick rust deposits
9.8	6.9	1796.6	10.8	Uniform rust film

The presence of hydrogen peroxide was observed to have a pronounced adverse effect on the corrosion resistance of the carbon steel. Heavy accumulations of rust were visible on all specimens, and the previously mentioned beneficial effect of increased initial pH was only of slight significance in these tests, probably because of the drop in pH during the test. A similar test is in progress where the pH is controlled to the initial value throughout the experiment. Pit depths of eight to 12 mils were recorded on the samples after cleaning. Thus, with hydrogen peroxide present in the water, the corrosion of 1030 carbon steel is markedly increased with the accumulation of voluminous quantities of corrosion products.

EFFECT OF SODIUM DICHROMATE ON CORROSION RESISTANCE OF CARBON STEEL

In an attempt to eliminate the adverse effect of hydrogen peroxide on the corrosion resistance of the carbon steel, various concentrations of sodium dichromate were added to the test medium. The pH was also varied. Tests were operated at 100°C for 2012 hours with duplicate specimens. The solution pH was not adjusted, but a concentration of 0.005 M hydrogen peroxide was maintained.

INITIAL pH	FINAL pH	Na ₂ Cr ₂ O ₇ (ppm)	WEIGHT LOSS (mg)	CORROSION RATE (mpy)	SAMPLE DESCRIPTION
7.8	4.5	100	36.2	0.23	Uniform dull yellow film
6.6	4.5	500	11.4	0.07	Bright metallic color
10.0	5.2	100	199.3	1.20	Few spots; bright color
9.7	4.2	300	21.0	0.13	Uniform green film
9.9	3.9	500	1.5	0.007	Bright metallic color

The effectiveness of sodium dichromate as a corrosion inhibitor in water containing hydrogen peroxide is clearly illustrated. Concentrations of 500 ppm were most effective at both pH ranges, although at an initial water pH of 10, its effect was 10 times better than at an initial pH of 7.7. Extremely mild corrosion attack on the carbon steel specimens was evident at 500 ppm concentrations. The samples retained their original metallic luster and there was no indication or sign of localized corrosion attack. Corrosion attack with 300 and 100 ppm, respectively, was only very slightly more intense. All three concentrations offered satisfactory results.

EFFECTS OF SODIUM CHROMATE ON CORROSION RESISTANCE OF CARBON STEEL

Similar tests were conducted using sodium chromate in place of sodium dichromate. These tests were operated for 2012 hours at 100°C in water with and without 0.005 M hydrogen peroxide. Various concentrations of sodium chromate were employed. The pH range for all tests was 5.5 - 6.5.

FINAL pH	HYDROGEN PEROXIDE M	Na ₂ CrO ₄ (ppm)	WEIGHT LOSS (mdm)	CORROSION RATE (mpy)	SAMPLE DESCRIPTION
6.8	None	125	3.7	0.03	Bright metallic color
3.9	0.005	100	68.5	0.42	Dull green film
3.6	0.005	300	25.2	0.16	Dull green film
3.8	0.005	500	16.6	0.10	Bright metallic color

Sodium chromate also proved effective for reducing corrosion attack on the carbon steel in the presence of hydrogen peroxide. It compared in similar manner to the results obtained with sodium dichromate. As the concentration was increased from 100 to 500 ppm, corrosion attack on the specimens decreased noticeably.

EFFECT OF 2S ALUMINUM ON CONTACT CORROSION OF CARBON STEEL

A study was made on the effect of water pH, hydrogen peroxide, and the use of inhibitors on the corrosion resistance of 1030 carbon steel in contact with 2S aluminum.

Tests were run for 2012 hours at 100°C. The test couples were made by means of 2S aluminum nuts and bolts.

INITIAL pH	HYDROGEN PEROXIDE	INHIBITOR (ppm)	MATERIAL	WEIGHT CHANGE (mdm)	CORROSION RATE (mpy)
5.8	None	None	1030	-24.7	0.15
			2S	+ 8.6	-
7.9	None	None	1030	-18.4	0.11
			2S	-25.1	0.44
9.9	None	None	1030	-11.5	0.07
			2S	-109.9	1.93
5.7	0.005 M	None	1030	-2033.3	12.26
			2S	-15.3	0.27
7.8	0.005 M	None	1030	-2088.7	12.6
			2S	-119.3	2.1
7.8	0.005 M	100	1030	-125.7	0.77
		Na ₂ Cr ₂ O ₇	2S	-29.7	0.52
7.8	0.005 M	500	1030	+ 2.4	-
		Na ₂ Cr ₂ O ₇	2S	-44.0	0.74
5.8	0.005 M	100	1030	-157.8	0.96
		Na ₂ CrO ₄	2S	+ 9.0	-
5.8	0.005 M	500	1030	- 4.1	0.03
		Na ₂ CrO ₄	2S	-20.9	0.37

The effect of increasing the pH of the water was beneficial to the corrosion resistance of the carbon steel, but at the same time it increased corrosion attack on the 2S aluminum. The corrosion rate on this material increased to nearly 2 mils/year as the pH was increased from 5.8 to 9.7. Corrosion attack on the carbon steel was 0.07 mils/year at this pH. The steel specimens were covered with a dull black film in these tests; the aluminum reacted similarly except around the contact area where it retained its original gray color. No signs of localized corrosion attack on any of the specimens were observed. In the pH range of 5.8, the steel was anodic to the aluminum; at a pH range of 7.9 - 9.9, the aluminum was anodic to the carbon steel.

The addition of 0.005 M hydrogen peroxide to the test solutions at a pH of 5.7 to 7.8 greatly increased the magnitude of corrosion attack on the carbon steel resulting in an average rate of 12.5 mils/year. Bulky rust depositions were very pronounced and pit depths of eight to 12 mils were recorded. The 2S aluminum specimens showed signs of corrosion attack and the surface areas, exclusive of the immediate contact area, were coated with a heavy brown colored film. The contact areas remained gray in color with spotty black markings. There were no indications of excessive pitting attack.

The addition of 100 - 500 ppm of sodium dichromate or sodium chromate to the test solutions containing 0.005 M hydrogen peroxide was definitely beneficial. Best results were obtained with 500 ppm of sodium chromate as evidenced by the corrosion rates on the carbon steel and 2S aluminum, 0.03 and 0.37 mil/year, respectively. In this case, both samples exhibited dull brown and black films but there were no formulations of voluminous corrosion products. Pitting attack was negligible. Favorable results were also obtained with additions of 100 ppm of either sodium chromate or sodium dichromate. The second phase of the reflector materials corrosion program was conducted at 200°C in clean stainless steel bombs. Specimens were insulated from the bomb by means of silica glass hooks. The tests were inspected weekly and new solutions were placed into the bombs before putting back into operation. The results of these tests appear in Table V.

TABLE V

The Corrosion of Reflector Materials in Water at 200°C

MATERIAL	EXPOSURE (hr)	INITIAL pH	HYDROGEN PEROXIDE	INHIBITOR (ppm)	WEIGHT CHANGE (mdd)	CORROSION RATE (mpy)
1030	336	5.1	None	None	- 9.5	1.7
1030	336	5.1	0.005 M	None	-23.9	4.4
1030	336	5.6	None	None	-11.1	2.0
2S Al					+ 4.4	-
1030	336	5.7	0.005 M	None	- 6.2	1.1
2S Al					- 9.3	4.9
1030	336	5.8	None	125	+ 3.3	-
2S Al				Na ₂ CrO ₄	- 3.6	1.9
1030	336	5.5	0.005 M	125	+ 2.7	-
2S Al				Na ₂ CrO ₄	+ 4.6	-
Zr	1512	5.7	None	None	+ 0.4	-
2S Al					+ 0.7	-

The results with 1030 carbon steel show the detrimental effect of the presence of hydrogen peroxide at 200°C. Corrosion attack was increased by a factor of two and one-half when peroxide was present in the water. The samples in both cases and especially in the test containing peroxide were irregularly spotted with depositions of corrosion products. Evidences of localized corrosion attack were apparent on both specimens. This study is being continued to investigate the use of sodium chromate and dichromate inhibitors at 200°C.

Best results on the 1030 steel:- 2S aluminum couple tests were obtained with 125 ppm sodium chromate present in the solution containing 0.005 M hydrogen peroxide. The samples exhibited weight gains of 4.6 mdd and 2.7 mdd for the aluminum and carbon steel, respectively. Both specimens showed dull colored films, but there were no voluminous corrosion products or signs of localized corrosion attack. The presence of 125 ppm sodium chromate in the absence of the peroxide was also beneficial although a mild corrosion attack on the 2S aluminum was reported. The most prominent corrosion attack was

observed on the specimens exposed to the solution containing 0.005 M hydrogen peroxide and no inhibitor. Both samples were pitted and had rather intensive scale formation.

The BM zirconium - 2S aluminum couple appears in excellent condition after 1512 hours in water at 200°C. Weight gains of 0.4 and 0.7 mg/dm²/day were reported for the zirconium and the aluminum, respectively.* No pitting attack has been found on these samples.

CORROSION RESISTANCE OF BORAL IN WATER

Tests have been started to determine the corrosion resistance of Boral in water at 100°C and at 200°C. Information at the latter temperature is not available at present. Tests have been conducted in water with and without 0.005 M hydrogen peroxide at 100°C for 672 hours to date. These results appear below.

EXPOSURE	INITIAL pH	WEIGHT GAIN (mdd)	
		NO PEROXIDE	0.005 M PEROXIDE
168	6.3	31.9	33.9
336	6.3	20.6	21.6
504	6.3	16.5	18.3
672	6.3	13.3	15.0

A slightly higher weight gain rate was observed on the specimen exposed to the peroxide solution indicating a heavier rate of film formation due to the availability of excess oxygen. Both samples appear in excellent condition with no signs of bulky film build-up or pitting type of corrosion.

MISCELLANEOUS CORROSION TESTS

TANTALUM

A piece of sheet tantalum has been exposed to 0.17 M uranyl sulfate contained in a silica tube at 250°C for 1344 hours (eight weeks). The sample was inspected weekly for measurement of corrosion attack. Results appear below.

EXPOSURE (hr)	WEIGHT GAIN (mdd)
168	2.9
336	2.1
504	1.0
672	0.8
840	0.7
1008	0.8
1176	1.4
1344	1.0

The sample has exhibited a dull brown film during the test with no indication of any corrosion damage. At the end of 1344 hours a slight yellow precipitate, identity as yet unknown, appeared in the silica liner containing the uranyl sulfate. This precipitate did not resemble the usual black residue formed when the uranyl ion was reduced by contact with certain materials. The test is being continued.

TITANIUM

A titanium sample was exposed to 0.17 M uranyl sulfate at 250°C in a silica tube. This test has operated 1344 hours to date. The sample was inspected weekly and results are listed below.

EXPOSURE (hr)	WEIGHT CHANGE (mdd)
168	+0.3
336	+1.3
504	+0.5
672	+0.3
840	+0.3
1008	+0.3
1176	+0.8
1344	-0.07

Not until the last week of exposure was there any indication of corrosion attack. The sample was reddish-brown in color with a few dark spots. A slight yellow precipitate, similar to that observed with the tantalum specimen, was found in the silica liner but there were no signs of the usual solution reduction phenomenon. This test is being continued.