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HOMOGENEOUS REACTOR PROJECT
QUARTERLY PROGRESS REPORT
for Period Ending May 15, 1951

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Reports previously issued in this series are as follows:

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SUMMARY OF PROGRAM AND PROGRESS

In recognition of the need for a broader developmental program to establish the feasibility of obtaining the potential advantages of homogeneous reactors for the production of fissionable materials and power, the ORNL Homogeneous Reactor Experiment Project (HRE), which was organized to develop, design and construct a pilot-scale homogeneous reactor, has been reconstituted as the Homogeneous Reactor Project. The ultimate objective of the ORNL program, based upon the studies of the Long Range Planning Group, is to provide the technical information required to determine the feasibility of a full-scale plutonium-power producing homogeneous reactor.

Homogeneous Reactor Program

The program of the Homogeneous Reactor Project which will be required to attain the above objective is conceived to be the following.

Completion of Pilot-Scale HRE. At present approximately 90% of the effort on the Project is directed toward the completion of the developmental, design and construction work for the pilot-scale HRE. Major emphasis is placed on chemical and engineering studies of the system UO_2SO_4-H_2O contained in 347 stainless steel under maximum conditions of 259°C and 1000 psi and of the mechanical components of the reactor system.

Experimental Operation of the HRE. A preliminary schedule for the start-up and experimental operation of the HRE was presented in the last progress report (ORNL 990). Detailed plans will be prepared prior to completion of construction. The experimental program should achieve the following:

1. Demonstration of the operability of a circulating aqueous-fuel reactor up to a maximum of 1000 kw, corresponding to a power density of 20 kw per liter.

2. Demonstration of auxiliary portions of the system, such as gas separation, gas handling, and recombination and control by variation of concentration.

3. Operating experience with this type of reactor.

4. Direct measurement of radiation decomposition and corrosion at flux densities comparable to those in a full-scale reactor.

1

Investigation of Alternate Systems and Reactor Types. Research on alternate fuel systems, materials of construction, and reactor types is currently being pursued on a small scale.

Design Development of Intermediate-Scale Homogeneous Reactor. Research and design leading to construction of an intermediate-scale homogeneous reactor has been undertaken. The reactor is now conceived as operating at a maximum of 40 mw and being of a size approaching that of a full-scale reactor, i.e., 8 to 10 ft diameter core tank vs. 15 to 20 ft for a full-scale reactor. The following are considered to be logical steps in this development:

1. Conceptual design of a full-scale (~2000 mw) reactor upon which to base plans of an intermediate-scale reactor.

2. Preliminary design of an intermediate-scale homogeneous reactor.

3. Research, component development, and detailed design of the intermediate reactor.

4. Construction and operation.

The major objectives of building such a reactor prior to a full-scale homogeneous reactor are considered to be (1) demonstration of the operability of a large-scale reactor system, (2) long-term testing of the reliability of handling a circulating aqueous-fuel system, and (3) testing of a chemical pilot plant to extract plutonium continuously from the fuel system.

Status of HRE

Construction. The 7500 Building which will house the reactor has been completed except for laying the concrete floor at the east side of the reactor.

The units comprising the reflector system, including the pressure vessel, have been constructed, with complete installation scheduled for July. This will be followed by pressure and leak testing.

Completion of the construction of components of the fuel system has been delayed pending results of current studies on chemical stability and on the gas-removal system.

Installation of the control system has been started. Mountings for the turbine, generator, and condenser have been constructed. Installation of components of the power system awaits delivery.

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Design. A design review group has been appointed to analyze critically the design of the entire HRE system with respect to its operability. The considerations of this group should be completed by August, 1951. During this quarter design work was directed toward completion of piping, flow sheet and shield drawings, and bills of materials.

Research and Development. Two general uncertainties must yet be resolved before the possibility of operating the HRE for a sufficiently long period to achieve the desired objectives will appear great enough to justify completion of the construction of the fuel system and initiation of operation. These are (1) establishment of the specific conditions required for stability of the fuel solution, i.e., UO_2SO_4-H_2O (30 to 40 g of uranium per liter) in 347 stainless steel at 250°C and 1000 psi, and (2) perfection of the gas-letdown system.

With regard to solution stability, it appears definitely established that maintaining oxidizing conditions in the system, for example by addition of oxygen, will provide stability. The optimum partial pressure of oxygen is now being determined. The effects of a number of variables including acidity, halide ions, various chemical pretreatments of the metal, the presence of corrosion products, the condition of the metal surface of the test pumps, and the presence of graphitar bearings have been studied in static bomb tests and pumped circulating loops.

Engineering studies of the gas-letdown system have led to modifications, specifically an increase in the flow of liquid removed with the gas and the addition of a surge tank, which show promise of eliminating the oscillations which have been observed in the original system. Work is being initiated to develop an alternate external gas separator.

Further work on the design and testing of graphitar and stellite bearings for the Westinghouse model 100A pump has given encouraging results.

Several methods for promoting mixing in partially stagnant regions of the reactor core have been studied, and one method produced encouraging results.

Because the recombination of essentially 100% of the H_2 and O_2 in stoichiometric mixtures has been demonstrated by the use of flame and catalytic recombiners, current effort has been devoted to investigating the feasibility of recombining with massive metal catalysts. Early tests gave unfavorable results with copper, silver, and platinum; therefore, this effort will be directed toward other more promising investigations in the next period.

3

The development of methods for chemical control of HRE fuel has continued to be centered on two instruments: the electromagnetic densitometer and Princo Densitrol for measurement of solution densities, and the ceramic-coated radiofrequency coil immersed in the fuel for indirect measurement of uranium concentration from the stored energy capacity.

Status of Long Range Studies

Studies of the phase equilibria of $UO_2(NO_3)_2$-H_2O and UO_3-H_3PO_4-H_2O systems have been continued in an effort to evaluate them as possible homogeneous reactor fuels. Ferric oxide produced by corrosion within the fuel system has been studied in connection with its effect on the critical solution temperatures of the UO_2SO_4-H_2O system; it was found that the effect was relatively small.

Although it has not yet been possible to prepare a uranium oxide slurry which is stable after heating, encouraging progress has been made. Slurries of thorium oxide containing 1000 g of thorium per liter have shown thermal and radiation stability characteristics that are promising.

Slurry pumping studies carried out on a small scale indicate that it may be possible to pump and control adequately an unstable slurry which settles relatively quickly.

Three methods of chemical processing for aqueous homogeneous reactor fuels have been investigated on a small scale. These include: (1) breakthrough adsorption on fuller's earth, Dowex 50 and Dowex A-1; (2) complete adsorption of fuel on Dowex 50 and Dowex A-1; and (3) precipitation followed by adsorption on Dowex 50 with Cu^{++} displacement and electrolysis. There is evidence that a process can be developed as a modification and/or combination of these methods.

Preliminary studies of boiling homogeneous reactors have been started and experiments are being designed to test the validity of theoretical calculations and to demonstrate flow rates, bubble formation, and rise time and the behavior of a solution heated in a manner simulating fission heat in a homogeneous reactor fuel.

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PART I. HOMOGENEOUS REACTOR EXPERIMENT

5-6

1. DESIGN AND CONSTRUCTION PROGRESS

C. E. Winters

Design	Assembly	Control
W. R. Gall	S. E. Beall	L. R. Quarles
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W. L. DeHieux, Jr.	D. T. Jones	C. A. Mossman
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T. H. Thomas	T. H. Mauney	B. P. White
F. C. Zapp	M. Shaw	J. E. Owens
F. L. Cauble		L. P. Inglis
R. H. Chapman		
R. W. French		
A. E. Strauchman		
W. Terry		
C. M. Wetzel		

In general, design work during the quarter has been aimed toward completion of piping drawings, flow sheet, shield drawings, and bills of materials. Emphasis has been placed on completion of the reflector system, and a thorough check of the complete system has resulted in numerous changes in details.

Major components still incomplete in final design are: (1) the low-pressure catalytic recombiners for fuel solution off-gas and the reflector off-gas, (2) a high-pressure catalytic recombiner for D_2 and O_2, (3) a heat exchanger between the letdown stream and the feed stream from and to the high-pressure fuel system, and (4) a liquid-level control for the fuel pressurizer.

All these components have been designed as tentative experimental models, but final designs will not be made until experimental data are available. The experimental catalytic recombiner is shown in Fig. 1.

A simplified HRE process flow diagram, giving process lines only with no instrumentation, is shown in Fig. 2; valves which are operated by automatic controls are shown as diaphragm valves. The general assembly of the reactor tank, including the pressurizer, control rod drives, instrument thimbles, and all connecting piping, is shown in Fig. 3.

Fuel Solution (Soup) System. Few changes have been made in the high-pressure part of the soup system since publication of ORNL-730 in June, 1950. The only significant change is transfer of the recombiner to the low-pressure system. The low-pressure gas-removal portion of the system, however, as shown in Fig. 1 represents a considerable change. Although the design of this portion as shown is tentative, pending outcome of a full-scale mock-up test, work is proceeding on the basis that it will be final.

SECTION A-A

CATALYST

GAS INLET

STEAM IN FOR
PREHEATING

ELECTRIC HEATER

A   A

CATALYST

CONDENSATE OUT

THERMOCOUPLE LEADS

OUTLET

FIG. 1.

EXPERIMENTAL CATALYTICAL RECOMBINER

8

Steam in
SILICA GEL ABSORBER
Water out
HELIUM STATION

STEAM DRUM
3000 lb/hr 200 psi Sat
SAFETY VALVE
BLOWOFF
2000 lb/hr 250 psi Sat Bldg Steam

CW Make-up
EMERGENCY COOLING WATER SURGE TANK
Vent
Drain
Liquid Freon
CW Tubes

He ~1050 psi
To Stack
CHARCOAL ABSORBER

CONTROL ROD SYSTEM
PRESSURIZER 1000 psi
1500# Steam in
Cond.

DEMIN. WATER 6 GPM 200 psi 286°F
SOUP PUMP
Oil out
HEAT EXCHANGER
Oil in
To Hot Waste
Trap
Bldg Cond Steam
To Stack
Vacuum Pump
CHARCOAL ABSORBED

GENERATOR
TURBINE

CATALYTIC RECOMBINER
D₂O GAS CONDENSER
Water out
Water
300°F

14,800 lb/hr 302°F
H₂O COOLER
Boiler Feed Water

407°F
482°F
41,600 lb/hr

From D₂O Cooler
To D₂O Cooler
Liquid Freon
CATALYTIC RECOMBINER
SOUP GAS FLAME RECOMBINER
COLD TRAP
Water out
CONDENSER
Atmos.
HOT WELL
Water out

COLD TRAP
Water in
D₂O OFF-GAS CONDENSER
Oil in
Oil out
D₂O PUMP
Rupture Disc
CORE
REFLECTOR VESSEL

Demineralized Water Make-up 1 GPM Max 228°F 20 psi Sat
HOT WELL PUMP
FEED WATER 125°F

VAPOR HEADER
Rupture Disc
D₂O DUMP VALVE
347°F
HEAT EXCHANGER
Rupture Disc
SOUP DUMP VALVE
PURGE PUMP
Decant Fill
Water in
CONDENSATE TANK
SOUP GAS COND.
CWD
FEEDWATER STORAGE

0.1 GPM/hr
D₂O DUMP TANK
D₂O Let-down Valve
Soup Let-down Valve
380 lb/hr Soup 70 lb/hr Steam 30 lb/hr Gas ~320°F

TURBINE PUMP
TRIPLEX PUMP

D₂O EVAPORATOR
D₂O FILTER
D₂O FEED PUMP 3.0 GPM Capacity
SOUP FEED PUMP
SOUP FILTER
To Hot Waste
CONDENSER
OUTER DUMP TANKS
Steam in
Cond out

CARRIER

SECRET

VALVE & LINE SYMBOLS
Instrument Operated Valve
Manual Operated Valve
Check Valve
Liquid Process Lines
Vapor & Gas Lines
Helium Lines

FIG. 2
HRE
SIMPLIFIED FLOW DIAGRAM
AT 1000 KW OPERATION
C-9598
Drawn: C.W.Day 5-15-51

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PRESSURIZER VENT

SAFETY PLATE DRIVE

PRESSURIZER

COOLING JACKET

HELIUM IN

GAS & SOUP LET DOWN

SOUP LEVEL LINES

SOUP OUT

PRESSURIZER STEAM IN

COOLING WATER OUT

SOUP IN

REFLECTOR IN

CATALYTIC RECOMBINER

CONDENSATE OUT

REFLECTOR VESSEL

HELIUM OUT

REGULATING PLATE

REFLECTOR FLOW LINER

CORE TANK

SAFETY PLATES

BRIDGE TUBE

ION CHAMBER THIMBLE

CORE TANK DRAIN

REFLECTOR OUT

APPROX. SCALE IN FEET

0   1   2   3

FIG. 3
REACTOR TANK ASSEMBLY

Study of gas generation in the soup feed pump indicates that a shutdown time of less than one minute will be sufficient to gas bind the pump. Provision is being made to bleed the gas out of the high-pressure side of the pump into the soup dump-tank vapor space.

Reflector System. Condensers for the reflector system are completed and installed as double pipe exchangers so that joints on the D_2O side will not be exposed to light water as would be the case with shell-and-tube type condensers.

Reflector dump tanks have been installed with cooling-water jackets for emergency cooling. These jackets have been designed to be welded to the tanks at only one point to eliminate stresses due to differential thermal expansion.

All piping design for the reflector compartment is complete and approximately 50% has been installed. Figure 4 is a pictorial view of the piping in this compartment.

Emergency Cooling System. A natural-convection cooling system is designed as shown in Fig. 5. Calculations for this system show that immediately following dump of the soup and reflector into the dump tanks, boiling will occur in the jackets until heat stored as enthalpy in the solutions at high pressure has been reduced to correspond to that at lower pressures in the dump tanks. An equilibrium condition will be reached after boiling approximately 30 gal of water, at which time the finned-tube natural-convection system will remove up to 28 kw of heat without boiling. Under this equilibrium load the following conditions will exist:

Heat-removal rate	95,500 Btu/hr
Velocity in 2-in. pipe	0.727 ft/sec
Mass flow rate	3,360 lb H_2O/hr
Temperature of hot leg	174°F
Temperature of cold leg	145°F

As a result of these calculations several changes have been made in design of the system. A pressure relief valve set at 15 psi gauge has been specified for the surge tank vent so that under boiling conditions the system will operate at that pressure giving a greater Δt for condensation of steam in the finned tubes. The surge tank has been placed at the top of the cold leg instead of the hot leg so that steam rising from the jackets must pass through the finned tubes before escaping. It is felt that with these modifications the quantity of water evaporated from the system will be held to a minimum.

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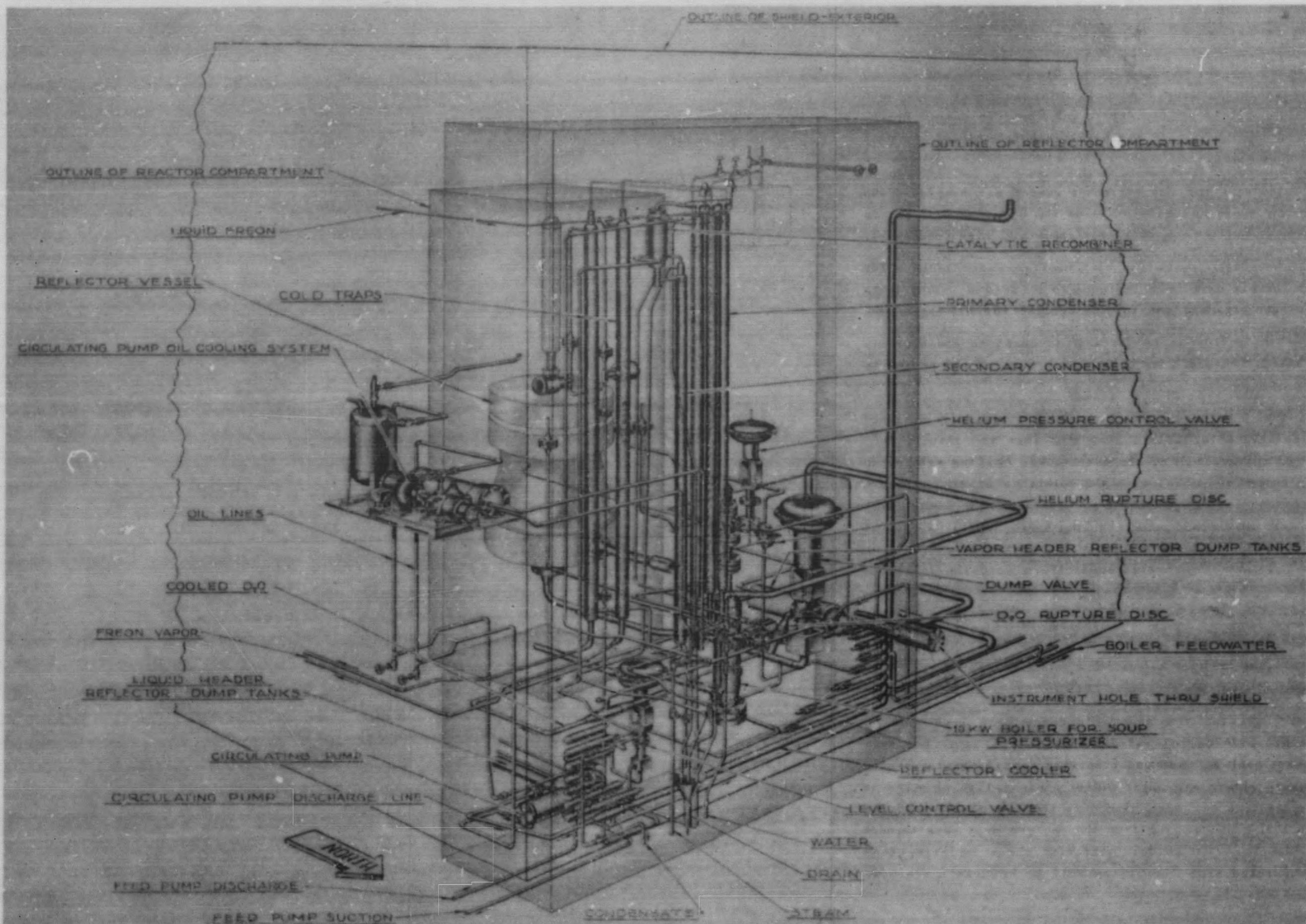
FIG 4
REFLECTOR COMPARTMENT PIPING

Labels:
- OUTLINE OF SHIELD-EXTERIOR
- OUTLINE OF REACTOR COMPARTMENT
- LIQUID FREON
- REFLECTOR VESSEL
- COLD TRAPS
- CIRCULATING PUMP OIL COOLING SYSTEM
- OIL LINES
- COOLED D2O
- FREON VAPOR
- LIQUID HEADER REFLECTOR DUMP TANKS
- CIRCULATING PUMP
- CIRCULATING PUMP DISCHARGE LINE
- FEED PUMP DISCHARGE
- FEED PUMP SUCTION
- OUTLINE OF REFLECTOR COMPARTMENT
- CATALYTIC RECOMBINER
- PRIMARY CONDENSER
- SECONDARY CONDENSER
- HELIUM PRESSURE CONTROL VALVE
- HELIUM RUPTURE DISC
- VAPOR HEADER REFLECTOR DUMP TANKS
- DUMP VALVE
- D2O RUPTURE DISC
- BOILER FEEDWATER
- INSTRUMENT HOLE THRU SHIELD
- 15 KW BOILER FOR SOUP PRESSURIZER
- REFLECTOR COOLER
- LEVEL CONTROL VALVE
- WATER
- DRAIN
- STEAM
- CONDENSATE

FIG 4

OFFICIAL USE ONLY
DWG. NO. D-8303

INNER DUMP TANKS

SHIELDING OUTLINE

CONDENSER

OUTER DUMP TANKS

FIG 3
H.R.E.
EMERGENCY COOLING SYSTEM

Steam System. Shop drawings of the 250-kw steam turbo-generator and the 400-ft^2 surface condenser have been completed by Worthington Pump and Machinery Company and approved by ORNL. Shipment of the condenser is scheduled for August 1, 1951, and the turbo-generator for October 1, 1951.

Drawings of turbine foundations and pipe trench have been approved and issued for construction.

Shield. Figure 6 illustrates the general arrangement of the reactor shield structure. Construction drawings of the shield have been approved and issued to the field.

It may be noted that access to all interior parts of the shield is from above, except for instrument tubes. The shield will be constructed primarily of solid concrete blocks, the outer two courses being laid in mortar and the inner ones being stacked. All blocks are of barytes aggregate and the first two courses next to the reactor tank contain colemanite ore to reduce the induced activity in the shield. Removable top plugs are of precast concrete.

Control. The principal effort of the control group has been devoted to checking out the control components and to a re-examination of the operation of the system in the light of new information. The D_2O system is now stablized and the changes in its control are indicated on the flow sheet. Study of the soup system is still open as component development progresses.

The essential changes in the D_2O system involve measurements in the off-gas section. The functioning of the recombiner will be checked by a temperature determination of the catalytic bed. For an insulated recombiner this temperature is an accurate indication of the composition of the gas passing through the bed. As a check against loss of D_2, the exit gas stream is analyzed by a platinum-filament hydrogen detector in the off-gas line beyond the cold traps. Water-flow and temperature instruments are provided on the recombiner condenser to permit a determination of the amount of gas being recombined.

The soup off-gas system control has been revised to function with the new off-gas system. Study of the gassing problem immediately after a shutdown indicated the need for a means of handling an appreciable amount of gas in the pressurizer. This is provided by operating the pressurizer vent valve by an excess pressure signal from the pressurizer pressure controller.

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DWG. NO. 12056

REMOVABLE
SHIELD PLUGS

EMERGENCY COOLING
WATER SURGE TANK

STEAM COMPARTMENT
4'-0"x 12'-0"x 16'-3"

REACTOR
COMPARTMENT
4'-6"x 4'-6"x 16'-3"

SOUP
COMPARTMENT
5'-6"x 9'-6"x 19'-6"

INSTRUMENT
HOLES

VALVE PIT

SOUP PUMP PIT

REFLECTOR PUMP PIT

STEAM PIPE
TRENCH

REFLECTOR
COMPARTMENT
5'-0" x 12'-4"x 19'-6"
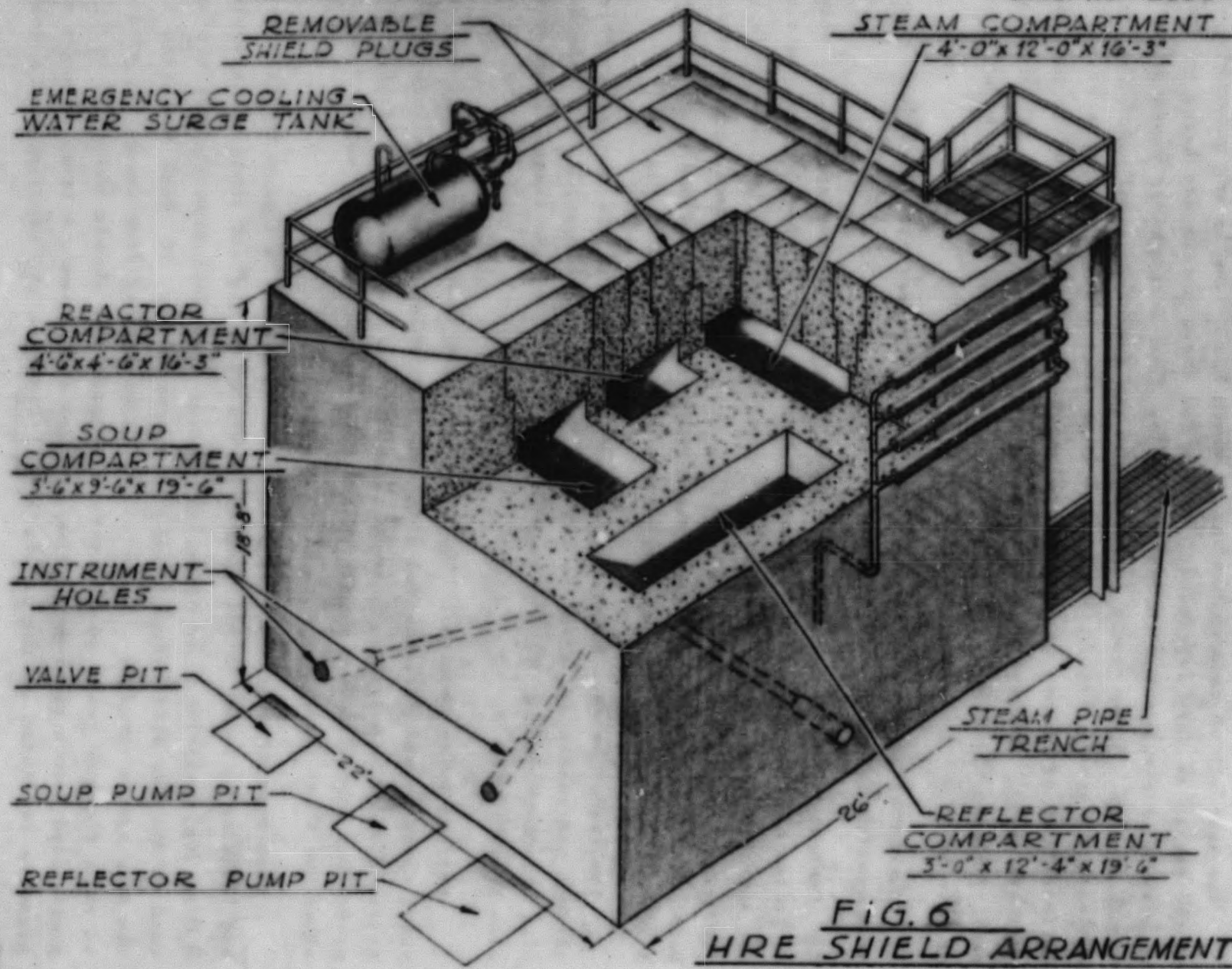
FIG. 6
HRE SHIELD ARRANGEMENT

The shut-off of soup-system valves which block flow to any external part of the system is very important. Valves for these points are being checked by measuring air leakage through the valve from atmospheric pressure to a vacuum chamber. These checks indicate that new stainless steel—stellite trim valves will give a liquid leakage of less than 1 cc/month for a pressure differential of 15 psi across the valve when the operator has 15 psi air pressure on it. Increasing the operator pressure will decrease this leakage still further. Stellite-stellite trim valves are worse than this by a factor of 5 to 10.

A control manual for the HRE will be written and published during the next quarter as a separate report.

Control Rod Drives. A complete assembly of one control rod and its drive mechanism has been built and is being tested. A 1/16-in. boral plate containing approximately 190 mg of boron per square centimeter has been successfully fabricated, and a sample assembly of control plates has been made in which boral plates are enclosed between stainless steel plates welded at the edges. A general arrangement of these drives and plates is shown in Fig. 3.

Instrument Holes. General arrangement and uses of the instrument holes through the shield are given in Fig. 7. Detailed construction of a tube and plug are shown in Fig. 8. The method of withdrawal of the fission chamber is also shown in Fig. 8.

Bellows Valve Operator. The endurance test of the experimental bellows valve operator was discontinued after 400,000 cycles owing to failure of the solenoid valve supplying air to it. On the basis of this test, design of a production model has been completed and drawings issued to the shop. Figure 9 shows the final design.

Leak-Detection System. It is planned to install a system for detection and location of leaks in all flanged joints in piping and vessels containing D_2O or fuel solution. Separate but similar leak-detection systems will be used on the two different liquids. As shown in Fig. 10, leak detection for the soup system consists of a pressurized tube leading from the gasket grooves of each flanged joint to a manifold outside the shield which is in turn pressurized from a receiver containing water and helium. A level detector and pressure indicator on the receiver will indicate the existence of a leak.

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FIG. 7

CODE TANK

REFLECTOR VESSEL

TYPICAL INSTRUMENT THIMBLE

TYPICAL INSTRUMENT LINER

FISSION CHAMBER OUTER PLUG

FISSION CHAMBER INNER PLUG

OUTER FACE OF SHIELD

SPACE FOR SHIELD MATERIAL

FISSION CHAMBER

INSTRUMENT LEADS

2'-9"
Instrument Travel

1'-0"

6'-0"
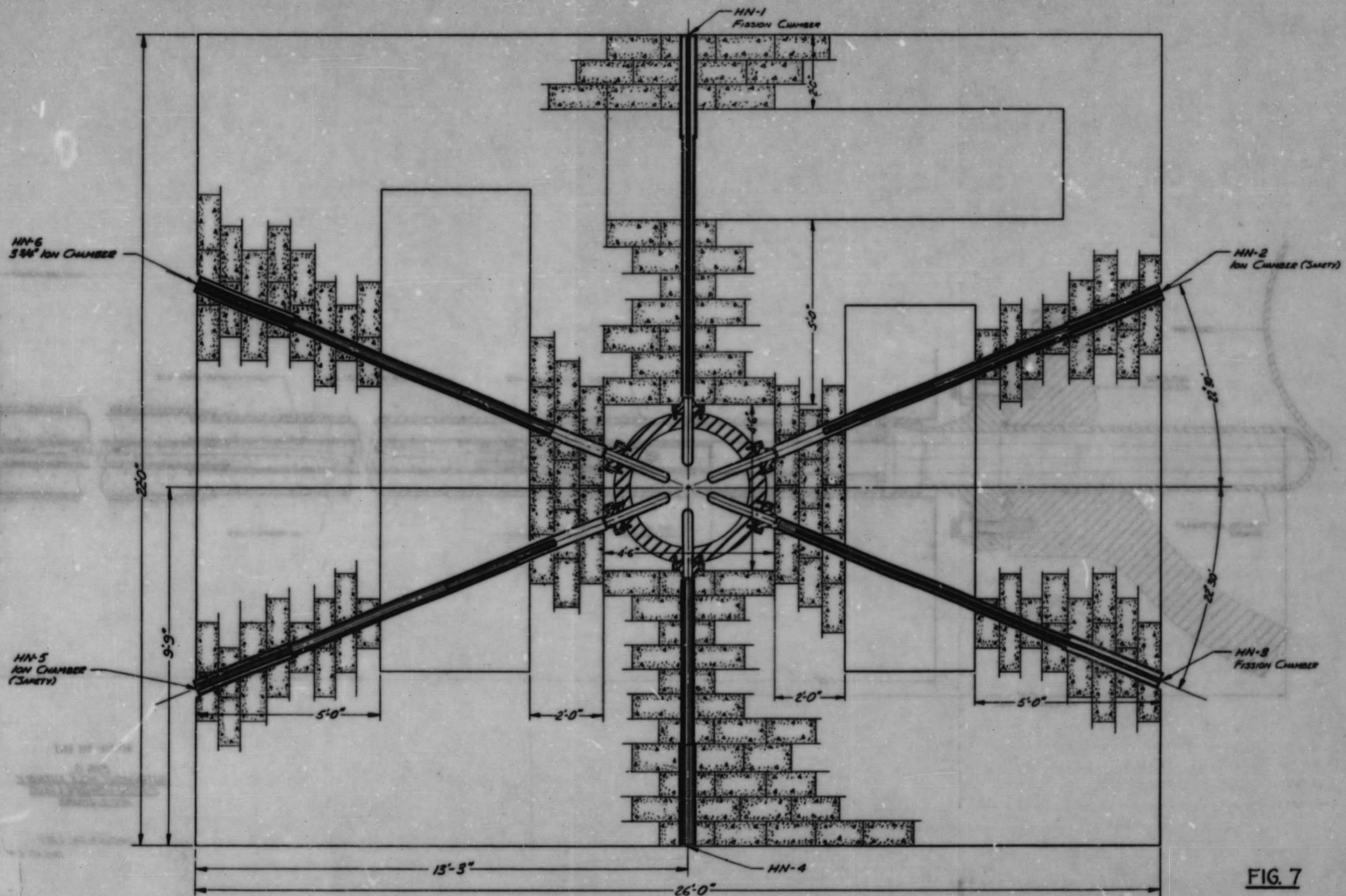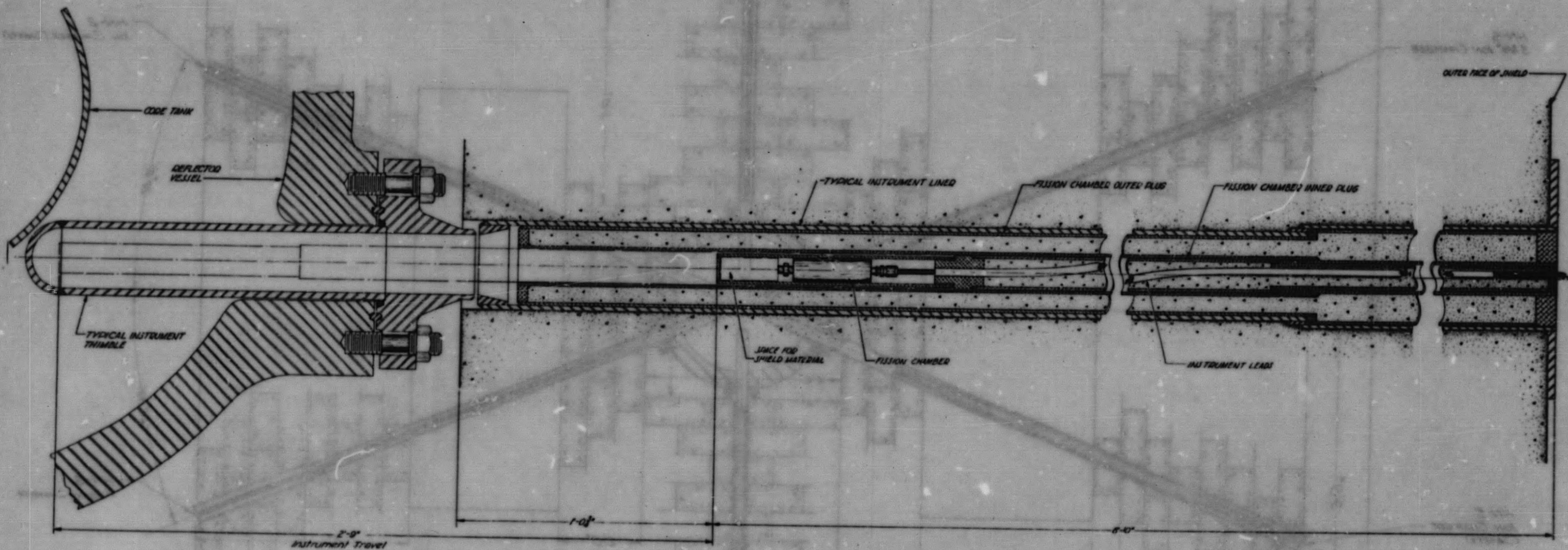
FIG. 8
INSTRUMENT HOLE ASSEMBLY
FISSION CHAMBER & PLUG
HN-1 SHOWN

Drawn C.W. Day 5-28-51

DWG. NO. E-8312

CAST ALUMINUM SPRING COVER

STEEL ADJUSTING NUT

STEEL SPRING FROM FOXBORO DIAPHRAGM
TYPE VALVE ACTUATOR

SOFT ALUMINUM GASKET

OILITE BRONZE BEARING

AIR IN FOR NORMALLY
OPEN OPERATION

CAST ALUMINUM SYLPHON CASING

CAST ALUMINUM BRACKET ADAPTER

BRASS SYLPHON BELLOWS ASSEMBLY

CAST ALUMINUM YOKE

AIR IN FOR NORMALLY
CLOSED OPERATION

STEEL BRACKET

YOKE AND BRACKET INTERCHANGEABLE
TO REVERSE OPERATION OF VALVE

FIG. 9
BELLOWS VALVE OPERATOR
FOR USE IN PLACE OF DIAPHRAGM OPERATOR
IN HIGH RADIATION ZONES

BELLOWS-SEAL VALVE

Pressurizing
Helium Line

Gauge

1100 PSI Helium

Liquid Level
Alarm

Liquid Level

Fill

Spark Plug

Drain

⅛"S.Steel Tubing

S.S. Autoclave Tubing

Autoclave Fitting

S.S. ⅛"Std. Tee

Weld

Silver Solder

Weld

S.S. ⅛"Std. Pipe

See Detail A

Header

DETAIL A
SHOWING TUBE & TEE FITTING
Typical All Header Fittings

Face of Shield

See Detail B

TYPICAL LEAK DETECTION FITTING
ALL FLANGES

Ring
Gasket

Autoclave Fittings

⅛"S.S Tubing

DETAIL B

FIG. 10
PROPOSED LEAK DETECTION SYSTEM
SCHEMATIC DIAGRAM

DWG. NO. B-9579
Drawn: C.W.Day Date: 6-4-51

Location of this leak may be determined by checking individual lines. Water pressure will be maintained slightly higher than the soup pressure so that leakage will all be into the soup system.

Status of HRE Construction. The new building for the HRE was occupied about March 1. Since that date all underground service lines have been installed and the shielding structure raised to the floor level. Equipment and piping for the heavy-water system is being installed as it becomes available. Over-all completion is approximately 20%. Progress of HRE construction is shown in Figs. 11 and 12.
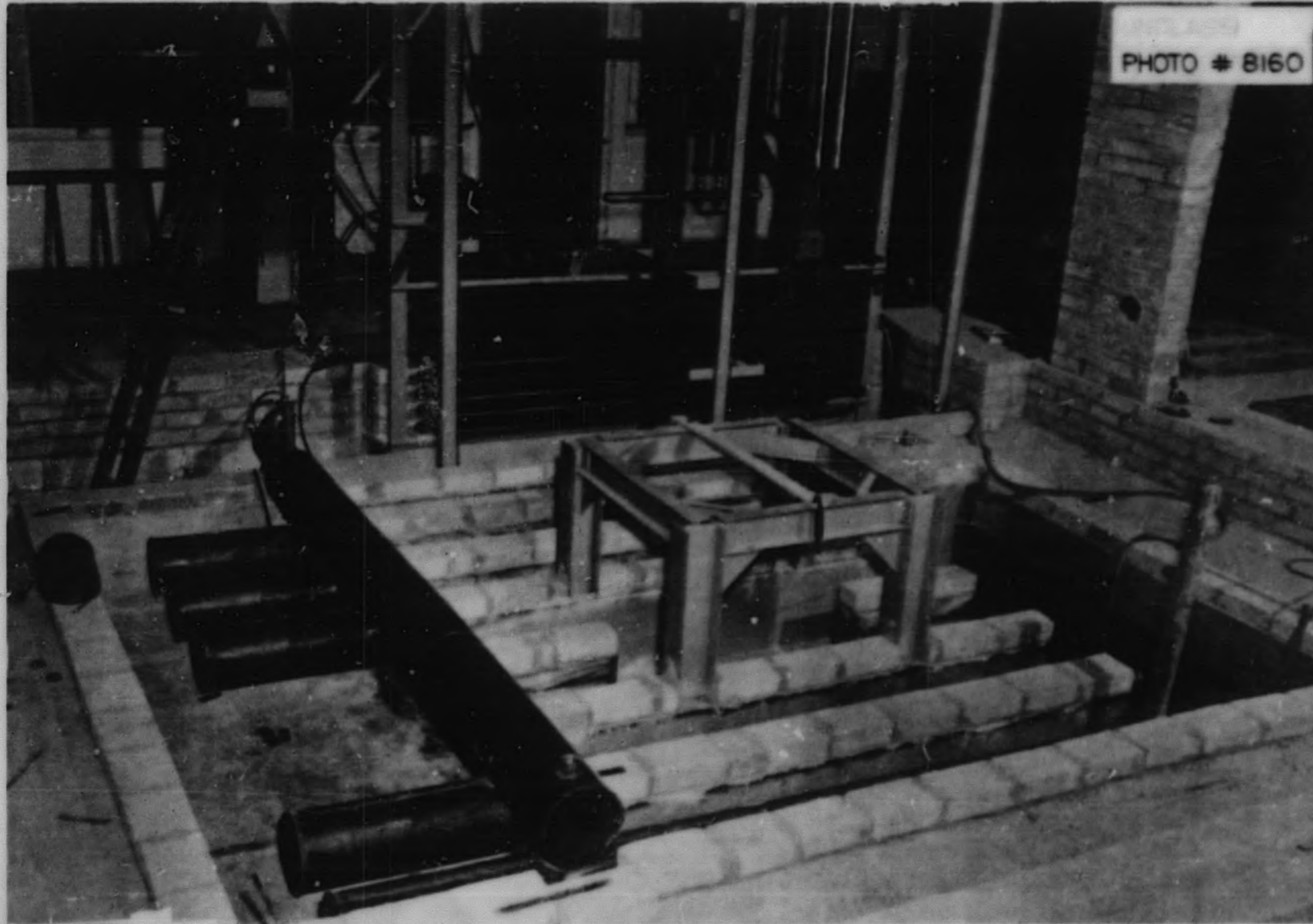
PHOTO # 8160

FIG. 11 PROGRESS OF HRE CONSTRUCTION

SHOWING PLACEMENT OF D_2O DUMP TANKS, D_2O CELL PIPING, AND REACTOR SUPPORT FRAME

PHOTO # 8159
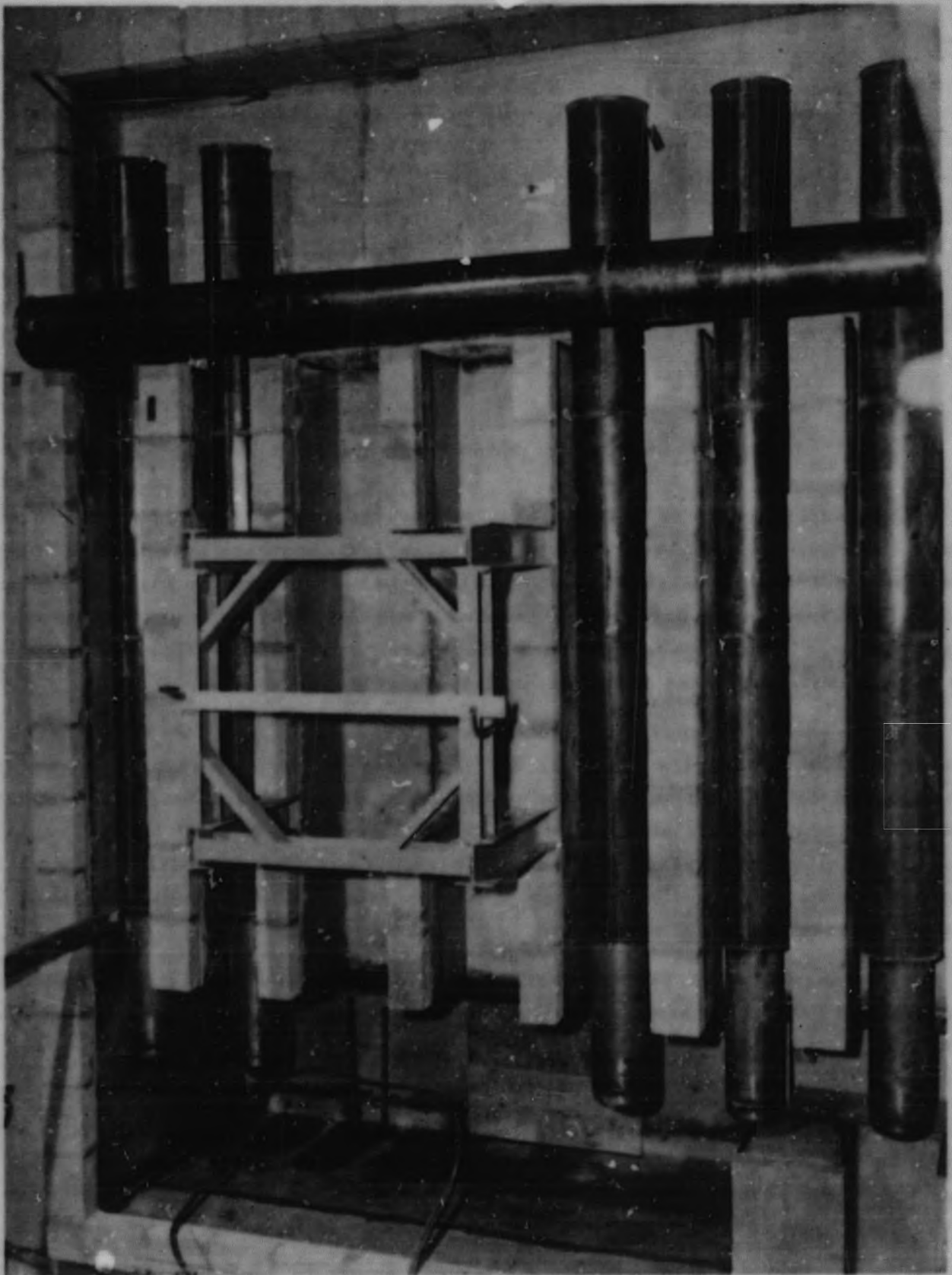
FIG. 12 PROGRESS OF HRE CONSTRUCTION
OVERHEAD VIEW OF D_2O DUMP TANKS AND REACTOR SUPPORT FRAME

2. CORROSION: UO_2SO_4—H_2O—347 STAINLESS STEEL SYSTEM

Static, Out-of-Pile Tests	Pump Loop Studies	Studies of Corrosion Variables
J. L. English	E. G. Bohlmann	Series I: M. H. Lietzke
A. R. Olson	C. G. Heisig	
J. Reed	H. C. Savage	Series II: M. D. Silverman
S. H. Wheeler	R. Wacker	
H. Barker	A. L. Davis	Electrochemical Corrosion Studies
J. W. Brown	C. M. Burchell	
L. L. Fairchild	W. B. Krick	J. C. Griess
R. F. Benson	R. Smith	
	J. F. Winsette	
	T. C. Weeks	

STATIC, OUT-OF-PILE TESTS

A general review of some aspects of the passivity imparted to stainless steel by chemical pretreatments and a program for study are presented. It was determined that the metal surface condition of test bombs in which stainless steel specimens were pretreated exerted a marked influence on the physical appearance of the samples. Old surfaces resulted in dull-appearing films while new metal surfaces produced lustrous sample surfaces.

The results of tests on the effectiveness of oxygen for maintaining a passive film in uranyl sulfate at 250°C were erratic. The inconsistency was attributed to the previous test history of the autoclaves used for the study. In untreated stainless steel systems at 250°C the reduction of uranyl sulfate was gradual during the first 4 hr, and reduction was nearly 100% complete during the next 4 hr. The thickness loss on untreated 347 stainless steel in uranyl sulfate at 250°C was 0.1 mil after 24 hr.

The operation of two thermal test loops in uranyl sulfate at 250°C is described. One loop was pretreated with 1% nitric acid; the other loop was not pretreated but the uranyl sulfate test solution was made 1% in nitric acid. Both runs were classed as successful.

The corrosion resistance of various types of titanium metal in uranyl sulfate at 250°C remains excellent. Zirconium metal containing 3 to 5% tin has shown excellent corrosion resistance.

Uranyl nitrate corrosion studies at 150°C were started. Of the materials tested, titanium and zirconium showed superior resistance. Uranyl fluoride tests at 150°C showed solution reduction at the end of 168 hr in untreated stainless steel bombs. There was no solution reduction when the bombs were initially pretreated in 1% nitric acid. Illium R exhibited the best corrosion resistance in an untreated condition to uranyl fluoride at 150°C contained in pretreated bombs; the corrosion rate was 0.4 mil/year after 500 hr.

The corrosion resistance of SAE 1030 carbon steel, of which the HRE pressure vessel is constructed, in distilled water containing small amounts of hydrogen peroxide was determined at 200°C. Galvanic couple tests with 347 stainless steel were investigated also. The addition of 275 ppm of trisodium phosphate served as an effective corrosion inhibitor even with hydrogen peroxide initially present.

Status of Corrosion Testing Equipment

Stagnant corrosion test autoclaves for use at 250°C have been increased to a total of 88. Plans are in process to fabricate approximately 20 thermal-convection test loops of various types of stainless steels suitable for uranyl sulfate exposure at 250°C. Ten 2-liter capacity autoclaves for stagnant corrosion testing will be fabricated from stainless steels, titanium, and zirconium.

Twelve new stainless steel autoclaves for stagnant corrosion studies at elevated temperatures have been received and will be used to investigate uranyl fluoride systems. The autoclaves have an individual capacity of 225 ml.

The six stainless steel thermal-convection loops previously described[1] have become inoperative owing to failure of the electrical heating system. These loops were designed for operation at 250°C by means of calrod heating elements metallized directly onto one leg of the loop. This type of heating arrangement resulted in frequent and early burn-out of the calrod units and localized hot-spots. New thermal loops are being designed using nichrome ribbon as a heat source. It is planned to fabricate 20 of these loops to study uranyl sulfate, uranyl nitrate, and uranyl fluoride systems at elevated

(1) J. L. English et al., "Out-of-Pile Corrosion," Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950, ORNL-925, p. 107, esp. 109 (Jan. 30, 1951).

temperatures. The loops will be constructed of type 309 niobium stabilized stainless steel, type 347 stainless steel, type 316 extra-low carbon stainless steel, type 316 niobium stabilized stainless steel, Carpenter 20, and titanium.

Six autoclaves, 1500 ml in capacity, are being designed for use in high-temperature studies. These autoclaves will be equipped with sample cells to permit solution withdrawal at operating temperature. The design will be such that interchangeable liners of various materials may be substituted. Titanium and zirconium corrosion will be investigated in this manner.

The component parts for a 150-gal dynamic system, 347 stainless steel construction, have been fabricated during the past quarter. This unit will operate with uranyl sulfate at 100°C and velocities approaching 25 ft/sec.

The Corrosion Laboratory is undergoing expansion to increase the 100°C corrosion test facilities by 30 units'. The total expanded capacity will be 100 units.

Corrosion Studies

The results of corrosion studies during the past quarter will be treated under the following headings: (1) Pretreatment Films on Stainless Steels, (2) Stainless Steel Thermal Loop Tests, (3) Corrosion of Titanium, (4) Corrosion of Zirconium, (5) Uranyl Nitrate Corrosion Studies, (6) Uranyl Fluoride Corrosion Studies, and (7) Corrosion of Reflector Materials.

1. **Pretreatment Films on Stainless Steels.** The use of either 1% by weight of 70% nitric acid or 2% by weight of chromium trioxide (CrO_3) at 250°C imparted passive characteristics on stainless steels used to contain uranyl sulfate solutions at 250°C. The characteristics of these pretreatment films, as determined by stagnant corrosion studies, were described in the last quarterly progress report.[2] Both types of films appear to be hydrous oxides. In the case of the nitric acid film, which has received the most study, it appears that passivity is not entirely due to the formation of a bulk oxide film. An additional factor, possibly chemisorbed oxygen or water of crystallization, may be an inherent component of the oxide film in the

(2) J. L. English and A. R. Olsen, "Film Studies on Pretreated Stainless Steel," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951*, ORNL-990, p. 43 (May 18, 1951).

over-all mechanism of passivity. This assumption is based on several rather conclusive laboratory studies as follows:

a. Passivity was not conferred on stainless steel merely by heating autoclave surfaces in circulating air at 250°C for periods of 24 hr. Such pretreatment could result only in a thickening of the normal oxide film on the stainless steel. In subsequent tests with uranyl sulfate at 250°C this oxide film alone was not sufficient to prevent reduction of the sulfate solution, i.e., there were no passive properties present.

These results indicate that with nitric acid pretreatments at 250°C. the presence of oxygen or nitric oxide from the thermal decomposition of the nitric acid serves not only to promote oxide film formation on the stainless steel surfaces. but also may become an essential part of the film as adsorbed atomic or molecular oxygen.

b. Stainless steel specimens pretreated in either nitric or chromic acids at 250°C lost the passivity effects imparted by these treatments if the specimens were allowed to remain exposed to air at room temperatures for periods exceeding 3 days. These specimens when later subjected to uranyl sulfate at 250°C caused reduction of the sulfate solution. Such behavior would indicate that initial film formation at 250°C was occurring under metastable conditions. Extended exposure to air at room temperature caused a reversion to the normal oxide film with a loss of some constituent, such as water of crystallization or possibly adsorbed oxygen, from the film. If, after pretreatment, the specimens were allowed to stand in water or uranyl sulfate at room temperature for periods exceeding 3 days. there was no resultant loss of passivity during subsequent exposure in uranyl sulfate at 250°C.

The two phenomena described in (a) and (b) are considered significant as affording a means to study more closely the general mechanism of pretreatment films. Future studies will be concentrated on these two phases with the ultimate objective of determining whether or not the passivity on stainless steels after pretreatment is a result of bulk oxide formation alone or whether other constituents, oxygen and/or water of crystallization, is contributing to the over-all mechanism of passivity.

Sufficient data have been collected on the stagnant corrosion behavior of pretreated stainless steels in uranyl sulfate at 250°C to conclude that:

a. If the protective film, obtained by nitric or chromic acid pre-treatments. is properly formed on stainless steel surfaces, there is no measurable loss in the uranium content of a 0.17 M uranyl sulfate solution (analyses are based on initial and final values over exposure periods of 1 week).

b.   Corrosion attack on various types of pretreated stainless steels
     is almost negligible (<1 mil/year) when condition (a) prevails.

For these reasons emphasis will be placed upon a study of the pretreatment
mechanism rather than a continuation of purely routine corrosion studies.   The
following investigations will be made during the forthcoming work period:

a.   The effect of temperature on the nature and properties of nitric
     acid and chromic acid pretreatment films. Temperatures of 150,
     200, and 250°C will be studied.

b.   The effect of metal surface condition on the characteristics of
     pretreatment films. This study will include various degrees of
     abraded finishes and chemically etched surfaces. Temperature
     variations will be included also.

c.   The effect of increasing concentrations of nitric and chromic
     acids and other oxidants on the stability of these films in
     uranyl sulfate solutions at 250°C.

These investigations will be supplemented by X-ray—diffraction studies and
chemical analyses of pretreatment films stripped from the metal surfaces.

Investigations completed during the past quarter concerned with pretreat-
ment films are discussed in the following paragraphs. In many cases, complete
analytical results were not available due to the time delay in processing
samples. In the interim, the criteria employed for judging whether or not a
specific corrosion test was performing satisfactorily were: (a) visual
observation of the test solution; (b) measurement of solution pH, and (c) phys-
ical appearance and weight variations of the corrosion test specimen. Proper
evaluation of these three conditions invariably resulted in valid interpreta-
tion of a corrosion test as verified later by the results of chemical analyses
on the test solutions.

*Effect of Surface Condition vs. Exposure Time on Nitric Acid Film Forma-
tion at 250°C.* The physical appearance of nitric acid—formed films on type
347 stainless steel specimens varied from specimen to specimen. Most of the
samples continued to remain highly lustrous with brilliant interference tints
after 24 hr in 1% by weight of 70% HNO_3 at 250°C. However, the samples
frequently showed dull-black coatings which were still extremely adherent but
much thicker than those which normally appeared on the treated specimens.

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These black colored specimens exhibited the same excellent degree of passivity in uranyl sulfate as the samples having thin, lustrous films. It was suspected that perhaps the previous test history of the stainless steel autoclaves (or bombs) was accounting for the differences in appearance. Many of the pretreatments were run in test autoclaves that had been pretreated many times, had been subjected to uranyl sulfate exposures with and without solution reduction, and had been chemically etched to remove adhering uranium oxides and corrosion products.

To determine exactly if the previous autoclave test history was influencing the appearance of the nitric acid pretreatment, four old and four new autoclaves were prepared for test. The old bombs selected had been in operation for 9 months during the uranyl sulfate-corrosion testing program. These bombs were first cleaned in a HNO_3-H_2O_2 mixture to dissolve any uranium oxides, washed and scrubbed in distilled water, etched 10 min in 10% HNO_3—4% HF—1% HCl (by volume) at 60°C, and washed and scrubbed thoroughly in hot distilled water. The new bombs had not been used previously for sulfate testing.

The new and old bombs with type 347 stainless steel samples were treated with 1% HNO_3 at 250°C for periods of 1, 4, 8, and 24 hr. The solutions were analyzed for iron, nickel, and chromium at the end of each run. Complete data are listed in Tables 1 and 2. The type 347 stainless steel specimens were prepared in the same manner for all tests. Preparation consisted of abrading on Nos. 80 and 120 grit paper followed by degreasing in acetone and alcohol.

An examination of the chemical analyses showed that:

a. The dissolved iron concentration in both new and old bombs leveled off at 1 ppm after 1 hr at 250°C. This is not a true measure of the dissolution rate of iron since it has been established that iron precipitates from solution as a Fe_2O_3. The small quantities of brown precipitate observed in five of the final test solutions were iron oxides.

b. The dissolved nickel gradually decreased in concentration from 32 to 8 ppm in the old bombs, while in the new bombs it increased steadily from 59 to 97 ppm. Chromium, on the other hand, exhibited a tendency to increase in concentration in the old bombs, and, with one exception, remained low and fairly constant in concentration during the 24 hr in the new bombs. Thus, it appears that on old surfaces nitric acid selectively attacks chromium in preference to nickel over an extended period of time while on newly machined surfaces the situation is reversed, i.e., nickel undergoes selective attack in preference to chromium.

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TABLE 1

Chemical Analyses of Nitric Acid—Pretreatment Solutions

BOMB TYPE	EXPOSURE (hr)	INITIAL pH	FINAL pH	DISSOLVED IONS (ppm)		
				IRON	NICKEL	CHROMIUM
Old	1	1.13	1.05	4	32	7
Old	4	1.13	0.72	1	11	20
Old	8	1.13	1.15	1	19	6
Old	24	1.13	0.50	1	8	33
New	1	1.13	1.05	5	59	4
New	4	1.13	0.82	1	65	<1
New	8	1.13	1.20	1	60	109
New	24	1.13	0.50	<1	97	8

TABLE 2

Corrosion Behavior of Type 347 Stainless Steel in 1% Nitric Acid at 250°C

BOMB TYPE	EXPOSURE (hr)	WEIGHT CHANGE (mg/cm²)	SOLUTION CONDITION	SAMPLE APPEARANCE
Old	1	-0.127	Water white; no precipitate	Shiny black-brown streaks
Old	4	-0.030	Pale yellow; slight brown precipitate	Dull gray-black film
Old	8	-0.015	Pale yellow; no precipitate	Dull gray-black film
Old	24	-0.066	Strong yellow color; no precipitate	Shiny black-brown color
New	1	-0.015	Water white; slight brown precipitate	Lustrous golden-pink color
New	4	+0.086	Water white; slight brown precipitate	Lustrous pink interference tint
New	8	* +0.015	Water white; slight black precipitate	Lustrous green-pink color
New	24	-0.056	Water white; no precipitate	Lustrous black color

Although the test specimens were prepared initially in the same manner, their resulting appearances as removed from both types of bombs were markedly different. Specimens removed from the new bombs were lustrous with brilliant colors due to interference patterns. The specimens removed from the old bombs were black in color, and, in two cases, they were dull in appearance. These samples have been submitted for X-ray—diffraction studies in order to discern any differences in the structure of the films. The yellow color appearing in the nitric acid solutions in the old bombs after 4, 8, and 24 hr was attributed to the oxidation of metallic chromium to chromium(VI) by the nitric acid.

Effect of Continuous Long-Time Exposure on Film and Solution Stability at 250°C. A group of tests was run with 0.17 M uranyl sulfate solution at 250°C contained in nitric acid—pretreated stainless steel bombs which remained closed for periods of 1 to 6 weeks. The object of these tests was to confirm the necessity for oxygen to repair and maintain the passive film. The test bombs were chemically cleaned and pretreated for 24 hr in 1% HNO_3 at 250°C. Type 347 stainless steel samples were treated in similar fashion. The uranyl sulfate solutions and samples were placed in the bombs and heated to 250°C. One bomb from the original group of six was removed weekly, so that continuous exposure was obtained over a period of 1 to 6 weeks. The data from these tests appear in Table 3.

TABLE 3

Effect of Continuous Exposure on Film Stability in Uranyl Sulfate at 250°C

Initial uranium: 38.7 g/liter

EXPOSURE (weeks)	INITIAL pH	FINAL pH	FINAL URANIUM (g/liter)	SAMPLE WEIGHT CHANGE (mg/cm²)	SAMPLE APPEARANCE
1	2.4	2.4	39.3	0.00	Dull black film
2	2.4	2.3	36.3	0.12	Shiny blue-black film
3	2.4	1.3	28.6	+3.55	Uranium oxide scale
4	2.4	2.0	39.7	+0.03	Lustrous red-brown film
5	2.4	2.4	40.5	-0.04	Shiny black film
6	2.4	2.3	Not available	-0.03	Dull black film

A decrease in total uranium content was found as the exposure time increased to 3 weeks. The sample removed at the end of the 3-week test exhibited a weight gain due to the accumulation of uranium oxides on the surfaces. A reduction of 26% in total uranium occurred during this run and the solution pH dropped from 2.4 to 1.3. Chemical analyses for the fourth- and fifth-week tests showed no reduction in total uranium content from the original value. This phenomenon was not expected after the behavior during the first 3 weeks. One possible explanation for the failure of the solutions to undergo reduction may lie in the previous test history of the bombs used in these tests. The bombs had been subjected to numerous pretreatments, solution reductions, and routine tests in uranyl sulfate at 250°C. Variations in surface condition may contribute to the erratic results.

Additional tests to investigate the oxygen effect on film stability will be run at 250°C in uranyl sulfate solutions. These will include:

a. Continuous exposure of 1 to 6 weeks in newly machined stainless steel bombs which were pretreated for 24 hr in 1% HNO_3 at 250°C.

b. Continuous exposures of 1 to 6 weeks in untreated newly machined stainless steel bombs. The uranyl sulfate solution will contain 1% HNO_3.

c. An investigation to study the effects of complete oxygen deaeration and various partial pressures of oxygen on nitric acid-- pretreated surfaces.

Uranyl Sulfate Solution Stability at 250°C as a Function of Exposure Time in Untreated Stainless Steel Systems. Corrosion tests were run in type 347 stainless steel bombs using 0.17 M uranyl sulfate solution. The bombs, previously used for other tests, were cleaned at room temperature for 4 to 6 hr in 20% hydrochloric acid containing 0.5% Rodine No. 60 (a high-molecular-weight complex organic compound used as an inhibitor). After thorough washing in distilled water, the bombs were further cleaned by exposure for 1 hr in 10% HNO_3 at 130 to 140°C. A final scrubbing and rinsing in distilled water followed. Type 347 stainless steel test specimens, 3.15 cm in diameter and 0.5 cm in thickness, were polished on Nos. 80 and 120 paper and degreased in acetone and alcohol. These specimens were tested in a cold-rolled condition; the volume of solution used in each bomb was 150 ml. Samples were suspended

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in the solution by means of quartz hooks. The total internal surface area of the test bomb, including the sample, was 335 cm^2. The solution-volume to surface-area ratio (ml:cm^2), therefore, was 1:2.2.

The oven used for heating the assembled test bombs was preheated to 250°C. Six bombs were weighed and placed in the oven and 1 hr was allowed for the bombs to reach this temperature. The bombs were then removed, one at a time, at intervals of 1, 2, 4, 8, 16, and 24 hr. The solutions were removed after cooling and filtered for chemical analyses of the filtrates and residues. Solution pH determinations were made immediately after the bombs were dismantled. The test specimens were dried and weighed, defilmed for 25 min at boiling temperature in 20% HNO_3, and reweighed to determine the amount of uranium oxides adhering to the surfaces. Residues were submitted for optical examination; the filtrates were analyzed for total uranium and uranium(IV).

The results of solution analyses, the condition of test samples and solutions, the corrosion data, and the amount of uranium removed from the samples by the HNO_3 defilming treatment, appear in Tables 4A-E.

TABLE 4A

Chemical Analyses of Test Solutions

Initial uranium: 40.5 g/liter
Initial uranium(IV):   56.0 ppm
Initial pH :   2.4

TIME AT 250°C (hr)	FINAL URANIUM (g/liter)	FINAL URANIUM(IV) (ppm)	FINAL pH
1	39.4	66.5	1.2
2	36.9	176.2	1.9
4	34.3	73.0	1.7
8	0.04	170.0	1.9
16	0.46	375.0	1.4
24	0.04	198.0	2.0

TABLE 4B

Condition of Test Specimens

TIME AT 250°C (hr)	SAMPLE APPEARANCE
1	Highly lustrous; uniform golden-pink interference tints
2	Highly lustrous; yellow-blue-green interference patterns
4	Brilliant yellow-red with traces of green interference colors
8	Dull black film; irregular scale formation
16	Dull green-black film; scaly product accumulation
24	Dull green-black film; scale accumulations

TABLE 4C

Condition of Test Solutions

TIME AT 250°C (hr)	SOLUTION APPEARANCE
1	Pale yellow color; muddy-brown colored residue
2	Pale yellow color; muddy-brown colored residue
4	Pale yellow color; muddy-brown and black colored residue
8	Light green color; heavy black residue
16	Light green color; heavy black residue
24	Light green color; heavy black residue

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TABLE 4D

Corrosion Data for Type 347 Stainless Steel Specimens

TIME AT 250°C (hr)	WEIGHT CHANGE AFTER HEATING		WEIGHT CHANGE AFTER HEATING AND DEFILMING		DEFILMED METAL THICKNESS LOSS (mils)
	(mg)	(mg/dm²)	(mg)	(mg/dm²)	
1	+3.1	+16.2	+5.0	+26.1	
2	+2.1	+10.9	+5.0	+26.1	
4	+3.2	+16.2	+5.2	+26.4	
8	+15.6	+81.4	-31.6	-164.9	0.083
16	+218.0	+1137.9	-34.4	-179.6	0.087
24	+55.7	+290.8	-38.9	-213.1	0.099

TABLE 4E

Total Uranium Recovered from Test Specimens

TIME AT 250°C (hr)	TOTAL URANIUM RECOVERED (mg)
1	7.2
2	5.0
4	7.2
8	36.0
16	160.0
24	62.0

Reduction of total uranium content proceeded steadily during the first
4 hr of test; during the 4-to 8-hr exposure period nearly complete reduction
of uranium from the original uranyl sulfate solution took place. The solution
pH dropped abruptly during the first hour from 2.4 to 1.2; this was the lowest
pH recorded during the entire test series. The pH results were erratic and no
direct correlation between total uranium content and pH was established. The
uranium(IV) results were less erratic and showed a definite increase from the
initial content of 56 to 375 ppm during the first 16 hr of test; a decrease to
198 ppm occurred during the last 8 hr of exposure. Iron, nickel, and chromium
contents were not determined on the filtrates and cannot be reported. The
residues, as identified in previous tests, undoubtedly consisted of mixtures
of UO_2, U_3O_8, and a Fe_2O_3.

The reduction of uranium from uranyl sulfate is probably accompanied by
the formation of small amounts of free sulfuric acid. The sulfuric acid, in
turn, accelerates corrosion attack on the stainless steel autoclave walls,
which results in the appearance of iron, nickel, and chromium ions in the
uranyl sulfate solution. The iron, and possibly chromium, forms insoluble
compounds which precipitate with the uranium oxides, giving more sulfuric
acid.

Variations in pH results may well be accounted for by the complex series
of chemical reactions which takes place while a uranyl sulfate solution is
undergoing reduction. These reactions could involve:

a. Progressive reduction of UO_2SO_4 to UO_2 (intermediate product may
   be uranyl sulfate; U_3O_8 has been definitely found).

b. Formation of small amounts of free sulfuric acid by the uranyl
   sulfate reduction process.

c. Reaction of the sulfuric acid with iron, nickel, chromium, and
   other constituents of the stainless steel test bombs.

The test specimens showed brilliant interference tints during the first
4 hr of exposure. The appearance of red and green tints on the samples ex-
posed 2 and 4 hr indicates second and third interference patterns, which, in
turn, indicate increasing film thickness as a function of time and temperature.
The specimens exposed 8, 16, and 24 hr were coated with a greenish-black

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scale. After defilming, low-power optical examination disclosed slightly etched surfaces with no signs of localized attack.

An apparent reduction in total uranium content was evident from the condition of the sulfate solutions during the first 4 hr. Although the filtrates from these solutions were characteristically yellow in color, fair amounts of brownish-black residues were collected which contained precipitated uranium and iron oxides. The solutions exposed 8, 16, and 24 hr were light green in color, showing the presence of soluble nickel, uranium(IV), and/or chromium. Bulky, black-colored residues were also present in abundant quantities.

No significant corrosion attack was observed on the type 347 stainless steel test specimens during the first 4 hr at 250°C. There did not appear, by visible examination, to be any adhering deposits of uranium oxides on the metal surfaces. Weight gains on these specimens averaged 2.8 mg on a surface area of 19.2 cm². Samples exposed 8, 16, and 24 hr showed much heavier weight gains, 218.0 mg being the greatest. All specimens were defilmed in boiling 20% HNO_3 for 25 min to remove uranium oxide scale. The samples exposed 1, 2, and 4 hr exhibited a greater than "as removed" weight increase even though small quantities of uranium were found in the analysis of the defilming solutions. The corrosion effect of the defilming treatment on unexposed test specimens was determined previously to be negligible. The increase in weight on the exposed specimens by the defilming operation indicates that at the same time dissolution of uranium oxides was occurring a reaction-produced pick-up from the HNO_3 was causing an increase in weight of the samples. The last three specimens, exposed 8, 16, and 24 hr, showed signs of corrosion attack. The metal thickness loss, for the actual time of exposure, was 0.083 mil for 8 hr and 0.099 mil for 24 hr. These values represent a uniform type of corrosion attack. No pitting corrosion attack was evident.

The amount of total uranium removed in the HNO_3-defilming solutions shows fairly good agreement with the weight increase originally determined on the test specimens "as removed" from the uranyl sulfate solutions.

Under the test conditions used, the following conclusions were reached:

a. In untreated type 347 stainless steel systems at 250°C, total uranium reduction is gradual but steady during the first 4 hr (15.3% reduction). Between 4 and 8 hr exposure total uranium reduction from the uranyl sulfate was nearly 100% complete.

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b. No definite correlation of uranium(IV) and solution pH vs. total uranium content was obtained, although, in general, uranium(IV) contents increased with decreasing total uranium concentration during the first 16 hr of test.

c. Type 347 stainless steel, after chemical defilming, showed a slight weight increase during the first 4 hr; a definite weight decrease was found on samples exposed 4 to 24 hr after defilming. The metal thickness loss did not exceed 0.1 mil in these cases.

2. **Stainless Steel Thermal Test Loops.** A stainless steel thermal loop described previously[1] was operated for 169 hr containing 0.17 M uranyl sulfate at 250°C. Several factors were present in the design of this loop which could cause or create unfavorable conditions for the operation of uranyl sulfate runs. These were:

a. Localized hot-spots on the metal wall beneath the heating elements could cause improper formation or deterioration of the nitric acid—pretreatment film. Whereas the normal temperature of operation is 250°C, the presence of localized heating may result in temperatures of 300 to 400°C or higher. This condition was found prevalent in those thermal loops which had calrod heater elements metallized directly to the stainless steel tubing. Above 300°C a two-phase region exists in the UO_2SO_4-H_2O system; one phase, the uranium-rich phase, is known to be quite corrosive.

b. The temperature at the base of the cold leg of the loop averaged 200°C during the operation of the loop at 250°C. Therefore, during the nitric acid pretreatment this portion of the loop was only at 200°C. Previous stagnant test data had shown that a nitric acid pretreatment at 200°C was not effective for subsequent operation in uranyl sulfate at 250°C.

This particular loop was used previously for a run of 633 hr with uranyl sulfate at 250°C. Near the end of this run the measured uranium content was 38.0 g/liter instead of the initial 39.0 g/liter. The accuracy of the analytical method rather than any actual reduction in the uranyl sulfate solution may have accounted for this difference. An addition of 10 ml of 70% HNO_3 was made to the uranyl sulfate and the loop was operated for 42 hr more. Total uranium again checked at 38.0 g/liter and the run was stopped. No precipitated uranium oxides were found in the sulfate solution after draining from the loop, which was then rinsed several times with distilled water and allowed to stand open to air.

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After standing 4 days open to air the loop was filled with 1050 ml of 1% by weight of 70% nitric acid and pretreated at 250°C for 12 hr. A small amount of brown-black precipitate, α Fe_2O_3, was found in the solution at the end of the pretreatment. The solution pH changed from an initial value of 0.95 to a final value of 1.3. Successive rinses with distilled water were water-white in color and free of any precipitated materials.

The unit was then filled with 1050 ml of uranyl sulfate containing 29.5 g of uranium per liter. The temperature of operation was 250°C. The loop was cooled daily to permit sample withdrawal. This cooling and reheating cycle involved a "down-time" of 2 hr. In removing samples, the sampling tube was first flushed with the test solution before an actual sample was taken.

Table 5 shows the results of solution analyses during the 169-hr run. The run was terminated at this time to permit rebuilding of the electrical control system.

TABLE 5

Chemical Analyses of Uranyl Sulfate Solution Contained in a Nitric Acid—Pretreated Type 347 Stainless Steel System at 250°C

SAMPLE TIME (hr)	SOLUTION pH	TOTAL URANIUM (g/liter)	URANIUM(IV) (mg/liter)	DISSOLVED IONS (mg/liter)		
				IRON	NICKEL	CHROMIUM
0	2.52	29.5	ND[a]	ND	ND	ND
10	2.60	28.3	25.0	IS[b]	IS	IS
36	2.55	28.8	23.0	IS	<1	IS
56	2.53	29.7	70.4	<1	ND	<1
76	2.59	30.3	27.0	ND	<1	6.6
98	2.60	29.5	22.8	2.3	<1	0.8
121	2.58	30.0	22.6	5.6	2.5	2.4
144[c]	2.59	29.8	34.0	5.0	<1	1.3
169	2.50	28.8	25.6	<1	3.5	3.9

(a) Analysis not determined.

(b) Insufficient sample for analysis.

(c) 260 ml of the original uranyl sulfate batch added to system (after sampling) to replenish solution removed by sampling.

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The final volume of solution, 1000 ml, drained from the loop was clear and yellow in color. A very small quantity, 5 to 10 mg, of α Fe_2O_3 was present.

The total uranium content remained fairly constant during the 169-hr run. The fact that four of the analyses were higher than the starting value may be a result of the analytical method accuracy.

Solution pH measurements, taken after cooling the samples to room temperature, were consistent. It has been observed in other tests that generally any lowering of the pH value indicates a reduction of the uranyl sulfate solution. No such indications were present in this run. Uranium(IV) analyses were of consistent magnitude except for one value of 70.4 mg/liter at the end of 42 hr. Unless determined within 4 hr after sampling, uranium(IV) values show only relative trends since the uranium(IV) ion is easily oxidized upon exposure to air.

After a consideration of the test method and testing conditions this 169-hr run was considered a successful one. The criteria for this conclusion were the consistency of pH and total uranium measurements, the absence of uranium oxides in the test samples, and the low concentrations of dissolved iron, nickel, and chromium found in the solutions. The amount of dissolved iron determined in the test samples is not a true measure of corrosion evaluation since iron precipitates from solution as an oxide.

A thermal loop test was run using an untreated type 347 stainless steel system. The test solution was uranyl sulfate containing 1% by weight of 70% nitric acid. The loop was first chemically cleaned and washed thoroughly in distilled water. The volume of test solution was 1200 ml and the unit was heated to 250°C. Samples were removed daily. The run continued for 154 hr after which time a shutdown was necessitated by heater element failure. The results of solution analyses appear in Table 6.

Total uranium analyses were consistent in value until the end of the run at which point a decrease from 29.7 to 28.0 g/liter was observed. The drop in pH from 1.2 to 0.8 was due to the addition of new solution containing 7.0 ml of 70% nitric acid. The dissolved ions, especially nickel, were considerably higher in concentration than encountered in runs with nitric acid-pretreated systems.

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TABLE 6

Chemical Analyses of Uranyl Sulfate Containing
1% Nitric Acid in an Untreated Type 347
Stainless Steel System at 250°C

SAMPLE TIME (hr)	SOLUTION pH	TOTAL URANIUM (g/liter)	URANIUM(IV) (mg/liter)	DISSOLVED IONS (mg/liter)		
				IRON	NICKEL	CHROMIUM
0	1.1	29.5	ND[a]	<1	<1	<1
9	1.2	29.7	36.0	<1	IS[b]	IS
23	1.1	29.0	33.5	<1	213.0	IS
42	1.2	29.3	60.0	<1	IS	68.0
62	1.1	29.4	21.6	IS	IS	IS
84	1.2	29.3	16.2	4.8	64.5	<1
107	1.2	28.8	22.4	<1	288.0	<1
130[c]	1.2	29.7	65.0	14.5	IS	43.8
154	0.8	28.0	21.0	<1	240.0	5.8

(a) Analysis not determined.

(b) Insufficient sample for analysis.

(c) Added 340 ml of original uranyl sulfate and 7.0 ml of concentrated HNO₃ (after sampling) to re-place solution withdrawn by sampling.

This particular type of thermal loop has been redesigned to eliminate overheating effects. Six of the new loops are nearing completion and will be placed into operation during the forthcoming quarter.

3. The Corrosion of Titanium. The corrosion program on titanium metal in uranyl sulfate solutions at 250°C is being expanded rapidly. Tests are being run at present in pretreated stainless steel bombs, but plans are in progress to fabricate two all-titanium autoclaves having a capacity of 1500 ml each.

Samples of commercial-grade titanium plate, 1/4 in. thick, have been tested in 0.17 M uranyl sulfate at 250°C for periods of 5 to 8 weeks. Samples

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were totally immersed, partially immersed, and totally exposed to vapor. The specimens were abraded on Nos. 80 and 120 grit paper and degreased prior to test. No other initial treatment was used. Tests were run in stainless steel test bombs which were pretreated every 2 weeks in 1% HNO_3 for 24 hr at 250°C. The test samples and solutions were inspected weekly.

The cumulative weight changes on these samples are included in Table 7 as a function of exposure time.

TABLE 7

Corrosion of Commercial-Grade Titanium in 0.17 M Uranyl Sulfate at 250°C

EXPOSURE (weeks)	CUMULATIVE WEIGHT CHANGE (mg/cm²)		
	TOTAL IMMERSION	PARTIAL IMMERSION	VAPOR EXPOSURE
1	+0.048	0.0	-0.006
2	+0.103	-0.017	-0.017
3	+0.080	0.014	-0.014
4	+0.070	0.025	-0.025
5	+0.048	0.017	-0.006
6	+0.042		
7	+0.054		
8	+0.042		

Although solution analyses have not been completed for these tests, results obtained thus far have not shown any indications of solution reduction and the initial and final solution pH measured for each weekly run have undergone little change. Final pH values average 2.2 to 2.3 as compared to the initial pH of 2.4.

The samples appeared in excellent condition throughout the tests. All exhibited a highly lustrous, uniform, golden-yellow color. No visible corrosion products or adherent uranium oxide scales were observed. On the specimen partially exposed to the liquid and vapor phases there were no signs of water-line corrosion attack.

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Several other grades of titanium metal were tested. These were obtained from Rem-Cru Titanium, Inc., and consisted of:

a. Tubing, 3/8 in. O.D. by 10 in. long, made by welding into a tube with 1/2 in. O.D., grinding the outside of the weld with a belt, and drawing to size.

b. Sheet, 1/8 by 12 by 12 in., containing 0.17% carbon and having a tensile strength of 94,000 psi and a yield strength of 86,000 psi.

c. Slab, 1/4 by 1 by 1½ in., made of the purest material that can be produced to date by the Kroll process. This material is low in carbon, oxygen, and nitrogen.

Results of corrosion tests in 0.17 M uranyl sulfate at 250°C appear in Table 8.

TABLE 8

Corrosion of Various Types of Titanium
in 0.17 M Uranyl Sulfate at 250°C

TYPE	CONDITION	EXPOSURE (weeks)	WEIGHT CHANGE (mg/cm²)	CORROSION RATE (mils/year)
Tubing	Not annealed; degreased	5	-0.30	0.26
Tubing	Annealed at 1200°F; descaled in sodium hydride	4	-0.10	0.13
Sheet	Annealed and degreased	4	-0.006	0.01
Sheet	Annealed; polished on Nos. 80 and 120; degreased	2	-0.14	0.17
Slab	As received; degreased	4	-0.20	0.03
Slab	As received; polished on Nos. 80 and 120; degreased	2	+0.04	

All samples were characterized by lustrous golden-yellow interference colors. No indications of solution reduction were observed. These tests are being continued.

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4. The Corrosion of Zirconium. The corrosion behavior of zirconium-tin alloys in uranyl sulfate at 250°C has continued to be excellent. These alloys contain a nominal 3 to 5% tin addition. To date, the corrosion resistance of this material has been superior to that of any Bureau of Mines zirconium tested.

One sample, containing 3% tin, has been exposed to 0.17 M uranyl sulfate at 250°C for a period of 11 weeks. The sample showed a cumulative weight gain of 0.3 mg/cm^2. A sample containing 5% tin has shown an equivalent weight gain after 8 weeks at 250°C in uranyl sulfate. Both samples exhibited highly lustrous, metallic-gray surfaces at the end of the tests. No formation of light-gray corrosion products was observed as encountered frequently on Bureau of Mines zirconium specimens.

Additional samples of 5% tin alloy produced by three melting techniques from various sources are undergoing corrosion tests in uranyl sulfate. These data are presented in Table 9.

TABLE 9

Corrosion of Zirconium Containing 5% Tin Addition in 0.17 M Uranyl Sulfate at 250°C

SOURCE	METHOD OF MELTING	MELTING STOCK	EXPOSURE (weeks)	WEIGHT CHANGE (mg/cm^2)	CORROSION RATE (mils/year)
MIT	Induction melted in graphite	BuMines sponge	7	+0.06	--
BuMines	Resistance melted in graphite	BuMines sponge	7	-0.11	0.05
BuMines*	Resistance melted in graphite	BuMines sponge	7	+0.11	--
BMI	Induction melted in graphite	BuMines sponge	5	-0.02	0.01
BMI	" W" arc melted	Crystal bar	5	-0.02	0.01

*Contains 3% tin.

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The specimens were dark brown in appearance at the end of the exposure periods. The "K" arc melted sample of crystal bar was more lustrous than the other specimens.

5. **Uranyl Nitrate Corrosion Studies.** A group of four tests was run at 150°C using uranyl nitrate solution containing 31.1 g of uranium per liter. These tests were conducted in untreated, chemically cleaned stainless steel bombs. The test samples were prepared by abrading on Nos. 80 and 120 grit paper and degreasing. Results for an exposure period of 1 week appear in Table 10.

TABLE 10

Corrosion of Various Materials in Uranyl Nitrate Solution at 150°C

MATERIAL	SOLUTION pH		TOTAL URANIUM (g/liter)		WEIGHT CHANGE (mg/cm²)	CORROSION RATE (mils/year)
	INITIAL	FINAL	INITIAL	FINAL		
347 SS	0.9	1.2	31.1	33.3	-0.86	2.20
309 Nb SS	0.9	1.2	31.1	32.9	-0.21	0.54
Titanium	0.9	1.3	31.1	31.8	+0.04	
BuMines zirconium	0.9	1.1	31.1	30.7	+0.05	

Type 347 stainless steel suffered the most intense corrosion attack. The sample was a lustrous brown-purple color with no indication of other than a uniform corrosion damage. Type 309 stainless steel exhibited more superior corrosion resistance, while titanium and zirconium showed the best corrosion resistance.

No reduction in total uranium content was found in these tests by chemical analyses. The solutions did contain, however, small quantities of insoluble brown-colored precipitate which were probably iron oxides.

6. **Uranyl Fluoride Corrosion Studies.** Previous tests have indicated that the austenitic stainless steels, titanium, tantalum, inconel, and other

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alloys consisting primarily of chromium, nickel, and iron, exhibited satis-
factory corrosion resistance to uranyl fluoride at 100°C. Specimens of
several of these metals were exposed to uranyl fluoride (29.4 g of uranium per
liter) at 150°C in untreated type 347 stainless steel bombs for 7 days.
Although chemical analyses of the test media are incomplete, the appearance of
a brownish-black precipitate accompanied by a decrease in solution pH indicated
the fluoride was reduced. The corrosion data for these tests are given in
Table 11.

TABLE 11

**Corrosion Behavior of Various Metals Exposed
to Uranyl Fluoride at 150°C in Untreated
Type 347 Stainless Steel Bombs**

MATERIAL	WEIGHT CHANGE ($mg/dm^2/day$)	PENETRATION RATE (mils/year)	SURFACE APPEARANCE
Titanium	+2.85		Reddish-brown interference colors
309 SS	+0.83		Green and red interference colors
304 SS	-1.75	0.31	Black uranium oxide scale
321 SS	-1.75	0.31	Black uranium oxide scale
316 SS	-3.81	0.69	Black uranium oxide scale
Inconel	-6.86	1.16	Bright metallic lustre
Durimet 20	-6.80	1.23	Bright metallic lustre
Carpenter 20	-7.77	1.40	Bright metallic lustre
Worthite	-16.1	2.91	Bright metallic lustre

Uranium reduction has not been observed in tests run at 150°C in pre-
treated bombs. The pretreatment consisted of heating the bombs at 250°C for
24 hr in 1% HNO_3. Untreated samples of 347 stainless steel and Illium R
exhibited corrosion rates of 1.10 and 0.42 mils/year, respectively, after
approximately 925 hr of exposure. The fluoride solutions were changed and
sampled 7 times during the course of these tests. The small variations in

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total uranium concentration were within the ±2% accuracy of the analytical method used for determining this element. The maximum tetravalent uranium concentration obtained was 68 mg/liter. No significant variations in solution pH from the original value of 3.25 were observed. Corrosion data for these tests are given in Tables 12 and 13.

TABLE 12

Corrosion Behavior of Untreated 347 Stainless Steel Exposed to Uranyl Fluoride at 150°C in Pretreated Bomb

CUMULATIVE EXPOSURE TIME (hr)	WEIGHT CHANGE (mg/dm²/day)	PENETRATION RATE (mils/year)	TOTAL URANIUM (g/liter)	URANIUM(IV) (mg/liter)
24	15.2	2.75	29.0	19
68	9.8	1.77	29.2	64
159	8.3	1.49	29.5	27
248	7.4	1.34	29.2	28
415.5	7.5	1.35	29.3	38
583.5	7.0	1.26	29.0	13
924.5	6.1	1.10		

TABLE 13

Corrosion Behavior of Illium R Exposed to Uranyl Fluoride at 150°C in Pretreated Bomb

CUMULATIVE EXPOSURE TIME (hr)	WEIGHT CHANGE (mg/dm²/day)	PENETRATION RATE (mils/year)	TOTAL URANIUM (g/liter)	URANIUM(IV) (mg/liter)
24	6.14	1.07	29.0	16.4
68	4.85	0.84	29.0	52.0
159	3.76	0.65	29.4	60.8
248	3.39	0.59	29.5	42.0
415.5	2.96	0.52	29.2	68.0
583.5	2.65	0.46	29.1	17
924.5	2.41	0.42		

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Other studies to determine the solution stability at 150, 200, and 250°C have been run in both untreated and pretreated type 347 stainless steel bombs. Chemical analyses for these tests are incomplete, and it is not known whether uranium reduction occurred. However, no voluminous precipitates have been observed in these tests, although the pH of the solutions used in the untreated bombs, especially at the highest temperature, usually showed a marked decrease.

7. **Corrosion of Reflector Materials.** Corrosion studies at 200°C with mild carbon steel (polished SAE 1030 carbon steel disks) exposed to distilled water containing small concentrations of hydrogen peroxide have resulted in initial corrosion rates of 7 to 10 mils/year. These rates decreased with exposure time to 2 to 3 mils/year after 18 weeks. The addition of trisodium phosphate to the test water was found to exert a marked influence for increasing the corrosion resistance of the carbon steel. Two concentrations of the phosphate inhibitor were used, 275 and 550 ppm. The results of stagnant corrosion studies in distilled water at 200°C containing these concentrations in the presence and absence of approximately 0.0005 M hydrogen peroxide are included in Table 14.

TABLE 14

Corrosion of SAE 1030 Carbon Steel in Water Containing
Trisodium Phosphate at 200°C

	EXPOSURE (weeks)	WEIGHT CHANGE (mg/cm^2)	
		275 ppm TRISODIUM PHOSPHATE ADDED	550 ppm TRISODIUM PHOSPHATE ADDED
Condition 1:	1	+0.073	-0.042
Distilled water;	2	+0.054	-0.033
no hydrogen peroxide	3	+0.054	-0.052
	4	+0.034	-0.118
	6	+0.005	-0.028
	8		-0.122
	10		-0.098
Condition 2:			
Distilled water	1	+0.114	-0.009
initially containing	2	+0.084	+0.009
0.0005 M H_2O_2	3	+0.070	-0.028
	4	+0.064	-0.061
	6	+0.020	-0.090
	8		-0.071
	10		+0.290

The initial solution pH of the water containing 275 ppm of trisodium phosphate was 11.1, as compared to 11.4 for the water containing 550 ppm. The final solution pH at the end of weekly runs averaged 9.7 and 10.2, respectively, for these solutions.

In the absence of hydrogen peroxide, 275 ppm of trisodium phosphate appeared a better corrosion inhibitor than the higher concentration. Whereas a weight gain of 0.005 mg/cm^2 was observed after 6 weeks in water containing 275 ppm, the sample exposed to 550 ppm showed a weight loss of 0.098 mg/cm^2 in 10 weeks, corresponding to a corrosion rate of 0.03 mil/year. Both specimens were comparable in appearance, having lustrous golden and tan interference patterns.

With 0.0005 M hydrogen peroxide present in the test medium, the lower concentration of trisodium phosphate again appeared to be the more effective inhibitor. The samples showed decreasing weight gains from 0.114 to 0.020 mg/cm^2 after 6 weeks of test. Samples exposed to 550 ppm of phosphate were slightly erratic in behavior. In general, weight losses occurred except for a sudden increase in weight during the last exposure period, from -0.07 mg/cm^2 to +0.29 mg/cm^2. The samples showed lustrous interference tints and were free of any type of bulky corrosion products. No signs of localized corrosion attack were observed.

Galvanic corrosion studies were made with type 347 stainless steel coupled to the SAE 1030 carbon steel specimens. A surface area ratio of 1 cm^2 of stainless steel to 1.7 cm^2 of carbon steel was used. Tests were run in distilled water at 200°C containing 0.0005 or 0.005 M hydrogen peroxide. The effect of hydrogen peroxide concentration on the corrosion of carbon steel coupled to stainless steel is shown in Table 15. Cumulative weight changes and corrosion rates are included. Data on the stainless steel are not reported since in all cases specimens remained unattacked and showed slight weight gains of 0.025 to 0.050 mg/cm^2 after 10 weeks of exposure.

The initial solution pH on these tests averaged 4.5; final solution pH at the end of weekly exposures averaged 6.2. The carbon steel specimens were anodically attacked in all tests. The marked effect of increased corrosion attack on the carbon steel is clearly evident by these data as the hydrogen peroxide concentration increased from 0.0005 to 0.005 M. In every case, the area in contact with the stainless steel showed intense blackening, corrosion product formation, and localized corrosion attack.

TABLE 15

Galvanic Corrosion of 1036 Carbon Steel Coupled to Type 347 Stainless Steel in Hydrogen Peroxide Solutions at 200°C

EXPOSURE (weeks)	CORROSION IN 0.0005 N H$_2$O$_2$		CORROSION IN 0.005 N H$_2$O$_2$	
	(mg/cm^2)	(mils/year)	(mg/cm^2)	(mils/year)
1	-1.88	4.8	-3.18	8.2
2	-3.66	4.8	-6.82	8.9
3	-5.30	4.6	-8.85	7.7
4	-7.70	5.1	-11.21	7.3
6	-8.48	3.7	-11.58	5.0
8	-9.49	3.1	-11.79	3.9
10	-9.83	2.6	-12.00	3.1

The effect of trisodium phosphate as an inhibitor to restrict galvanic attack on carbon steel in distilled water at 200°C was investigated. Tests were run in the absence and pressure of 0.0005 N hydrogen peroxide. The concentration of trisodium phosphate used for these tests was 550 ppm, resulting in an initial solution pH of 11.4. Corrosion data for the carbon steel coupled to 347 stainless steel are included in Table 16.

TABLE 16

Galvanic Corrosion of 1030 Carbon Steel Coupled to Type 347 Stainless Steel in Distilled Water Containing 550 ppm of Trisodium Phosphate at 200°C

EXPOSURE (weeks)	CORROSION WITH NO H$_2$O$_2$		CORROSION IN 0.0005 N H$_2$O$_2$	
	(mg/cm^2)	(mils/year)	(mg/cm^2)	(mils/year)
1	+0.28	0.2	0.0	
2	+0.39		+0.27	
3	+0.34		+0.25	
4	+0.23		+0.15	
6	+0.25		+0.14	
8	+0.28		+0.11	
10	+0.29		-0.04	0.01

The initial solution pH was 11.4; final solution pH averaged 10.2. In
the absence of hydrogen peroxide, the corrosion behavior of the carbon steel
was consistently good; a steady weight change prevailed during the course of
the test. The samples were highly lustrous on the outer areas while the
contact area was discolored but free of corrosion product formation and
localized attack. The addition of 0.0005 M hydrogen peroxide to the inhibited
test solution resulted in only a minor change on the corrosion of the carbon
steel. The rate of weight increase, mg/cm^2, decreased with time until an
actual weight loss was observed after the final 2 weeks of exposure. This
loss was extremely slight, 0.04 mg/cm^2. The condition of the samples was very
similar to the condition of specimens exposed to distilled water in the absence
of hydrogen peroxide. There were no indications of accelerated corrosion
attack due to the presence of hydrogen peroxide.

This type of test is being repeated using lower concentrations of tri-
sodium phosphate.

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While the static tests on corrosion and solution stability of uranyl sulfate in 347 stainless steel gave very encouraging results[3] provided the steel was suitably pretreated, attempts to duplicate these results in dynamic tests in simple pump loops were unsuccessful. Although this suggested that the flow itself might be the source of the difficulty, two other possibilities needed investigation before this conclusion could be accepted. These were: (1) the effect of the presence of materials other than 347 stainless steel in the pump, e.g., 410 stainless steel, 316 stainless steel, tantalum, stellite, inconel, and graphite; and (2) the effect of the presence of dissolved oxygen in the uranyl sulfate solution.

Experimental Work and Results

Analytical Work. In the static tests and first loop runs, color changes, examination of metal test specimens, and total uranium concentration analyses were used to determine solution breakdown and/or corrosion. In the loop tests samples were withdrawn through a valve at the back of the pump, and in the static tests samples were withdrawn by cooling the container bombs to room temperature and opening. In the loop tests discussed below samplers were attached to the loops so that samples could be taken directly from the system while in operation since the pump is constructed in such a way as to limit mixing between the pump armature chamber and the rest of the system. This slow rate of mixing meant that the results of analyses performed on pump samples were not representative of conditions in the loop itself. An expanded analytical program was also instituted to attempt to build up a picture of the changes taking place in the uranyl sulfate solution during operation under various circumstances. In addition to pH measurement, the samples were analyzed for total uranium, uranium(IV), iron, chromium, and nickel. When precipitates were obtained, spectrographic and X-ray analyses were made. At present the

(3) J. L. English et al., "Static Out-of-Pile Tests," this report, p. 24; see also other sections on out-of-pile corrosion tests in previous HRE quarterlies (listed on p. 4).

results of the analyses suggest the following:

1. The most sensitive indication of change in solution composition is given by the concurrent change in pH. It has been observed that corrosion and/or precipitation of the uranium in solution is accompanied by the release of hydrogen ion. Since the natural pH of 30 to 40 g of uranium per liter of uranyl sulfate solution is approximately 2.5, small changes in hydrogen ion concentration corresponding to slight corrosion and/or uranium precipitation produce relatively large pH changes. These pH changes have provided the best means of detecting breakdowns in the loop experiments which have been completed thus far. Unfortunately, this will not be the case at higher uranium concentrations where the natural pH of the solutions is appreciably lower and, as a consequence, a considerably larger change in hydrogen ion concentration is necessary to change the pH by an easily measurable amount.

2. Changes in total uranium concentration have been the next best measure of breakdown in loop operations and present the best information, as might be expected, on the extent of solution breakdown and/or corrosion.

3. Nickel analyses have given some trouble; however, recent data obtained with an improved analytical method suggest that an increase in the concentration of nickel in the uranyl sulfate solution is a very good indication of serious corrosion.

4. An increase in uranium(IV) concentration appears to accompany corrosion and uranium precipitation. However, the data obtained thus far are somewhat questionable because of the probable re-oxidation during sampling. The hydrolytic precipitation which follows the formation of the uranium(IV) under the existing conditions also makes it difficult to get more than an indication of trouble from rising uranium(IV) concentrations during long operations.

5. Analyses for iron and chromium in the uranyl sulfate solution also give a somewhat confused picture because of the hydrolytic precipitation of these ions under loop experimental conditions. Again, an increase in their concentration in the uranyl sulfate solution indicates serious corrosion, but it gives no reliable estimate of the extent of such corrosion.

In subsequent work further attempts will be made to get a satisfactory analytical picture of solution changes during precipitation and/or corrosion.

Loop Tests. After completion of a loop test which was deliberately set up to fail in order to get an analytical picture of what transpired in the

uranyl sulfate solution during precipitation of the uranium and/or corrosion of the steel, an attempt was made to isolate the several doubtful materials in the pump armature chamber from the loop proper. The need for such isolation of the pump armature chamber was emphasized by quartz-tube and static steel bomb tests which showed that the presence of graphite in uranyl sulfate solution at 250°C caused substantial precipitation of uranium in less than 100 hr. The graphite bearings of the pump were therefore a probable cause for some of the failures encountered in the dynamic loop tests. These attempts were unsuccessful, however, because of mechanical difficulties which could not immediately be corrected.

At this stage in the program a review of the available information suggested that the stability of a uranyl sulfate solution—347 stainless steel system might be related to or dependent on the presence of oxygen in the system. This possibility was suggested by the following:

1. The well-known high corrosion resistance of stainless steels to oxidizing media.

2. The fact that oxygen is the common decomposition product of the pretreatment agents, HNO_3 and CrO_3, which the static steel bomb tests had shown would produce a satisfactory protective coating on 347 stainless steel.

3. The coating produced on the stainless steel in contact with the gas phase was as good as that obtained where the stainless steel contacted the liquid phase.

4. In-pile tests indicated that the oxidizing atmosphere produced by the radiation decomposition of the water was beneficial.

5. Quartz-tube and static steel bomb tests set up as a result of the above observations failed uniformly when oxygen was removed by evacuation or by bubbling nitrogen through the solution; practically no failures were observed under similar conditions when the oxygen was not removed.

In order to test the effect of the presence of oxygen in solution on pump loop operation an experiment was started in which oxygen pressures of 300 to 500 psi were maintained over the solution during operation. This test was operated 135 hr at 250°C without precipitation of the uranium. A subsequent test ran 287 hr without precipitation in spite of the fact that the oxygen pressure over the solution was progressively reduced from 500 to 25 psi in the course of the test and despite the presence of graphite bearing in the pump.

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The total gas pressure was maintained at approximately 500 psi with He. It is also significant that this run was carried out in a loop which was not pre-treated with HNO_3 or CrO_3 solution. Analytical data are not complete, but the available data indicate no serious corrosion. Unfortunately, the results have been confused by the discovery that the uranyl sulfate used in all the loop tests run this quarter probably contained 10 to 70 mole % of $(NH_4)_2SO_4$ or H_2SO_4. Analyses of the specific reagent used in the various tests have not been completed nor has the effect of the presence of these impurities on the results been evaluated; thus, detailed descriptions of the tests and the results obtained are being deferred until the next quarterly report.

Future Work

In addition to checking on the results obtained with the impure uranyl sulfate with new pure material, future effort will be concentrated on evaluation of the oxygen concentration necessary to stabilize uranyl sulfate solutions in stainless steel. The approach will involve determination of the minimum oxygen concentration necessary for stabilization under various conditions.

EFFECT OF VARIABLES ON CORROSION: SERIES I

The corrosion experiments described in this report were performed in 8-mm-I.D. quartz tubes 4½ in. long. The quartz-tube method for studying corrosion at high temperatures has many advantages. The solutions and specimens can be easily observed and the progress of corrosion followed. Many experiments can be run simultaneously with a minimum of equipment, and only simple equipment is required. A possible disadvantage might be the effects of dissolved silica in the solutions from the quartz tubes.

In carrying out the experiments 1-in. pieces of nitrate-passivated 347 stainless steel or untreated steel along with 2 ml of the solution to be investigated were sealed in the tubes. The tubes were heated either in aluminum block furnaces provided with a slit so that the tubes could be observed, or in a box in a large oven. The aluminum block furnaces and the box in the oven were mounted on rockers so that the solutions and specimens

were oscillated during the heating. All the corrosion experiments were conducted at 250°C and were of at least 100 hr duration.

The uranyl sulfate solution investigated contained 30 g of uranium per liter which corresponded to a 0.13 f uranyl sulfate solution. The uranyl phosphate solution was prepared by dissolving uranyl phosphate in 1.5 M phosphoric acid to give a concentration of 30 g of uranium per liter. The solutions were frozen in the tubes prior to sealing to minimize losses due to evaporation.

Experimental Results

Passivated vs. Unpassivated Steel. The uranyl sulfate solution alone and in the presence of the nitrate-passivated 347 stainless steel appeared to be perfectly stable. When the solution was heated with unpassivated steel, however, there was extensive reduction and precipitation of uranium from the solution. The uranium(IV) content of the solution increased to over 1 mg/ml. The pH of the solution dropped from 2.5 to about 1.0. The steel specimen showed evidences of general corrosion, and iron(II) was found in the solution to the extent of over 1 mg/ml. Analysis showed that the black precipitate of UO_2 also contained iron and chromium, while the nickel stayed in solution.

Effect of pH. The pH of the solution was varied from 3.2 to 1.5. The high values were obtained by dissolving UO_3 in UO_2SO_4 solution. The total uranium concentration was kept at 30 g/liter. The low pH values were attained by adding H_2SO_4 to the UO_2SO_4 solution. When solutions with pH values between 2.5 and 1.5 were heated with passivated steel there was no evidence of change. When solutions with pH values between 2.6 and 3.2 were heated with passivated steel a small amount of yellow precipitate formed. The uranium content of the solution decreased slightly and the pH dropped to about 2.0. The precipitate was presumably a hydrated uranium(VI) oxide.

Effect of Uranium(IV) Concentration. When 10 mg $U(SO_4)_2 \cdot 4H_2O$ per milliliter of the uranyl sulfate solution was added and the solution was heated with passivated 347 stainless steel, failure of the solution invariably occurred. Some of the uranium precipitated as UO_2. The pH of the solution

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dropped to 1.0 to 1.5 and there was sometimes slight corrosion of the steel.
With higher concentrations of uranium(IV) pitting sometimes occurred. Smaller
concentrations of uranium(IV) had no effect on the system. Since a large part
of the uranium(IV) sulfate was oxidized to uranyl sulfate by the oxygen in the
tube, it was probably necessary to add an excess above this amount before
failure of the solution occurred.

Effect of Graphite. When powdered graphite was added to tubes containing
uranyl sulfate solution and a piece of passivated steel, there was extensive
reduction of the uranium content of the solution. The pH of the solution
decreased to about 1.0, while the concentration of uranium(IV) increased. Some
general corrosion of the steel occurred, and appreciable concentrations of
iron(II) appeared in the solution. When no steel was present the only effect
of graphite was to increase the uranium(IV) concentration in the uranyl sulfate
solution. Apparently the reaction of the uranium(VI) with graphite to produce
uranium(IV) with subsequent oxidation of the uranium(IV) to uranium(VI) pro-
ceeded until the oxygen supply in the tube was exhausted. Then further pro-
duction of uranium(IV) in excess of the 50 γ/ml concentration could take place.

Effect of Corrosion Product Salts. 1. $FeSO_4$. When 1 mg $FeSO_4$ was added
to 2 ml uranyl sulfate solution and the oxygen removed from the tube and
solution prior to sealing, a black precipitate containing both iron and uranium
formed. The pH of the solution dropped to about 1.3. When the oxygen was not
removed, the iron(II) was oxidized to iron(III) which underwent a hydrolytic
reaction to give a reddish precipitate of $Fe_2O_3 \cdot xH_2O$. In this case there was
no precipitation of uranium.

In the presence of passivated steel 1 mg $FeSO_4$ per 2 ml uranyl sulfate
solution caused complete precipitation of the uranium as U_3O_8. There was no
noticeable corrosion of the steel specimen. With $Fe_2(SO_4)_3$ the same behavior
was observed as in the absence of steel; the iron(III) hydrolyzed completely
but there was no precipitation of uranium and no corrosion of the steel.

2. $Cr_2(SO_4)_3$. Chromic sulfate (1 mg per 2 ml uranyl sulfate solution)
was hydrolyzed completely to Cr_2O_3 both in the presence and in the absence of
passivated 347 stainless steel. There was no precipitation of uranium and no
corrosion of the steel. The presence of 1% HNO_3 in the solution caused
oxidation of the chromium(III) to chromium(VI).

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3. *NiSO₄*. There was no observable change when 1 mg $NiSO_4$ was heated with 2 ml UO_2SO_4 solution either in the presence or in the absence of passivated steel.

Addition of Na_2MoO_4 and Na_2WO_4. Na_2MoO_4 and Na_2WO_4 were tried as corrosion inhibitors at high temperature. In both cases 1 mg of the salt was added to 2 ml of uranyl sulfate solution. In each case a small amount of yellowish precipitate was formed which contained uranium and either molybdenum or tungsten. The solution to which Na_2MoO_4 had been added was stable in the presence of passivated steel and graphite, while there was extensive reduction and precipitation of uranium as UO_2 and U_3O_8 from the solution to which Na_2WO_4 had been added. Neither salt was effective in preventing solution breakdown when 10 mg $U(SO_4)_2 \cdot 4H_2O$ was added to 2 ml of uranyl sulfate solution in the presence of passivated steel.

Effect of Oxygen. A series of experiments in the presence of both passivated and untreated steel was performed to determine the importance of oxygen in the corrosion process. The results are summarized in Table 17.

TABLE 17

Effect of Oxygen on the Uranyl Sulfate—Steel System

MATERIAL	TREATMENT	RESULT
Untreated steel	Air	Precipitation of uranium
	Solution aerated prior to sealing	Precipitation of uranium
	O_2 bubbled through solution prior to sealing	Red flakes of $Fe_2O_3 \cdot xH_2O$, but no precipitation of uranium
Passivated steel	Air	No precipitation
	O_2 bubbled through solution prior to sealing	No precipitation
	Air removed from solution	Precipitation of uranium

These results seem clearly to indicate the importance of oxygen in stabilizing the uranyl sulfate—passivated steel system.

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Addition of Nitric Acid. When 1% HNO_3 was present in UO_2SO_4 solution in contact with graphite and a piece of passivated steel there was no failure of the solution in 100 hr. In the absence of HNO_3 uranium precipitated from the solution in a few hours.

Effect of Halogen Ions. The presence of 100 ppm Cl^- in uranyl sulfate solution in contact with passivated steel did not have any effect in enhancing corrosion or causing precipitation of uranium. In the presence of 1800 ppm Cl^- there was some corrosion of the passivated steel specimen. The solution, however, appeared to remain stable.

In another experiment a uranyl sulfate solution containing 25 ppm Cl^- was placed in a long tube (10-in.) with a piece of passivated steel. The tube was heated at one end only so that the solution refluxed constantly. There was no change in 2 weeks.

Uranyl Phosphate Systems. Preliminary experiments with the solution of uranyl phosphate in 1.5 N phosphoric acid gave very promising results. There was no failure of the solution in the presence of treated steel, untreated steel, or treated steel and graphite. There was no noticeable corrosion of the steel, although the specimens were covered with a green crystalline deposit.

Conclusion

Table 18 summarizes some of the important results obtained in the uranyl sulfate system.

Precipitation of uranium from uranyl sulfate solution in the presence of passivated steel was observed in the absence of air or oxygen, in the presence of graphite, and in the presence of high uranium(IV) concentrations. In all of these cases the uranium was reduced as well as precipitated. At higher pH (2.6 to 3.2) there was precipitation but not reduction of uranium. Corrosion of the steel specimens was often observed when the uranium was reduced and precipitated. The presence of an oxidizing agent (viz. O_2 or 1% HNO_3) seems to be necessary in preserving the stability of the system.

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TABLE 18

Effect of Various Factors on the Stability of the UO_2SO_4 System

FACTOR	RESULT

A. NO STEEL PRESENT

FACTOR	RESULT
Graphite	Increased the uranium(IV) content
$U(SO_4)_2 \cdot 4H_2O$ (10 mg/ml)	No change
$U(SO_4)_2 \cdot 4H_2O$ (10 mg/ml)	No change in presence of air; precipitation of uranium content down to 2 mg/ml $UO_2(SO_4)_2 \cdot 4H_2O$ when air was removed from solutions
Chrome alum	Complete hydrolysis to Cr_2O_3; no precipitation of uranium
$NiSO_4$	No change
$FeCl_3$ or $Fe_2(SO_4)_3$	Complete hydrolysis to $Fe_2O_3 \cdot nH_2O$; no precipitation of uranium
Graphite + Na_2MoO_4	Slight precipitation of uranium; no further change
Graphite + Na_2WO_4	Slight precipitation of uranium; no further change
$U(SO_4)_2 \cdot 4H_2O$ (10 mg/ml) + Na_2MoO_4	Slight precipitation of uranium; no further change
$U(SO_4)_2$ + Na_2WO_4 (10 mg/ml)	Slight precipitation of uranium; no further change

B. PASSIVATED STEEL PRESENT

FACTOR	RESULT
100 ppm Cl^-	No change
1800 ppm Cl^-	Small amount of corrosion; solution stable
Graphite	Reduction of uranium content of solution; decrease in pH
Graphite + 1% HNO_3	No change
$U(SO_4)_2 \cdot 4H_2O$ (10 mg/ml)	Precipitation of uranium; slight corrosion of steel
$NiSO_4$	No change
$FeSO_4$	Complete precipitation of uranium as U_3O_8
$Fe_2(SO_4)_3$	Complete hydrolysis to Fe_2O_3; no precipitation of uranium
Graphite + Na_2MoO_4	Slight precipitation of uranium; no further change
Graphite + Na_2WO_4	Extensive precipitation of uranium
$U(SO_4)_2 \cdot 4H_2O$ (10 mg/ml) + Na_2MoO_4	Complete reduction; precipitation of uranium
$U(SO_4)_2 \cdot 4H_2O$ (10 mg/ml) + Na_2WO_4	Complete reduction; precipitation of uranium
pH 3.18	Precipitation of uranium as yellow $UO_3 \cdot nH_2O$; decrease in pH
pH 2.60	Same as pH 3.18
pH 2.20	No appreciable change
pH 1.98	No appreciable change
pH 1.72	No appreciable change
pH 1.44	No appreciable change

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EFFECT OF VARIABLES ON CORROSION: SERIES II

Several series of ampoule tests were run as out-of-pile experiments in order to determine the effects of numerous variables on the corrosion resistance of 347 stainless steel in uranyl sulfate systems.

The experimental procedure was as follows: Type 347 stainless steel rods approximately 1½ in. in length and 1/16 in. in diameter were inserted in 6-mm-I.D. quartz (vitreosil) ampoules. Enough uranyl sulfate, of concentration 30 g of uranium per liter, was added to completely cover the steel specimens, leaving a vapor space approximately equal to that occupied by the liquid. The solutions were frozen in a dry-ice bath and the ampoules then sealed. The tubes were "housed" in hollow brass cylinders and rocked in a stainless steel box in a large high-temperature oven at 250°C for various lengths of time. The solutions and specimens were observed daily. Although originally planned to run 100 hr, numerous tests were extended further when it appeared that this additional time would give more conclusive results. At the end of each run, the solutions were analyzed for pH and uranium concentration (sometimes iron and nickel), and the test specimens of stainless steel were examined under a microscope. The variables examined included (1) the type of passivation treatment, (2) the presence of nitrate, (3) chloride and iodide in varying amounts, (4) the presence or absence of oxygen, and (5) the length of time of the experiments.

The data and results are listed in Table 19. Two main criteria have been largely used to determine the success of a test run. The first is the appearance of the test specimen under the microscope and the second is the condition of the uranyl sulfate solution at the end of the test, i.e., uranium concentration, pH, precipitates, etc.

Numerous observations and several conclusions from these experiments are summarized in the following paragraphs.

1. Chloride ion is definitely detrimental to 347 stainless steel in concentrations of ≤ 500 ppm under the essentially *static* conditions of these experiments. The uranyl sulfate solutions are reduced to U_3O_8 and UO_2, and the test specimens show considerable flaking and some pitting. Concentrations of 10 to 200 ppm of chloride do not reduce uranyl sulfate solutions in 120 hr, but the test specimens show the formation of a fairly heavy layer of coarse-grained oxide.

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TABLE 19

Effect of variables and Additives on Corrosion of 347 Stainless Steel by Uranyl Sulfate Solutions

NO. OF SAMPLES	PRETREATMENT	ADDITIVE	pH*	REMARKS
20	Nitrate	Cl⁻, 10 - 2000 ppm	1.9 - 2.1	Definite attack in all cases at ≥ 500 ppm; coarse-grained oxide film present at lower concentrations
10	Nitrate	I⁻, 100 - 2000 ppm	1.9 - 2.1	Attack of 2 specimens, one at 2000 and other at 1000 ppm; coarse-grained oxide film present at lower concentrations of I⁻
12	Nitrate	Air	1.8 - 2.0	Solutions and specimens OK
2	None	Air	1.6	Bad attack of specimens
6	Nitrate	Degassed	1.6 - 1.8	All solutions reduced completely; all specimens attacked
2	None	Degassed	1.8	
2	Chromate	Air	1.9 - 2.1	Solutions OK; specimens excellent
4	Chromate	Degassed	1.1 - 1.5	U concentration in solution reduced materially; specimens begin to show attack
2	Nitrate	1 atm O₂	2.40 - 2.5	Solutions and specimens OK
2	None	1 atm O₂	1.85	Small red precipitate; specimens acquired thin oxide film
2	Nitrate	10 atm O₂	2.45	Solutions and specimens OK
2	None	10 atm O₂	2.40	Small red precipitate; specimens acquired thin oxide film
2	Oxygen	Air	2.1	Solution and specimens OK
2	Nitrate	1% HNO₃		500 ppm Ni present in all solutions; specimens good
2	None	1% HNO₃		

*The pH values listed in this column are those measured at the end of each experiment. The pH of the starting solution in all cases was 2.55.

2. Iodide ion is extremely unstable in uranyl sulfate solutions which have not been degassed of atmospheric oxygen, so that in this series of tests we are essentially dealing with free iodine. Duplicate samples containing 2000 and 1000 ppm of iodide gave opposite results; in each case one solution was reduced to U_3O_8 while the other remained stable. However, the test specimens, even in the stable solutions, showed some signs of attack such as flaking off of the oxide layer. Concentrations ≤ 500 ppm of iodide did not reduce the solutions or materially affect the test specimens in 140 hr except for the formation of the coarse-grained layer of oxide similar to that noted above in the case of chlorides.

3. The absence of oxygen was found to be very detrimental, resulting in reduction of the solutions and serious attack of the steel specimens. Oxygen was eliminated from these ampoules by degassing on a vacuum line ($\sim 10^{-4}$ mm). This technique appears to offer considerable promise as a means of testing the durability of any passivation film, and, simultaneously, the elapsed time necessary for breakdown of both the solution and steel specimen gives a direct indication of the relative toughness of these films or oxide layers. For example, all six separate nitrate-pretreated specimens (from different pretreatment batches) were attacked, and the uranyl sulfate solutions completely reduced in less than 40 hr at 250°C; four of these failed completely in less than 24 hr. In contrast to these, two chromate-pretreated specimens were run for at least 120 hr and two more for 150 and 170 hr before material reduction of the uranium in solution was evident; furthermore, none of the steel test specimens showed the deep attack and pitting which were noted with nitrate-pretreated specimens.

4. Several runs were made in which excess oxygen was present in the system. One atmosphere of oxygen was obtained in some samples by bubbling oxygen through the solutions, while in others hydrogen peroxide was added in such amounts that its decomposition would give a pressure of about 10 atm of oxygen measured at room temperature above the solution. Passivated (nitrate) and unpassivated specimens were used. The former showed no change nor were the solutions affected after 100 hr, but the latter appeared to have acquired a thin film of oxide, simultaneously depositing a small red iron oxide precipitate from solution. These latter oxygen-pretreated specimens were then placed in fresh solutions of uranyl sulfate (air present) and run an additional 80 hr without any evidence of breakdown. Whether this oxygen pretreatment will provide a durable passivation film is now being tested by the degassing technique.

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5. Several runs were made on both passivated (nitrate) and unpassivated specimens in which 1% nitric acid was added to the uranyl sulfate solutions. Small reddish precipitates of iron oxide were noted after 24 hr, and the color of the solutions had changed from yellow to a decided greenish yellow; analyses indicated that at least 500 ppm of nickel had been leached out of the steel specimens into solution. The specimens themselves had a good appearance; they were gray in color, having a thin crystalline layer above a lustrous background.

6. Small yellow precipitates, which appeared to be of the rhombohedral type and contained on the average about 5% of the uranium present, were found in almost every ampoule (except where the uranium was reduced) heated at 250°C for at least 80 hr. Several of these precipitates, which were analyzed spectrographically, were found to contain large amounts of uranium and medium amounts of silicon. X-ray—diffraction patterns at first appeared to indicate that the crystalline material was similar to that obtained by Marshall,[4] which he postulated as an orthosilicate compound $(UO_2)_2SiO_4 \cdot 3H_2O$. However, closer examination revealed that there were enough discrepancies between the patterns to indicate that they are not the same crystalline phase. Since these precipitates contain silicon and are very difficult to dissolve in nitric acid, it is believed that they consist largely of uranium silicates formed from long contact of the uranyl sulfate solutions with vitreosil at 250°C.

ELECTROCHEMICAL CORROSION STUDY

Corrosion studies of an electrochemical nature have been continued during the past quarter. These studies have been directed toward obtaining a general picture of the corrosion mechanism and the subsequent uranium removal from solution by precipitation of either $UO_3 \cdot xH_2O$, U_3O_8, or UO_2.

Experimental

The utility of the cell passivated stainless steel|UO_2SO_4|passivated stainless steel, at 100°C in the presence of chloride ions has previously been

(4) W. L. Marshall and J. S. Gill, "The Compound Uranyl Orthosilicate Trihydrate," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870, p. 25 (Mar. 1, 1951).

demonstrated.[5] This same system was also found to indicate the onset of rapid corrosion at 250°C in the presence of chloride ions.

At 100°C in the absence of chloride ion it has been impossible to observe any evidence of corrosion even after 5 days exposure time. Neither microscopic examination of the surface nor potential measurements indicated active corrosion. When a uranyl sulfate solution was heated to 250°C in a passivated steel bomb for 1 week the entire uranium content was precipitated and corrosion products were found both in solution and in the precipitate. During the run the potential of the walls of the vessel versus a central passivated steel wire was recorded and there was no evidence of a potential change. The potential of the cell, passivated stainless steel $|UO_2SO_4|$ passivated stainless steel, remained at zero throughout the experiment even though complete uranium precipitation occurred during the run. It appears that the system, passivated stainless steel $|UO_2SO_4|$ passivated stainless steel, is of little or no value in the absence of the chloride ion.

The first stage of uranium precipitation probably consisted of the reduction of uranium(VI) to uranium(IV). The uranium(IV) was subsequently precipitated by hydrolysis and the uranium oxide adhered to all available surfaces. Both electrodes became coated with the precipitate and hence were equivalent.

In the above run the uranium precipitated as a shiny, black, adherent coating on the walls of the vessel as well as the central electrode. An X-ray analysis of the precipitate showed it to be 100% UO_2.

If the above assumption is correct, it would be impossible to use any metallic indicator electrode because when it became coated with UO_2 it would be equivalent to the passive surface also covered with the same oxide. In the near future a platinum-indicator electrode will be used to see if the same result is obtained.

The effect of removing oxygen from the uranyl sulfate solution in which a passivated stainless steel specimen was immersed has been investigated. A passivated piece of steel was mounted in the bottom of a conventional electrolysis cell and 15 ml of UO_2SO_4 (30 g of uranium per liter) solution was placed above it. A stream of oxygen-free nitrogen was bubbled through the solution

(5) "Potentiometric Corrosion Studies," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951, ORNL-990, p. 91 (May 18, 1951).

and the potential of the steel vs. the S.C.E. was recorded. Before passing
nitrogen through the cell, the potential of the steel was +0.52 v vs. S.C.E.

During the first 4 hr of passing nitrogen through the solution the
potential changed in a negative direction by about 50 mv. During the next
hour the potential changed by 350 mv so that the potential of the steel was
about +0.10 v vs. S.C.E. Further bubbling of nitrogen had no additional
effect on the potential of the steel. When oxygen was substituted for nitrogen
in the gas stream, the potential changed in about 1 hr to its original value,
i.e., +0.52 v vs. S.C.E. The cycle could be repeated by the alternate passing
of nitrogen and oxygen through the solution.

It thus appears that oxygen was at least partially responsible for the
noble behavior of the passivated steel. Since the time required to observe
the change in potential was so long, it seemed likely that the oxygen held on
the surface of the steel was released only slowly.

It has been shown conclusively that the presence of 100 to 300 ppm of
silica in a uranyl sulfate solution improves the corrosion resistance of
passivated stainless steel to chloride ion attack. When passivated steel
specimens were immersed in a uranyl sulfate solution at 100°C containing 0.05
M potassium chloride the passivity was destroyed in 10 to 40 min. If the
uranyl sulfate solution contained 100 to 300 ppm silica the passivity was
destroyed only after 20 to 24 hr. To date no extensive study of this system
has been made, but a more detailed study is planned for the future.

Discussion

At least a part of the results of the corrosion studies reported to date
can be explained fairly well by an electrochemical mechanism similar to that
proposed by Uhlig.[6] The anodic reaction consists of the oxidation of iron,
nickel, and chromium. At the cathodic areas there are three possible reactions:

$$\tfrac{1}{2}O_2 + 2H^+ \longrightarrow H_2O - 2e$$
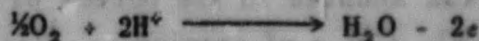
(6) H. H. Uhlig, *Corrosion Handbook*, p. 125-143. Wiley, New York, 1948.

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$$2H^+ \longrightarrow H_2 - 2e \tag{2}$$

$$UO_2^{++} \longrightarrow UO_2 \text{ (or } U_3O_8) - 2e \tag{3}$$
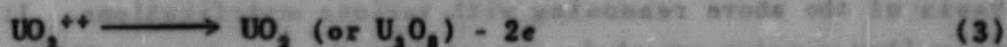
Equations (1) and (2) consume hydrogen ions, leaving a decreased acidity in the near vicinity of the cathodic surface. Hence, if oxygen is present and if either oxygen or hydrogen ions are more easily reduced than uranyl ions, corrosion of the alloy can proceed without reduction of uranium. However, if the reduction of either oxygen or hydrogen ions at an appreciable rate constitutes the cathodic reaction there would be an increased pH near the cathodic surface and the hydrolytic precipitation of uranyl ion appears possible.

The consumption of hydrogen ions at the cathode is nearly offset by the liberation of hydrogen ions produced from the hydrolytic precipitation of the anodic corrosion products. At 250°C both iron(III) and chromium(III) are completely precipitated as oxides, liberating hydrogen ions in an amount nearly equal to that consumed at the cathodic areas. Experiments have indicated that the precipitates of iron and chromium oxides are frequently colloidal in nature and could easily be overlooked during an analysis of the solution. Hence, an analysis of the solution does not necessarily indicate the occurrence of active corrosion.

There are several reasons that corrosion may not be apparent at lower temperatures:

1. Hydrolytic precipitation of uranium(IV), iron(III), and chromium(III) does not take place in uranyl sulfate solutions, at least to completion, until temperatures in excess of 100°C are reached.

2. In a closed system where the reduction of oxygen is the controlling factor the rate of corrosion doubles for each 30°C rise in temperature,[6] resulting in a corrosion rate almost 200 times faster at 250°C than at 25°C.

3. Oxidation-reduction potentials, overvoltages, and conductivity of the solution possibly become more favorable for an increased corrosion rate at increased temperatures.

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The data obtained to date indicate that corrosion encountered in the HRE work is an electrolytic type. Nearly all the data can be explained on the basis of the above reasoning with various modifications. It appears that the so-called passive steel is not completely passive at 250°C in uranyl sulfate but undergoes continuous corrosion. The rate of corrosion is undoubtedly dependent on numerous physical properties of the steel and its oxide coating. Since each melt of steel is not completely identical and since each method of working the steel is different, the degree of reproducibility of corrosion rates can be expected to be low. The data obtained bear out the last statement.

Future work will be directed at getting a clearer picture of the corrosion mechanism and determining what effect, if any, silica in the uranyl solution has on corrosion rates.

3. STABILITY AND CORROSION UNDER RADIATION

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During the past quarter the efforts of the Radiation Stability Group have been directed toward the following general lines of investigation:

1. Long-term radiation stability tests at the maximum flux of the graphite pile.

2. Short-term exploratory tests at the much higher fluxes of the LITR.

3. Out of pile studies of corrosion and solution stability using the bomb-fitting-tubing assemblies designed for in-pile testing.

4. Preliminary radiation stability studies of the components of the heavy-water reflector system of the HRE.

5. Preliminary radiation stability studies of uranyl nitrate solutions.

The conclusions of principal interest to the HRE which have arisen from the work of the group during the quarter are as follows:

1. The presence of oxygen is necessary for the maintenance of the passivity of type 347 stainless steel surfaces in contact with uranyl sulfate solutions at 250°C, and may possibly be sufficient for the achievement and maintenance of passivity. (This finding is supported by the work of other groups who approached the problem from different points of view, and it is not intended that any credit should be taken from them. The conclusion, nevertheless, is presented here because the work of the Radiation Stability Group establishes it with certainty.)

2. Surfaces pretreated with chromic acid appear outstandingly better than those pretreated with nitric acid when tested for ability to maintain passivity in contact with degassed solutions of uranyl sulfate.

3. A group of five stainless steel bombs containing enriched uranyl sulfate solutions has been exposed to the full flux of the X-10 pile for 7 weeks with pressures substantially in excess of steam pressure, indicating that the uranium remains in a soluble form.

4. A preliminary experiment in the LITR has been carried out successfully.

LONG-TERM IRRADIATIONS IN THE X-10 PILE

As part of the continuation of long-term irradiation studies, five bombs were placed in hole 60 about 7 weeks ago. These bombs, developed through the out-of-pile testing program described later in this report, were free from chloride and non-stainless steel components. At the time the bomb assemblies were prepared the importance of oxygen for out-of-pile maintenance of passivity had not been established, and the conditions were not optimal in the light of present knowledge. Three of the bombs showed no reduction of uranium when heated in the absence of radiation; one showed a slight amount of reduction, and the other showed complete reduction. All the bombs, after insertion, were subjected to low-temperature activation treatment in the presence of neutron radiation, and throughout the 7-week period they have all shown pressures substantially in excess of steam pressure. This implies that there is uranium in solution after this length of exposure.

An automatic control device has been perfected and attached to a "slave" kwh meter indicating pile power; the device lowers the temperature of the bombs by $50^{\circ}C$ every time the pile is shut down and restores the temperature 30 min after the pile comes up again. This prevents the exhaustion of oxygen by recombination during a pile shutdown, and the temperature to which the surfaces are exposed in the absence of radiation is reduced. In this way it is hoped that only the corrosion occurring in the presence of radiation will be measured.

It seems probable that some weight changes will be noted when the corrosion samples in these bombs are eventually examined. This assumption is based on the fact that all the assemblies received out-of-pile heating to test their ability to contain uranyl sulfate. We now know that in the absence of large positive oxygen pressures the small amount of oxygen present in the air would be rapidly consumed, followed by corrosion and reduction of the uranium if the heating were continued. It appears significant that the two bombs which had shown partial or complete reduction of uranium has been pretreated with nitric acid, whereas the other three had been pretreated with chromic acid. As will be shown in a later section of this report, it appears that chromate pretreatment offers much better protection against uranyl sulfate solution in the absence of oxygen than does nitrate pretreatment. Thus these bombs, and their corrosion samples, should show less corrosion than the bombs treated with nitrate.

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As the out-of-pile testing program continues with its evaluation of oxygen and other agents for the achievement and maintenance of passivity, it should be possible to obtain a new and better set of bombs to replace those now in hole 60.

IRRADIATION STUDIES AT HIGHER FLUXES USING THE LITR

Under present authorization the LITR can achieve a flux of around 10^{13} at a 1000-kw power level. This is a factor of 10 to 20 over the fluxes obtainable in the X-10 graphite pile and gives a radiation level comparable with that expected for the HRE. Moreover, the ratio of gammas and fast neutrons to slow neutrons is about 10 times that achieved in the graphite pile. This higher ratio is also expected for the HRE. It is therefore believed that experiments in the LITR represent, as well as can be obtained short of the HRE itself, the operating radiation levels expected from the HRE at half power.

During the past quarter the design and fabrication of apparatus was completed and a preliminary experiment was carried out. One purpose of the experiment was to check the effectiveness of the control equipment and the procedures for loading and unloading at high radiation levels. On the whole, the equipment performed exceedingly well. It was found that auxiliary heating was not necessary at power levels above 320 kw, enough heat being obtained from fission and gamma heating to hold satisfactory temperature levels. Insertion and withdrawal of the aluminum tube containing the bomb and furnace were accomplished without difficulty or excessive radiation of personnel.

The second purpose of the experiment was to become oriented with respect to the pressures achieved at any given combination of temperature and flux, particularly at fluxes above those obtainable in the X-10 graphite pile. Since the experiment has just been completed, it is not possible to present a complete analysis of the data. However, several points are clear and should be discussed. First of all it seems probable that the uranyl sulfate solution originally put into the bomb was decomposed to insoluble oxides of uranium during the period of temperature and pressure checking which preceded insertion into the LITR. Thus the experiment was started with a "dead" bomb, and no pressure build-up was observed at an initial temperature of 250°C and power levels of 6, 60, and 80 kw. This situation was not completely unexpected in

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view of the out-of-pile studies which were being carried out concurrently. Two things which contributed to uncertainty in interpreting results were (1) the absence of a large positive oxygen pressure over the solution during the heating and pressure tests, and (2) the lack of any analyses of the solution after these tests. The reason for the first condition was an unwillingness to add the possible complicating factor of oxygen pressure to the recombination which was subsequently to occur; the lack of analyses was a calculated risk, based on the greater risk involved in breaking and attempting to remake the pressure seals after the initial pressure tests.

Having been satisfied that the solution was initially bad, the temperature was lowered while maintaining the neutron flux level in order to permit the build-up of a peroxide concentration sufficient to oxidize the reduced uranium back to the uranyl state. This maneuver was successful in bringing a major portion, if not all, of the uranium back into solution.

With an apparently satisfactory solution a variety of temperature-pressure combinations were explored at a power level of 320 kw (1/3 full flux). An interesting set of self-consistent data was obtained, revealing no effects of unexpected magnitude attributable to the higher slow-neutron flux or to the gamma and fast-neutron fluxes. In anticipation of higher pressures at higher fluxes, it was decided to reduce the pressure to a low value by using a high temperature (295°C) and a very low flux, hoping in this way to maintain a protective concentration of oxidizing radicals while recombining most of the hydrogen and oxygen. Apparently this maneuver was unsuccessful; when the flux level was raised to 2/3 and then to full flux (640 and 1000 kw) the pressure response was much lower than anticipated. When the power level was reduced to 320 kw the response indicated that most of the uranium had been lost from solution. Although subsequent efforts to reactivate the solution were unsuccessful, recombination data at higher fluxes were obtained which will be useful in future work.

It is planned to continue these preliminary experiments in the near future, and, using chromate pretreatment supplemented by an auxiliary oxygen pressure in the absence of radiation, there seems to be no reason for anticipating trouble with the solution. The data already obtained on recombination rates will allow us to explore the effects of higher flux in an orderly manner so as to obtain dependable data in the shortest possible time.

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As the third phase of operations in the LITR, it is planned that a study be made of long-term effects on solutions and stainless steel surfaces. For these experiments it is planned to use the horizontal thimble holes. Calculations are now under way, which, coupled with the information obtained in the preliminary experiments, will lead to designs for bombs, furnaces, shielding, etc. that will permit satisfactory experiments in the horizontal holes.

OUT-OF-PILE STUDIES OF STAINLESS STEEL BOMB-FITTING-TUBING ASSEMBLIES

As reported in the previous quarterly,[1] suspicion had been focussed on two factors which were thought capable of causing solution instability and corrosion, even in the absence of neutron irradiation. The first factor was the presence of chloride ion, and the second was the use of a bomb fitting containing a silver-soldered joint 2 in. above the liquid phase and at a lower temperature than the body of the liquid. It will be recalled that every assembly containing such a fitting showed reduction of the uranium solution to black oxides and evidence of corrosion in the formation of ferrous ions.

Analyses of hot water rinses put through the bomb indicate the extent of removal of chloride ions. The hot rinses also served to lower the chloride ion concentration to minimal values prior to the introduction of uranyl sulfate solution.

With respect to the fittings, designs have been modified so that the thermocouple well has been eliminated and the capillary tubing is sealed to the fitting by means of a small stainless steel ferrule or swage ring. Thus there are no heated joints and no non-stainless steel portions of the fitting. Preliminary designs of a small bomb having two openings in its head, one for a thermocouple and one for the capillary tubing (both being held in place by means of small stainless steel ferrules), have been tested and bombs of this type are now under construction.

Table 20 gives some of the early results obtained with the new style fittings.

These results are in striking contrast to the results obtained earlier with the old-style fittings and appear to confirm the suspicion previously noted. However, there were two cases of complete reduction and one case of

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(1) J. W. Boyle et al., "In-Pile Studies," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951*, ORNL-990, p. 79 (May 18, 1951).

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TABLE 20

Out-of-Pile Tests of Assemblies Containing Swage-Type Fittings

BOMB NO.	PRETREATMENT	RESULT OF HEATING FOR AT LEAST 24 hr AT 250 TO 300°C
316	Nitrate	Good; no loss of uranium
324	Nitrate	Good
325	Nitrate	Good
321	Nitrate	Good on first test; then partial loss of uranium to 28.7 mg/ml on second heating
327	Nitrate	Bad; uranium content less than 1 mg/ml
317	Nitrate	Good; steam leak left all uranium in soluble form
320	Nitrate	Good; steam leak left all uranium in soluble form
335	Nitrate	Good; steam leak left all uranium in soluble form
330D	Chromate	Good
330S	Chromate	Good
328	Chromate	Good; small water loss by steam leak; water replaced
331D	Nitrate	Good on first test; complete loss of uranium of second test

partial reduction which were not immediately explained. These suggested that some further factor must be operating to confuse the situation. During the past quarter results from our ampoule experiments and from test-loop and electrochemical work by other groups began to indicate that the presence of oxygen was necessary for the maintenance of passivity. This provides an explanation for the failures associated with the old-style fittings; the silver-soldered joint presented a clean, reduced, silver-copper eutectic surface which would be almost ideal for reaction with oxygen at temperatures of around 200°C. When the limited supply of oxygen in the system had been depleted the passivity would no longer be maintained and active reduction of the uranyl sulfate with corrosion of the metal could begin. This would also help explain the in-pile experience using old-style fittings; when radiation was present to provide an oxidizing atmosphere or when large partial pressures of oxygen were present the bombs would remain passive, but during long shutdowns at high temperatures the oxygen might have become depleted, allowing corrosion to take place. The high concentrations of chloride ion present in some in-pile tests would tend to accentuate the effect of losing oxygen pressure.

Based on the concept of the presence of oxygen as a necessary (perhaps sufficient) condition, it was decided to set up a series of experiments in which the stainless steel bombs were not pretreated in the ordinary nitric acid or chromic acid solution but in which oxygen was used as the only pretreatment agent.

The results to date, listed in Table 21, indicate clearly that oxygen alone is capable of achieving and maintaining a passive condition in a stainless steel bomb-tubing solution assembly. When critical conditions for passivity have been defined with such assemblies, in-pile radiation tests will be initiated using these conditions. Information received from the pump loop tests indicates that satisfactory out-of-pile conditions can be maintained in larger dynamic systems.

TABLE 21

Oxygen as a Passivating Agent

RUN NO.	ADDED OXYGEN PRESSURE DURING TEST (psi)	PRETREATMENT CONDITIONS	RESULTS		
			24 hr	100 hr	500 hr
336	200	200 psi; wet		Good	
337	400	400 psi; wet		Good	
339	400	400 psi; dry		Good	Good
340	200	None		Bad (?) (leak-low volume)	
341	400	None		Good	
342	600	None		Good	
343	None	200 psi; wet		Bad	
344		600 psi; wet		Bad	
345		400 psi; dry		Bad	
346		None	Bad		
347		None	Bad		
348		None	Bad		

PRELIMINARY IRRADIATION STUDIES OF THE HEAVY-WATER REFLECTOR SYSTEM

At a meeting of the Homogeneous Reactor Project Steering Committee, April 26, the reflector system was discussed extensively, and the Radiation Stability Group was requested to study the associated components (D_2O, 347 stainless steel, 1030 carbon steel, and trisodium phosphate) with particular reference to the rate of gas formation under radiation. This study is now under way, using H_2O instead of D_2O, both in quartz ampoules and in bombs of 1030 carbon steel. In addition to trisodium phosphate, other agents for achieving a pH above 10 (considered to be the effective anticorrosion agent) are being studied, including 0.005 N NaOH and a saturated solution of MgO.

PRELIMINARY IRRADIATION STUDIES OF THE URANYL NITRATE SYSTEM

Studies of the uranyl nitrate system were initiated early in the quarter. Purified uranyl nitrate solutions were prepared and analyzed. Analytical methods and equipment for determining the composition of the gaseous radiation products were perfected, and quartz ampoule experiments were under way when the program was interrupted to carry out the investigation of the heavy-water reflector system reported above. The work on uranyl nitrate and other uranium compounds will be resumed as soon as the heavy-water work is completed.

PROJECTED WORK FOR THE NEXT QUARTER

Additional preliminary experiments will be carried out at the higher fluxes obtainable in the LITR, using the vertical hole into the active lattice. Apparatus for long-term experiments in the horizontal thimble holes will be completed and experiments will be started. An exploration of uranium peroxide formation as a function of temperature and flux will be carried out in the LITR using the vertical experimental hole.

Long-term experiments will be continued in horizontal hole 60 of the X-10 pile. If the present set of bombs is removed for any reason a new set will be inserted.

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Exploration of the radiation decomposition of the heavy-water reflector system of the HRE will be carried out by means of experiments in hole 12 of the X-10 pile.

Preliminary exploration of the radiation decomposition of uranyl nitrate solutions will be continued, and studies on uranyl fluoride and possibly uranyl phosphate solutions will be initiated, using hole 12 of the X-10 pile.

Out-of-pile studies of bomb-fitting-tubing assemblies will be continued as a basis for interpretation of the in-pile radiation results. Solutions of higher concentration will be checked, following which radiation studies will be initiated in hole 12.

Out-of-pile studies of the rates of recombination of hydrogen and oxygen in our bomb-fitting-tubing assemblies at high pressures may be initiated in order to provide better interpretation of the significance of data obtained in the presence of radiation, particularly in the pressure "hump" frequently observed in radiation experiments.

If possible, work on the interaction of oxygen with stainless steel surfaces, using O^{18} as a tracer and by measurement of the rates of consumption of ordinary oxygen, will be initiated for its significance in connection with passivity.

It is hoped that it will also be possible to start investigating the interaction of stainless steel components with uranyl sulfate solutions under a variety of conditions, using irradiated stainless steel as a source of radioactive components. This technique should provide a very sensitive measurement of the ability of protective measures to prevent the escape of the stainless steel metallic components, i.e., to prevent corrosion.

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4. RECOMBINATION OF HYDROGEN AND OXYGEN

H. M. McLeod

Laboratory-Scale Studies	Pilot Plant Tests
D. W. Kuhn	K. O. Johnsson
A. A. Palko	T. S. Mackey
A. D. Ryon	D. Phillips
	M. J. Fortenberry

LABORATORY-SCALE STUDIES

During the past quarter work was concentrated on studies of the feasibility of recombining an essentially 100% stoichiometric mixture of hydrogen and oxygen by means of massive metal catalysts and on methods of removing iodine from the gas stream. Work was also started on development of a method for the catalytic recombination of the relatively small quantity of gas formed in the HRE reflector system.

Efficiency of Conversion. Although it has already been demonstrated that the efficiency of conversion in the hydrogen-oxygen reaction using a platinum catalyst may exceed 99%, it is of interest to know precisely what fraction of 1% of the gas may be expected to pass through the catalyst. Since this residual gas may require further treatment, its quantity should be known as accurately as possible. Hence, experiments were conducted in which the quantity of catalyst was varied from about 400 to 1500 g, the temperature in the catalyst bed was varied from 200 to 700°C, the composition of the gas was varied from about 3 up to 15%, and the combined gas-steam flow rate varied from about 25 to 110 liters/min. In these tests the gas was preheated to the desired temperature prior to entering the catalyst chamber, and only one pass was made through the catalyst. The data are given in Table 22 and show that the conversion efficiency averaged 99.79% with the maximum at 99.99 and the minimum at 99.1. Although there was a wide variation in the conditions employed in the tests, the conversion efficiencies were fairly uniform. Therefore, there does not appear to be any correlation between temperature, space velocity, and gas composition. The possibility of reducing the unrecombined portion of the stream leaving the catalyst by condensing most of the steam and then passing the noncondensed portion through a second small catalyst bed will be investigated.

TABLE 22

Efficiency of Conversion in the Catalytic Recombination of H_2 and O_2

0.3% Platinum-on-Alumina

WEIGHT OF CATALYST (g)	PREHEAT TEMPERATURE (^{o}C)	MAXIMUM CATALYST TEMPERATURE (^{o}C)	FLOW RATES (liter/min)		ELECTROLYTIC GAS (%)	SPACE VELOCITY (hr^{-1})	EXIT GAS (cc/min)	PERCENT CONVERSION
			STEAM	ELECTROLYTIC GAS				
390	175	360	25	1.5	5.7	2700	4.3	99.71
390	200	310	50	1.5	2.9	5300	2.3	99.84
390	130	193	100	1.5	1.5	10500	1.4	99.91
1200	200	415	100	9.0	8.3	3700	85.0	99.1
1400	120	430	17.5	1.5	7.9	560	0.09	99.99
1400	150	600	17.5	3.0	14.6	600	15.6	99.5
1400	120	230	50	1.5	2.9	1500	0.04	99.94
1510	180	625	22	3.0	12.0	670	1.5	99.95
1510	140	425	50	4.5	8.3	1450	1.6	99.97
1510	155	685	50	9.0	15.3	1450	3.5	99.96

Recombination of Essentially Pure Electrolytic Gas. Studies were begun on methods for recombining hydrogen and oxygen mixtures containing little or no diluent steam in the presence of a catalyst less active than the platinum-on-alumina type. The principal advantage in carrying out full-scale recombination of such mixtures is that it would eliminate the necessity of adding diluent steam. In these studies the gas mixture was passed through platinum, silver, and copper tubing at various temperatures and flow rates. The important conditions and the results of these tests are summarized below.

Platinum Tubing. In these tests the platinum tubing (¼ in. diameter, 10 ft long) was immersed in an oil bath which could be heated as high as 170°C. Employing gas flow rates varying from about 0.25 to 9.5 liters/min and temperatures of 125, 150, and 170°C, the efficiency of conversion of a hydrogen-oxygen gas mixture, saturated with moisture at room temperature, was found to be dependent on both temperature and space velocity. With temperatures fixed, the conversion efficiency decreased with increased velocity; with velocity fixed, the efficiency increased with increased temperature. The results indicated that a surface area of about 1 sq ft would be required for each liter per minute of gas at 170°C to obtain a conversion efficiency of 90%. Aqua regia was then passed through the tube, followed by distilled water, in an attempt to increase the surface activity. In subsequent tests the temperature inside the tube quickly rose to the point where a flashback occurred. In view of these results no further consideration will be given to the use of a massive platinum surface as the catalyst.

Silver Tubing. Tests similar to those carried out with the platinum tube were conducted using an 18-in. length of ¼-in. diameter copper tube lined with silver foil. The efficiency of conversion was very low at any of the temperatures available when using an oil bath. Silver tubing has been ordered and will be tested at higher temperatures in a fused salt bath.

Copper Tubing. Tests were carried out using a 20-ft length of 3/8-in.-diameter copper tubing immersed in a fused salt bath (sodium nitrite—potassium nitrate mixture). At 350°C and with a gas flow rate of 0.5 liter/min, flame recombination was promoted which occasionally flashed back to the generator; at temperatures below 350°C recombination did not occur to any appreciable extent.

Conclusions and Future Work. In view of the unfavorable results it was decided that no further work would be carried out using massive metal surfaces as the catalyst with the exception of a few tests using the silver tubing when available. Also, it was decided to conduct exploratory tests using catalysts other than platinum; information on such catalysts is now being sought from manufacturers.

Removal of Iodine from Gas Stream. An evaluation of stainless steel as a medium for trapping iodine from an electrolytic gas mixture is now in progress. The first test extended over a period of 480 hr. Type 316 stainless steel turnings were packed in a glass tube, and a mixture of electrolytic gas and iodine vapor was passed through the tube at room temperature. The gases were then mixed with preheated steam and passed through a heated bed of platinum-on-alumina catalyst. Flow rates were:

Steam	11 liters/min
Electrolytic gas	0.72 liters/min
Iodine	19 mg/hr
Space velocity	16,000 hr^{-1}
Weight of catalyst	30 g

The catalyst temperature ranged from 330 to 420°C, and the conversion fell from 98.6% at the start to 53.4% after 480 hr. The moist iodine attacked the stainless steel to form reddish-brown droplets of liquid which were water soluble. A section of stainless steel weighing 7.2 g was completely dissolved in this manner during the 20-day period.

A second and similar experiment is now in progress. The present test is being run at a higher iodine flow rate, and the temperature of the catalyst is maintained at 230 to 250°C. After 700 hr of operation, a considerable portion of stainless steel adjacent to the gas inlet tube was dissolved, and about 50 g of dark colored solution was withdrawn from the trap. The catalyst conversion efficiency fell off during the first 2 weeks from 97.7 to 93.2%, and during the next 2-week period it remained fairly constant at about 93.5%.

Future Work. Emphasis is now being placed on the development of a satisfactory method for recombining hydrogen and oxygen formed in the reflector side of the HRE. The initial tests will be carried out under conditions of temperature, pressure, and composition simulating those expected during operation of the HRE, and the efficiency of conversion obtained by employing a platinum-on-alumina catalyst located in the gas space of the reflector will be determined.

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In-Pile Test. The bomb from the first in-pile catalyst test was examined, and it was found that the uranium had precipitated from solution. The aqueous portion contained approximately 12 ppm chloride which may have caused the precipitation. The effect of chloride in the bombs is discussed under Sec. 1, p. 59. This experiment, then, was inconclusive, but further studies are to be made using the platinum-on-alumina (rather than on charcoal) catalyst which appeared to be satisfactory in other tests.

PILOT PLANT TESTS

During the past quarter the combustion range of the burner orifice was established; tests which were started in the previous quarter for the purpose of determining the quantity of steam necessary to dilute the off-gas to ensure quenching of flashbacks were completed; and most of the planned pilot plant runs were carried out although the data on these runs are not yet correlated.

Burner Orifice Range. To determine the combustion range of the burner orifice in terms of gas flow rates, tests were first carried out with the burner-chamber top plate located in the open to permit visual observation of the performance of both the burner and spark plug. The gas flow rate (no steam added) was varied slowly from about 17 to about 0.5 cfm, which was the lowest flow at which combustion was sustained. It was noted that as the gas flow decreased, the distance between the face of the burner orifice and the point in the gas stream at which combustion started also decreased. With a gas flow rate of about 2.5 cfm the burner orifice overheated, causing a flash-back, indicating the need for increasing the velocity of the gas over the low flow range by adding a fixed flow of steam. The quantity of steam necessary to prevent overheating of the orifice was determined by holding the gas flow rate constant at 2.5 cfm and varying the flow of steam; at 1 cfm of steam the orifice no longer overheated and at 1.5 cfm the orifice did not become heated with gas flow rates as low as 0.5 cfm. Consequently an orifice was installed to provide a constant flow of 1.5 cfm of steam which was introduced into the gas stream at a point near the burner orifice. Subsequently, tests were conducted with the burner orifice and cover plate in place. The results of these tests showed that the minimum flow rate of gas that would sustain combustion was 0.5 cfm; from 0.5 down to 0.3 cfm intermittent burning occurred, and below 0.3 cfm ignition occurred only when the burner chamber became sufficiently

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filled with gas to ignite. It is interesting to note that with a gas flow rate of 0.3 cfm the composition of the mixture entering the burner orifice was only about 17% gas, a composition which, according to the previously reported data on explosion limits, is noncombustible. Since an ignition transformer with a secondary potential of 10,000 v operates the spark plug, it is possible that in passing through the cool orifice a part of the steam condenses into small droplets which are ionized and collected on the neighboring metal in a manner similar to the operation of high-voltage electrostatic precipitators.

Quantity of Steam Necessary to Dilute the Off-Gas to Ensure Quenching of Flashback. During the previous quarter work was started on determining the range of gas compositions which would provide a noncombustible mixture between the dump tanks and the primary condenser in the HRE recombiner system. These tests were carried out using equipment similar to that which will be used in the HRE and under conditions simulating those expected during operation of the HRE. The equipment, testing procedures, and preliminary data were reported in the preceding HRE quarterly report.[1]

The minimum quantity of steam necessary to quench flashbacks at each of several different gas flows was determined. In these tests, the threshold value of steam flow was obtained approximately for each flow of gas, after which the steam flow was varied above and below the threshold value to more closely establish the flow below which flashbacks would penetrate beyond the primary condenser. The gas flows employed were 0.7, 0.9, 1.2, 9, and 16 cfm; in conducting the tests about 12 flashbacks were initiated by means of the auxiliary spark plug at each gas flow rate. The data obtained in these tests are given in Table 23.

The results showed that with a gas flow of 16 cfm and introducing the steam at a point 6 ft upstream from the condenser the maximum concentration of gas for which flashbacks could be repeatedly quenched was about 30%; with 9 cfm gas flow the maximum concentration was 24%. When the steam was introduced at a point 10 ft upstream from the condenser, using 16 cfm gas flow, the maximum concentration was about 32%. A fixed flow of 32 cfm of steam successfully quenched flashbacks at all gas flows below 9 cfm.

These results indicate that the relationship of the gas flow rate and the amount of steam necessary to quench flashbacks is not linear and that the

(1) H. M. McLeod, Jr., et al., "Pilot-Scale Tests of the Flame Recombiner," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951*, ORNL-990, p. 99, esp. p. 100 (May 18, 1951).

TABLE 23

Minimum Amount of Steam Necessary to Quench Flashbacks

FLOW RATES AT 70°F AND 1 atm (cfm)				GAS COMPOSITION (vol %)			
COMBINED GAS	H_2	NO_2	STEAM	H_2	NO_2	STEAM	RESULTS
Steam Mixed with Gas 6 ft Before Entering Condenser							
0.648	0.430	0.218	32	0.013	0.007	98.0	Flame quenched
0.910	0.602	0.308	32	0.018	0.009	97.5	Flame quenched
1.22	0.815	0.405	32	0.025	0.012	96.5	Flame quenched
9.0	6.0	3.0	29.	15.8	7.9	76.2	Flame not quenched
9.0	6.0	3.0	32	14.6	7.3	78.0	Flame quenched
16.05	10.55	5.5	36	20.2	10.5	69.0	Flame not quenched
16.05	10.56	5.5	37.5	19.6	10.3	70.0	Flame quenched
Steam Mixed with Gas 10 ft Before Entering Condenser							
15.95	10.55	5.4	27	24.5	12.6	63.0	Flame not quenched
15.95	10.55	5.4	30	23.0	11.8	65.5	Flame quenched

effect of the length of noncombustible zone between the dump tanks and the primary condenser in the recombiner system is significant over the range employed. Since the length of piping from the dump tank to the condenser will be about 14 ft in the HRE, it has been recommended that the composition of the gas in this section be maintained at not greater than 30% and that a constant steam flow of 1.5 cfm be maintained for gas flows below 5 cfm.

Testing of the Burner System. A number of pilot plant runs were made, both with low gas flow rates and with and without the follow-up catalytic recombiner. The data obtained during these runs are now being correlated, and the results will be reported in the next quarterly report.

5. ANALYTICAL CHEMICAL CONTROL OF THE HOMOGENEOUS
REACTOR SOLUTION

W. H. Davenport and R. H. Powell

During the past quarter a full-scale laboratory model of the electro-magnetic densitometer was assembled and exploratory runs using water were made in order to observe the response, sensitivity, and reproducibility of the instrument.

The Princo Densitrol instruments, which also measure density, are being fabricated by the Precision Thermometer and Instrument Company and the delivery date is estimated to be July 1, 1951. The dynamic testing of this apparatus will require a test loop.

A bomb was recently completed which is designed to test the various Q coils in the presence of varying concentrations of uranyl sulfate for mechani-cal strength of gasketing, performance at HRE temperatures, and equilibrium steam pressures.

In-pile experiments are continuing on the gamma- and neutron-absorbing glasses received from A. Silverman.[1] A new approach in making a glass with a combination of chemical stability and radiation stability is being taken by Penberthy Instrument Company of Seattle, Washington. It is attempting to reduce radiation damage in a glass by using materials which transmit the neutron radiation relatively well and offer low stopping power to gamma radiation. Such a glass would not be a shielding material but might be very useful for observation purposes in the high-pressure HRE system. The first attempt at a glass of this type has been received and will be corrosion tested.

ELECTROMAGNETIC DENSITOMETER

A type 347 stainless steel bomb (Fig. 13) was used for the exploratory distilled-water runs. Bomb and float were first cleaned electrolytically, then pretreated with 1% nitric acid for 4 hr. The tail of the float fitted into a cylindrical extension at the base of the bomb. The vertical movement

(1) W. H. Davenport and R. H. Powell, "Analytical Chemical Control," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951*, ORNL-990, p. 115 (May 18, 1951).
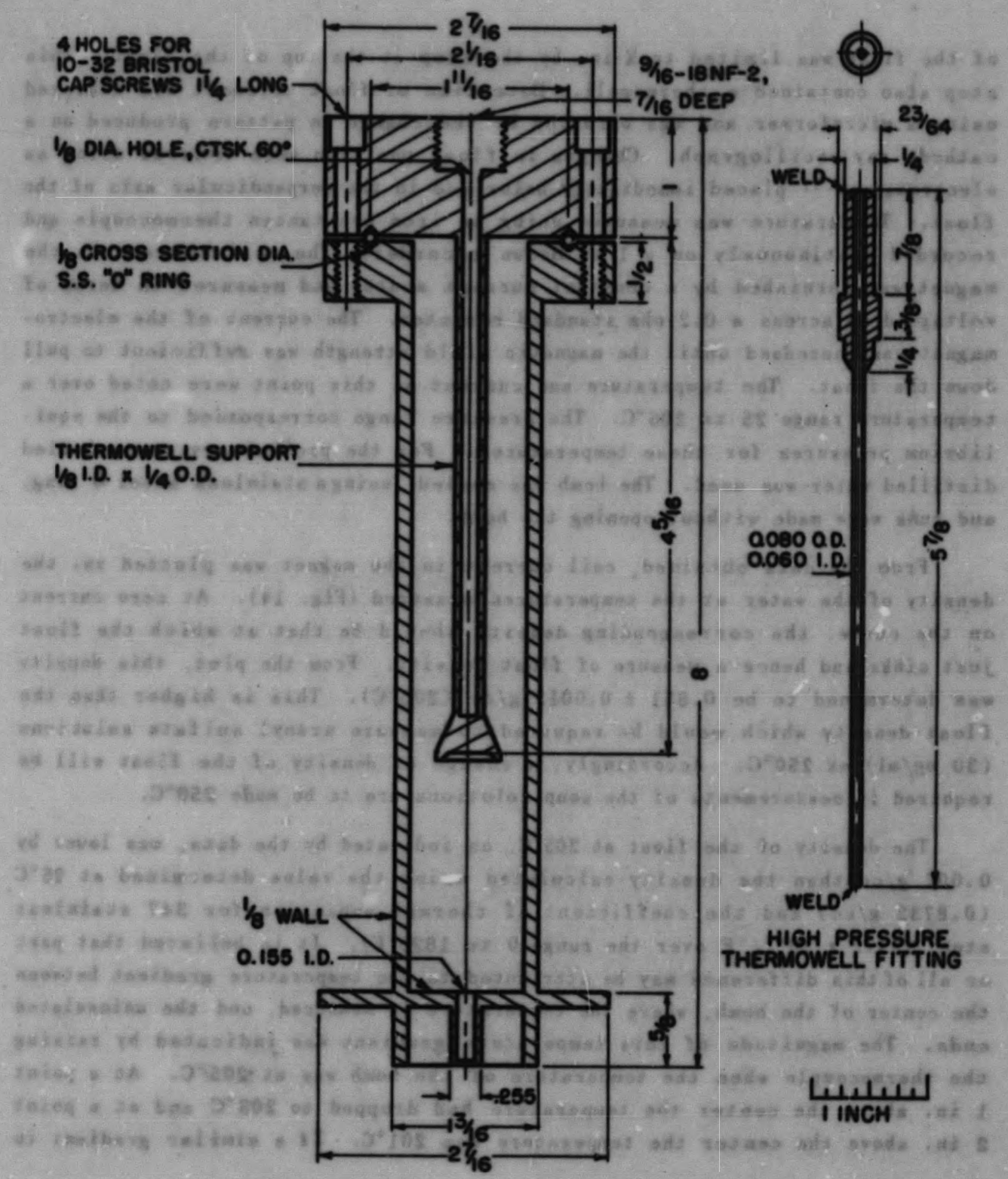
FIG. 13
ELECTROMAGNETIC DENSITOMETER
LABORATORY TEST BOMB
MATERIAL — 347 S.S.

of the float was limited to ¼ in. by the stop at the top of the float. This stop also contained a thermowell. Detection of float movement was achieved using a microformer and was observed by the change in pattern produced on a cathode-ray oscillograph. Changes in float position were induced using an electromagnet[2] placed immediately below and in the perpendicular axis of the float. Temperature was measured using an iron-constantan thermocouple and recorded continuously on a 1 mv Brown recorder. The coil current in the magnet was furnished by a constant current source and measured in terms of voltage drop across a 0.2-ohm standard resistor. The current of the electromagnet was increased until the magnetic field strength was sufficient to pull down the float. The temperature and current at this point were noted over a temperature range 25 to 206°C. The pressure range corresponded to the equilibrium pressures for these temperatures. For the preliminary runs, boiled distilled water was used. The bomb was sealed, using a stainless steel O ring, and runs were made without opening the bomb.

From the data obtained, coil current in the magnet was plotted vs. the density of the water at the temperatures measured (Fig. 14). At zero current on the curve, the corresponding density should be that at which the float just sinks and hence a measure of float density. From the plot, this density was determined to be 0.851 ± 0.0015 g/cc (205°C). This is higher than the float density which would be required to measure uranyl sulfate solutions (30 mg/ml) at 250°C. Accordingly, a change of density of the float will be required if measurements of the soup solutions are to be made 250°C.

The density of the float at 205°C, as indicated by the data, was lower by 0.007 g/cc than the density calculated using the value determined at 25°C (0.8732 g/cc) and the coefficient of thermal expansion for 347 stainless steel (11.2×10^{-6}/°F over the range 0 to 1825°F). It is believed that part or all of this difference may be attributed to the temperature gradient between the center of the bomb, where the temperature is measured, and the uninsulated ends. The magnitude of this temperature gradient was indicated by raising the thermocouple when the temperature of the bomb was at 205°C. At a point 1 in. above the center the temperature had dropped to 203°C and at a point 2 in. above the center the temperature was 201°C. If a similar gradient in

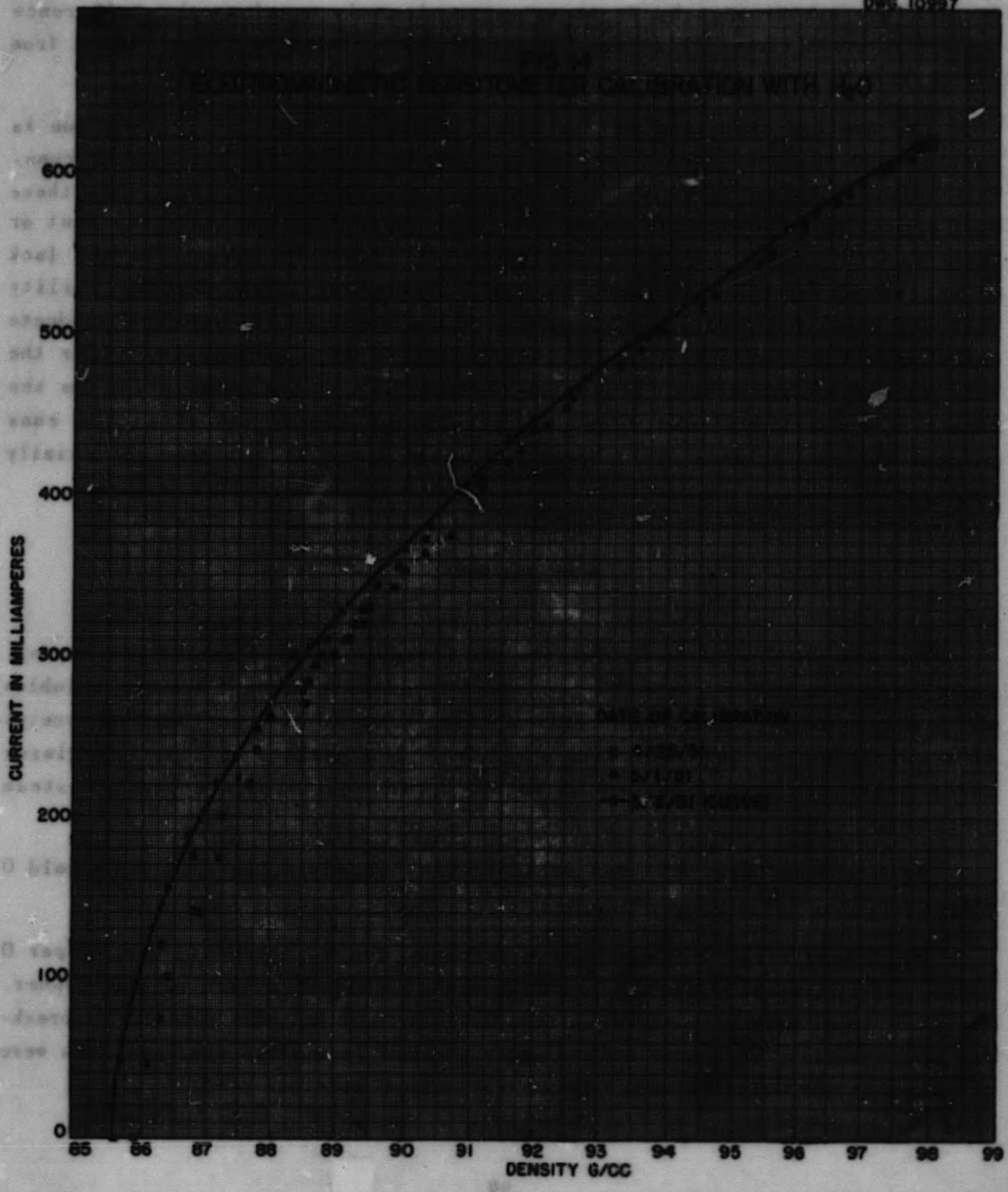(2) W. H. Davenport and R. H. Powell, "Analytical Chemical Control of the Homogeneous Reactor Solution," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950,* ORNL-925, p. 260 (Jan. 30, 1951).

FIG. 14
ELECTROMAGNETIC IONSTONE(?) CALIBRATION WITH H₂O

CURRENT IN MILLIAMPERES

600

500

400

300

200

100

0

65 86 87 88 89 90 91 92 93 94 95 96 97 98 99

DENSITY G/CC

temperature is assumed to exist at the lower end of the bomb, the average density of the solution will be higher than the density at the point of temperature measurement by an amount approximately equal to the difference between the calculated float density at 205°C and the density determined from the curve.

The average deviation of the points from the curve for a given run is smaller, ±0.001 g/cc, than the spread between curves for successive runs. This spread becomes appreciable, 0.004 g/cc at lower-density level, but there does appear to be a definite trend with time toward either higher-current or lower-density measurement or a combination of both. The reason for the lack of reproducibility between runs is now being investigated. The possibility that the density of the water changed with the addition of corrosion products seems unlikely since the density, as determined by a pycnometer, after the runs agreed within 0.0002 g/cc with the density of the water prior to the runs. The density of the float was determined before and after the runs using a Westphal balance. This density also was found to have been essentially unchanged.

Q MEASUREMENT

The degree of success or failure attributable to the glazes (two types), which have been put on powdered-compressed-fired Lava Gnade M ceramic thimbles which encase copper coils, has remained unanswered to date pending the receipt of a suitable type 347 stainless steel bomb and gaskets to test the glazes under gasketing conditions of 25 to 250°C and equilibrium saturated steam pressures.

Such a bomb, Fig. 15, has recently been received together with gold O rings.

Stainless steel O rings were eliminated due to hardness, and copper O rings were eliminated due to probable uranyl sulfate attack on the copper. The gold rings were prepared in a Lava Grade A mold and were removed by breaking the ceramic. They were subsequently pressed in a steel die, and then were annealed at 600°C for 30 min. Twenty-four carat gold was used.

DWG. 11001

AMERICAN INSTRUMENT CO.
SUPER PRESSURE ELECTRICAL
CONNECTOR
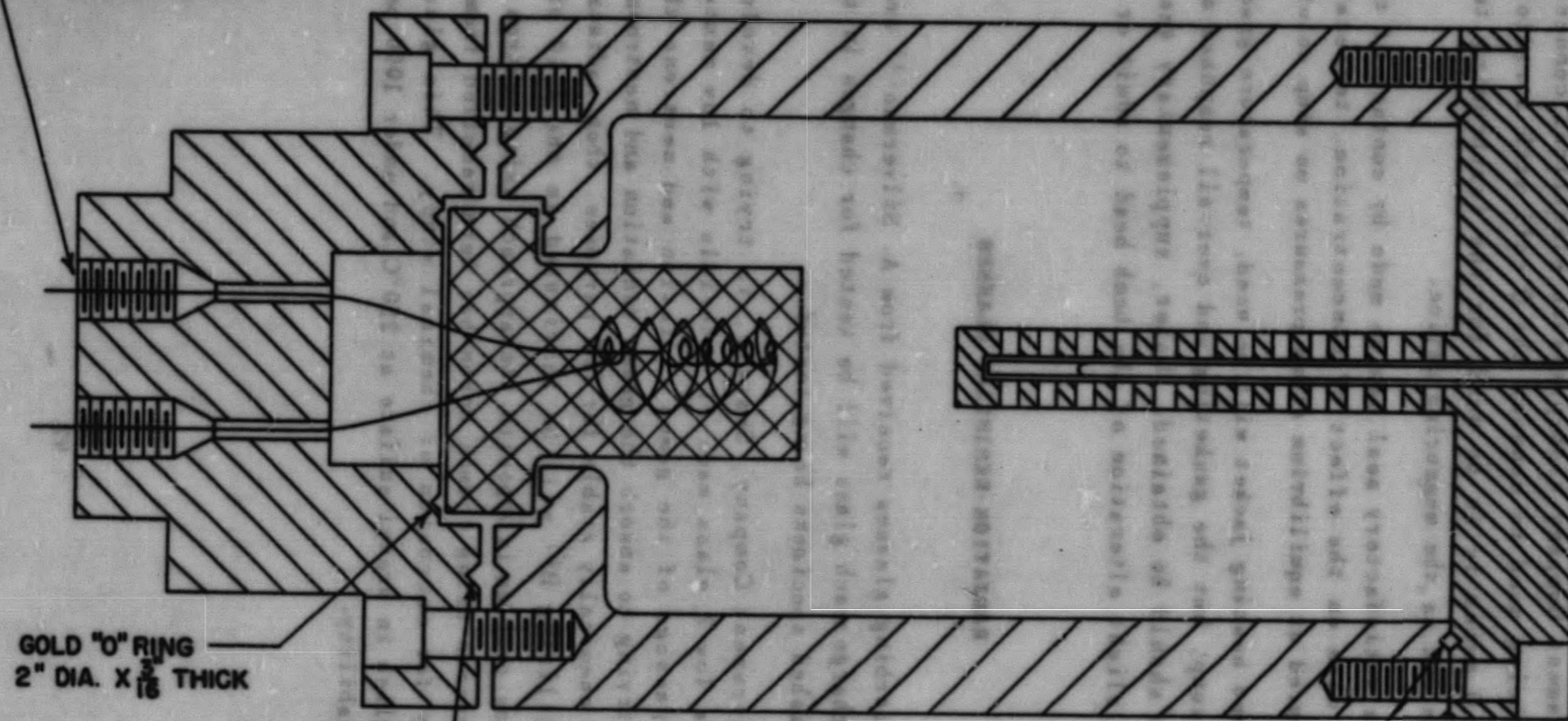
GOLD "O" RING
2" DIA. X $\frac{3}{16}$ THICK

GOLD "O" RING
3" DIA. X $\frac{1}{4}$ THICK

GOLD "O" RING
3 $\frac{3}{4}$ DIA. $\frac{3}{16}$ THICK

FIG. 15   BOMB TO TEST Q COILS PERFORMANCE

American Instrument Company high-pressure electrical connections and pressure seals are being used to connect the Q coil with a radiofrequency source. A Boonton Q meter is to be used for the forthcoming tests as a radiofrequency source and as the measuring device.

Assuming that a satisfactory seal can be made by contact of the gold O ring on the glaze, data on the effect of concentration, temperature, and pressure will be secured at equilibrium steam pressures on soup solutions.

Since an open-end heating jacket will be used, temperature gradients can be expected in the soup, but the gasketing and over-all response of Q under the bomb conditions should be obtained. Later, supplementary gas pressure could be added by a slight alteration of the bomb head to admit or discharge pressurizing gas.

RADIATION-RESISTANT GLASSES

The neutron-absorbing glasses received from A. Silverman[1] are still in the pile. Upon discharge each glass will be tested for changes in the optical spectrum of the polished specimens being tested.

Penberthy Instrument Company, Seattle, is trying to develop for our purposes a suitable low Z glass made of materials with low neutron cross-sections to allow passage of the gamma radiation and neutrons through the glass, rather than trying to absorb the gamma radiation and neutrons. If such a glass can be made chemically stable for HRE purposes, then radiation testing of such a glass utilizing B^{11} will be instituted in the X-10 pile. This approach to the glass problem is opposite the approach using neutron absorbers. The first glass specimen using common boron has been received from Penberthy Instrument Company for corrosion or chemical study. This glass will be tested by J. L. English in uranyl sulfate at 250°C and under 1000 psi pressure for its chemical stability.

6. ENGINEERING COMPONENT STUDIES

C. B. Graham

W. G. Atkinson   G. P. Letz
J. O. Bradfute   W. L. Ross
J. S. Culver   H. C. Savage
P. N. Haubenreich   I. Spiewak
C. G. Heisig   W. K. Stair
W. S. Hogan   R. VanWinkle
H. I. Kreig   R. H. Wilson
              C. D. Zerby

Experimental results indicate that vortex instability occurring from mixed flow in the letdown heat exchanger and valve may be eliminated by the use of a surge tank, restriction, and an up-flow in the exchanger and valve. Vortex stability may be further improved by increasing the rate of flow of the feed (pulsafeeder). Additional equipment must be installed before stability can be studied in a true mock-up of the HRE. Pressure-drop data for the system components under various temperature conditions are given. The flame recombiner system has been installed on the mock-up and is ready for testing.

Methods for reducing bearing loads and for increasing the load-carrying capacity of bearings are described. One set of graphitar bearings has operated satisfactorily for 1040 hr under very severe conditions. A stellite bearing-journal combination has been tested and a set of bearings has been installed in a pump. Although operation time has been short, and bearing design has been limited by availability of castings, promising results have been obtained, and the pump is still running satisfactorily after 300 hr of operation in water.

Mixing rates have been measured under isothermal conditions in various regions of the core. Introduction of hot and cold water did not result in observable changes. Several different baffles were tested, and one consisting of simple rods located on radii produced good results. Further efforts will be made to appraise the effect of density differences in the core in an attempt to prove that baffles are unnecessary.

Vortex Stability. As reported in a previous quarterly progress report,[1] the gas-removal systems for the core developed an oscillation which caused the vortex void in the core to change volume at a regular frequency. Since this condition is undesirable in the reactor, a development program was undertaken to eliminate it.

The oscillation was observed in all components of the letdown system and had a frequency of 15 to 30 cycles/min. The magnitude of the fluctuation was 50 to 100 cc in the pressurizer level. This represents the pulsation in the entire circulating and letdown systems. Observations through windows in the core showed an estimated volume change in the vortex void of 22 cc at gas flows comparable to maximum reactor conditions. This is .05% of core volume.

All evidence to date indicates that the letdown valve in conjunction with the compressible volume in the pressurizer is the source of the oscillation. Tests described in ORNL-990 showed that the oscillation occurred when gas was admitted between the core and the letdown heat exchanger with or without circulation in the core. This would indicate that the vortex oscillation is a result of, rather than the cause of, the oscillation.

Status of Stability Testing. The mock-up (see Fig. 16) is presently being reconstructed, incorporating the features developed in the experimental program and additional equipment which will permit 250°C operation. These features are shown in Fig. 17, and the experimental results which suggested them follow. Various combinations of these features resulted in stability up to 110% of the design gas flow (at 1000 kw power level, assuming 50 ev per molecule of H_2O decomposed) at 230°C, and 218% of gas flow at 150°C. Lack of heating capacity prevented operation at higher temperatures in both cases.

1. Letdown Stream in the Annulus of the Letdown Heat Exchanger. This arrangement was the result of considerable testing, a discussion of which is given in ORNL-990. Before successful means of controlling oscillation were discovered, tests in the letdown heat exchanger on tubes of various lengths and diameters showed the annular passage to be far more stable than a tube of

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(1) J. S. Culver, R. H. Wilson, and C. D. Zerby, "HRE Core-Gas-Removal System," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951*, ORNL-990, p. 22 (May 18, 1951).
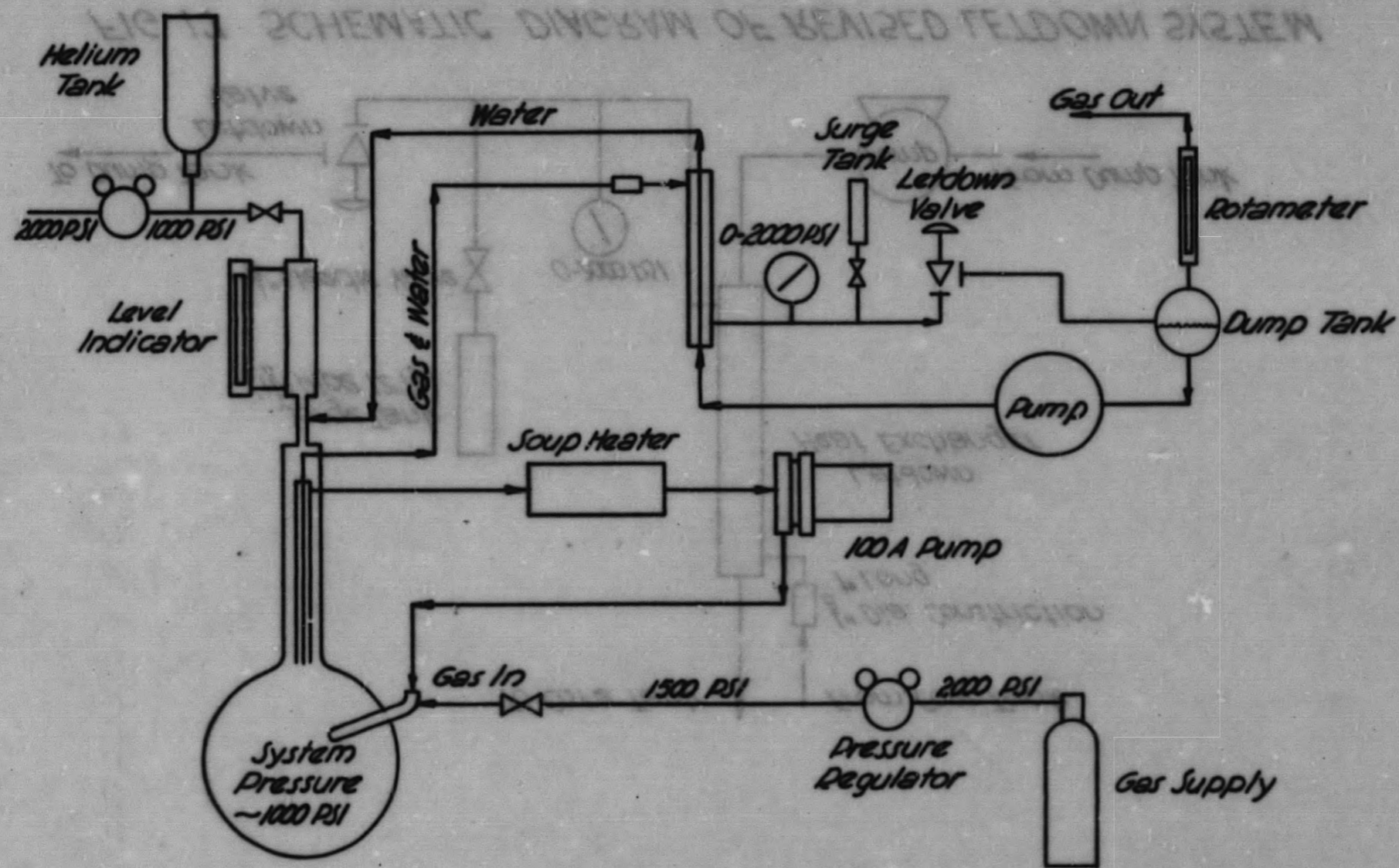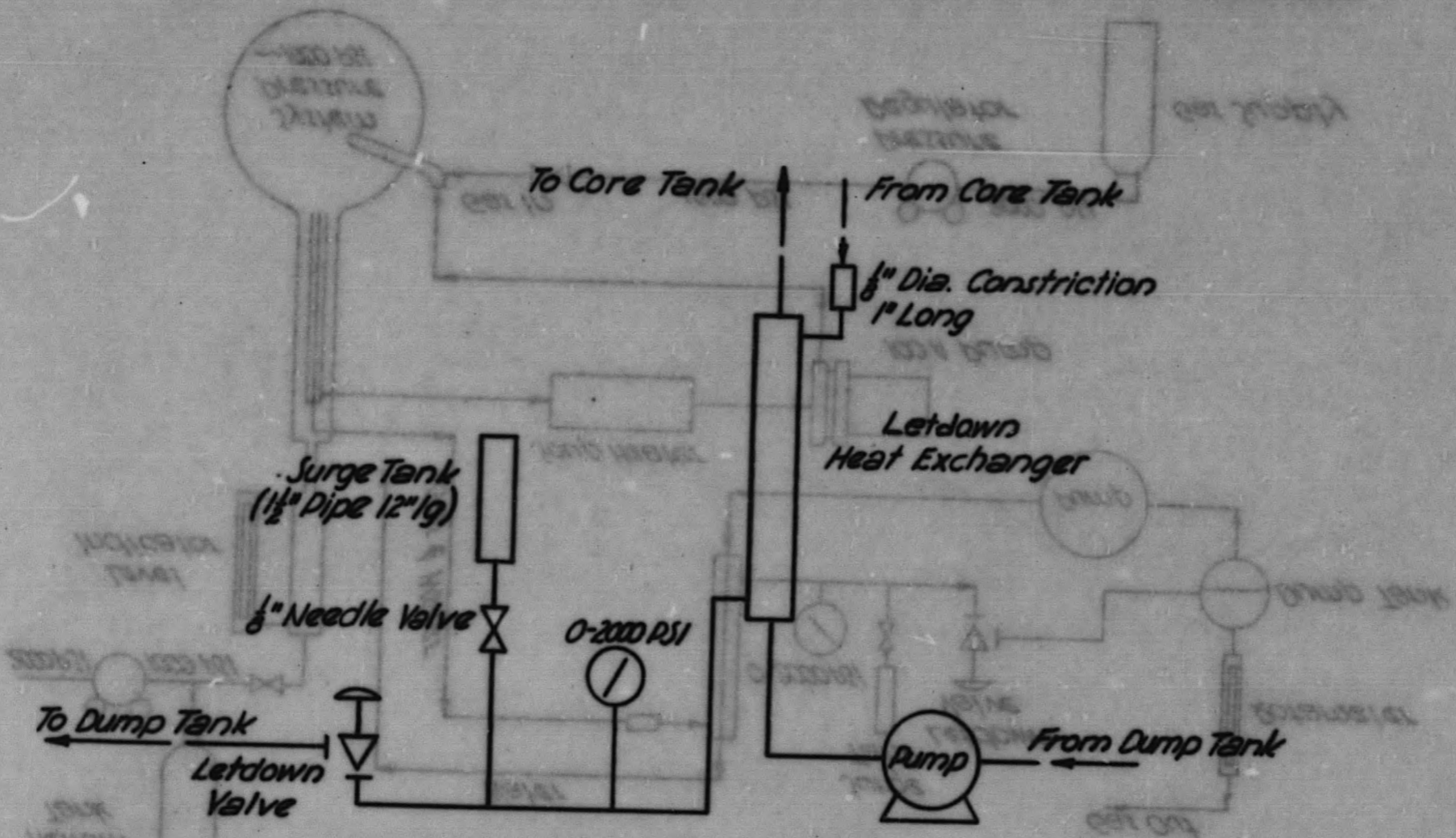
FIG. 16   SCHEMATIC DIAGRAM OF HRE MOCKUP

FIG. 17 SCHEMATIC DIAGRAM OF REVISED LETDOWN SYSTEM

equivalent cross-section. The test exchanger was a 20 ft length of 1/4-in. pipe inside 1/2-in. pipe. The proposed design for the reactor is 50 ft long and is now being installed in the mock-up for testing.

2. *Upward Approach to the Letdown Valve.* In a paper by O. P. Berglin[2] it was pointed out that a two-phase flow in vertical pipes produces bubbles, slugging, and annular flow if the flow is upward. Only slugging and annular flow are observed in a downward flow. The severity of the slugging should be less in the former case.

These effects were observed in a high-pressure gauge glass in the letdown stream. Since slugging was thought to initiate the oscillation at the letdown valve, the piping was arranged to provide a vertical approach to the valve. This change made a great improvement in the smoothness of operation.

3. *1/8-in. Orifice Upstream of the Letdown Heat Exchanger.* Early tests in which a hand valve was inserted in the letdown line above the heat exchanger showed a beneficial effect on operation with the valve open. Throttling with the valve produced a high-frequency oscillation in the vortex. Removal of the valve developed a slight instability at certain gas flow rates which had not previously appeared. On the basis of these observations a constriction 1 in. long and 1/8 in. diameter was substituted for the valve. It is believed that this orifice tends to damp out oscillation between the letdown valve and the compressible volume in the pressurizer. The combination of steps (1), (2), and (3) allowed steady operation up to 200°C.

4. *Surge Tank Upstream of Letdown Valve.* Since all evidence indicated that the letdown valve was the source of the oscillation, one solution to the problem would be to damp out fluctuations that might initiate oscillation at this point. To accomplish this a surge tank and throttling valve were installed, as shown in Fig. 17. Varying the setting of the 1/8-in. throttling valve established an optimum position which was later calibrated and found to be equivalent to an orifice .0345 in. in diameter. This arrangement allowed operation without oscillation up to 230°C and a gas flow of 1100 cfh. The expected maximum in the reactor is 1000 cfh at 1000 kw. Limitations on the heating system prevented operation at higher temperature.

(2) O. P. Berglin, "Flow of Gas Liquid Mixture," *Chem. Eng.* 56, 104 (May 1949).

5. *Increased Flow in Liquid Letdown Stream.* Preliminary testing on the mock-up was performed by a small triplex pump, replacing the pulsafeeder pump, which originally delivered only 0.67 gpm. However, repacking the pump increased the flow to 1 gpm and produced a marked improvement in stability.

Further tests were made on letdown liquid streams greater than 1 gpm. By changing pulleys the pump was made to deliver 1.8 gpm. Because of limitations in the heating system this could be operated only up to 150°C and showed no tendency to oscillate at a gas flow exceeding 2000 cfh. A further test was made by diverting the letdown stream through the inner tube of the heat exchanger and removing the surge tank. Previously, such a system would oscillate at 50°C when the gas flow exceeded 100 cfh; with the increased flow the same system did not oscillate at 150°C and a gas flow of 2180 cfh.

Modifications planned for the pulsafeeder are expected to increase delivery from 0.6 to 1.6 gpm with piping identical to the reactor.

The improvement in operating stability with the surge tank and 1.8 gpm letdown stream is shown in Fig. 18. The points shown for the improved system represent the maximum conditions which could be obtained on the apparatus, rather than a maximum stable condition. It should be noted that a stable system does not become unstable as the temperature or gas flow is reduced.

Plans for Future Stability Testing. The completed mock-up will have a new soup heater and a 40-kw steam boiler which will allow continuous operation at 250°C and perhaps at higher temperatures. The letdown system will be tested using the valve and heat exchanger which were built for use in the reactor. Stability checks will be run under all conditions expected in the reactor, and low-temperature—low-pressure runs will be made to assure stability during the proposed preliminary low-power tests of the reactor. In addition, a program to develop and test an external gas separator as an alternative procedure will be initiated.

When the steam pressurizer designed for the reactor is available it will be installed and tested with the level controller in operation, all preliminary testing being done with water and helium.

After all components have operated satisfactorily, the system will be converted to soup operation. This will involve replacing the present sphere, which has windows, and rebuilding the 100A pump to the latest specifications.

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FIG. 6 MAX. GAS FLOWS FOR STEADY OPERATION OF 28 FT LETDOWN HEAT EXCHANGER
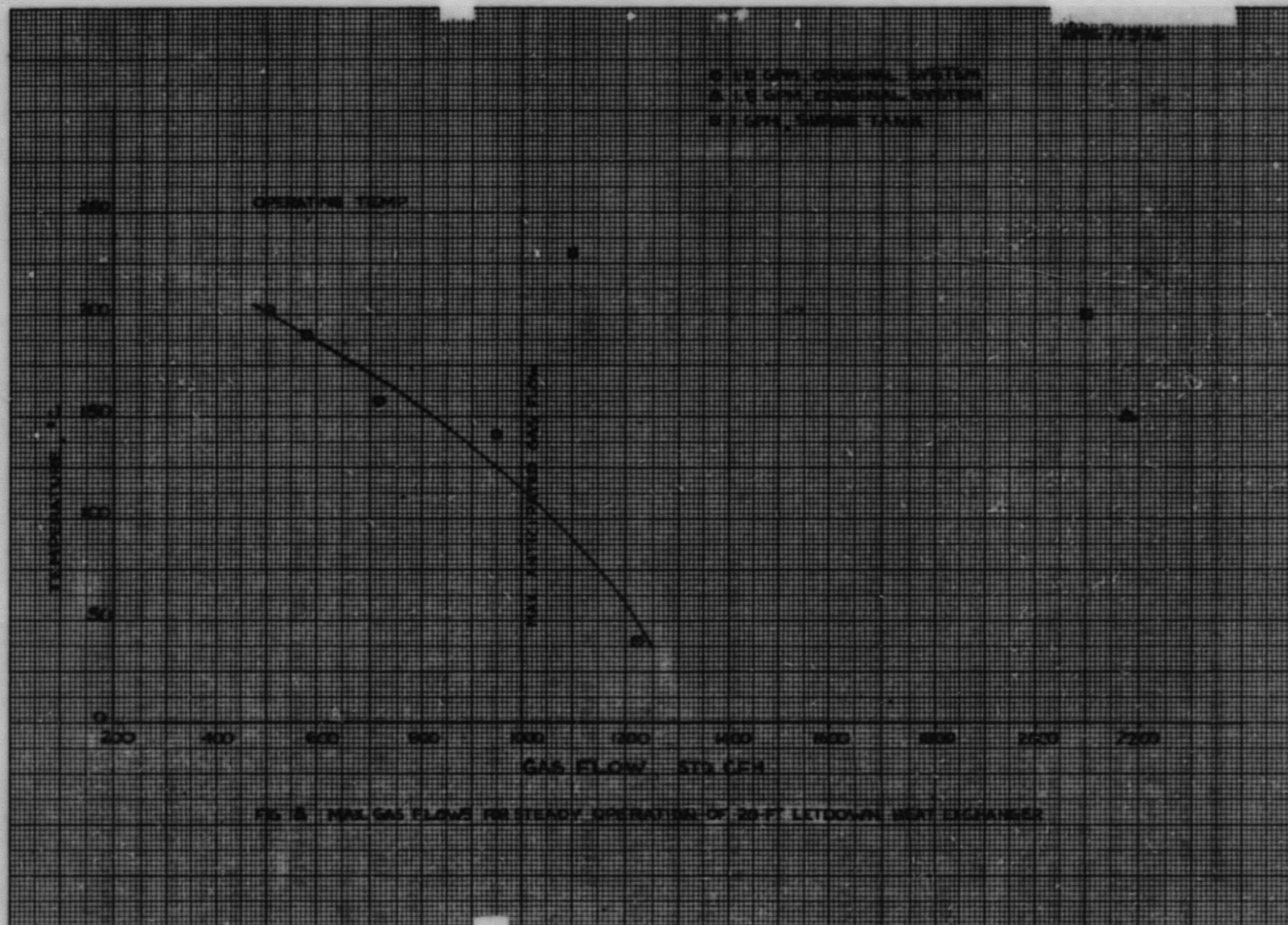
Limiting Conditions To Be Considered when Planning Low-Pressure Experiment. In regard to stability, lower operating pressures decrease the tendency to oscillate by permitting a greater opening in the letdown valve. However, as the pressure drop across the valve decreases, the range of control is reduced until the valve can no longer hold the pressurizer level constant. A minimum pressure drop of 250 psi across this valve was found to be adequate on the test apparatus.

The two-phase flow in the letdown stream produces a large pressure drop across the letdown heat exchanger at high gas flow rates. Data for the reactor exchanger cannot be obtained until the actual heat exchanger is tested; however, the experimental equipment gives values in the order of 250 psi. These two factors are additive, hence a minimum operating pressure of 500 psi will be required if gas flow rates in the order of the reactor maximum are to be experienced.

Pressure-Drop Measurements. To add to the general knowledge on the hydraulics of the circulating system, pressure-drop measurements and pump performance in a typical reactor circuit were measured. The results are presented in Fig. 19.

Pulsafeeder Tests. A pulsafeeder pump was installed in the mock-up with all piping designed to duplicate the size, length, and number of bends found in the reactor. After carefully eliminating all air from the system the pump would reliably deliver only 0.6 gpm.

Calculation of available piston displacement corrected for compressibility of oil and water in the pipes showed the maximum possible delivery to be 0.785 gpm. On this basis it is planned to substitute a larger cylinder in the oil pump which will give a calculated delivery of 1.6 gpm.

Flame Recombiner for HRE Mock-Up. The flame recombiner and associated control instruments have been installed in the HRE mock-up and are ready for testing. When sufficient tests have been completed to prove the operation of the mock-up recombiner as a separate unit, and the hydrodynamics of the gas letdown system has been satisfactorily resolved, the two systems will be joined and operated as a unit. The apparatus is available for injecting measured flows of hydrogen and oxygen directly into the reactor core at the
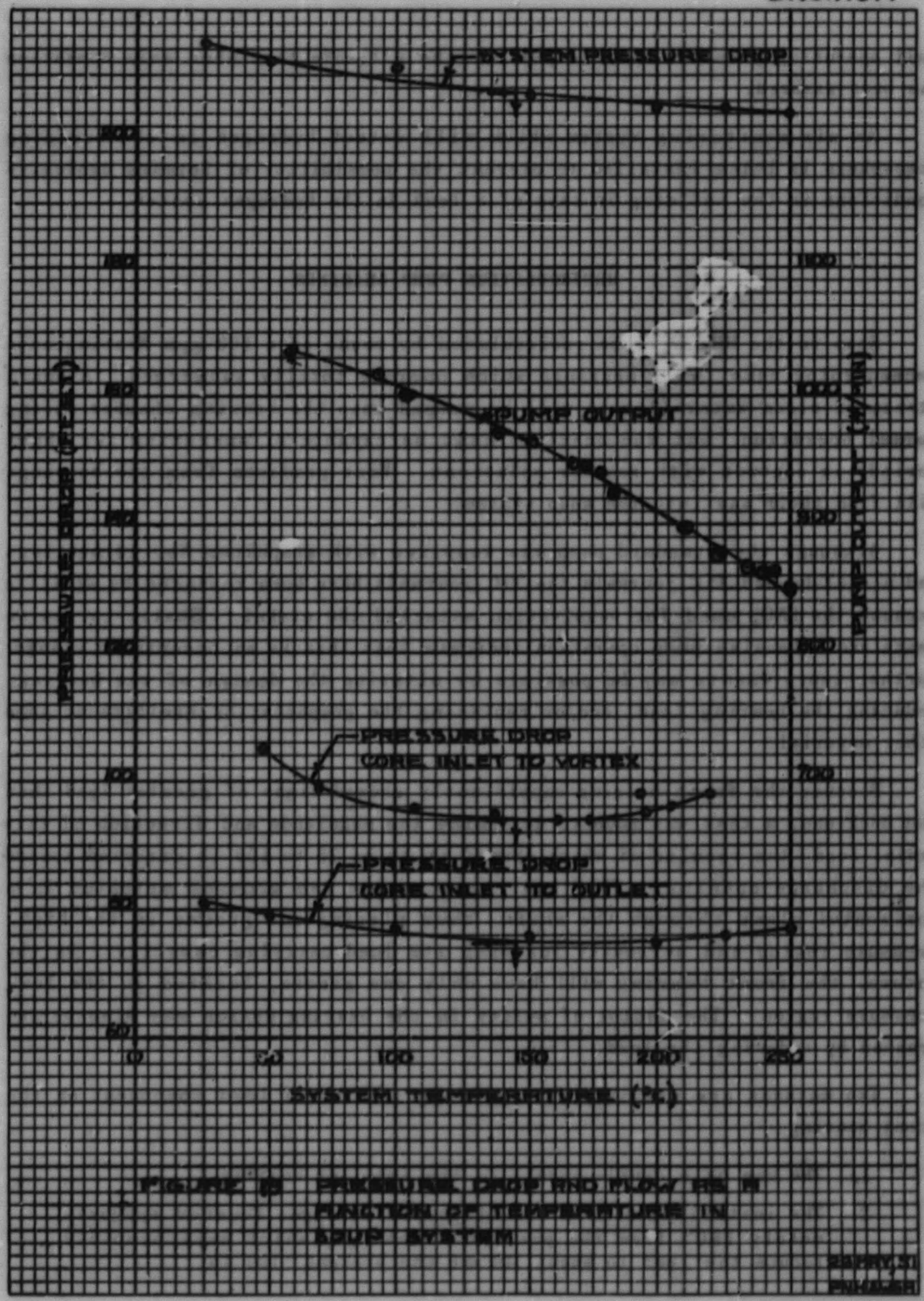
full operating pressure of 1000 psi for the ultimate test when safe operation has been assured.

An air-monitoring system which will detect hydrogen in the building atmosphere is being installed to prevent the possibility of forming explosive conditions in the building in case of a leak in the hydrogen system.

RECIRCULATION PUMP BEARINGS

Soup in the HRE will be recirculated by means of a 100-gpm Westinghouse canned rotor pump, with bearings which operate totally submerged. A small stream of clean water (1 gph) will be pumped into the bearing chamber during normal operation, but the bearings must be capable of operating for short periods in contact with reactor solutions. Wear products from the bearings will find their way into the soup system.

Although the standard pump was supplied with graphitar No. 14 bearings and nickel-bonded TiC journals, the TiC journals have been replaced by stellite because the HNO_3 used for passivation attacked the nickel. Static corrosion tests and extensive pump operation indicate that this is an acceptable change. Further improvements may be possible by altering the design of the bearing, reducing the bearing load, and/or replacing the graphitar by stellite or some other material.

Because the front bearing consistently showed signs of greater load than the back one, a test was made to determine the magnitude and direction of this radial load, the results of which showed it to be 75 to 100 lb directed toward the discharge opening. This bearing contains two grooves oriented in a horizontal plane through the shaft, thus placing one groove in the high-pressure region and seriously lowering its load-carrying capacity. In the future, the front bearing will have only one groove, located in the low-pressure region. The factor of safety in the bearing design may also be increased by reducing the load.

Two methods are possible for reducing the radial load component on the front bearing:

1. The use of a double scroll in the impeller housing.

2. The installation of a second pump discharge, located approximately 180° from the present discharge, which will probably reduce the load to about 10% of the present ~100 lb.

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Method (1) was discarded because alteration of the present pumps to incorporate this feature would be difficult, and extensive testing would be necessary. Although method (2) is undesirable because two matched discharge pipes are required for satisfactory results, one of the pump housings is being modified to test this scheme.

Thrust bearing studies have been made and tests using a model bearing are under way to appraise possible improvements. It is apparent that this bearing cannot be expected to carry heavy loads. The pump has four pads welded in the impeller housing, making it possible to reduce or eliminate thrust loads by adjusting the position of the impeller on the shaft, the adjustments being made after each pump alteration. Unless it becomes necessary to remove the pads, the present thrust bearings appear satisfactory; however, local erosion marks indicate that pad removal may be desirable. Alternate means of handling thrust loads are under investigation, and it is believed that the installation of a Kingsbury-type thrust bearing is the most simple solution to this problem. It will be possible to determine if this change is necessary when the soup recirculation test loops have been operated for longer periods.

One of the 100A pump loops has now operated 1040 hr with soup in the loop and bearing chamber. The graphite pump bearings were inspected after 600 hr of operation with only negligible wear being observed; on the front bearing the wear was approximately 0.0005 in., and on the rear it was 0.0002 in. Some scratches were noted on the front (graphitar) bearing, resulting from abrasives in the liquid, and the stellite journal showed slight signs of chemical attack.

The test is considered more severe than will be encountered in the reactor because: (1) the soup was precipitated frequently, providing abrasives which damaged the bearing; (2) many starts and stops were necessary in testing soup stability and changing operating conditions; and (3) the soup was continuously in the bearing chamber, no water injection being used. Graphite bearings are therefore considered to be very promising.

There has been some evidence that graphitar No. 14, the original bearing material, may cause soup precipitation, and in view of this 25 alloys are undergoing corrosion tests in a preliminary study to find other suitable journal-bearing combinations.

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Bearing tests on stellite 98M2 have been made and one journal-bearing combination using this alloy was operated continuously in water under simulated load for 250 hr, completing 550 start-stop cycles under overload conditions before failure occurred.

One 100A pump has been fitted with stellite 98M2 bearings and journals and is presently being tested, a 300-hr operation in water having been logged to date. An examination after 18 hr showed thrust wear, resulting from loads forced on the bearings while making adjustments to eliminate the thrust load, but the radial section was satisfactory. The bearings were again installed in the pump without repairing the damaged thrust faces. Watt meter readings indicate that operation is satisfactory.

These stellite bearings have two lubricant grooves because suitable castings were not on hand when the bearings were machined; however, new castings have been received and a single, or possibly no groove, will now be used. This change will greatly increase the load-carrying capacity of the bearing. The present bearings were aligned by line lapping while mounted in the pump. As a possible improvement in maintaining precise alignment a self-aligning bearing mount is being considered.

A 17-7 PH stainless steel bearing was tested against a stellite 98M2 journal and operated continuously for 72 hr in water under load; however, this combination failed quickly under start-stop operation.

MIXING IN THE HRE CORE

A study has been in progress to evaluate the mixing characteristics of the HRE core and to attempt to improve the mixing in partially stagnant regions. This work has been carried on in a transparent, full-scale plastic sphere. Data are obtained by introducing and studying variations in temperature and dye concentration with time. Observations are made at various points in the vessel by means of movable probes.

As described in the previous quarterly report[3] it has been found that liquid rotates in a stable orbit in the body of the sphere and mixes with streams bypassing along the walls of the vessel. In the northern hemisphere,

(3) I. Spiewak and J. O. Bradfute, "Mixing in the HRE Core," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951*, ORNL-990, p. 31 (May 16, 1951).

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which includes the inlet and outlet connections, this bypass goes directly from the inlet to the outlet. In the southern hemisphere the stream finds a vertical path up through the central axis of the sphere and out.

As a result of this mechanism, there is a region, located in a cylinder with an inside radius of about 6 cm and an outside radius of 11 cm, in which mixing takes place rather poorly, compared to average mixing in the reactor. (The sphere radius is 22.9 cm.) The flow pattern is described more fully in ORNL-990.

Quantitatively, mixing in this region requires approximately six times as long as the average for the entire vessel, with no density gradients in the liquid. The southern hemisphere is slightly worse in this respect than is the northern hemisphere. There appears to be no significant change in these figures with a 2.5-fold change in viscosity obtainable between 10 and 50°C. Also, if the flow rate is halved, mixing is twice as slow throughout.

It was hoped that introducing cold water into a sphere filled with hot water would improve the mixing of the stagnant region by virtue of the centrifugal effects on density variations. The density differences obtainable within the limits of the apparatus (0.9%) produced no observable difference in the rate of mixing. The density variation in the reactor operating at 1000 kw will probably amount to about 5%. Further study of the effect of density differences in this range will be made at room temperature with methanol solutions.

Unless this density effect is appreciable, to avoid local overheating in stagnant areas it may be necessary to use mechanical obstructions which distribute the flow properly. These baffles would have to strike the proper balance between (1) effect on mixing, (2) effect on gas removal, (3) effect on reactivity, and (4) structural strength and resistance to fatigue.

Various types of baffles have been tried in the sphere with partial success. In no case was the amount of metal inserted unfeasible from the nuclear standpoint. These include:

1. *Cylindrical Rods.* Cylindrical rods were mounted along radii in the horizontal equatorial plane of the sphere. The rods were either 1/8 or 3/16 in. in diameter. The optimum length was 7 in., bringing the rods out from

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the sphere wall, through the stagnant layer, and just into the updraft going to the outlet. The rotational flow is normal to these rods, producing a turbulent pressure loss behind them. This low-pressure area draws liquid through the stagnant region and into the central updraft. For roughly 2 in. on both sides of the plane of the rods the maximum residence time was found to be about 15% above the average residence time for the sphere. The remainder of the stagnant region is affected to a lesser degree and its residence time is about twice the average, which still is a great improvement over the condition with no baffles. The effectiveness of the rods in a given vertical location appears relatively insensitive to the number of rods or to their diameter. One, two, and three rods were tried with similar effectiveness.

The turbulence induced by the rods had the effect of increasing the precession of the vortex. The degree to which this occurs, however, is not serious. Vertical rods have been found to have a greater effect on the vortex.

Resonance vibrations were present in a particular rod over a flow range of about 30%. Only minor oscillations were present at all other flow rates. The flow rate at which resonance exists is determined by the length and moment of inertia of the rod and by the velocity of fluid slipping past it. Eight-inch stainless steel tubing in resonance failed very soon. Failure occurred usually where there were scratches or threads. Over ten million cycles were obtained on mild steel 3/16 in. rod without any failures. Unless stress corrosion is a serious problem, there should be no failures after this, according to literature fatigue data. If rods are used in the reactor, they will be nonresonating within the expected flow range.

2. *Streamline Baffles*. Airfoils about 1 in. wide and 3/16 in. high at the maximum were mounted in position similar to the rods. These provided only skin friction to pull liquid in toward the center, with a minimum of turbulence. The vibration problem was alleviated, and the vortex was stabilized. However, the reduction in residence time of the stagnant region was only 20%. Apparently it is necessary to increase turbulence to bring about the desired mixing.

3. *Vertical Fins*. Six vertical fins, 5 in. high and 1½ in. wide, were mounted in pairs on three symmetrical cylindrical rods in an effort to produce slug flow through the sphere. The fins were curved slightly to follow

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the flow lines, and the rotational flow intersected the fins at a small angle. A definite slug flow component was observed at the elevation of the fins, but stagnation persisted at other elevations. This was the only slug flow ever obtained in the plastic model. The vortex was quite unstable.

4. *Horizontal Fins.* Surfaces intersecting the flow lines at about a 45° angle were placed lengthwise on three equatorial rods. This seemed to throw the flow up into the northern hemisphere and down into the southern hemisphere, destroying the tendency of the liquid to rotate, which is essential for gas removal.

5. *Bell.* An inverted bell-shaped device mounted near the bottom of the sphere was designed to divert part of the updraft into the stagnant region. The maximum residence time was lowered somewhat, and the stagnant region was shifted more toward the outside of the sphere. The flow pattern through the sphere was considerably modified. However, the bell was not properly aligned, and the vortex was quite unstable. It appears to be impractical to consider this device for the HRE on the basis of alignment problems alone.

If baffles are to be used in the reactor, horizontal rods appear to be the best type. Additional testing and analysis will be required before the desirability of using baffles can be definitely determined.

PART II. LONG RANGE STUDIES

7. PHASE STABILITY OF ALTERNATE SYSTEMS

W. L. Marshall

Pressure Studies   **Phase Studies**

H. O. Day, Jr.   J. S. Gill
H. W. Wright

PRESSURE STUDIES OF AQUEOUS FUEL SYSTEMS

The purpose of this investigation is to provide fundamental thermal-pressure data for the current fuel medium (UO_2SO_4-H_2O) and for the UO_2F_2-H_2O and $UO_2(NO_3)_2$-H_2O systems. The work has been divided into two parts, namely, low-temperature investigation up to 150 to 175°C and investigation from these temperatures up to the critical region.

Apparatus for the low-temperature measurements has been designed and constructed. A precision thermostat which can maintain the temperature within ±0.002°C for long periods at temperatures of 50 to 165°C has been made. The entire apparatus has been designed with the goal of high precision and accuracy in mind.

Actual laboratory work on the high-pressure region has not yet begun. However, much thought has been given to the problem of getting highly accurate results, and experimental work is to be started in the near future.

THE URANYL NITRATE—WATER SYSTEM ABOVE 180°C

The experimental investigation of the uranyl nitrate—water system above 180°C is given in previous reports.[1,2] Briefly, hydrolytic decomposition of uranyl nitrate—water solutions occurs above 184°C in a closed system of 1:1 liquid-to-vapor volume ratio. The precise temperature of precipitation of a yellow solid is dependent on concentration. The precipitation temperature is about 260°C in very low concentrations and increases to a maximum of about 345°C for a 55 wt % solution. The temperature then decreases to 184°C at the theoretical composition of uranyl nitrate dihydrate.

(1) W. L. Marshall, J. S. Gill, and C. H. Secoy, "The Uranyl Nitrate—Water System Above 180°C," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951,* ORNL-1053, p. 22 (to be issued).

(2) W. L. Marshall and J. S. Gill, "Aqueous Uranyl Nitrate and Uranyl Nitrate—Nitric Acid—Water Solutions Above 100°C," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951,* ORNL-990, p. 136 (May 18, 1951).

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The temperature at which a red-brown vapor phase appears is about 285°C in the dilute region and decreases to approximately 184°C in the saturated solution.

This vapor-phase coloration phenomenon is reversible with temperature; however, the yellow solid appearing at the upper temperature is of questionable reversibility.
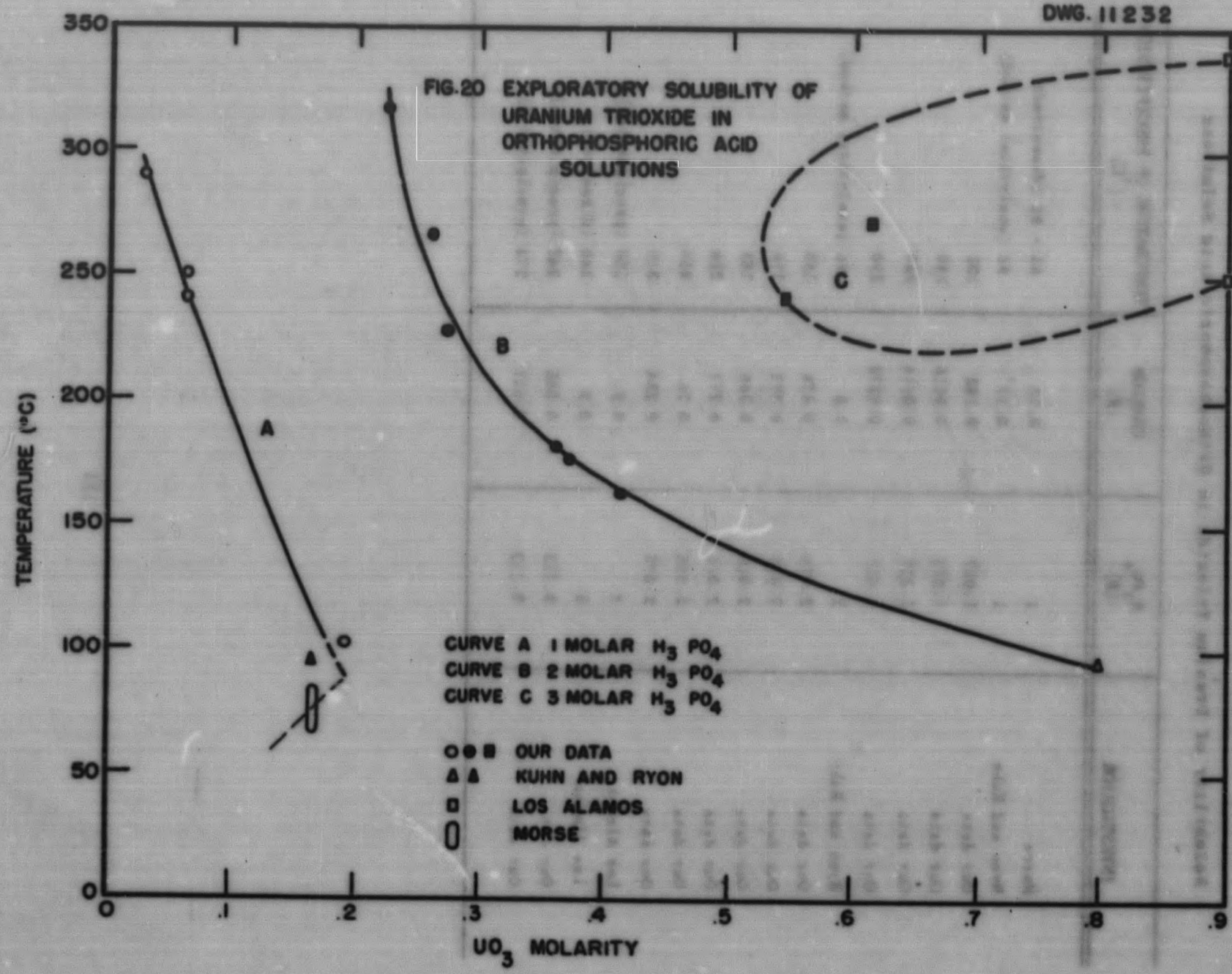
THE URANIUM TRIOXIDE—PHOSPHORIC ACID—WATER SYSTEM

A fundamental investigation is under way on uranium trioxide solubility in phosphoric acid solutions up to the critical temperatures of the systems. In this investigation exploratory solubility determinations have been made in the range 100 to 300°C using 1, 2, and 3 M orthophosphoric acid. As a result of this work, concentration of effort is to be on solubilities in 2 M acid. After phase equilibrium conditions are established for this system, solubilities will be determined in other acid concentrations. Therefore, with these data the concentration of acid necessary to dissolve a given amount of uranium trioxide at a fixed temperature might be determined.

Current Experimental Status. A synthetic method described previously[3] has been used. Experimental data obtained by this method are given in Table 24 and are shown in Fig. 20. Exploratory data from Los Alamos[4] and elsewhere[5,6] are included.

In the work at ORNL, in 2 M acid solutions bulky, gelatinous type precipitates appeared upon reaching the given temperatures. These precipitates seemed to change character to form long crystalline needles. When the temperature was lowered 50 to 75°C for 10-hr periods, the crystals did not appear to redissolve. Until this point of precise solubility is established the solubility curves in Fig. 20 must be considered as only tentative.

(3) W. L. Marshall, J. S. Gill, and C. H. Secoy, "The Uranyl Fluoride—Water System," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950,* ORNL-795, p. 22 (Oct. 1, 1951).
(4) R. P. Hammond, Los Alamos Scientific Laboratory, private communication.
(5) A. D. Ryon and D. W. Kuhn, *Solubility of Uranyl Ammonium Sulfate,* Y-381 (April 1, 1949).
(6) L. Morse, Chemical Technology Division, Oak Ridge National Laboratory, unpublished data.

FIG. 20 EXPLORATORY SOLUBILITY OF
URANIUM TRIOXIDE IN
ORTHOPHOSPHORIC ACID
SOLUTIONS

CURVE A 1 MOLAR $H_3 PO_4$
CURVE B 2 MOLAR $H_3 PO_4$
CURVE C 3 MOLAR $H_3 PO_4$

O ● ◙ OUR DATA
△ ▲ KUHN AND RYON
▢ LOS ALAMOS
◖ MORSE

DWG. 11232

TABLE 24

Solubility of Uranium Trioxide in Orthophosphoric Acid Solutions

INVESTIGATOR	H_3PO_4 (N)	URANIUM (N)	TEMPERATURE OF PRECIPITATION (°C)
Morse	1	0.17	65 - 85 (dissolved)
Ryon and Kuhn	1	0.17	96 (analytical method)
Our data	1.017	0.192	102
Our data	1.017	0.0616	240
Our data	1.017	0.0616	250
Our data	1.017	0.0278	290
Ryon and Kuhn	2	0.8	96 (analytical method)
Our data	2.075	0.414	163
Our data	2.075	0.373	176
Our data	2.075	0.366	183
Our data	2.075	0.271	228
Our data	2.075	0.26	266
Our data	2.075	0.224	316
Los Alamos	3	0.9	250 (precipitated)
Los Alamos	3	0.9	340 (dissolved)
Our data	3.113	0.546	242 (precipitated)
Our data	3.113	0.617	273 (precipitated)
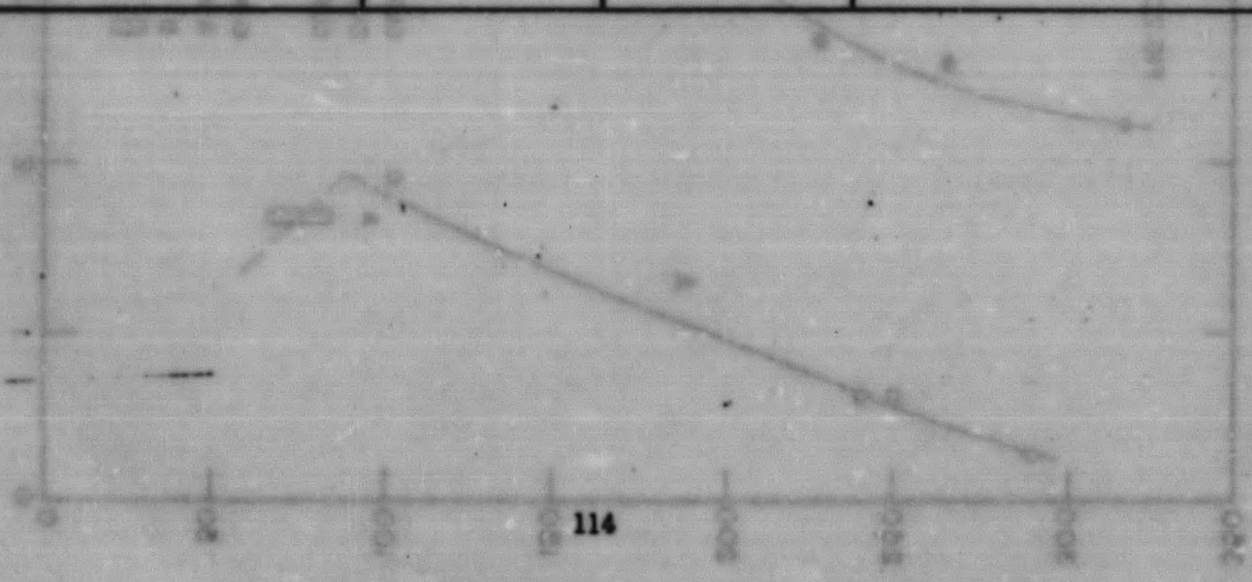
The initial alternate speculations are as follows:

1. Curve B in Fig. 20 is a metastable curve, and the system has subsequently converted to a stable phase possessing a low solubility change with temperature.

2. Curve B in Fig. 20 is a stable curve, but the return approach to equilibrium is slow.

3. The data reported along Curve B are the results of superheating phenomena, and the true solubility points are at lower temperatures.

After a consideration of the above factors, it has been decided to change to an analytical method for the study of this system. Work in this direction is in progress.

EFFECT OF FERRIC OXIDE ON CRITICAL SOLUTION TEMPERATURES OF THE URANYL SULFATE—WATER SYSTEM

A visual study has been made of the effect of ferric oxide on the critical solution temperature on the uranyl sulfate—water system. Previous studies of the uranyl sulfate—sulfuric acid—water system showed an elevation of the critical solution temperature proportional to the amount of excess sulfuric acid.[7]

In the present investigation it was thought that ferric oxide might alter the two liquid-phase phenomenon to such an extent as to change conditions for a homogeneous reactor solution at 200 to 300°C.

Experimental. Uranyl sulfate trihydrate prepared by the Y-12 Chemical Department was used. This material was checked for purity and excess acidity by analysis and by pH determinations. Ferric oxide powder, c.p., was obtained from Baker and Adamson.

Approximately 1.3 ml each of aqueous uranyl sulfate solutions of 4.6, 9.7, 19.6, and 30.0 wt % was sealed in silica tubes of 11 cm length and 4 mm I.D. containing approximately 100 mg Fe_2O_3. In addition, a blank was prepared using distilled water. These tubes were rocked in a special rocker-heater

(7) R. E. Leed and C. H. Secoy, "Further Study of the Two-Liquid Phase Region of the System UO_2SO_4-H_2SO_4-H_2O," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870, p. 29 (Mar. 1, 1951).

device, the temperature was raised or lowered, and observations were made through a slit. Details of the method have been given previously.[a]

In all runs, including the blank, the ferric oxide particles appeared to increase in size and settle faster in the tubes as the temperature was raised. At the critical solution temperature the solid ferric oxide collected in the heavier liquid phase, thus stopping all random motion of the particles. The temperature appeared to be lowered 3 or 4°C under that of a ferric oxide—free uranyl sulfate solution, but this effect is not certain. No such phenomenon was observed in the blank.

When the temperature was lowered, the return to complete miscibility could be delayed as much as 10 or 15°C if the solution was cooled as fast as 1 or 2°C per minute. The delay is proportional to the cooling rate, indicating a possible physical effect of the particles.

Analysis of the supernatant after a run showed no change in the uranium concentration. A negligible amount of iron was present in solution.

In effect, ferric oxide powder might possibly lower the critical solution temperature of uranyl sulfate solutions several degrees, at least up to 30 wt % salt. No visual effects were noted below these temperatures. Higher accuracy could not be obtained because of observational difficulties in the presence of ferric oxide.

DECLASSIFIED

8. SOLUBILITY OF FISSION PRODUCT SULFATES

B. Zemel

The determination of the high-temperature solubilities of the more insoluble fission product sulfates is continuing using radioactive tracers, stainless steel bombs, and filter disks. The filter disks enable separation of solution and precipitate at a given temperature before cooling down.

In order to avoid corrosion problems in determining the solubilities in the presence of uranyl sulfate solutions, the bombs were provided with platinum liners and the stainless steel filter disks were replaced by alundum disks.

Solubility studies were made of $SrSO_4$, $BaSO_4$, and $Y_2(SO_4)_3$ in UO_2SO_4 (30 g of uranium per liter). After this work was completed the UO_2SO_4 was found to be impure, and the studies will therefore be repeated. Studies were also made of $La_2(SO_4)_3$ and Ag_2SO_4 in water. Because of the short half-life of the lanthanum activity available and the difficulties involved in its puri- fication, the complete $La_2(SO_4)_3$ curve has not yet been prepared. The values obtained for Ag_2SO_4 are given in the range 145 to 330°C and were checked by potentiometric titrations. An attempt was made to run at least part of the Ag_2SO_4 solubility curve (Fig. 21) by the quartz-tube method as a further check, but the compound proved to be photosensitive and the results were considered unreliable.

TABLE 25

Solubility of Ag_2SO_4 in H_2O

TEMPERATURE (°C)	CONCENTRATION (g/100 g of solution)
145	0.894
157	0.65
199	0.45
199	0.376
250	0.40
250	0.35
305	0.329
305	0.295
330	0.28

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FIG. 21

SOLUBILITY OF Ag_2SO_4 IN H_2O

O SEIDELL
□ DATA FROM TRACERS
△ DATA FROM TITRATIONS

(Ag_2SO_4) g/100gms. SOLN.

TEMPERATURE °C
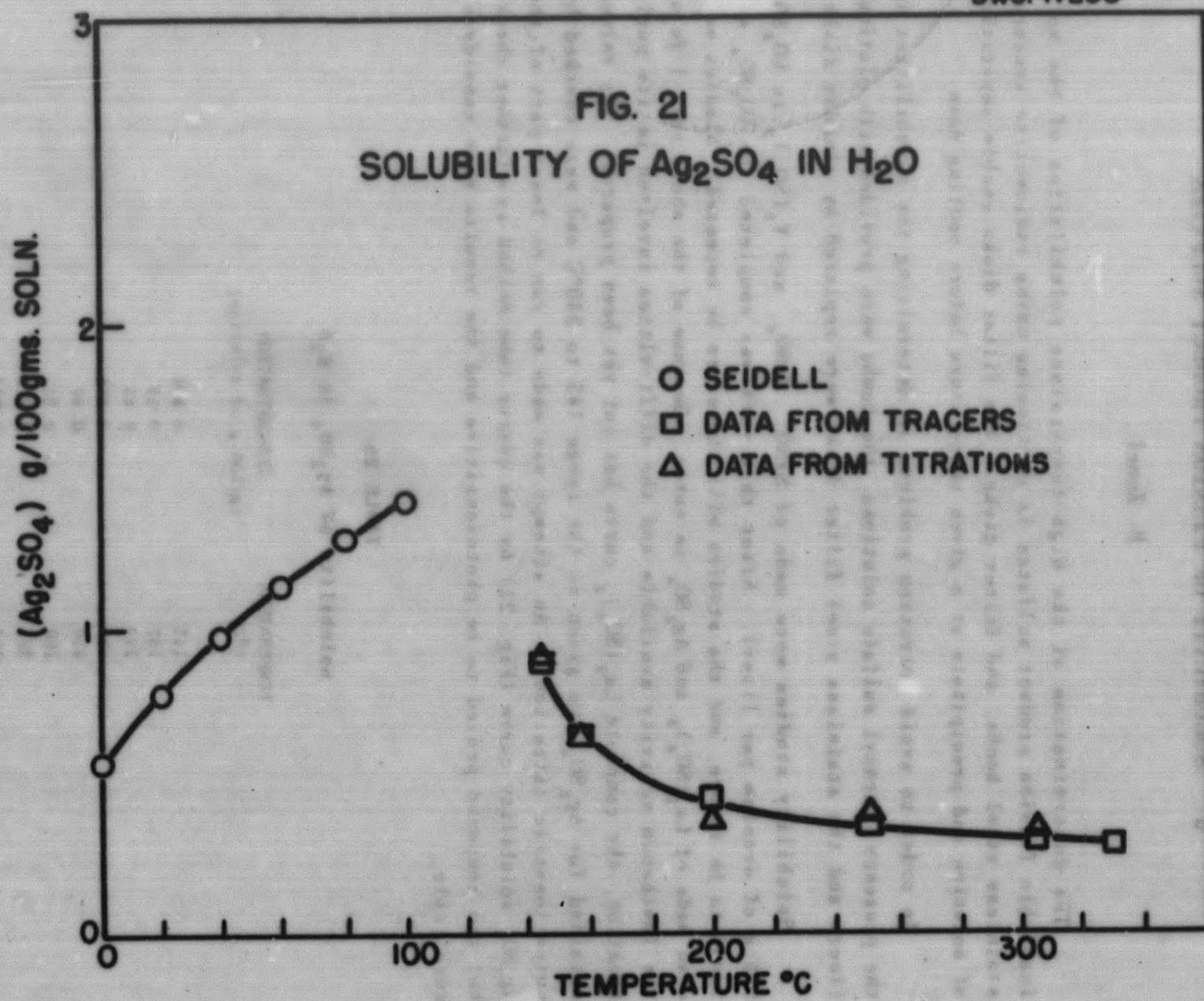
9. SLURRY STUDIES

Uranium Oxide Slurries   *Thorium Oxide Slurries*

L. E. Morse   T. C. Runion
G. A. Eaton   J. L. Bamberg
C. P. Johnston   V. L. Fowler
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URANIUM OXIDE SLURRIES

During the past quarter further investigations were made into the preparation of uranium oxide slurries suitable for use in the homogeneous reactor project.

The slurries will contain 40 g of uranium per liter and must be stable with respect to sedimentation upon shutdown of the slurry-circulating system. The reactor will operate at 250°C and 1000 psi pressure.

Preliminary experiments on the irradiation of natural uranium oxide slurries stabilized with bentonite were completed. It appears that samples of the slurries irradiated for 1 week while being heated at 250°C were comparable in stability towards sedimentation with control samples of the slurries which were only heated at 250°C.

Electron micrographs of heated uranium trioxide—water slurries have been obtained with and without bentonite which indicate that one function of the bentonite is to hinder the growth of larger particles.

Investigations were also begun into methods of preparation of uranium peroxide which is used as the source of anhydrous uranium trioxide. There are no data currently available on the relation between the method of preparation and the slurry stability.

Preliminary Experiments on Irradiation of Natural Uranium Trioxide—Water Slurries. The experimental details and results of this irradiation test are presented in Table 26.

The agreement between the irradiated and unirradiated heated slurries is good. Further, the fact that the results varied with the individual oxides indicates that the small diameter of the tubes does not affect the sedimentation process greatly, although circulation of the slurry was limited during the heating period as evidenced by some clumping in the slurry.

TABLE 26

Preliminary Experiments on Irradiation of Natural Uranium
Trioxide—Water Slurries at 250°C

Slurry composition:

Uranium (natural), 40 g as anhydrous UO_3

Bentonite, 1000 ml of a suspension of 13 g of dialyzed bentonite
   solids; average particle size below 25 mμ

Heating conditions: 250°C for 1 week

Irradiation: hole 12 of ORNL reactor (neutron flux ~ 5 x 10^{11})

Settling time: 3 weeks at room temperature

Experiments carried out in 4-mm-I.D. sealed quartz tubes in duplicate

	VOLUME RATIO OF SETTLED SOLIDS TO TOTAL SLURRY	
	HEATED ONLY SLURRY (control)	HEATED AND IRRADIATED SLURRY
H oxide, anhydrous UO_3 (Harshaw) prepared by decomposing $UO_2(NO_3)_2$; appeared to contain some undecomposed $UO_2(NO_3)_2$	0.63 0.67	0.69 0.69
M oxide, anhydrous UO_3 from decomposed $UO_4 \cdot 2H_2O$ prepared by adding 30% H_2O_2 (excess) to a $UO_2(NO_3)_2$ solution at pH 2.5; this type of oxide was used in all previously reported results	0.81 0.85	0.83 0.99
E oxide, anhydrous UO_3 from decomposed $UO_4 \cdot 2H_2O$ prepared by adding $UO_2(NO_3)_2$ solution dropwise to excess 3% H_2O_2, both solutions being 0.1 N in free HNO_3	0.70 0.80	0.69 0.75

It is interesting that a slurry of the M oxide which had been heated for
8 days in a stainless steel bomb that had been agitated by rocking showed a
settled-solids-volume/total-volume ratio of 0.88 after a long sedimentation
time. This is in good agreement with the quartz-tube results given above.

It appears then that the effects of radiation on the stability of these
natural uranium oxide slurries are not more adverse than thermal effects.

Function of Bentonite in Slurry Stabilization. An attempt has been made
to elucidate the nature of the function of bentonite in slurry stabilization.

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For this purpose particle-size determinations were made by electron microscopy on unheated and heated UO_3 slurries and heated UO_3 slurries containing bentonite. The oxides and slurries used were those described in Table 26. The results are given in Table 27.

TABLE 27

Particle-Size Determinations in Uranium Trioxide—Water Slurries of Composition Shown in Table 26

Heating conditions: 50 hr at 250°C in sealed quartz tubes

Particle-size measurements made in electron microscope;

MATERIAL	UNHEATED UO_3 IN H_2O PARTICLE SIZE (μ)		HEATED UO_3 IN H_2O PARTICLE SIZE (μ)		HEATED UO_3 IN BENTONITE SUSPENSION PARTICLE SIZE (μ)	
	AVERAGE	RANGE	AVERAGE	RANGE	AVERAGE	RANGE
H oxide	0.1	0.02 - 0.4	0.2	0.02 - 5	0.5	0.02 - 14
M oxide	0.1	0.02 - 0.5	0.5	0.02 - 8	0.2	0.02 - 3.5
E oxide	0.2	0.05 - 1	0.5	0.02 - 15	0.3	0.02 - 1

Although in all cases there is an increase in the average size on heating, the presence of bentonite considerably narrows the range of particle sizes, especially with respect to formation of the larger particles.

One possible explanation for this may be that the bentonite tends to coat the oxide particles and prevent them from coalescing. This is in keeping with the previously noted behavior that smaller amounts of bentonite consisting of very fine particles are as efficient as larger amounts of bentonite containing larger particles since in the former case a given weight of bentonite will yield more particles.

Methods of Preparation of Uranyl Peroxide. A fairly general phenomenon noted in the aging of precipitates at elevated temperatures is for the larger particles to grow at the expense of smaller ones, for example, as occurs in

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the aging of $BaSO_4$. It appears that if it is possible to obtain a very uniform particle size, the growth process may be retarded. Thus, in the case of uranium trioxide—water slurries, if, once the optimum particle size has been chosen, the particle-size distribution spread could be made very narrow about that size, it might be possible to minimize the effect of particle growth as a contributing factor toward slurry instability.

In all these experiments anhydrous UO_3 is prepared by decomposing $UO_4 \cdot 2H_2O$; therefore an investigation was begun on the effect of variations in the methods of preparation of $UO_4 \cdot 2H_2O$. There are as yet no qualitative evaluations of these methods available in terms of particle-size distribution or slurry stability.

It has been reported that, depending on the order of addition of $UO_2(NO_3)_2$ solution and H_2O_2 to each other, peroxides of different physical characteristics have been obtained. A series of experiments was carried out in which the order of addition of the two reagents as well as the acidity was varied. The reagents used were: $UO_2(NO_3)_2$ solution, 210 g/liter; and 3% H_2O_2 (1.4 liters).

When $UO_2(NO_3)_2$ solution was added dropwise with agitation to the hydrogen peroxide solution heated to 60°C, the uranyl peroxide settled very rapidly on standing whether the precipitation was carried out in 0.1 N free nitric acid or at pH 2.5. However, when the order of addition was reversed, the precipitate settled very slowly, especially at pH 2.5. After 1 week of standing, the uranyl peroxide precipitate occupied about 80% of the total volume.

The peroxides prepared by adding $UO_2(NO_3)_2$ solution to H_2O_2 were more deeply yellow-colored after five washings with water. The oxides prepared from these precipitates were brick red and were also more intensely colored.

One possible application of these results may be the possibility of making the slurry self-stabilizing under reactor conditions. Measurements of acidities of slurries yield values between pH 3 and pH 4; thus if it were possible previous to reactor shutdown to operate the reactor under such conditions that large amounts of H_2O_2 were generated, the possibility is that sufficient uranyl peroxide would be formed under conditions which yield a very slowly settling material. The situation, however, is complicated by pumping problems associated with uranyl peroxide slurries which in turn lead to difficulties in maintaining sufficient circulation to keep the reactor below 100°C, which is necessary to prevent excessive peroxide decomposition.

Another variation in the preparation of uranyl peroxides was made by carrying out the precipitation in the presence of ammonium citrate. It is known that the ammonium citrate forms complexes with UO_2^{++}, and it was found that as the citrate concentration was increased the period between the mixing of the $UO_2(NO_3)_2$ and H_2O_2 and the formation of a precipitate could be varied from a few minutes to several hours. At higher concentration of ammonium citrate, the yield of uranyl peroxide was decreased, and the product was contaminated by a second solid phase of a deep golden-yellow color. The reagents finally decided upon were the following: solution 1, 100 ml, containing 5 g of $UO_2(NO_3)_2$ and 5 g of ammonium citrate; solution 2, 100 ml, containing 5 ml of 30% hydrogen peroxide.

It was found that with solutions of these compositions the time interval between addition and precipitation was sufficient to permit thorough mixing of the reagents. The precipitate, when it did form, appeared uniformly throughout the volume of solution. Other experimental variations were made in which the precipitations were carried out in more dilute final volumes.

The precipitates formed in the presence of ammonium citrate differed from other uranyl peroxides in that they showed strong adhesion between precipitate particles. On sufficient vigorous agitation they appeared to form uniform dispersions in water which then settled rapidly.

The physical nature of these uranyl peroxides has not been further investigated although there are strong indications that they may consist of extremely small particles.

THORIUM OXIDE SLURRIES

Two types of thorium oxide slurries have been investigated for use in 23 breeder blankets. Each contained 1000 g of thorium per liter as the oxide. A preliminary evaluation of heat and radiation stability has been made for each variety with results that were generally promising.

Finely Divided Thorium Oxide with No Additives. Table 28 shows the settling rates of ThO_2 as calculated by Stokes' law for the settling of spherical particles. Using a value of 9 for the density of ThO_2, a 0.1- to 0.5-μ fraction of calcined ThO_2 was separated by repeated sedimentation and

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TABLE 28

Settling Velocity of Various Sizes of ThO$_2$ in H$_2$O at 25°C

PARTICLE SIZE (μ)	TIME REQUIRED TO SEDIMENT 10 cm IN H$_2$O
0.1	1438 hr
1.0	86.3 min
10.0	51.0 min
20.0	12.75 sec
50.0	2.04 sec

decantation. A slurry of this material required 24 hr for complete settling
and showed slight thixotropic properties (Table 29). As measured at the
slowest speed (lowest rate of shear) of a model LVF Brookfield viscosimeter
the viscosity was 1200 to 1400 centipoises. At the highest rate of shear
(60 rpm) on the instrument the viscosity registered 140 to 150 centipoises.

TABLE 29

Viscosity of Finely Divided ThO$_2$ Slurries at 20°C

Model LVF Brookfield viscosimeter, No. 2 spindle

SPINDLE SPEED (rpm)	VISCOSITY (centipoises)
6	1400
12	688
30	270
60	140
30	290
12	612
6	1250

Such finely divided particles are rather surface active, tending to form
loosely bound agglomerates. However, after standing for periods as long as 1
month the material was easily redispersed.

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From the standpoint of physical properties such slurries have good engineering features, i.e., the viscosity is low, corrosion is negligible, settling rates are acceptable, and the data of Hiskey and Eidinoff have shown that the particle size is in the range of minimum erosion effects.

Since the available quantity of finely divided ThO_2 (0.1 to 0.5 μ) is rather small, large-scale heating experiments have not been completed. However, experiments are being carried out in small quartz tubes to determine if particle-size growth can be detected. No change in the average particle size has been observed in slurries containing bentonite when heated for periods up to 150 hr at 250°C. In addition, no evidence of caking was observed in samples irradiated in quartz tubes in the pile at neutron fluxes of 5×10^{11} cm^{-2} sec^{-1} for periods of 1 week at 100°C.

A small program is underway to investigate certain of the naturally occurring silicates as antipacking agents. Such low-cross-section materials would be added to the slurries, not as dispersing agents but merely to prevent packing in the event that the slurries had to stand for considerable lengths of time without agitation. Certain varieties of the crysotile (asbestos) variety look promising.

Thorium Slurries Stabilized with Additives. Using 0.75 to 1.0 wt % fractionated bentonite, stable thorium slurries have been prepared along the lines suggested by the work of Morse. These slurries have been irradiated in the pile for periods up to 1 week without evidence of radiation decomposition. The experiments were carried out in quartz tubes at the operating temperature of hole 12 (about 100°C).

Various tests of the heat stability of the slurries have been conducted at 250°C in quartz tubes for periods up to 2 weeks with no appreciable changes in properties. However, similar tests in a stainless steel autoclave under strong agitation have always resulted in the deposition of bentonite on the walls of the container and consequently failure of the slurry. The reason for this behavior is not clear since this bulk of the bentonite is apparently unaltered chemically and may be readily reslurried with the thorium to give a stable suspension at room temperature.

The amount of bentonite required for stable slurries varies directly with the particle size. With 0.75 to 1.0 wt % bentonite of particle sizes less than 25 mμ, stable slurries containing 1000 g of thorium per liter as the

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oxide are obtained. With naturally occurring bentonite nearly three times as much bentonite is required since the particle sizes are more nearly 10 to 25 μ.

Decreasing the size of the thorium oxide particles also decreases the amount of bentonite required. However, no appreciable advantage was observed using particle sizes smaller than 1 μ. The deleterious effect of iron on bentonite-stabilized uranium slurries was also verified. However, attempts to remove the iron completely were unsuccessful. Electrodialysis and ion-exchange remove ionic iron or iron that is readily replaceable with H^+, but this represents only a small percentage of the total amount. It was observed during the course of fractionating out the 25-mμ particle-size bentonite in a supercentrifuge that most of the iron was eliminated with the heavy fraction of bentonite. It was also observed that the iron could be completely hydrolyzed after 48 hr in an autoclave at 250°C to give a ferric hydroxide colloid. However, the iron was so intimately mixed with the bentonite that no separation could be accomplished without chemically altering the bentonite.

It now seems apparent that the preparation of stable slurries containing 1000 g of thorium per liter will of necessity produce mixtures of high viscosity (Table 30). Using a Brookfield model LVF viscosimeter, a typical range of viscosities with varying rates of shear is from 10,000 to 2,000 centipoises. At lower viscosities the slurries settle rapidly, and at higher values stiff gels results. The expenditure of power in pumping such viscous slurries may be prohibitive. This aspect of the problem should be evaluated at an early date before much additional work with bentonite additives is done.

TABLE 30

Viscosity of Typical Stable Thorium Oxide Slurries at 20°C

1165 g of ThO$_2$ per liter, 0.5 to 1.0 μ particle size; 0.75 to 1.0 wt %
bentonite, about 25 mμ particle size; model LVF Brookfield viscosimeter

BENTONITE ADDITIVES	SPINDLE SPEED (rpm)	VISCOSITY (centipoises)		SUPERNATANT VOLUME (%) AFTER ABOUT 1-min AT 0.25°C
		pH 5 to 6	pH 3 to 4	
5% unfractionated containing about 1% Fe, pH 5.0	6	26,500		None
	30	7,000		
	60	4,060		
3.5% unfractionated, low Fe content (about 0.1%) (B. Preiser Co.)	6	6,800	9,200	5
	30	1,900	2,300	
	60	1,100	1,270	
3.0% (same as above)	6	3,900		10
	30	980		
	60	560		
1.3%, less than 25-mμ particle size, less than 0.1% Fe	6		3,600	5
	30		1,340	
	60		730	

10. CONTINUOUS FUEL PROCESSING

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The primary objective of this study is to selectively remove high cross-section fission products and plutonium from an aqueous solution plutonium-producer and, by so doing, minimize processing which is required before re-enrichment of the uranium. It is also of some concern to remove all the fission products from an enriched core reactor, such as the HRE, without changing the chemical form of the fuel since re-enrichment is not necessary. Precipitation, surface adsorption, ion-exchange adsorption, and electrolysis have all been applied. A combination of procedures which do not change the chemical form of the fuel is used to take advantage of particular properties of different fission products.

For an 18.6-ton (92 g of uranium per liter) plutonium producer, the following processing scheme is proposed. One-fifth or 40,000 liters of the reactor fuel is cooled 1 day and passed through about 500 liters of Dowex 50 for removal of plutonium, rare earths, and strontium. At less frequent intervals the fuel is also passed through about the same volume of fuller's earth for the removal of zirconium and cesium, and through Dowex A-1 anion resin for the removal of molybdenum, iodine, tellurium, and ruthenium. The ruthenium, the hold-up uranium, and the bulk of the fission products are stripped from the adsorbers with nitric acid and run through Purex. The plutonium is purified and the uranium is decontaminated for handling in the re-enrichment plant.

For the processing of enriched fuel the same system of adsorbers can be used with about 5% of the fuel processed per day being held up on the adsorbers. Since re-enrichment is not required, this fuel hold-up is objectionable. Another process must be used for decontamination before reconverting the fuel to the original chemical form. A process has been developed using a combination of cation exchange and electrolysis which returns all the fuel to the reactor as UO_2SO_4. Barium and zirconium are removed by filtration. Rare earths and strontium are adsorbed on a cation exchange resin. Molybdenum, iodine, tellurium, and ruthenium are electroplated. The only appreciable

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uranium hold-up is on the cation resin and this is displaced selectively with Cu^{++} ion. The small excess of Cu^{++} in the effluent UO_2SO_4 is removed by electrolysis with only a very slight pH reduction. A total uranium loss of 0.001% has been demonstrated.

If the problem of converting UNH containing excess HNO_3 to neutral UO_2SO_4 is simple and can be carried out by remote control, another ion-exchange process is attractive. In this method all the uranium processed per day is adsorbed on a cation resin. Unadsorbed fission products go on to waste. The uranium is stripped selectively from the cation resin and completely adsorbed again on anion resin with breakthrough of unadsorbed fission products again. The uranium is again stripped selectively but is in the nitrate form in an excess of HNO_3.

Table 31 roughly compares three systems for treating HRE fuel. The runs were made at full chemical scale assuming 5% of the reactor loading to be processed per day. One-day-cooled tracer and dead fission products equivalent to one day's production were added. The fission products which precipitated naturally were barium, zirconium (10 days production), tellurium, and portions of molybdenum, iodine, and ruthenium. The flow was probably too high for the fuller's earth used, which, on separate runs, caught practically all the cesium. Some strontium losses were higher than necessary because the resin volume, 50 ml, was at a minimum. The efficiency of electrolysis and anion exchange for molybdenum, iodine, tellurium, and ruthenium were remarkably similar.

In conclusion, it may be said, neglecting precipitation, that fuller's earth or the inorganic ion exchangers are the only good methods of removing zirconium and cesium from SO_4 fuel. Cation exchange is most specific for plutonium and the rare earths but adequately covers barium and strontium. Electrolysis is most satisfactory and probably can be more highly developed for molybdenum, ruthenium, iodine, and tellurium.

TABLE 31

Comparison of Three Processes for Decontaminating HRE UO_2SO_4 Fuel

A. Breakthrough adsorption on fuller's earth, Dowex 50, and Dowex A-1

B. Complete adsorption of fuel on Dowex 50 and Dowex A-1

C. Precipitation followed by adsorption on Dowex 50 with Ca^{++} displacement, followed by electrolysis

RESULTS ON DAILY BASIS

	A	B	C
Percent of fuel in form other than neutral UO_2SO_4 (in excess HNO_3)	0.6%	100%	0
Percent of uranium hold-up on adsorbers	0.011%	0.013%	<0.001%
Total volume of adsorbers per day	150 ml	2000 ml	50 ml
Percent of fission products left in fuel			
Rare earths	4%	0.8%	8%
Barium	7%		<10%
Strontium	28%	1.1%	31%
Cesium	62%	5.5%	100%
Zirconium	27%	45.6%	28%
Columbium		44.0%	
Ruthenium	85%	6.5%	45%
Molybdenum	48%	45.3%	57%
Iodine	33%	0.6%	11%
Tellurium	33%	1.3%	18%
Neptunium	>75%	19.5%	>75%

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11. ENGINEERING RESEARCH ON ALTERNATE REACTOR SYSTEMS

Slurry Reactor

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Boiling Reactor

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H. W. Hoffman

SLURRY REACTOR STUDIES

A longer range experimental program was initiated this quarter to determine and to overcome the problems associated with the substitution of a UO_3 slurry for the solution of uranyl sulfate in the HRE. It is anticipated that difficulties may arise from at least four sources: (1) lack of stability of the slurry resulting in lack of uniformity; (2) caking upon shutdown; (3) excessive growth or comminution of the slurry particles; and (4) abrasion of the system components. Preliminary results have been obtained on the first two problems, and construction has started on equipment for preliminary study of the latter two problems.

Stability and Uniformity of Circulated Slurry. In order to determine to what extent the slurry becomes inhomogeneous while circulated in a closed system, a glass and stainless steel apparatus was built which pumped a 25 g/liter UO_3 slurry through a small sphere and through a liquid cyclone separator. The finer fraction from the separator was passed through a pump, while the coarser fraction was returned to the finer stream at the throat of a venturi on the high-pressure side of the pump.

In early tests using barytes instead of UO_3, samples taken from regions at five different radial positions in the sphere indicated that the solids content varied between 35% solids at 15 gpm and 50% solids at 8 gpm. Barytes (density 4.2) were used for convenience in early tests. The results of these tests are believed to give a quantitative indication of the results to be expected in a slurry of UO_3 (density 7.3).

With UO_3 slurry the flow patterns in the sphere and in the separator were found to be similar to the pattern in the solution system.[1] However, it was

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(1) J. S. Culver and R. Wilson, "Model II (Plastic Sphere Test System," *Homogeneous Reactor Experiment Report for the Quarter Ending February 28, 1950,* ORNL-630, p. 60, esp. p. 78 (Apr. 21, 1950).

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found necessary to remove the slurry from both ends of the vortex in order to avoid accumulation of solids at one end.

No pumping or settling difficulty was encountered in other parts of the system. During the tests, UO_3 changed in color from a bright yellow to a dirty yellow-green. Samples have been submitted for analysis to determine the cause of this change.

The UO_3 charged into the system originally passed 200 mesh and was retained on 325 mesh screen. During operation, an increasing proportion of solids passed over with the overflow from the separator, indicating a reduction in the particle size. A sampling procedure has been instituted to determine the extent of particle size reduction.

The operating temperature of this equipment has been increased to 75 to 80°C and protracted operation has begun to determine the slurry and particle stability at this slightly higher temperature.

Caking. Initial tests bore out reports by previous investigators that fine calcined UO_3 in stagnant water will harden into a solid cake. On the theory that this hardening is due to recrystallization with water, samples of the calcined powder were dispersed in distilled water and heated at 250°C for 24 hr. Crystals as large as 300 to 400 μ were formed which, after filtering, washing, and screening, showed no caking tendency. The UO_3 in the current system has been hydrated in that fashion.

Abrasion. Design of equipment to determine the abrasive properties of UO_3 crystals has started. This equipment is similar to a standard Brinnell abrasion wear tester. Initial tests will be simple, comparative hardness tests, but flow impingement tests may be necessary later.

Separator Tests. Should abrasion and caking prove serious in the pump or heat exchanger it may be necessary to use a separator to remove the solids from the system before entering the pump and heat exchanger. A Dorr-Clone liquid cyclone separator has been ordered for testing in this connection.

Crystal Growth and Comminution. It has already been demonstrated that crystals of hydrated UO_3 will grow in a relatively stagnant water environment,

while reduction in crystal size was observed in the initial circulating system. A system has been designed to study these tendencies in a circulated slurry in which the temperature is cycled between 110 and 150°C. Qualitative information on the equilibrium between crystal growth and crystal refinement can be obtained from such a system, and when this is compared with lower temperature tests, it is possible that quantitative indications of the two process rates can be obtained.

Full-Scale Circulating System. Design of a full-scale 150°C HRE slurry-system mock-up has started, but many of the design decisions must await the outcome of the foregoing tests. Machining of the 18-in. stainless steel sphere is under way, and a number of other components have been collected.

BOILING REACTOR STUDIES

A small program was initiated this quarter to determine the feasibility of a boiling type of homogeneous reactor. The purpose of this program is to yield data which will permit the calculation of the maximum rate at which heat can be removed from the reactor by boiling and to accumulate information on the formation and collapse of bubbles for use in evaluating the control problems of such a reactor.

Theoretical Analysis. Approximate calculations for the vapor phase velocity and fluid circulation rate in a cylindrical geometry have been completed. Approximate densities, void space, power level, pressure, and cylinder dimensions were assumed and the velocities or circulation rates were evaluated from a first law energy balance for a flow process. These velocities varied widely and were dependent largely on the magnitude of the loss coefficient used in the calculations.

A heat balance type of calculation of resident voids for an assumed power level of 1000 megawatts in a 30-ft diameter right cylinder indicates that the percentage voids in the bulk fluid may become excessive (over 20%) at vapor circulation velocities in the natural-convection range. If the natural circulation vapor velocity in the core is of the order of 10 ft/sec, preliminary computations indicate the resident voids to be about 5% of the total cylindrical fluid volume. Such high vapor velocities can be assured by relying on forced circulation.

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Experimental Studies. A design has been completed and the apparatus is under construction for a "T" experiment. The object of this study is to observe the behavior of a dilute salt solution with uniform electrical resistance heating. No attempt has been made in this experiment to simulate the heat generation due to the flux distribution in a reactor. Instrumentation for temperature, pressure, and power dissipation are included in the design of the apparatus.

In an effort to produce higher heat-generation rates near the center of the liquid, an experiment has been operated in which two isolated circuits were connected at right angles to each other across a cylindrical container of dilute acid. By holding the current in one circuit 90° behind current in the other circuit, some increase in power generation near the center was expected. Electrolysis and boiling at the electrodes hampered effective operation. It is believed that better electrode cooling and addition of a depolarizing agent will reduce these difficulties.

Another system which has been designed uses a vertical insulating baffle to concentrate the current at the center of a sphere. This system, indicated in Fig. 22, consists of a hollow copper sphere divided into two hemispheres by an insulating separator. The system is filled with a conducting solution, e.g., 1% hydrochloric acid; a voltage is impressed between the two hemispheres, with the separator serving to give a power distribution which simulates to some extent the distribution to be expected in a boiling reactor. The system is provided with view ports so as to enable visual, as well as photographic, observation of phenomena occurring in the center of the sphere. It will also be possible to determine circulation patterns and rates by means of pitot-tube traverses.
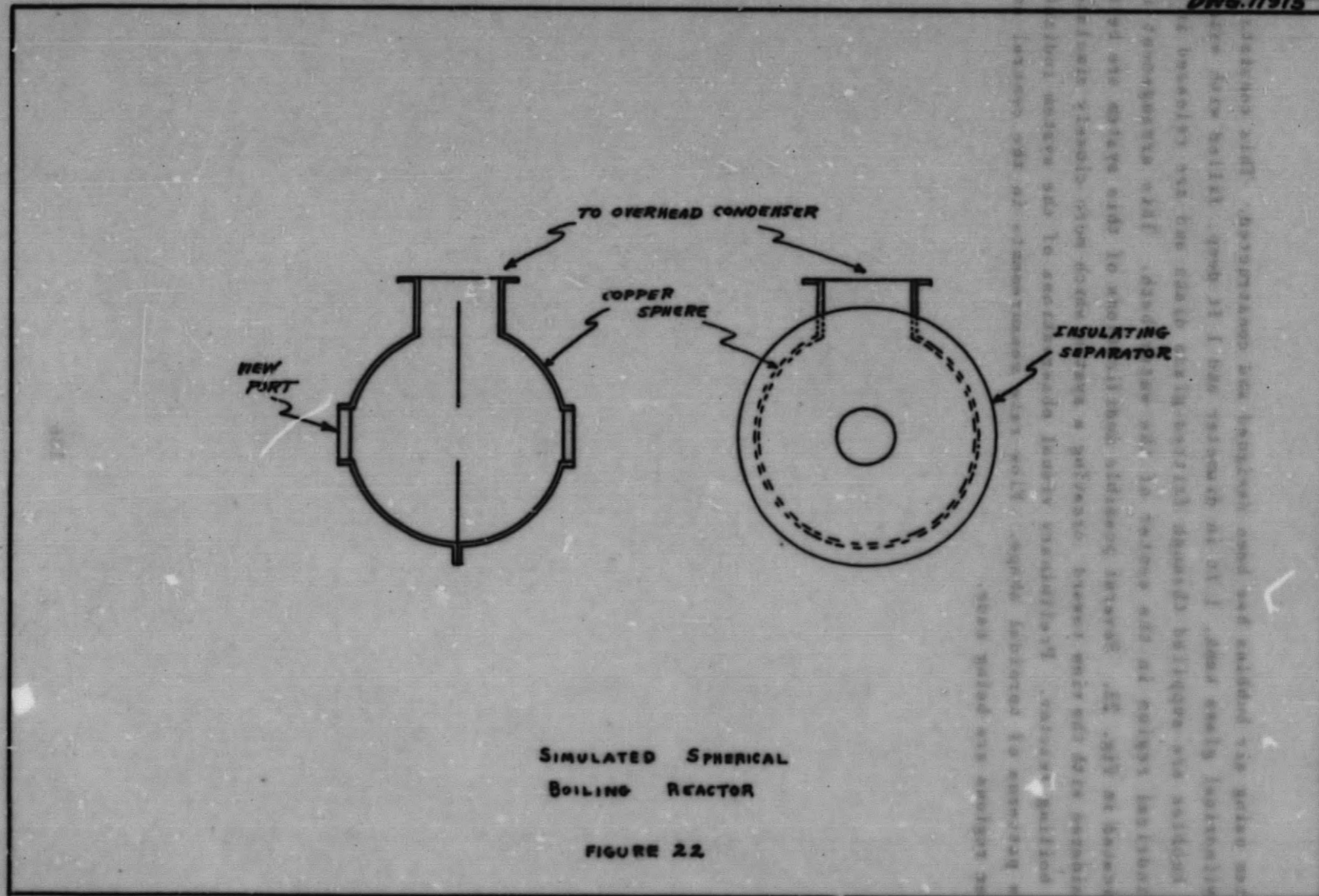
A few efforts to use light for transmitting heat to the center of the tube have been unsuccessful to date because of high absorption and high reflectivity of the water surface. Efforts along this line are continuing.

Ultrasonic energy has been used in another investigation for obtaining internal heat source in a 2 x 4 in. cylinder. Limitations on available equipment prohibit immediate investigation on a suitable scale.

In a preliminary effort to obtain some information on the circulation patterns and the rates of flow in a boiling homogeneous reactor, a simulated
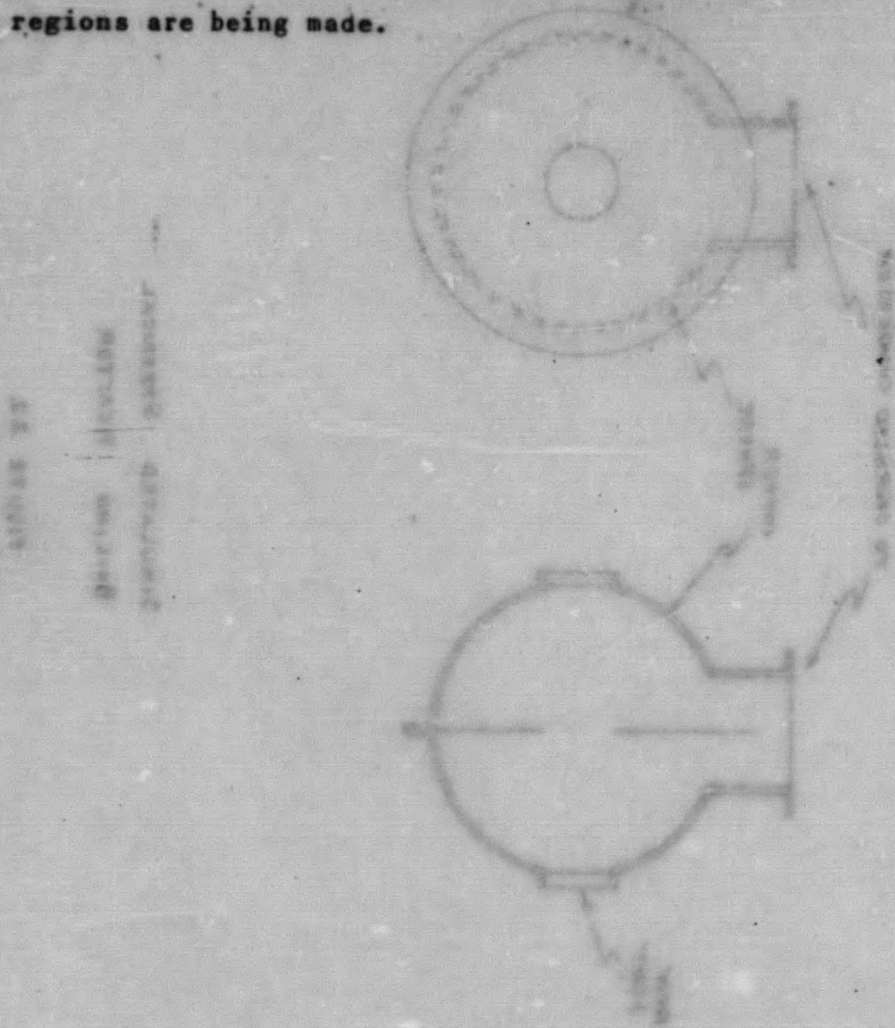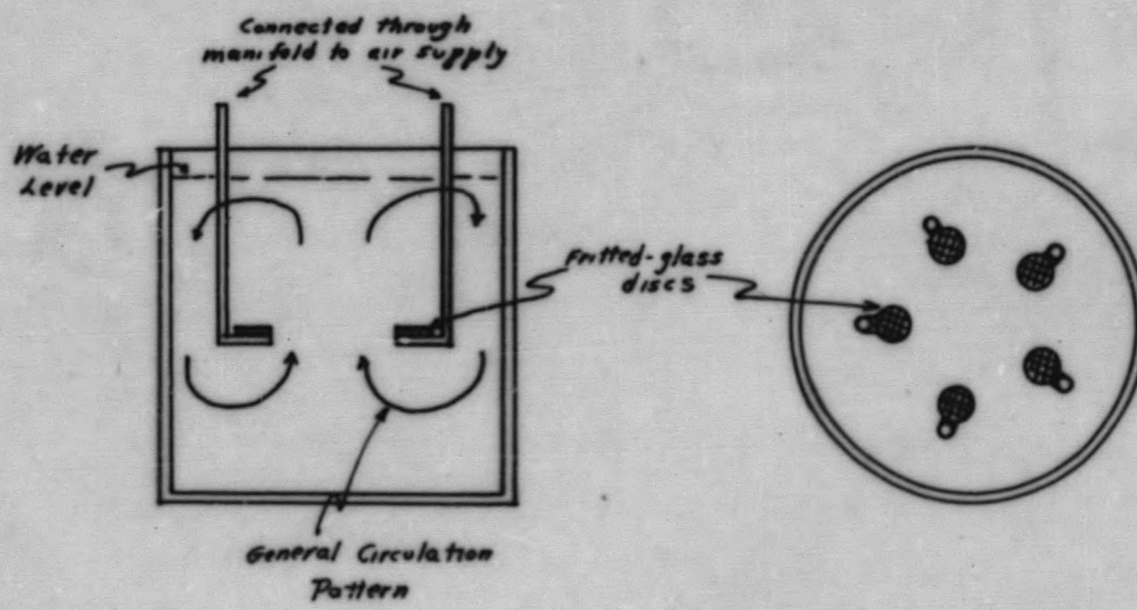
DECLASSIFIED

TO OVERHEAD CONDENSER

COPPER SPHERE

VIEW PORT

INSULATING SEPARATOR

SIMULATED SPHERICAL
BOILING REACTOR

FIGURE 22

system using air bubbles has been designed and constructed. This consists of a cylindrical glass tank, 1 ft in diameter and 1 ft deep, filled with water. The bubbles are supplied through fritted-glass disks and are released in a cylindrical region in the center of the water bath. This arrangement is indicated in Fig. 23. Several possible modifications of this system are being considered with the view toward creating a system which more closely simulates the boiling reactor. Preliminary visual observations of the system indicate flow patterns of toroidal shape. Flow rate measurements in the central and outer regions are being made.

Connected through
manifold to air supply

Water
Level

Fritted-glass
discs

General Circulation
Pattern

SYSTEM FOR CIRCULATION STUDIES

FIGURE 23