ORNL-630

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REACTOR TECHNOLOGY DIVISION

**HOMOGENEOUS REACTOR EXPERIMENT
REPORT FOR THE QUARTER ENDING FEBRUARY 28, 1950**

C. E. Winters, Editor

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I. SUMMARY

Solution Stability

The solution stability experiments indicate that if the uranium sulfate solution is at a temperature of 65°C , and at ORNL Reactor Flux that 1 to 2 excess molar sulfuric acid is necessary to prevent precipitation of UO_4 . One experiment at 250°C at the same flux indicates that the excess acid is unnecessary. Gas formation rates at 65°C and below indicate that one molecule of H_2O is decomposed per 50 e.v. of fission energy, and that pressures greater than 10,000 psi are generated in a closed system, indicating that at this temperature, decomposition rates considerably exceed recombination rates, and that the application of reasonable pressures to suppress the gas formation rate is of little practical help. One experiment at 250°C indicated that at a total pressure of 900 psi a psuedo equilibrium was established, indicating presumably that recombination was occurring at a rate approximately equal to the formation rate. This experiment indicates that going to higher pressures and temperatures are in the right direction for the minimization of the bubbling problem. Experiments at temperatures between 65°C and 250°C are planned.

Corrosion

Short term corrosion experiments at 250°C generally confirm the selection of zirconium as the material of construction for the Homogeneous Reactor Tank. The experiments also indicate that if one takes too many liberties with solution compositions that corrosion difficulties may be experienced. Stainless steels of a wide variety of composition are generally attacked by uranyl sulfate at 250°C . Addition of extra sulfuric acid greatly accelerates the attack and after a sufficiently long period of time in a sealed vessel, reducing conditions are set up with the resulting reduction of the uranyl ion to lower insoluble oxides, principally U_3O_8 .

Additions of oxidizing agents in moderate quantities in the form of H_2O_2 , HNO_3 , CrO_3 , to the vessels, stop the uranyl reduction and reduce the attack on the stainless itself to tolerable values. Unfortunately, one series of experiments with uranyl

I. SUMMARY (Con't.)

Corrosion (Con't.)

sulfate plus stabilized HNO_3 , with or without excess sulfuric acid, showed a very serious form of intergranular type of attack on zirconium, similar to that experienced at Argonne National Laboratory Naval Reactor Corrosion Tests on Bureau of Mines Zirconium. A single experiment with CrO_3 did not produce this type of attack. Experiments will continue and in addition, the effects of H_2 and O_2 gas will be observed.

Overall, it continues to appear that there are several conditions under which a uranyl sulfate Homogeneous Reactor is feasible. One may operate at 250°C with uranyl sulfate without excess acid if one uses a zirconium tank, and with the external system constructed of zirconium, and perhaps titanium or certain of the precious metals. One may operate at 100°C using a wide variety of materials of construction, including stainless steel, if one incorporates sufficient excess acid in the solution to prevent precipitation. Insufficient work has been accomplished to demonstrate feasibility at intermediate temperatures, but there is little reason to doubt that suitable conditions can be found if desired and provided a proper balance is made between the temperature, the excess acidity, an oxidizing agent and the materials of construction.

Physics

Aside from minor dimensional corrections to conform to mechanical design values the calculations of critical mass are complete and indicate a favorable assembly. The question of shimming, and of safety and regulating rods is still incomplete but no trouble is anticipated in getting adequate reactivity built into these functions.

The transient operation of the reactor is such as to sustain instantaneous changes of reactivity amounting to 2% effective. There is evidence that the damping due to delayed neutrons and cooling will be of such magnitude that oscillations about equilibrium power will be very small.

Preliminary investigation of the origin of reactivity changes shows that all such changes take place over a reasonable time interval and that estimates made on the basis of instantaneous changes are very conservative.

22
11
11

I. SUMMARY (Con't.)

Physics (Con't.)

The interpretation of the overall physical picture that one is forced to adopt is that the Homogeneous Reactor is self controlling for a reactivity change far in excess of that which would completely destroy most of the other types of reactors so far proposed.

Engineering and Design

Preliminary designs given for the reactor and auxiliaries. A program is in progress to design and construct a non-nuclear model to demonstrate the feasibility of operating at 1000 psi and 250° C. This will require roughly 3 months to reach a stage when the engineering feasibility can be reasonably conclusively demonstrated.

Site Plans

The Laboratory plans to recommend a site in the valley to the south and somewhat east of Oak Ridge National Laboratory about 1/2 mile from X-10. The details are to be presented in a separate report to be issued at a later date.

II. DESIGN

A proposed tentative design of the Homogeneous Power Reactor Pilot Plant is illustrated graphically by Figures II-1 through II-5 inclusive. Since a description of the system as a whole has been given in the Technical Division Quarterly Report of December 28, 1949, (Report ORNL-527), subsequent discussion of the design in this section will be confined to these figures.

A vertical section through the centerline of the reactor is illustrated by Figure II-1. The accompanying table is a nomenclature of the components which go into the reactor. Pile fluid (fuel and moderator mixture) will be introduced tangentially into the reactor core through a one and one half inch schedule 80 nominal size zirconium inlet pipe (Item 21) welded to the core tank. Centrifugal action tends to separate the gases of dissociation, which are withdrawn through the gas removal tube (Item 2) to a recombiner unit. The gas removal tube is concentric with the pressurizer pipe (Item 22), which is welded to a diffuser outlet located on top of the reactor core. In passing through the diffuser, the velocity head induced in the pile fluid due to the tangential inlet will be substantially converted to pressure head, thus resulting in a lowered system pressure drop. Immediately after passage through the diffuser ports, the pile fluid divides; the main stream is conducted through the outlet pipe (Item 23) to the main heat exchanger. A part of the fluid will remain stagnant in the pipe to the pressurizer, which will serve to maintain the desired 1000 psi pressure on the system. This arrangement gives the shortest and most direct connection between the core tank and the pressurizer; thus, any volume or pressure change induced by a sudden increase in the reactivity of the pile may be absorbed in the pressurizer as a surge tank to minimize harmful effects so introduced.

In order to completely drain the system of pile fluid, a small tube (Item 11) is shown connecting the bottom of the core tank to the pile fluid storage system. This pipe is conducted through the top flange closure by making it concentric with the outlet pipe. In order to compensate for the cross sectional area of this pipe occupied by the drain tube, the outlet pipe from the core through the cover flange will be specified as a two inch, schedule 80 pipe. Thereafter, it may be reduced to a one and one half inch schedule 80 pipe in the run to the heat exchanger.

With this arrangement of pipe connections between the top flange and the core tank, differential expansions due to unequal temperatures should be automatically compensated. The weight of the reactor core and contents will be carried primarily by the pressurizer pipe (Item 22) as a member in tension suspended from the top flange. The elbows in the separate inlet and outlet pipes act as expansion bends to take up differences in expansion

II. DESIGN (Cont'd)

in these pipes. The concentric pipes will operate at substantially the same temperatures, hence, no particular trouble is anticipated with thermal strains in these members.

Figure II-2 is a detail showing a proposed method of attaching the zirconium inlet and outlet pipes to the top flange. This construction was chosen in order to minimize the quantity of zirconium required for the flanges. It is required that there shall be no mechanical joints placed in the reactor which would increase the probability of leakage of fluids between the core and reflector. Therefore, the zirconium pipe is a continuous section from the core through the top flange. A disc of zirconium with a flat on one side for a gasket-groove and a sphere on the opposite side is welded directly to the pipe at the plane of the bottom of the top flange. This disc, with the ring joint gasket, is held in place against the bottom of the top flange, which is also grooved for the gasket, by means of a steel backing flange and bolts. Thus, the condition of no mechanical joints between the pipe fluid and the reflector is satisfied, and, simultaneously, the reflector is effectively and reliably sealed. There will be three such joints required on the under side of the closure flange for sealing off the inlet, outlet, pressurizer, gas draw-off, and drain pipes with the concentric construction shown.

Item 10 is a typical control rod guide thimble which will be fabricated from hafnium-free zirconium. Using rods as the control elements, six of these are required. However, space has been allowed between the top level of the reflector and the bottom of the flange for insertion of alternate safety plates should these be proven necessary. The outside diameter of the reactor core tank sphere is 19 in., and the inside diameter of the cylindrical neck of the reflector shell is 24 in., which leaves a maximum of two and one half inch radial clearance for insertion of the thimbles. Therefore, for adequate clearance the maximum outside diameter of the thimbles is specified as two inches.

Obviously, the thimbles in which the control rods are guided must never be allowed to collapse. Also, it is imperative for control purposes to have the minimum thickness of wall compatible with safety. A very heavy walled thimble will absorb too many neutrons, thus, detracting from the sensitivity of the rod. Figure U-1, paragraph U-20 of the ASME Code for Unfired Pressure Vessels recommends a thickness to diameter ratio of 0.120 for a working stress of 10,000 psi in the tube wall, with a working pressure of 1000 psi. Therefore, the required wall thickness, according to the code, for this stress and pressure is 0.240 in. The specified wall thickness for ordering the zirconium tubing has been given as 0.250 in. In

II. DESIGN (Cont'd)

an effort to determine whether or not this thickness could be safely reduced, the literature was surveyed for data on the design of tubes subjected to external pressure.

Of the formulae quoted in the literature for determining the collapsing pressure of long slender tubes ($L/D \geq 8$), those derived by Timoshenko and Bryan are generally accepted. Substitution of the proper elastic constants of zirconium in either equation results in the following formulae:-

$$p_c = 26.4 \times 10^6 \left(\frac{t}{d} \right)^3$$

where p_c = collapsing pressure, psi
 t = tube wall thickness, in.
 d = mean diameter of tube, in.

Assuming the outside diameters of the control rod thimbles constant at two inches, and substituting various tube wall thickness, a curve of collapsing pressure versus tube thickness may be obtained. Thus, from this curve, the collapsing pressure of a two inch outside diameter, one-fourth inch thick walled zirconium tube is 76,800 psi. However, this assumes a perfectly cylindrical tube with absolutely uniform wall thickness and homogeneity of material. Apparently, therefore, if sufficient care is exercised in fabrication, the tubes as specified should be more than adequate to withstand the differential pressures likely to be encountered in the reflector region of the reactor.

However, if it is conceded that the ASME, Code results in ultra conservative results and that wall thicknesses as determined by Bryan's or Timoshenko's equation are valid, then, it should be possible to specify a greatly reduced wall thickness for the control rod guide thimbles. Thus, according to these equations, a two inch O.D. zirconium tube with a wall thickness of one-eighth of an inch should withstand a collapsing pressure up to 8000 psi.

The control rod thimbles are to be secured to the top flange by the same type of joint as used for the piping. However, the backing flange used may have a guide extension (Item 3) welded to it in order to provide a proper guide for the upper end of the control rod, and to provide a housing for a shock-absorber spring, linear bearings, etc., and an upper support for the mechanism which actuates the rods.

Item 5 is the proposal for the top closure flange. This will consist of a standard 24-inch nominal pipe size 1500 psi at 750°F blind flange which may be obtained as a stock item from the

II. DESIGN (Cont'd)

Taylor-Forge Company or others. This flange is to be modified as required for the inlet and outlet pipes and the control rod thimbles. An analysis for stresses induced in the flange and holding studs due to internal hydrostatic pressure has been made in the memorandum report (CF-49-11-152) from Segaser to Winters. An analysis for stresses induced by thermal gradients is being prepared.

Vendors have been contacted for the fabrication of the reflector pressure shell (Item 7). Tentative specifications have been written for this vessel, as described in the memorandum from Segaser to Winters (CF-50-1-70). Substantially, the final design of this vessel will be as described in this memorandum with the exception of certain of the openings which are to be changed both in size, number and location. Final design drawings are now being prepared.

In order to reduce induced activity in the steel of the pressure vessel, it is proposed to line the vessel with a thermal neutron absorbing substance (boral sheet), Item 8. Because of the shape of the vessel, that portion of the liner for the spherical container could be fabricated in the form of orange-peel-shaped segments which would be formed to fit the curvature of the inside of the vessel. These could be fastened to the inside of the vessel with small flat head screws and each segment edge welded to form a continuous and seamless liner.

Because of the fact that the wall of the pressure vessel will act as a thermal shield, considerable heat may therein be developed by absorption of neutrons and gamma rays. This heat may be sufficient to induce severe thermal gradients in that portion of the vessel not in contact and cooled by the reflector (the reflector will operate at various levels as a shim control). Calculations are currently being made to determine the magnitude of this effect. If the calculations indicate that these stresses are of a serious magnitude, it should be possible to provide auxiliary cooling on the inside or outside of the pressure wall by brazing or welding steel cooling coils between the wall and the liner. A recess in the inside wall of the reflector vessel would have to be provided for these coils, as indicated by the dashed lines on Figure II-1. This should be feasible since the walls are 60% thicker than required by the ASME code, and the coils could be of tubing not more than one-half inch O.D. through which ordinary water could circulate. It should not be necessary to cool below the centerline of the reactor core.

Inlet and outlet pipes to the reflector coolant heat exchanger and circulating pump are shown by Items 13 and 17. It has been

II. DESIGN (Cont'd)

assumed that one inlet and one outlet each are adequate for all positions of reflector height. These connections must obviously be located well below the anticipated minimum reflector level.

Item 15 is a three inch nominal size drain pipe for the reflector. This pipe connects to a pneumatically or electrically operated "dump" valve and hence, to a system of always safe dump tanks. This system is provided as an alternate safety device for the reactor. However, the value of dumping the reflector as a high speed safety device is marginal, since, assuming the most optimistic conditions, calculations show that the reflector will not be discharged from the tank in less than about two and one half seconds: (See ORNL, Central Files No. 49-12-48, "Discharge Times of Homogeneous Reactor Pilot Model Reflector Flowing Through Two Inch Pipe From Pressure Tank").

Thimbles are provided in the reflector region of the reactor seven and one half inches below the core centerline for the purpose of introducing the necessary instruments (counters, ion chambers, etc.) for adequate control of the pile. A typical instrument thimble and bridge tube construction is shown by Items 18 and 19. As in the case of the control rod thimbles, the instrument thimbles must be proportioned to withstand collapse, although it is not as mandatory to have a minimum wall thickness. Southwell, in the paper, "On the General Theory of Elastic Stability" has developed an equation for the collapsing pressure of a short tube ($L/d \leq 8$) which considers the effect of limited length and end restraints on the elastic behavior of the cylinder. If the effective length of the zirconium instrument thimbles is assumed as approximately 14 in. and the outside diameter as three and one half inches, and substituting the proper elastic constants, this equation may be reduced to:-

$$p_c = 2.1 \times 10^6 \left(\frac{t^2}{d} \right) \left(\frac{t}{d} \right)^{\frac{1}{2}}$$

where p_c = collapsing pressure, psi

t = tube wall thickness, in.

d = mean diameter of tube, in.

This equation may be used to plot a curve of collapsing pressure versus wall thickness. The zirconium specified for procurement corresponds to a three inch by schedule 160 nominal pipe. This pipe size has a wall thickness of 0.437 inches, which, according to the curve would not collapse until a pressure of 47,000 psi was reached. Therefore, it appears reasonable that the inside diameter of the pipe may be bored out to correspond to a size compatible with a practical instrument size. If it is assumed that the instruments can be made of a size to fit in a three inch diameter hole, the

II. DESIGN (Cont'd)

resulting wall thickness of the 3.500 O.D. pipe will be 0.250 in., which according to Southwell's equation, will not collapse until a pressure of 11,000 psi is reached. Since the operating pressure in the reflector is expected to be of the order of 1000 psi, tube dimensions of this size will give a factor of safety of at least eleven, or five and one half for an operating pressure of 2000 psi.

Items 12 and 16 in Figure II-1 constitutes the supporting framework for the reactor and components. Item 9 is a stainless steel sheet metal splash guard which may be erected around this frame and reactor for the purpose of preventing loss of pile or reflector fluid if a high pressure leak should develop in the system. Item 14 is an optional high density auxiliary shield which may be placed adjacent to the pile for the purpose of supplementary shielding of equipment; especially in locations where it is unavoidably necessary to remove some of the concrete block for the placement of equipment.

The relative locations of the instrumentation thimbles, control rod thimbles, core tank, drain pipe and supporting structure are shown by Figure II-3. Six instrument thimbles and six control rod thimbles are required. Therefore, in order for the instrument thimbles and connecting bridge tubes to clear the supporting structure and not interfere with the control rod thimbles, an unsymmetrical arrangement is necessary as shown. Figure II-5 is a horizontal section through the reactor and shielding on the plane of the instrument thimble centerlines. This view illustrates how the instrument thimbles connect to the exterior of the pile shield in order to vary the location of each instrument relative to the core tank for optimum efficiency.

An overall view of the reactor, shielding and certain of the major items of equipment is shown by Figure II-4, which is a vertical section taken through the shielding in a plane just missing the central supporting structure. This view is lacking several items, but serves to illustrate the general visualized construction. The reactor and auxiliaries will be supported within a biological shield as a minimum consisting of an outer wall two feet thick by 18 ft - 0 in square by 18 ft - 0 in in height from the basement floor. The equipment within this shield will be supported at the proper levels by structural steel framing within the two foot wall and fitted around the equipment will be place pre-cast concrete blocks supported over the dump tanks as illustrated. Thus, by removing the upper concrete slabs and the necessary blocks, any item may be exposed for removal and maintenance. Certain of the equipment, such as Pulsafeeder return pumps, the heater for the concentrator tank, etc., are visualized as being in pits on two opposite sides of the reactor. Access to these pits will be by

II. DESIGN (Cont'd)

manholes with removable concrete covers outside of the pile shield. A slight suction pressure could be applied to the shield with air ducts as shown, in order that any air leakage will be in instead of out for safety and health reasons. An operating floor is shown 10 ft - 0 in above the ground floor on which a turbine could be mounted as well as the necessary control panels.

NOMENCLATURE FOR FIGURE II-1

1. Inlet pipe elbow
2. Gas removal tube
3. Regulating rod upper guide
4. Regulating rod thimble backing flange
5. Flange closure
6. Ring seal
7. Reflector pressure shell
8. Reflector shell liner
9. Splash shield around reactor
10. Regulating or control rod guide thimble
11. Bottom drain pipe
12. Support beam
13. Reflector fluid cooling pipe return
14. Optional auxiliary high density shielding
15. Pipe to reflector dump tanks
16. Supporting columns
17. Reflector fluid cooling pipe exit
18. Bridge tube for instrumentation
19. Reentrant thimble for instrumentation
20. Reactor core tank
21. "Soup" entrance pipe
22. Pipe to pressurizer
23. "Soup" outlet pipe
24. Pressure shell cooling coils

FIG. II - 1

PROPOSED ARRANGEMENT OF HOMOGENEOUS REACTOR PILOT PLANT

Scale - 1/8 in. = 1 in.

NOT CLASSIFIED

FIG. II-2

DESIGN STUDY
METHOD OF SEALING ZIRCONIUM PIPING
TO TOP FLANGE
SCALE - FULL

Dwg. 8686

FIG. II-3

SECTION A - A THROUGH CENTER LINE OF INSTRUMENTATION THIMBLES

Scale: 1/8 in. = 1 in.

19

Dwg. 8687
~~SECRET~~

FIG. II-4

VERTICAL SECTION THRU REACTOR SHOWING PROPOSED
ARRANGEMENT OF MAJOR ITEMS OF EQUIPMENT

SCALE, $\frac{1}{2}$ " = 1'-0"

III. PHYSICS

A. Statics

Calculations of the critical mass of the homogeneous reactor have been completed for some time. These have been made by L. C. Noderer and are on the basis of two group diffusion theory. Unfortunately design dimensions are somewhat different from those used in these calculations and some recalculation is in order.

Thus far information accumulated amounts to the following:

1. Critical Mass	grams/liter	kc
a. With full reflector (norm temp)	20.5	1.42
b. With empty reflector (norm temp)	65	1.82
c. With empty reflector (cold)	34.3	1.56
*d. Completely mixed core and reflector		> 1.75
e. With full reflector (variable temp)		
2. Flux Distribution - with full reflector		

The mixed core and reflector calculations (*) are for the purpose of investigating the hazards of a core tank rupture.

The variable temperature calculation is for the purpose of obtaining the temperature coefficient of reactivity. There have been three such calculations made giving the following data.

1. Tank considered completely elastic (sustains no pressure change) and no loss of fluid giving $\frac{\partial k}{\partial T} = 1\%$ change in reactivity per 10 °C temperature rise.
2. Tank considered rigid expansion excess escaping. This gives 1% reactivity change per 7 °C temperature rise.
3. Effect of nuclear cross section changes only giving 1% reactivity change per 70 °C temperature rise.

III. PHYSICS (Con't.)

Statics

None of these calculations yields the temperature coefficient necessary for dynamic calculations. For this reason a set of calculations are underway for getting three new coefficients of reactivity.

1. $\left(\frac{\partial k}{\partial T}\right)_{P,g}$ Temperature coefficient for constant pressure and gas concentration
2. $\left(\frac{\partial k}{\partial P}\right)_{T,g}$ Pressure coefficient for constant temperature and gas concentration
3. $\left(\frac{\partial k}{\partial g}\right)_{T,P}$ Gas concentration coefficient for constant temperature and pressure

These three coefficients are being calculated in the light of actual elastic properties of the gas, the core tank and the coolant.

The critical mass calculations for a full and empty reflector give the end points of information desired for a variable reflector level. The calculation of critical mass for variable reflector levels is exceedingly complicated and will require considerable numerical calculations. The available methods for solving this problem will be outlined in ORNL-631 to be released shortly.

Preliminary calculations of mixed core and reflector indicate a decrease in reactivity compared with normal conditions. This indicates a reasonable degree of safety in case of core tank failure.

The control rod configuration and requirements have as yet been only approximated and it seems advisable that such questions be answered in view of the proposed use of thimbles to house the rods and the accumulative dependence being placed on the temperature coefficient.

B. Dynamics

The dynamical behavior of the Homogeneous Reactor has been considered primarily on the basis of effects of step increases in reactivity. Thus for the origin of such step increases in the Homogeneous Reactor is rather obscure but calculations made on this basis are on the conservative side.

III. PHYSICS (Con't.)

Dynamics

In advance of considering such calculations it is necessary to study the equations of motion of all as parts of the reactor. For this purpose the reactor has been considered to be made up of the following five interconnected systems:

1. Nuclear - neutron economy
2. Thermal - heat transfer and temperature coefficients
3. Chemical - gas generation and effect on reactivity
4. Hydrodynamical - flow and pressure relations
5. Mechanical - control drives

A complete discussion of these systems can be found in ORNL-632 to be released shortly.

Solutions of the equations of motion have been attempted by analytical and numerical methods. The equations simplify considerably if the motion is considered for a short period of time, i.e., the first four seconds. This four second period results from the following considerations.

If the temperature and power level is taken at some mean position in the reactor the effects of changes may be measured from time $t = 0$ corresponding to the initial state of equilibrium. The incoming coolant temperature is not changed from its equilibrium value until two seconds after the disturbance because it takes two seconds for a slug of coolant to traverse the external system if it starts from the exit of the reactor. This two seconds plus the time required for this slug to reach a point in the reactor corresponding to average conditions amounts to four seconds on the basis of the equations of motions.

Effect of Temperature Coefficient

For these first four seconds the cooling is essential of constant magnitude because of the constant temperature of the incoming coolant. This could be written

$$\frac{dT}{dt} = S(P - P_0) \quad (1)$$

where P_0 is the equilibrium power level.

III. PHYSICS (Con't.)

Effect of Temperature Coefficient (Con't.)

This simple law of cooling in combination with the negative temperature coefficient of reactivity

$$k_c = k_{c0} + \alpha(T - T_0) \quad (2)$$

and the relation for power generation

$$\frac{dP}{dt} = \lambda_0 [k - k_c] P \quad (3)$$

form a complete system of equations defining the change of power and temperature with time. Due to the non-linearity of this system it cannot be integrated analytically so the time may be eliminated and the power expressed as a function of temperature. This is given by

$$P - P_0 \log \frac{P}{P_0} - P_0 = - \frac{\lambda_0 \alpha}{2S} [T - T_0] \left[T - T_0 - \frac{2e}{\alpha} \right] \quad (4)$$

The initial temperature is T_0 and e is the δk introduced at time $t = 0$. The maximum temperature excursion is

$T_0 + \frac{2e}{\alpha}$ and the maximum power excursion which occurs at $T = T_0 + \frac{e}{\alpha}$ is

$$P_{\max} - P_0 \left[\log \frac{P_{\max}}{P_0} + 1 \right] = \frac{\lambda_0 \alpha}{2S} \left(\frac{e}{\alpha} \right)^2 \quad (5)$$

or approximately

$$P_{\max} = \frac{\lambda_0 \alpha}{2S} \left(\frac{e}{\alpha} \right)^2 \quad (6)$$

The minimum power is given by

$$- \log \frac{P_{\min}}{P_0} - 1 = \frac{\lambda_0 \alpha}{2S P_0} \left(\frac{e}{\alpha} \right)^2 \quad (7)$$

This represents an oscillation which for the Homogeneous Reactor may be evaluated from the following constants:

III. PHYSICS (Con't.)

Effect of Temperature Coefficient (Con't.)

$$\lambda_0 = 10^4 \text{ sec}^{-1} \quad \frac{\delta k}{k} = \frac{e}{1.5}$$

$$\alpha = .001 \text{ } ^\circ\text{C}^{-1}$$

$$S = .00571 \text{ } ^\circ\text{C/K.W.S.}$$

$$P_0 = 1000 \text{ KW}$$

We may tabulate the results as follows:

e	T _{max}	P _{max} /P ₀	t _m	P _{min} /P ₀	$\frac{\delta k}{k}$
.005	10° C	26	.09	0(e ^{-22.9})	.333%
.01	20° C	93	.056	0(e ^{-88.5})	.667%
.015	30° C	213	.042	0(e ⁻²⁰⁸)	1.00%
.02	40° C	356	.036	0(e ⁻³⁵⁰)	1.33%

These values of maximum power are reached in time t_m shown above.

It is interesting to note that for very small values of e the oscillations are sinusoidal defined by

$$\left[\frac{P}{P_0} - 1 \right]^2 = \frac{\lambda_0 \alpha}{S P_0} \left(\frac{e}{\alpha} \right)^2 - T^2 \quad (8)$$

The frequency of these small oscillations is

$$f = \frac{1}{2\pi} \sqrt{\lambda_0 \alpha S P_0} \quad (9)$$

which for the above constants give

$$f = 1.2 \sim / \text{sec}$$

The magnitude of the oscillations in relation to $\frac{\delta k}{k}$ is shown in the following table:

III. PHYSICS (Con't.)

Effect of Temperature Coefficient (Con't.)

e	$P_{\max}/P_0$	$\frac{\delta k}{k}$	$\% \frac{\delta k}{k}$
2.39×10^{-6}	1.01	1.60×10^{-6}	.00016
7.31×10^{-5}	1.10	4.88×10^{-5}	.005
5.92×10^{-4}	2.00	3.95×10^{-4}	.04

It looks like very small disturbances will set the pile in oscillation. Fortunately the frequency of these oscillations is small and a rapid control system could compensate for the changes.

The time spent during one cycle at powers below normal are as follows:

$\frac{\delta k}{k}$	$t(P < P_0)$	t total cycle
very small	.42 sec	.82
.33%	1.75 sec	1.93
.67%	3.50 sec	3.61
1%	5.25 sec	5.33
1.33%	7.00 sec	7.07

This rough analysis has so far been based on a system with no delayed neutrons, no gas generation and no coolant loss from the core tank.

Effect of Gas Generation

If we take into account the gas generation we must rewrite equation (2) for the k required for criticality. This gives

$$k_c = k_{c0} + \alpha(T - T_0) + B(v_g - v_{g0}) \quad (10)$$

where v_g is the volume of gas as a fraction of core volume, v_{g0} being the equilibrium value. From static calculations B has been shown to be equal to 1.

III. PHYSICS (Con't.)

Effect of Gas Generation (Con't.)

We must now add an equation for gas generation.

$$\frac{dv_g}{dt} = r(P - P_0) \quad (11)$$

where r is the gas generation per unit core volume and equal to 4×10^{-6} .

Since the gas and temperature enter the analyses in exactly the same way the preceding analysis may be used with new constants.

The maximum power may now be written (instead of (5)):

$$P_{\max} - P_0 \left(\log \frac{P_{\max}}{P_0} + 1 \right) = \frac{\lambda_0}{2(\alpha S + Br)} e^2 \quad (12)$$

which gives the numerical values

$\frac{\delta k}{k}$	$P_{\max}/P_0$	$(P_{\max}/P_0)_S$
.33%	16	
.67%	56.5	
1.00%	135	120
1.33%	212	225

The values $(P_{\max}/P_0)_S$ are those obtained from stepwise numerical calculations which take into account the escape of coolant during a power surge. Apparently this escape does not affect the reactivity very much.

Pressure Rise

The primary reason for the stepwise numerical calculations was to obtain the pressure rise. A rather rough calculation will give us the order of magnitude of pressure rise.

III. PHYSICS (Con't.)

Pressure Rise (Con't.)

Taking into account thermal expansion and compressibility of the coolant, we may write its density

$$\rho = \rho_0 \left[1 - \beta(T - T_0) + \gamma(p - p_0) \right] \quad (13)$$

The tank can change its volume by elastic expansion due to pressure (thermal expansion neglected because of slowness of heating). This volume may be written

$$V = V_0 \left[1 + \epsilon(p - p_0) \right] \quad (14)$$

The mass of coolant in the tank may then be written

$$M = \rho V = \rho_0 V_0 \left[1 - \beta(T - T_0) + (\gamma + \epsilon)(p - p_0) \right] \quad (15)$$

If coolant is allowed to escape we must have the continuity condition satisfied

$$-\frac{dM}{dt} = \rho_0 A v \quad (16)$$

where A is the area of the relief pipe leading to the pressurizer and v is the velocity into this pipe.

From (15) and (16) we have

$$v = \frac{V_0}{A} \left[\beta \frac{dT}{dt} - (\gamma + \epsilon) \frac{dp}{dt} \right] \quad (17)$$

The equation of motion for the material in the relief pipe is

$$M_r \frac{dv}{dt} = p - av^2 \quad (18)$$

The condition for a maximum $\frac{dp}{dt} = 0$ yields

$$v = \frac{V_0}{A} \beta \frac{dT}{dt} \quad (19)$$

giving a pressure

$$P = a \left[\beta \frac{V_0}{A} \frac{dT}{dt} \right]^2 \quad (20)$$

III. PHYSICS (Con't.)

Pressure Rise (Con't.)

From equation (1) we have

$$\frac{dT}{dt} = SP_0 \left(\frac{P}{P_0} - 1 \right) \quad (21)$$

giving for the pressure

$$p = \frac{a}{144} \left[\beta \frac{V_0}{A} SP_0 \right]^2 \left(\frac{P}{P_0} - 1 \right)^2 \quad (22)$$

Using the following constants

$$\beta = .00153 \text{ } ^\circ\text{C}^{-1}$$

$$S = .00571 \text{ } ^\circ\text{C}/\text{KW sec}$$

$$V_0 = 3060 \text{ m}^3$$

$$A = 1.765 \text{ m}^2 \text{ (1 1/2" diam pipe)}$$

$$P_0 = 1000 \text{ KW}$$

$$a = .0143 \text{ psi sec}^2/\text{ft}^2$$

We then get

$$p = .0227 \left(\frac{P}{P_0} - 1 \right)^2 \quad (23)$$

The following tabulation gives the pressures based on maximum power figures:

$\frac{Sk}{k}$	$P_{\max}/P_0$	$P_{\max}(\text{psi}) - P_0$	$P_{\max}(S) - P_0$
.33	16	5	
.67	56.5	70	
1.00	135	407	960
1.33	212	1020	2300

III. PHYSICS (Con't.)

Pressure Rise (Con't.)

The values $P_{\max}(s)$ are those obtained from stepwise numerical calculation. The 2300 value corresponds to a velocity in the relief pipe of 401 ft/sec. Working with velocities this high results in extreme uncertainty and makes it questionable whether extensive numerical calculations should be continued.

The bursting pressure for the tank is 4000 psi which would correspond to a prompt reactivity $\frac{\delta k}{k}$ of 1.5% from stepwise calculation and a $\frac{\delta k}{k}$ of 1.75% on the basis of the simple calculations.

Effect of Delayed Neutrons

The inclusion of the effect of delayed neutrons is extremely difficult and involves past history in the same way as the true temperature dependence. However, here again we may deal with conventional delay phenomena for the first four seconds which is long enough to study the power and pressure peaks. The previous discussion involves the prompt $\frac{\delta k}{k}$ only and of course there must be added to this the effect of the delayed neutrons.

For the serious power surges which occur in about .03 seconds the total additional $\frac{\delta k}{k}$ for all delay groups is .01% which is negligible. Hence the total $\frac{\delta k}{k}$ which can be tolerated are the figures shown above plus .75% reaching a possible 2.5%.

For longer times after the disturbance the picture is not so simple and it will be necessary to take into account the complete delayed neutron effect which includes the past history of values at 4 seconds, 6 seconds and 10 seconds earlier. This is expressed in the relation

$$a_1(t) - a_1(t-10)e^{-10\lambda_1} = C_1(t) - C_1(t-4)e^{-4\lambda_1} + C_1(t-6)e^{-6\lambda_1} - C_1(t-10)e^{-10\lambda_1} \quad (24)$$

III. PHYSICS (Con't.)

Effect of Delayed Neutrons (Con't.)

where a_1 is the density of delayed neutron emitters and C_1 is the density of delayed neutron emitters if the coolant flow is zero.

It is best to treat this relation in conjunction with the true temperature which is another difference relation given by

$$T(t) - gT(t-10) = (1-g)T_h + T_S(t) - T_S(t-4) + g T_S(t-6) - gT_S(t-10) \quad (25)$$

where T is the actual temperature and T_S is the temperature given by the treatment in the section on temperature coefficient.

Long Time Response

The response to a change in reactivity after four seconds is of importance in considering the stability of operation during which sudden accidental jumps in reactivity may occur.

We have seen in the previous discussion that the solutions are of an oscillatory nature and the question of the degree of damping must be answered.

Since the nature of the long time effects is determined only by the relation (24) and (25) above we will see how these expressions alter the picture.

The delayed neutron effect is small compared with the temperature coefficient and the damping produced by it should be small compared with the damping one might expect from the thermal equation (25).

The temperature being defined by (25) results from the finite transit time of the coolant and may be approximated by a Newtonian type of cooling given by

$$\frac{dT}{dt} + h(T - T_0) = S(P - P_0) \quad (26)$$

where the second term is added to account for cooling. (Compare with equation (1)).

III. PHYSICS (Con't.)

Long Time Response (Con't.)

This approximation to (25) is more likely one of degree rather than of kind and serves a reasonable basis for a preliminary investigation of damping.

The introduction of such a cooling into the picture yields a period for small oscillations given by

$$m = - \frac{h}{2} \pm \sqrt{\left(\frac{h}{2}\right)^2 - SP_0 \alpha_0} \quad (27)$$

The criterion for aperiodic motion is

$$\left(\frac{h}{2}\right)^2 > SP_0 \alpha_0 \quad (28)$$

Using 24.1 as the value of h most closely approximating true conditions this criterion is satisfied indicating that after 4 seconds following a small disturbance the motion will be non-oscillatory.

For large disturbances the combination of equations (2), (3) and (26) has been studied by R. R. Coveyou who has found that damping is present. The degree of damping in this case has not been studied but there is no good reason to believe that the damping will decrease as the disturbances get larger.

Solution by Electric Simulation

The possibility of electrically simulating the complete set of equations of motion has been given considerable thought and plans are underway to construct such a simulator.

This simulator will differ from conventional pile simulators in that such factors as temperature coefficient and gas generation will be taken into account. Also the inclusion of delayed neutrons will conform to equations (24) instead of the conventional delay equations.

The inclusion of the temperature and gas coefficients of reactivity require a multiplying circuit in order to multiply these changes by the neutron flux before feeding the product to the integrator.

III. PHYSICS (Con't.)

Solution by Electric Simulation (Con't.)

The temperature equation (1) and the gas equation (11) are treated the same as normal delayed neutron emitter equations, the output of the temperature circuit being T_S which can be considered the input to the circuit which generates T in accordance with (25). Likewise the output of the delay circuits being C_i can be considered the input to circuits which will generate a_i in accordance with (24).

By studying the characteristics of the six delay groups one finds that such relations as (24) need be applied only to one group (group III $\lambda_1 = .456$, $\beta_1 = .0024$) the others being quite closely simulated by attenuation of conventional delayed circuit outputs. Groups I and II ($\lambda_1 = 14, 1.61$; $\beta_1 = .00029, .00084$) can be handled in normal fashion since the periods are so short that all significant changes take place within the core. Groups IV, V and VI ($\lambda_1 = .154, .0315, .0125$; $\beta_1 = .0021, .0017, .00026$) are handled likewise in conventional circuits except that the output is reduced by 20% to account for losses in the external cooling circuit.

The output of the temperature and gas circuits is reactivity and must feed a multiplying circuit as mentioned above. The multiplication can be done with a servo mechanism driving a potentiometer but all the servos which are readily available have considerable time lag and could not follow fast enough to give the power peaks which may occur in as little as .03 seconds.

Other multiplying devices are being studied by the instrumentation group and it is likely that a simple electronic multiplier will be used even though the multiplication is not very accurate. This seems reasonable in the light of no reasonable assurance that the coefficients of reactivity will be linear.

The simulation of equations (24) and (25) will require memory devices from which information at times $t-4$, $t-6$, and $t-10$ may be obtained. At present it is planned to use magnetic tape recorders to perform this operation. Since only one delayed neutron group will be treated in this way it will be necessary to have four tapes (a_{III} , C_{III} , T_S , T) each continuous and making a complete cycle in 10 seconds. One recorder and one eraser are necessary for each tape

III. PHYSICS (Con't.)

Solution by Electric Simulation (Con't.)

in addition to a total of 8 pickups for all tapes. The procedure of memorizing in this fashion is apparently well worked out and should not present insurmountable problems.

The building of the simulator is planned on a piece by piece basis so that at intervals as each unit is added it will be possible to check calculations which have already been made.

Origin of Reactivity Changes

The calculations on the effect of changes of reactivity have been made on the basis of instantaneous changes. In considering the various circumstances which give rise to reactivity changes none have been found which occur rapidly enough to be considered even approximately instantaneous.

A list of 60 such circumstances has been prepared by C. B. Graham. This list includes many trivial cases which can be dispensed with immediately. It is impossible in a reasonable period of time to analyze all those remaining. The more important of them have been singled out and thus far none have given dangerous excursions of temperature and pressure. Two cases in particular which have been studied are:

1. Tank failure with consequent mixing of core and reflector.
2. Pump startup after reactor has been in equilibrium at high power levels.

The first of these has been mentioned in the section on statics where it was stated that complete mixing always results in a subcritical assembly. The probability of such an occurrence is minimized by the fact that it is a subsequent condition to an already improbable occurrence (tank rupture). The second of these has been analyzed by H. C. Savage and is accompanied by $\frac{\delta k}{k}$ of 1% in 2 seconds.

This kind of disturbance should not have serious consequences.

Further work is to be done on these disturbances and will include a system of weighting the various circumstances in such a way that any set of circumstances which have a probability below some fixed value will be disregarded.

Safety Considerations

In conjunction with the preparation of a report to the Safeguards Committee it is advisable to study the possible accidents from all causes. The plan of such a study will conform to the following outline:

A. Condition of System

- I. Course of Construction (including setup)
- II. Completed (not operating)
- III. Completed (operation)

B. Stimuli

- I. Intentional
 - II. Accidental
 - a. Local
 - b. External
 - III. Sabotage
 - a. Local
 - b. External
- { 1. Human error
2. Mechanical

C. Response

- I. Normal
- II. Shutdown
- III. Low range failure
 - a. Non-contaminating
 - b. Contaminating
- IV. Explosion

Here again the ramifications of such a study is endless unless some probability considerations are taken into account.

Control Requirements

The control requirements of the Homogeneous Reactor depend in a very large measure on factors which have not been completely analyzed. This is especially true of such circumstances which arise from sabotage. The hopes of making a completely foolproof control system will not be satisfied in any case and the most reasonable procedure is to adopt a

Control Requirements (Con't.)

system of control similar to that used on the MTR reactor and depend upon the temperature coefficient to act as a gremlin-proof watch dog in case of unusual or unexpected circumstances.

The actual amount of reactivity to be included in control and shim rods will depend more upon what can be obtained within reasonable space limits than what the nebulous considerations above would dictate is necessary. So far it appears that it will not be too difficult to build about 4% into all the rods. This combined with the shimming of 40% afforded by the change of reflector level should be ample.

IV. CHEMISTRY

A. Chemical System Preliminary Survey

During the last few months considerable progress has been made in the design of a small, power-producing homogeneous reactor. Thought has been and is being given to mechanical and hydraulic features, to the control system, to the heat exchanger and to many other aspects of the reactor. However only incidental consideration has been given to the accompanying chemical system which will be required for any prolonged continuity of operation. It is the purpose of this section to survey, in as specific a manner as seems possible at this time, the requirements of such a chemical system for a simple homogeneous reactor. Incidentally, the lack of adequate specificity at any point should be interpreted to indicate the necessity for additional research.

By definition the thermal homogeneous reactor in its simplest form must contain a fluid system of at least two components, fuel and moderator. Other components may be required to provide thermal, chemical, and radiation stability to the system. In addition a large number of additional chemical species will always be present as a consequence of the fission process. We have, therefore, at the outset an extremely complicated, multi-component system over which chemical control must be maintained. The extent and precision of this control, i.e., the ability of the control mechanism to compensate for any and all chemical changes in the system, will probably determine the lifetime of continuous operation. On one extreme, if no chemical control were exercised the reactor could at best operate only a limited time until it either shut itself down or presented a hazardous condition. If, on the other hand, the control operated continuously and ideally compensated for all the possible chemical changes operation would be limited only by mechanical or other type of failure. The realization of the latter would constitute a major chemical achievement.

In order to proceed to a discussion of the component parts of a control system one should first have an intimate knowledge of the state of affairs in a stable reactor fluid. He should also know what changes may occur during operation, the rates at which these changes may occur and the magnitude of their effect on the system. Prediction could then be made as to how to prevent or compensate for these changes and as to the rate of response required. Since such a complete

IV. CHEMISTRY (Cont'd)

Chemical System Preliminary Survey

knowledge is not available for any of the possible homogeneous reactor systems, we shall choose, for a more detailed treatment, that system which is under study for the pilot model homogeneous reactor, the enriched uranyl sulfate- light water system. Operating conditions are to be 250°C and 1000 psi pressure. The reactor core is to contain 50 liters of solution at a concentration of 40 grams of U²³⁵ per liter with a maximum thermal flux of 10^{13} yielding a power level of 1000 kw.

The chemical effects over which the necessity for control can be anticipated are, (1) the consumption of uranium by the fission process, (2) corrosive action between the solution and the reactor vessel, (3) the production of hydrogen, oxygen, and peroxide by the irradiation decomposition of water, (4) build-up of fission product gases, and (5) build-up of other fission products. The possibility of radiation-induced decomposition of uranyl sulfate is not included because the results of radiation studies to date indicate that the uranyl sulfate is stable. This list is certainly not exclusive since other chemical phenomena may occur the existence of which has not been indicated by the comparatively short term experiments that have been done. However, those listed are certain to occur and their control constitutes the major task of the chemist in so far as the homogeneous reactor is concerned. Each will be discussed in turn.

Concentration Control

The consumption of uranium at the maximum power of 1000 kw will be about 1 gram per day. This, in a 50 or 60 liter system, produces only a very small concentration change which can easily be balanced by periodic additions to the system. However control of the concentration of the liquid provides a useful means of controlling pile reactivity and therefore a continuous knowledge of the uranium concentration and a means of varying it at will is desired. In addition it may be found necessary to maintain a prescribed H₂SO₄ concentration in the system and it may also be necessary to maintain a small but finite amount of some oxidizing agent. The amount of free H₂SO₄ required depends on the concentration level of peroxide in the system. The peroxide level in turn depends on the temperature of operation. Experiments to date indicate that very little or no free acid is required for operation at

IV. CHEMISTRY (Cont'd)Concentration Control

250°C while something between 1 and 2 normal is required at 60°. It may be that acid concentration can be correlated with and controlled by the temperature of the reactor.

These variables are lumped together here because they all involve the same type of control mechanism, namely, a means of determining concentrations, either periodically or continuously, by analytical and/or physical measurements, followed by a means of adding prescribed components to the system.

Insofar as the pilot homogeneous reactor is concerned, the question arises as to whether the control measurements must be made in the high temperature - high pressure zone. A system which provided a continuous measurement in the high pressure zone would provide the ultimate in minimizing external hold up and in reducing the time interval between the measurement and the compensating action. However, it would seem an exceedingly difficult if not impossible task to devise such a system. If a not too frequent periodic check is all that is required and if the permissible time lag in compensating action is not too short the problem presents no great difficulty. Samples could be removed from the bleed stream leading to the dump tanks, the necessary analytical and physical data obtained, and concentration changes introduced to the system through the booster pump. All chemical work would, of course, have to be performed from behind appropriate shielding. The required chemical determinations might include total uranium content, presence of reduced uranium, acidity, presence of suspended solids and their nature, and others. Adequate information might be obtained by a suitable combination of physical measurements such as pH, density, electrical conductivity or others along with empirical correlations of these measurements with chemical composition.

There is some belief that the only factor that will have to be followed with reasonable continuity will be the uranium concentration and that this might be done by density determinations alone. This would be adequate provided that all other changes have negligible influence on the density and assuming that the density dependence on temperature, concentrations, and pressure has been previously determined over the entire range of the variables which may occur. If these conditions are true other factors would need only periodic checks.

IV. CHEMISTRY (Cont'd)

Concentration Control

It would seem that the importance of this problem would warrant the assignment of competent personnel whose responsibility, on a short term basis, would be to design and test a composition control system adequate for the pilot reactor and, on a longer term basis, to explore the feasibility of continuous control operating in the high pressure zone. The full scale, dead uranium model of the pilot reactor would provide a convenient tool for testing chemical control systems.

Corrosion Problems

The question of interaction between the solution and the reactor vessel must be considered from two aspects; first, the effect of the solution on the vessel and, second, the effect of the vessel on the solution. The corrosion problem is largely a pre-operative one, a matter of selecting the solution and the reactor material such that corrosion rates will be adequately slow. The group in the Technical Division under Mr. English seem to have this problem well in hand and appear to be headed toward a satisfactory solution as far as the uranyl sulfate pile is concerned. Details are given in another section of this report. However, according to their results, it may be necessary to maintain a certain concentration level of some oxidant and perhaps also to maintain acidity within certain limits. This is just another facet of the problem of control of chemical composition discussed in the previous section.

Radiation Stability

Radiation studies carried on in the graphite pile by E. Shapiro and being continued by J. W. Boyle indicate that uranyl sulfate is radiation stable. However the solvent, water, does undergo decomposition to form free radicals and ions which in turn react to yield hydrogen gas, oxygen gas and hydrogen peroxide. Unless removed gas pressures will continue to build up until the rate of recombination of the gases balances the rate of their formation. When this happens a constant equilibrium gas pressure will exist in the system. At low temperatures ($\sim 60^{\circ}\text{C}$) this pressure may be very high, in fact, it has been followed up to over 700 atmospheres with only slight indication of leveling off. However, at 250°C the partial pressure levels off at ~ 20 -25 atmospheres. This is attributed, at least for the most part, to an acceleration of the recombination reaction rather than any change in the

IV. CHEMISTRY (Cont'd)

Radiation Stability

rate of gas production. This is indicated by the fact that the initial rate of gas production is relatively independent of temperature.

It would thus appear that a homogeneous water reactor could be operated at 250° and a total pressure of 1000 psi (68 atmospheres) with no additional mechanism for accelerating gas recombination. The partial pressure of hydrogen would be of the order of 14 atmospheres, that of oxygen 7 atmospheres and the balance of the pressure would be due to saturated steam. However, the question arises as to whether or not such a gaseous mixture falls in the explosive range. If it does a hazard would be present not only because of possible rupture of the system but also because of the effect of the compression wave on the pile reactivity. The Chemistry Division at Y-12 under Mr. Clewett are initiating an investigation of the explosive limits of hydrogen-oxygen-steam mixtures which should provide an answer to this question.

In case this mixture does lie in the explosive region, an additional mechanism for accelerating the recombination reaction would be desired. This mechanism might take the form of a bulk catalyst, such as platinum, in the vapor phase. Such a catalyst would unquestionable recombine the gases until its activity was poisoned by some component of the system. Investigation of the effective lifetime of catalysts under pile conditions should be made as time permits. An alternate procedure would be the incorporation of a catalytic agent in the liquid phase. Again the catalyst is subjected to poisoning effects of the solution. It is not known whether the recombination is primarily a vapor phase reaction or a liquid phase reaction nor whether the surface of the vessel plays a predominant roll. Agreement between the results obtained in stainless steel vessels with those obtained in quartz indicates that the reaction is not dependent on the nature of the surface.

The effect of hydrogen peroxide on the system may be two-fold. As previously mentioned, peroxide may cause the precipitation of UO_4 . It has also been found that the presence of peroxide prevents the reduction of uranyl ion to U_3O_8 by components present in stainless steel. Other oxidizing agents such as nitric acid or chromic acid will also do this. The question arises as to whether the peroxide concentration level during operation at 250° is high enough to prevent the reduction of uranyl ion even though it is inadequate to cause precipitation

IV. CHEMISTRY (Cont'd)

Radiation Stability

of UO_4 . Such an event would be an amazingly fortuitous circumstance, but from preliminary results may actually be the case. At any rate the need for precise, and perhaps continuous, control over the composition of the liquid is indicated.

Fission Product Gases

It has been estimated that a maximum of 1.5 cc (STP) of gaseous fission products will be produced per hour. The principal components will be xenon, krypton, and iodine. The manner in which this material can be removed and disposed of will depend on the manner in which hydrogen-oxygen production is controlled. If a vapor-phase catalytic recombiner is used there will be a continuous evolution of gas from the reactor which will efficiently strip the fission gases and remove them to the gas recombiner chamber. Here they may be allowed to decay. If this is not the case the amount of gas liberated may be too small for efficient stripping. In this event it will probably be necessary to maintain a small side stream from which the gas will be removed by flash cooling. The gas can then be collected for storage by a suitable adsorbent material such as activated charcoal.

Disposal of the fission gases does not seem to present a difficult problem. However a satisfactory solution should be demonstrated and it would seem desirable that someone be given the responsibility for the development and demonstration of a successful system.

Other Fission Products

The exact valence state in which all of the fission products will appear is not known and is, in some cases, difficult to predict. The species which appear will be determined, at least for the most part, by the environment of the atom at the time of its formation. In the somewhat acidic and somewhat oxidizing uranyl sulfate-water system, it would seem reasonable to expect most of the fission product elements to appear as cations in the solution and, if encountered in the solid state, to come down as sulfates. The transition elements which display variable valence and those whose ions are amphoteric and subject to hydrolytic action do not present a clear basis for prediction particularly in a solution at 250°. It may be expected that in some cases more than one ionic species of a given element will be present. Iodine, for example, would not be expected to appear as the iodide ion but rather as free

IV. CHEMISTRY (Cont'd)

Other Fission Products

iodine and iodate ion. The periodate ion seems somewhat less likely at the elevated temperatures. Other anions which may be encountered include arsenite, arsenate, selenite, selenate, tellurate, molybdate, ruthenate, columbate, etc.

The operation of the reactor at an elevated temperature introduces an element of uncertainty into a prediction of what precipitates might form. In general sulfates, even though their solubility may be increasing with temperature at room temperature, become "insoluble salts" before the critical temperature of water is reached. For example, cadmium sulfate which is soluble to the extent of about 1400 g per liter at room temperature is insoluble at 190° and above. Solubility products have not been determined at temperatures above 100° and it is therefore impossible to predict how soon and to what extent fission product sulfates would precipitate at 250°. It is reasonable to expect some precipitate formation within a matter of seconds after start-up. Co-precipitation phenomena may play an important role and the formation of radio-colloids may even be encountered. The possible development of a filtration or centrifugation method for the removal of a large percentage of the fission product activity is a field that should not be overlooked. Research in this field with emphasis on the uranyl sulfate and uranyl fluoride systems should be started.

There is a possibility that the centrifugal reactor which has been developed by the Technical Division for the separation of gas bubbles might also be utilized for the separation of solids. Heavier solid particles would be accelerated outwards by centrifugal force and would accumulate along the periphery of the reactor. The efficiency of such a separation would depend on the relative magnitudes of the tangential and radial velocity components as well as the relative density of the solids and liquid. If a means of collecting and removing the accumulated solids could be devised this method would offer promise of a continuous clean-up of suspended solids with no external hold-up.

The development of a closed-cycle, low-holdup separations process by either ion-exchange adsorbers or by solvent extraction methods will require a research effort of considerable magnitude. The adsorption method appears to offer the most promise but there remains to be demonstrated the stability of the resins in the intense radiation field which would be encountered with a stream of fluid fresh from the reactor. Either of these methods

IV. CHEMISTRY (Cont'd)Other Fission ProductsTABLE IV-1CALCULATED EQUILIBRIUM FISSION PRODUCT LEVELS

		V = 16 gal.		a = 0.0417 grams/hr (1 g per day)		
v, gal./hr.	f	∞	10^3	10^2	10	2
0.12		5.560	5.566	5.616	6.178	11.120
1.2		0.5560	0.5566	0.5616	0.6178	1.112
12.0		0.0556	0.0557	0.0562	0.0618	0.1112
120.0		0.0056	0.0056	0.0056	0.0062	0.0111

Table 1 gives calculated values of $x_{\max}$ in grams of total fission products in the reactor system under equilibrium conditions for selected values of v and f. The total volume of the system was taken to be 16 gallons (~60 liters) and the rate of fission product formation to be 1 gram per day. It is evident from the table that, if a separation factor of 10 or greater can be obtained, the rate of flow through the separation system becomes the only important factor in maintaining a low level. Figure IV-1 shows the variation of x with time for the particular case where v = 1.2 gallons per hour and f = 10^2 .

The only point to the preceding discussion is to emphasize the value and importance of a continuous process with as high a flow rate as possible.

Present Status of the Research Program

The following outline will give an indication of the scope of the present research program and plans for increases in scope.

- A. Problems of immediate importance in which satisfactory progress is expected with the present effort or with planned additions.
 1. Phase stability of aqueous reactor solutions. No additions contemplated.
 2. Corrosion Studies - The addition of a highly competent physical chemist to attack the problems in this field from a fundamental viewpoint is under consideration.

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FIGURE IV-1
Variation of Fission Product
Level in the Homogeneous Reactor
with a Continuous Decontamina-
tion Process.

IV. CHEMISTRY (Cont'd)Present Status of the Research Program

3. Radiation stability of solutions. Immediate addition of one man and renovation of an additional hole in the ORNL reactor is planned.
4. Explosive range of hydrogen-oxygen-steam mixtures and recombination rates. No additions

B. Problems of immediate importance on which work has not started.

1. Chemical control. The assignment of one man from the Chemistry Division to this field is planned.
2. Fission product precipitation. The assignment of one man is expected.

C. Longer Range Studies

1. Slurry work. No additions.
2. Fission product separation. Applied research will be started in the near future by personnel available in the Separations Section of the Chemistry Division.

B. Radiation Effects

Possible radiation effects on the solution in the homogeneous reactor are thought to be the following: decomposition of the water, decomposition of the anion ($\text{SO}_4^{=}$) of the solute, oxidation of the uranium with precipitation of UO_4 . and alteration in corrosion resistance of the metal of the container. These possible effects are discussed separately below.

Decomposition of the water is considered to be not a critical matter for the prototype reactor, since the contribution of the maximum conceivable gas production to the reactivity will be too small, because of the high pressure, to make control difficult. This decomposition will, however, be important in full-scale piles, and is being studied at present. The apparatus employed is a bomb of stainless steel connected through a capillary tube to an external pressure recorder. The solution is placed in a liner in the bomb and the whole encased in a furnace and lowered into the pile. In the one experiment completed, the pressure at 250°C leveled off after about an hour at about 25 atmospheres.

IV. CHEMISTRY (Cont'd)

B. Radiation Effects

Similar and other experiments done previously at 60°C showed the pressure still rising at 700 atmospheres. Hence the effect of temperatures is as predicted, a decrease in steady state pressure. Although the pressure ceased its rapid rise quickly at 25 atmospheres, there was a slow increase amounting to about 25 atmospheres for the seven days the sample was irradiated. This may be the result of corrosion introducing an ion favoring decomposition (almost all solutes do) or of some more subtle mechanism. Further insight should be gained when the bomb is unloaded and the solution and liner are cool enough to be examined.

Decomposition of the sulfate anion is not thought likely, but will be looked for in the irradiations made for following the water decomposition. Precipitation of sulfur from such solutions under irradiation has apparently never been observed at this Laboratory, although hundreds of exposures have been made. Reduction to sulfite would be surprising since the equilibrium between it and sulfate is rapidly attained, and the species produced by radiation from water are oxidizing and reducing in equal numbers.

Oxidation of the uranyl ion to UO_4 occurs under pile irradiation. At 60°C precipitation of UO_4 occurs rapidly in uranyl sulfate solution (40 g U^{235} /liter) exposed in Hole 12 of the Oak Ridge pile. If the solution is made 1.0M in H_2SO_4 , the precipitation is prevented. Also if a non-acidified solution is irradiated at 250°C no precipitation occurs, presumably because of the lower peroxide concentration at that temperature.

Corrosion experiments have shown that at least under some conditions stainless steel can reduce uranyl sulfate solution giving a precipitate of a lower oxide of uranium. This was shown to be prevented by a suitable oxidant, e.g., nitric acid. Since radiation produces oxidizing species (e.g. H_2O_2) there is some chance that this corrosion effect might be modified under radiation. Experiments to this end will be carried out in conjunction with the studies of water decomposition by including corrosion samples in the bombs.

IV. CHEMISTRY (Cont'd)

C. Phase Rule Work

In preliminary radiation studies at 250°C of acidified and neutral uranyl sulfate solutions containing 40 grams uranium per liter, Boyle has shown no precipitation of uranium peroxide to occur as was experienced at 100°C. Therefore, in order to reduce corrosion difficulties of uranyl sulfate it might be feasible to decrease the solution acidity by the addition of basic uranium trioxide.

The purpose of this study was to determine the thermal stability of uranyl sulfate solutions containing varying amounts of uranium trioxide, the total uranium content being held constant at 40 grams per liter. This concentration is desirable in connection with the homogeneous reactor.

Experimental

The solutions were prepared by dissolving varying amounts of chemically pure uranyl sulfate trihydrate and uranium trioxide in water to give exactly 40 grams uranium per liter of solution. The densities and pH values were determined.

The experimental methods are those of Secoy¹. Quartz, capillary tubes of the respective solutions of known concentrations were prepared and placed in a steel bomb containing an observation slit. The bomb was rocked and slowly heated, the solution tube being observed at all times.

Results

The data are presented in Table IV-2 and shown graphically in Figures IV-2 and IV-3. The pH data are shown in Figure IV-2. Curve XY indicates experimentally obtained data. Curve ZY gives comparison data² for equivalent uranyl sulfate solutions, no uranium trioxide present.

The phase diagram data are shown in Figure IV-3. Upon raising the temperature of a known solution an irreversible precipitate occurs along the line AB. This precipitate appears as a yellow-orange gel very similar to the hydrogen gels of Al_2O_3 and Fe_2O_3 . The precipitate appeared to increase with

1 CNL-18, ORNL-176, p. 58.

2 Helmholtz and Friedlander, LAMS 30 (1943).

FIGURE IV-2

The pH of UO_2SO_4 - UO_3 - H_2O Solutions at 25°C
 (40 grams Uranium/Liter held constant with UO_3 and UO_2SO_4)
 $\odot$ = Our Data; $\triangle$ Comparative Data (No UO_3 but equivalent UO_2SO_4)

FIGURE IV-3
The UO_2SO_4 - UO_3 - H_2O System (40 grams Uranium/Liter held constant with UO_3 and UO_2SO_4)

IV. CHEMISTRY (Cont'd)C. Phase Rule Work

temperature. Initial experimental tubes in the BC concentration range showed a very slight scum on the quartz sides around the meniscus edge but no further precipitation upon temperature elevation. Subsequent tubes showed no scum in this region. At uranium trioxide concentrations lower than the concentration at point C no precipitation or scum appeared in any tube; therefore, line CD does not indicate experimental data, but rather shows an extrapolated portion of ABCD. Curve DEF represents the two liquid phase appearance temperatures. These values along DEF were obtained with no difficulty although the precipitate occurring along AB was still apparent in this range. In the region GH, the gel precipitate appeared to change character and form a more compact solid.

Conclusion

Curve BCD is drawn in consideration of the apparent linearity of AB, the recognition of the uniqueness of point D, and the scum appearance in preliminary solutions in the BD range. Subsequent solutions in the same region were clear up through the two phase separation curve, DEF. If the extrapolated line BCD represents the true curve then the above discrepancies might be explained in terms of a metastable solution existing above line BCD, the precipitate not appearing in the samples studied. However, BE is drawn in accordance with actual experimental observations along lines AB and ED and also in consideration of some theoretical assumptions to be presented later.

The ultimate conclusion is that the system, $\text{UO}_2\text{SO}_4 - \text{UO}_3 - \text{H}_2\text{O}$ (40 g U/l held constant) appears thermally stable below the curve ABCD of Figure IV-3 and probably stable in the region BCDE.

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TABLE IV-2

THE $\text{UO}_2\text{SO}_4 - \text{UO}_3 - \text{H}_2\text{O}$ SYSTEM, 40 G U/L HELD CONSTANT

Sol'n No.	Grams U/l added as UO_3	Grams U/l added as UO_2SO_4	Density	pH	Precipitation Temp.	Precipitate Character	Two Liquid Phase Appearance
Initial (See Ref. 1)	0.0	40.000	1.052	2.43	None	None	310°C
1	2.500	37.500	1.046	2.79	-	None	308
2	3.750	36.250	1.047	3.11	-	None	310
3	5.000	35.000	1.043	3.23	-	None	305
4	6.250	33.750	1.051	3.30	192°C	Very slight scum	304
5	6.875	33.125	1.052	3.40	178°C	Haziness (no final decomposition)	Stopped run at 300
6	7.500	32.500	1.047	3.45	158°C	Haziness (no final decomposition)	302
7	7.500	32.500	1.047	3.45	165°C	Gel type	305
8	10.000	30.000	1.045	3.68	110°C	Gel type	307
9	15.000 (satn point)	25.000	1.058	3.93	25°C	Gel type	313
10	15.000 (satn point)	25.000	1.058	3.93	25°C	Gel type	308

IV. CHEMISTRY (Cont'd)D. Recombination Program

The problem at hand is to determine in a general way the conditions under which hydrogen and oxygen can be made to combine rapidly, though not explosively, in the presence of various proportions of steam. Exploratory experiments have been planned which are intended to define the temperature limit above which a given mixture of hydrogen and oxygen mixed with steam will combine at a reasonable rate. At the same time, the effect of varying the partial pressures of H_2 , O_2 , and steam can be studied. The required apparatus is now being constructed and assembled. In the meantime, a survey of the literature has been conducted by A. D. Ryon, the results of which are summarized below.

Literature Survey on the Combination of Hydrogen and Oxygen

A rather extensive literature survey has been made of books and periodicals. Although no information was found for the specific conditions in which we are interested, the references provide a good background for the work.

The composition explosion limits of hydrogen are between 5% and 90%. These limits change very little with pressure or nature of the diluting gas. There are three pressure-temperature explosion limits on mixtures of H_2 and O_2 within the composition limits. (1) At pressures below 20 mm the ignition temperature falls rapidly with increased pressure; (2) from 20 to 100 mm the temperature of ignition rises; (3) and above 100 mm the ignition temperature drops slowly. Nothing is reported on the limits above 1000 mm total pressure. Extrapolation of the limit to 500 lb/sq in gives the ridiculous temperature of $-480^\circ C$. Apparently the third explosion limit changes very little at high pressures.

The rate of reaction below the explosion limits is slow (about 20 mm pressure drop per minute at about $10^\circ C$ below the limit). At rates greater than 20 mm/minute, the system is not isothermally stable, and the explosion limit is exceeded. Since we are interested in much higher rates (1500 mm/min.), the recombination reaction will probably have to be attained by flame combustion or catalytic combustion. The flame combustion is to be preferred over catalysis because of the danger of poisoning the catalysts. To maintain a flame without explosion of large volumes of gas, it probably will be necessary to pass the gas through jets with the gas impinging on a surface maintain at about $600^\circ C$ for ignition. The water formed could be returned to the system with pumps.

IV. CHEMISTRY (Cont'd)E. Slurry Work

During the past quarter, the preparation of uranium-oxide-water slurries suitable for use in the homogeneous reactor was further investigated.

The slurry will contain 40 grams of uranium as the oxide in a liter of water and must be stable with respect to sedimentation on shutdown of the reactor pumps. The operating conditions are 250°C and 1000 lbs/sq in pressure.

Previous work had shown that the slurries prepared by dispersing anhydrous uranium trioxide in water, while stable at room temperature sediment very rapidly after being heated at 250°C in a closed system for one hour.

The work of the past quarter was concerned with the behavior of some other oxides of uranium in slurries and the use of bentonite as a stabilizing agent for slurries.

The Stability of Some Uranium Oxides Slurries at 250°C

Slurries were prepared using several other uranium oxides besides the anhydrous UO_3 in concentrations to yield 40 grams of uranium per liter. The following oxides were tested:

anhydrous uranium trioxide - UO_3
uranyl peroxide - $\text{UO}_4 \cdot 2\text{H}_2\text{O}$
the "violet" oxide - $\text{U}_3\text{O}_8 \cdot x \text{H}_2\text{O}$ (?)
the green oxide - U_3O_8

The slurries prepared from these oxides were unstable after being heated at 250°C for one hour, the final products being muddy yellow sediments.

Examination of the crystalline structures indicated some conversion to the hydrated UO_3 except in the case of U_3O_8 which appeared to be unaffected by water alone. However the addition of H_2O_2 followed by heating indicated that the U_3O_8 would be converted to the hydrated oxide. Only the $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ and the anhydrous UO_3 slurries were stable at room temperatures.

These results indicate that under continuous pile operating conditions, all the oxides would be converted to hydrated UO_3 which in itself is incapable of forming a stable slurry.

IV. CHEMISTRY (Cont'd)E. Slurry WorkThe Use of Bentonite as a Stabilizing Agents for Slurries

The use of bentonite for stabilizing suspensions of many materials in water is a well-known chemical art. The mechanism of stabilization is attributed to the ability of bentonite to absorb large quantities of water with the resulting increase in the viscosity of the system. And since, by controlling the viscosity of the suspending medium, it is possible to control sedimentation rates, it seemed worthwhile to determine if bentonite would be applicable to the slurry problem.

Bentonite is a natural clay having cation exchange properties. The analysis of a typical bentonite as shipped is given below:

<u>Constituent</u>	<u>Percent</u>	<u>Constituent</u>	<u>Percent</u>
SiO ₂	64.32	CaO	0.52
Al ₂ O ₃	20.74	MgO	2.30
Fe ₂ O ₃	3.03	Na ₂ O	2.59
FeO	0.46	K ₂ O	.39
TiO ₂	0.14	SO ₃	.35
P ₂ O ₅	0.01	chemically held H ₂ O	5.14
		minor constituents	0.01

The sodium and potassium are exchangeable ions and the chemically held H₂O is an integral part of the bentonite structure.

The slow neutron cross section calculated from its chemical composition indicates that one gram of natural bentonite has a total cross section that is smaller by a factor of 2 than the sulfur in the amount of UO₂SO₄ necessary to provide 40 grams of uranium per liter of solution. This means a gain in neutron economy for breeding purposes is possible if the amount of bentonite required for stabilization is one gram per 100 ml of slurry or less.

It has been shown that bentonite consists of mixture of particles ranging in size from macroscopic to colloidal. The

IV. CHEMISTRY (Cont'd)E. Slurry Work

separation of particle sizes can be readily accomplished in a Sharples supercentrifuge by varying both the velocity of the centrifuge and the feed throughput rate of the suspension being fractionated. The smaller bentonite particles are most effective in controlling the viscosity of water.

Using bentonite as the stabilizer, two slurries were prepared which showed good stability with respect to sedimentation after being heated at 250°C and 575 lbs/sq in pressure for one hour in a stainless steel bomb. The details are given in Table IV-3 below:

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TABLE IV-3

THE STABILITY OF URANIUM TRIOXIDE-WASTE SLURRIES CONTAINING BENTONITE AS A
STABILIZING AGENT - URANIUM ANALYSES AT VARIOUS SLURRY COLUMN HEIGHTS

Composition:

Anhydrous UO_3 - 48 grams H_2O - 1000 mlHeating Data 250°C and 575 lbs/sq in pressure for one hour

Stabilizing Agent - 3% natural bentonite Settling time - 96 hours			Stabilizing Agent - 1.4% fractionated bentonite - ave. particle size=28.6 milli- microns Settling time - 66 hours		
Sampling Level in Slurry Column Height cm	U Conc. mg/ml	Percent U (A)	Sampling Level in Slurry Column Height cm	U Conc. mg/ml	Percent U (A)
0	-	-	0 (top)	34.0	89.5
4.8	37.3	79.5	3.5	35.3	92.9
8.8	37.3	81.2	7.0	36.7	96.6
13.0 (bottom	52.5	113.4	11.0	37.3	98.1
well mixed sample	46.3	-	14.5 (bottom)	39.0	102.6
			-	-	-
			well mixed sample	38.0	-

(A) This value is calculated on the basis of analysis of the well mixed sample.

IV. CHEMISTRY (Cont'd)E. Slurry Work

These slurries were further tested for stability by heating for 18 and 72 hours in a stainless steel bomb using the same conditions.

It was observed that the slurries became unstable after such treatment and the amount of hydrated UO_3 sedimented increased with a longer heating period. The supernatant had taken on a pink color.

When a suspension of bentonite alone was heated in the same bomb for 18 hours at 250°C , the color of suspension changed from golden yellow to the same pink color noted in the case of the slurries. Viscosity measurements showed that as a result of heating the viscosity of the suspension was increased by a factor of 4.

The pink color was identified as being due to the presence of iron and spectrographic analysis did not indicate that corrosion of the bomb was a contributing factor. Therefore, it was concluded that the iron came from the bentonite.. A subsequent test made by heating a bentonite suspension in a sealed quartz tube under the same condition verified that the bentonite was the source of the iron.

The iron may be liberated from the bentonite either by decomposition of the clay at 250°C or else by a cation exchange process. Further experiments are now under way to determine which process is responsible for liberation of the iron and what remedial steps may be taken.

The manner in which the iron interferes with the stabilizing power of the bentonite is probably the following. The small bentonite particles in suspension are negatively charged and since the iron is in the Fe^{++} state it will neutralize the negative charges on the bentonite, allowing the bentonite to clump together. This will result in an increase in the viscosity of the suspension due to the larger sizes of the particles and finally when the particles become sufficiently large they will precipitate.

V. EXPERIMENTAL ENGINEERING

A. Model II (Plastic Sphere Test System)

The beginning of the period covered by this report is approximately the time that the transition was made from the original one tenth size glass model to the full size plastic sphere. Since the bulk of the work done on the glass model is covered in the report ORNL-527 it will only here be referred to occasionally.

It became apparent from early tests that unless special precautions are taken to avoid it, a vortex of some sort will appear in a spherical vessel when fluid is pumped through it. This vortex tends to align itself with the outlet port but may be unstable or oriented in such a manner that any entrapped gas cannot leave the sphere with ease. This observation gave rise to a program to develop a geometry which will maintain a steady predictable condition which provides a reliable exit for entrapped gases at fluid flow rates expected in the Pilot Reactor. (See Figure V-1).

Since the type of flow encountered in such a device does not fall in the two common types of vortices treated in the literature, i.e., forced and free vortices, it became desirable to study two phases of the problem. First to empirically develop a satisfactory geometry for the reactor, and second to establish the theory pertaining to such a system to permit design of reactors, of any size.

Description of Apparatus (See Figure V-2)

The apparatus consists of a plexiglas sphere made of two flanged hemispheres bolted together between back up flanges. (See Fig. V-3)

The hydraulic system consists of a 10 hp centrifugal pump in a closed circuit. A surge tank fitted with an overflow near the top permits regulating the pressure of the system. By admitting tap water from an 80 psi line to the suction of the pump and then throttling the overflow on the surge tank and pressure up to 80 psi can be obtained at the pump suction. The overflow provides cooling necessary to retain mechanical strength in the plastic.

Suitable valves are provided to regulate the water flow, throttle the discharge or by pass the sphere if desired.

FOR OFFICIAL USE ONLY

PHOTO 9900

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FIGURE V-1
BUBBLE TRACKS

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00

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Figure V-2

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PHOTO 9902

FIGURE V-3
PLASTIC SPHERE
SHOWING VORTEX VOID

V. EXPERIMENTAL ENGINEERING (Cont'd)

Description of Apparatus (Cont'd)

An air connection is available with pressure reducer, gauge, flow meter and regulating valve.

All water lines have pressure gauges, an orifice and Foxboro flow meter continuously indicate flow rate.

Development of A Satisfactory Geometry

The evolution of the present design will be considered first since it was necessary to obtain steady operation before any data could be taken. The vessel consisted of two plastic hemispheres clamped together between metal flanges. During fabrication of the hemispheres, which were free blown from plexiglas, a large radius (one half inch or more) is left at the intersection of the plane of the flange and the inside surface of the hemisphere. This left a large "V" shaped groove around the inside of the vessel in the plane of the flanges which caused considerable trouble as will be pointed out later.

Several geometries were tried which are shown schematically in Figure V-4 .

The figures are in the order in which the geometry was evolved and the results obtained were as follows:

Type I - this geometry was an attempt to get a true tangential inlet at a right angle to the axis of rotation. Since it was not practical to put the inlet at the "Equator" because of the flanges, it was arbitrarily placed 45° "North Latitude" and the outlet also moved over 90° away. It was hoped that the flanged joint between hemispheres would not prove bothersome since the vortex tends to align itself with the outlet. This only proved to be partially true and the vortex ran near but not into the outlet pipe. The net result was that all entrapped air rushed into the vortex and could not escape.

This condition was partially corrected by an 18 in. diameter ring baffle two inches wide, which when placed at 90° to the axis of the discharge straightened out the flow sufficiently to make the vortex hit the one and one half inch pipe outlet. The pressure drop from inlet to outlet was less than theory on the glass model predicted

Figure V-4

V. EXPERIMENTAL ENGINEERING (Cont'd)

Development of A Satisfactory Geometry

but the vortex was not stable and precessed about the one and one half inch outlet pipe, often missing it entirely.

Type II - this modification was short lived but quite significant in that it stabilized the vortex to such an extent that the predicted pressure drop of 50 psi was realized on the first run and both hemispheres were ruptured. It also showed promise for an inlet at a point "North of the Equator".

Type III - this design incorporated an inlet flange 35° north of the equator with the incoming stream of water entering on a chord and since it was on a flange could be tilted up and down in $22 \frac{1}{2}^{\circ}$ steps.

The original outlet was made of three and one half inch pipe fittings so that the pressure drop would be less. This system with a gas outlet tube of one fourth inch pipe in the center worked fairly well, but the slight precession of the vortex caused it to miss the gas pipe and hence spill over except when passing the end of the tube. A steel plug two inches diameter on the end of the gas tube giving an annular outlet with small gas openings showed much improvement since the vortex did not spill into the outlet stream when not aligned with the gas outlet. Instead the cylindrical void in the center of the vortex would dwell on the end of the two inch plug and grow until it passed the gas pipe at which time it would discharge with some water. Although intermittent in operation this resulted in an efficient gas separator since no visible bubbles appeared in the outlet stream. Pressure drop as predicted by theory was about 20 psi.

Type IV - this geometry was only a change in the outlet to provide a more finished system. A plastic assembly was built which incorporated the annular outlet with a spherical end on the central plug which was two and one fourth inches in diameter in the center of a three and one fourth inch diameter outlet. This plug had a three eighth inch hole through which the gas was drawn off.

V. EXPERIMENTAL ENGINEERING (Cont'd)

Development of A Satisfactory Geometry

A minor but important detail in the construction of these parts in a radius on the edges of all holes, etc., to minimize turbulence in the central core which rotates at quite high speed. (See Figure V-4).

Pressure drop in this system is about 10 psi at 100 gpm flow.

This geometry in general was the most satisfactory to date however several minor changes were tried in an effort to reduce precession of the void in the center of the vortex. The introduction of inlet water on a chord rather than tangentially was not too bad and has some advantages in the mechanical design of the final reactor. Also the stream can be directed toward either pole up to 45° without any appreciable change. This again may prove advantageous from a design standpoint.

To observe the effect of the groove left where the hemispheres were bolted together the groove was filled with modeling clay. There was no apparent change, hence one might conclude that if such a groove lies in a plane perpendicular to the axis of the outlet, it has little effect on the operation of the system.

The last two changes were an attempt to cut down the volume of the void as follows: first a small baffle was installed over the inlet pipe to more nearly approximate a tangential inlet. This, as might be expected increased the angular velocity and improved stability probably due to less turbulence at the inlet. The baffle was then modified to decrease the inlet area and provide a narrow slot which gave a higher velocity tangential inlet. As might be expected the time for an air bubble to travel from the enter diameter to the center was reduced, however all previous attempts to speed up rotation had produced so much instability as to show no net gain.

The second modification was an insert placed in the outlet to reduce the area and diameter of the annulus. This it was hoped would increase the angular velocity in the central core and improve separation at the possible expense of some pressure drop. The pressure drop did not increase a measurable amount and holdup of gas did decrease to a new low.

V. EXPERIMENTAL ENGINEERING (Cont'd)

Tests Conducted on Residence Time and Gas Holdup

The primary purpose of the plastic mock-up was to measure gas holdup and residence time of the gas. All the foregoing was necessary however to get a reasonably satisfactory system which gave reasonable and reproducible results.

Two principle methods were employed in measuring holdup, namely, measuring the size of the bubble trapped in the sphere after shutting off the system and by running the vortex into a calibrated vessel with the pump still running but with air inlet and outlet closed simultaneously.

Much time has been consumed attempting to get a mechanical or electrical system which is fast enough to give reliable results where the time of transit of the air bubbles from diameter to center is about one fourth second, as shown on slow motion movie film.

All solenoid valves readily available had such small ports that they provided a definite impedance to the flow of air and water at the gas removal point. Due to the low pressures at which we were forced to operate this made reliable measurement impossible.

The system now in use is composed of two lever operated one half inch gate valves mechanically linked together as shown in Figure V-2.

The air and water outlet valve closes as the air bypass opens. Pressure in the sphere stops air flow immediately and the sudden rise in discharge pressure in the air and water outlet causes the void in the center of the vortex to recede from the outlet and hence, effectively prevent further escape of air.

The data which follows was taken with the pump running. The air inlet and air and water outlet valves were operated simultaneously and the entrapped air was then run up into a calibrated vessel filled with water. The volume was recorded after running the pressure of the entire system up to original air inlet pressure. This latter operation was done with the pump off. All flows recorded for air were at inlet pressure hence, the air expands to a larger volume near the center of the vortex where the pressure is lower.

V. EXPERIMENTAL ENGINEERING (Cont'd)

Tests Conducted on Residence Time and Gas Holdup

This effect will be reduced when the higher pressure plastic spheres are put into use. The error introduced by this expansion does not favor the separator and hence figures quoted should be conservative. In addition to this practically all air is admitted near the equator and in one plane so that most bubbles must travel the maximum possible distance.

The following theory and data reflect the thinking and physical progress to date.

Gas Holdup

The problem of removing gas bubbles from the homogeneous reactor has brought up the question as to whether gravity or a vortex should be utilized for removing the gas. The following theoretical treatment, which is in turn followed by test data, is an attempt to provide some definite reasons why one system or the other should be developed for practical use.

The figure is a sectional view of a sphere of radius R with an inscribed cylinder. The figure and the quantities designated on it are explained and referred to in the mathematical treatments which follow under the headings, Gravity and Vortex. The first treatment takes up the gravity system and finds the average path h of all bubbles which rise vertically along the cylinder walls of an infinite number of inscribed cylinders and then rise along the inside walls of the spherical segments above these cylinders.

V. EXPERIMENTAL ENGINEERING (Cont'd)Gravity System Calculation

h = length of average path of bubbles rising along wall of inscribed cylinder

$(h + d)$ = total length of bubble path

dv = incremental volume of bubbles that follow path $(h + d)$

$\bar{h}$ = average bubble path

$$\bar{h} = \frac{\int_0^{\frac{\pi}{2}} (h + d) dv}{V}$$

V = volume of sphere, $\frac{4}{3} \pi R^3$

$d = R \theta$

$dv = 2\pi r \cdot 2h \cdot dr$

$h = R \cos \theta$

$r = R \sin \theta$

$dr = R \cos \theta d\theta$

$dv = 4\pi R^3 \sin \theta \cos^2 \theta d\theta$

$$\int_0^{\frac{\pi}{2}} (h + d) dv =$$

$$\int_0^{\frac{\pi}{2}} (R \cos \theta + R \theta) (4\pi R^3 \sin \theta \cos^2 \theta d\theta) =$$

$$\int_0^{\frac{\pi}{2}} 4\pi R^4 (\sin \theta \cos^3 \theta + \theta \sin \theta \cos^2 \theta) d\theta =$$

$$\int_0^{\frac{\pi}{2}} 4\pi R^4 (\sin \theta \cos^3 \theta + \theta \sin \theta (1 - \sin^2 \theta)) d\theta =$$

V. EXPERIMENTAL ENGINEERING (Cont'd)Gravity System Calculation

$$4\pi R^4 \int_0^{\frac{\pi}{2}} (\sin \theta \cos^3 \theta + \theta \sin \theta - \theta \sin^3 \theta) d\theta =$$

$$\int_0^{\frac{\pi}{2}} (h + d) dv = \frac{17}{9} \pi R^4$$

$$\bar{h} = \frac{\frac{17}{9} \pi R^4}{\frac{4}{3} \pi R^3} = \frac{17}{12} R$$

$$= 1.415 R$$

Residence time, t, for average bubble,

$$t = \frac{\bar{h}}{u}$$

$$u = \text{velocity of bubble}^*$$

$$t = \frac{1.415 R}{u}$$

For the 18-inch diameter sphere, $R = 22.9$ cm.

J. A. Lane's memo to the Reactor Steering Committee gives 20 cm/sec. as the velocity of bubble rise for the average bubble.

Then

$$t = \frac{1.415 \times 23}{20} = 1.63 \text{ sec}$$

* Assumed to be constant- the velocity actually is considerably reduced as it moves across the top of the sphere and then speeds up as it approaches the outlet.

V. EXPERIMENTAL ENGINEERING (Cont'd)

Holdup Measurement in a Gravity System

Air was admitted to the sphere of water through six sintered glass inlets at the rate of 200 cc sec., the maximum anticipated rate of gas evolution. The bubble size is unknown and is believed to be larger than the average bubble considered in the reactor. The water displacement caused by this rate of gas flow was measured and found to average out to 155 cc over several runs. In this case:

$$\text{Residence time} = \frac{155}{200} = 0.775 \text{ sec.}$$

It will be noted that this residence time is much lower than that calculated above. The bubbles appeared to have a much larger diameter than 0.25 cm (as used by Mr. Lane), and hence would be expected to rise faster than 20 cm/sec.

In an actual reactor one would expect small bubbles; so that the calculated value seems more applicable.

Vortex System Calculation

In the vortex system the bubbles move directly from the cylinder wall to the axis and then vertically along the axis.

$$r = \text{distance bubbles travel from cylinder wall to axis} = R \sin \theta$$

$$dv = \text{incremental volume of bubbles that follow path of length } (r + R)$$

$$R = \text{radius of sphere} = \text{average distance traveled by bubbles at the axis} = 22.9 \text{ cm}$$

$$\bar{h} = \text{average path}$$

$$\bar{h} = \frac{\int_0^{\frac{\pi}{2}} (r + R) dv}{V} ; V = \frac{4}{3} \pi R^3$$

$$dv = 4 \pi R^3 \sin \theta \cos^2 \theta d\theta$$

V. EXPERIMENTAL ENGINEERING (Cont'd)Vortex System Calculation

$$\int_0^{\frac{\pi}{2}} (r + R) dv =$$

$$\int_0^{\frac{\pi}{2}} (R \sin \theta + R) (4\pi R^3 \sin \theta \cos^2 \theta d\theta) =$$

$$4\pi R^4 \int_0^{\frac{\pi}{2}} (\sin^2 \theta \cos^2 \theta + \sin \theta \cos^2 \theta) d\theta =$$

$$\int_0^{\frac{\pi}{2}} (r + R) dv = \frac{\pi^2 R^4}{4} + \frac{4}{3} \pi R^4$$

$$\bar{h} = \frac{\frac{\pi^2 R^4}{4} + \frac{4}{3} \pi R^4}{\frac{4}{3} \pi R^3} = R \left(\frac{3\pi}{16} + 1 \right)$$

$$\begin{aligned} \bar{h} &= \frac{3\pi R}{16} + R \\ &= 0.589 R + R \end{aligned}$$

Residence time, t , for average bubble,

Let u_1 = average velocity of bubble approaching axis or vortex filament

u_2 = average velocity of gas in the vortex filament.

$$t_1 = \frac{0.589 R}{u_1} ; t_2 = \frac{R}{u_2}$$

$$u_2 = \frac{Q}{a} = \frac{Q}{2a} \text{ where,}$$

Q = gas flow/unit time.

a = area of vortex filament cross section

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V. EXPERIMENTAL ENGINEERING (Cont'd)

Vortex System Calculation

Fig. V-6 shows that the gas holdup is reduced by increased operating pressure. This results from the fact that the vortex operates at a higher pressure thus increasing the pressure drop from the vortex to atmosphere, increasing the volume of flow from the vortex.

It should be noted that the volume of gas introduced into the system in Fig. V-6 is measured at inlet pressure. Also the holdup volume is measured at inlet pressure. While the gas expands as it travels through the sphere, this factor is compensated by the fact that the holdup volume is measured at inlet pressure. The error in this method has been calculated to be less than 10% and more accurate results will be available when operation at higher pressure is possible.

Photographic Techniques in Measurement of Gas Holdup

Moving pictures taken from directly over the "north pole" show a very definite path, and may, when time permits, provide a curve representing a typical bubble path. Since the system is constantly changing, moving pictures give many exposures of known duration. It is possible that the length of bubble "tracks" can be measured if a suitably clear picture can be had. From these measurements, bubble velocities can be calculated as a function of radius. Also introduction of a dye stream might be tried and the relation of water path and bubble path studied.

By counting frames it was found that a bubble leaving the outer edge took 17 frames or $\frac{17}{64}$ sec to reach the center.

Since the average path in this stream is less than half the radius of the sphere ($\frac{\pi R}{8}$), it is apparent that the major problem is the removal of gas from the void at the center.

Behavior of Solids in Sphere

Although no planned experiments have been run on the introduction of solids with $sp\ gr > 1$, occasionally bits of rubber gasket material, wire, glass, modeling clay and mercury have been accidentally introduced into the system with the pump running. In general the material follows an erratic orbit around the inner wall of the sphere usually below the equator. The material cannot be pumped out, and cannot get into the center of the core.

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V. EXPERIMENTAL ENGINEERING (Cont'd)

Future Plans

Heavy walled ($> 1/2"$) plastic spheres are almost ready for operation and should allow pressures up to 100 psi which may allow tests on which one might predict higher pressure operation. These should be in operation by February 15, 1950.

Arrangements are complete and the order has been written for a 347 stainless steel ball for 1000 psi operation with normal soup if desired. It is hoped to have this available in April 1950.

Pressure Drop

The first versions of the reactor core models utilizing vortices for gas removal had quite high pressure drops across the vortex. This is not desirable from the standpoint of pumping costs; so a combined theoretical and empirical study of the vortex has been made. A presentation of this study and some conclusions follow.

A relationship between the velocity and the pressure drop from the center to the periphery of any vortex is given by the following equation:

$$dp = \frac{\gamma}{g} \frac{v^2}{r} dr^* \quad (1)$$

where,

dp = pressure increment
v = tangential velocity
r = radius corresponding to v
 γ = specific weight
g = conversion factor

It has been proved that for a liquid in frictionless rotation

$$vr = \text{a constant}^*$$

in a so-called free vortex. To check this, a velocity scan was made from the center to the periphery of the vortex in the 18 inch diameter spherical vortex. The result is shown in Figure V-7. (Note that the radius of the sphere is 0.75 and of the outlet is 0.125). In the range $0.12' \leq r \leq 0.75'$ an

*Russel, G. E. Hydraulics, Holt, New York, 1942.

FIGURE-V-7

VELOCITY vs RADIUS
IN A
SPHERE 1.5 ft. I.D.
102 G.P.M.

Inlet 2-in I. D. on a chord
at $r = 0.61$ ft.

V. EXPERIMENTAL ENGINEERING (Cont'd)Pressure Drop

approximate formula for the velocity as a function of r takes the form

$$v = Kr^{-n} \text{ or } v = \frac{K}{r^n} \text{ or } v r^n = K \quad (2)$$

$$\begin{aligned} \text{In this case } n &\approx 0.78 \\ K &\approx 4.7 \end{aligned}$$

A general solution of equations (1) and (2) gives,

$$r_1 \Delta p r_2 = \frac{\gamma K^2}{2g} \cdot \frac{1}{n} \left[\frac{1}{r_1^{2n}} - \frac{1}{r_2^{2n}} \right] \quad (3)$$

$r_1 \Delta p r_2$ = Pressure drop from r_1 to r_2 .

In the range of $0 < r \leq 0.120'$ the vortex is a forced vortex where

$$v = r \omega$$

$$\omega = \text{angular velocity} \quad (4)$$

A general solution of (1) and (4) gives,

$$\begin{aligned} r_0 \Delta p r_1 &= \frac{\gamma}{2g} \omega^2 \left[r_1^2 - r_0^2 \right] \\ \omega^2 &= \frac{K^2}{r_1^{2n+2}} \\ r_0 \Delta p r_1 &= \frac{\gamma}{2g} \cdot \frac{K^2}{r_1^{2n+2}} \left(r_1^2 - r_0^2 \right) \quad (5) \end{aligned}$$

Combining (3) and (5)

$$r_0 \Delta p r_2 = \frac{\gamma K^2}{2g} \left[\frac{1}{n} \cdot \left(\frac{1}{r_1^{2n}} - \frac{1}{r_2^{2n}} \right) + \frac{1}{r_1^{2n+2}} \left(r_1^2 - r_0^2 \right) \right] \quad (6)$$

V. EXPERIMENTAL ENGINEERING (Cont'd)Symbols

- v = tangential velocity
 dp = pressure increment
 r = radius corresponding to v
 γ = specific weight
 g = conversion factor
 Δp = pressure drop
 r_1 = inner radius of "free" vortex
 r_2 = outer radius of "free" vortex
 r_0 = radius of vortex filament or void
 n = exponent (empirical)
 ω = angular velocity
 K = constant (empirical)

Pitot tube readings were taken along the radius of the vortex in the plane of the sphere's "equator". From these data the total pressure drop and velocities were evaluated, and the Δp calculated from the velocities was compared to the measured Δp in three different cases, using tap water in the sphere and flow system.

<u>Case</u>	<u>GPM</u>	<u>K</u>	<u>N</u>	<u>Calculated Δp</u>	<u>Measured Δp</u>	<u>Diff.</u>
1	102	4.7	0.78	8.3 psi	6.2 psi	2.1 psi
2	80	3.7	0.78	5.1 psi	3.1 psi	2.0 psi
3	42	1.53	0.78	0.9 psi	1.2 psi	-0.3 psi

It is believed that higher pressure drops could be more precisely calculated and measured, and hence better agreement would be obtained. Caution must be used in the extrapolation of equation (6) to larger spheres, in that the evaluation of K and n is empirical. Roughly, K is one-half of the inlet velocity and n lies between 0.7 and 0.8. Without viscous shear in the liquid, K would be numerically equal to the inlet velocity and n would be unity.

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FIGURE V-8
TEST LOOP FOR WESTINGHOUSE PUMP

V. EXPERIMENTAL ENGINEERING (Cont'd)

D. Soup Dump System

Design of Dump Tanks

Calculations indicate that a range of concentrations from 17 to 40 grams U^{235} per liter may be desired in the operation of the pilot model homogeneous reactor.* Using 60 liters as the volume of the soup recirculating system (reactor, pump, boiler, pressurizer and piping) the maximum amount of U^{235} required would be 50 grams/liter x 60 liters = 3000 grams.**

These 3000 grams of U^{235} will require 200 liters of solution to give the minimum concentration of 15 grams per liter. Thus, it will be necessary to provide at least 200 liters of storage volume outside of the reactor recirculating system.

Report K-343 indicates that a 7" I.D. stainless steel cylinder sheathed by 0.44 g/cm² of cadmium and immersed in an infinite water reflector is an "Eversafe" vessel for solutions of UO_2F_2 . This same report also indicates that the minimum critical mass for an 8" I.D. stainless steel reactor under the same conditions is about 5.2 kg of U^{235} . Since the maximum amount of U^{235} in the homogeneous reactor is expected to be about 3 kg., and UO_2SO_4 solutions instead of UO_2F_2 solutions will be used, the soup dump tanks will be constructed of 8", Schedule 40, 347 stainless steel pipe coated outside with boral or cadmium. There will be two soup dump tanks mounted horizontally, each 12' 8" long (including pipe caps at ends), providing 245 liters of volume. Their mass will be 753 lbs without fittings.

They will be pitched slightly so that the hold-up of solution will be minimized when operating the reactor at the highest concentration. Each liter of hold-up in the soup dump tank adds approximately 50 grams of U^{235} to the 3 kg required for the reactor recirculating system at the maximum concentration.

* The system has been designed for a concentration range of 15 to 50 gms/liter.

** Actually the maximum calculated requirement is $40 \times 75 = 3000$ gms.

V. EXPERIMENTAL ENGINEERING (Cont'd)

Concentrator and Pulsa-feeder Circuit

Fig. V-9 is a diagram of a piping arrangement in which hold-up in the concentrator will be minimized. The two horizontal dump tanks are placed so that the end of the tank that provides suction head for the pulsa-feeder pump is the lowest point and the corresponding end of the other tank is the highest point of the two tanks. The difference in these two levels may be about 2 inches. A 22" length of steam jacketed 1 1/2" pipe will extend vertically downward from the bottom of the highest end of the highest soup tank. This 1 1/2" pipe will be connected to the lowest end of the two soup tanks with a 1/2" pipe. The volume of this 1/2" pipe and 1 1/2" pipe connecting the ends of the two soup tanks is calculated to be 976 cc, which is, then, the absolute minimum hold-up in the concentrator.

Uniform concentration in the two tanks will be provided by heating the 1 1/2" down pipe from the highest end with a steam jacket and cause circulation to occur by the decrease in apparent specific gravity with the formation of steam in this pipe, lifting the solution up 2 inches and allowing it to trickle down through the soup tanks to the lowest point in the soup tank system. The volume of liquid trickling from the high end to the low end will be determined experimentally.

The pulsa-feeder pump which feeds soup into the reactor will take suction from the lowest point in the concentrator. The solution will be passed through a filter and a cooler before it reaches the pulsa-feeder to prevent plugging or vapor flashing in the pump. This pump will operate at about one gallon per minute. The filter medium will be removable so that solids may be removed from the system at this point.

Vapor from the flashing or evaporation will be taken off the highest dump tank through a 2 inch pipe to the condenser which will be mounted at an angle. Vapors will be condensed and dropped either into the condensate receivers if concentrating or back into the dump tanks if total reflux is desired. An over-flow line from the condensate tank to the soup tank will be provided to prevent evaporation to dryness in the concentrator. The condenser will be designed to dissipate approximately 300,000 BTU/hr at 200° F saturation temperature on the tube side using 10 gpm of 80°F cooling water on the shell side.

FIGURE V-9
 DIAGRAMATIC DRAWING OF REACTOR SYSTEM

V. EXPERIMENTAL ENGINEERING (Cont'd)

Concentrator and Pulsa-feeder Circuit

The condensate tanks will be constructed of eight inch, Schedule 40, 347 stainless steel pipe, 8 feet-2 inches long, two in number, with a total volume of 152 liters and mass of 488 pounds without fittings.

The condensate tanks will be mounted vertically, and interconnected at the bottom. There will be a liquid level indicator in one tank, indicating the volume of water contained in the two condensate tanks. Knowing this volume, and assuming no leakage into or out of the soup dump system, the volume of solution in the reactor, the total volume of solution in the system and the mass of U^{235} in the system, the concentration of solution in the reactor and dump tanks may be calculated at any time. A liquid level indicator will also be installed on the soup dump tank. Although this liquid level indicator will give considerably less accurate readings of volume (because the soup tanks are horizontal) it will give a direct indication of the volume and, hence concentration, in the reactor and soup tanks, and will thus serve to detect large leaks and give a cross-check on the concentrations obtained from the more precise values obtained from the reading of the level in the condensate tank.

Further concentration checks will be made occasionally by sampling the liquid in the soup tank. Some circulation from the reactor to the dump tanks, through the pulsa-feeder pump may be desirable to keep the concentrations equal in the reactor and dump tanks.

A line with a valve in it will connect the bottoms of the condensate receiver to the suction line of the pulsa-feeder pump to enable quick dilution of the soup in the reactor if desired.

Heat Dissipation During Dumping and After Shut Down

A quick dump of soup from the reactor to the dump tanks is necessary only to minimize intermixing of reflector and soup in case of a break in the zirconium sphere. An estimated two minute dump time is considered to be the most practical from the standpoint of the dump valve considerations.

Assuming no heat removal other than that absorbed in heating the metal in the dump tanks, which have a heat capacity of about 88 BTU per $^{\circ}F$, and flashing steam into the 8 cubic foot

V. EXPERIMENTAL ENGINEERING (Cont'd)

Heat Dissipation During Dumping and After Shut Down

vapor space, 106 lbs of water at 250° C and 1000 psi dumped into the soup tank initially at 200° F would increase the pressure in the soup tank to a calculated 140 psia.

A condenser operating with a heat removal of 300,000 BTU/hr would reduce this pressure to 73 psia if two minutes were allowed for dumping. At this pressure, less than 5 pounds of liquid remain in the reactor sphere.

A calculated maximum time of 4.9 minutes is required to cool the whole system to 212° F, which would be atmospheric pressure, with the condenser operating at 212° F on the tube side with a 10 gpm flow of cooling water. It is likely that during dumping the condenser will operate at tube temperatures higher than 212° F which would increase the average rate of heat dissipation and therefore decrease the time required to reduce the pressure of the system to atmospheric. A probable minimum time is estimated to be about four minutes. This minimum time will be carefully calculated using transient conditions.

These calculations neglect the energy of radiation from the fission products, but the emergency cooling system will be designed to remove this heat. It has been calculated that this energy amounts to 38 kw 10 seconds after shut down, and 9.55 kw one hour after shut down if the pile has been operated 1000 hours at a power level of 1000 kw.

An emergency cooling system utilizing a stored tank of water will be developed to dissipate heat from radiation of fission products in case of a complete failure of utilities.

If the soup remains in the core after shut down, calculations indicate that natural convection of heat to the heat exchanger will be adequate to prevent overheating.

E. Thermal Stress- Reflector Tank

The total amount of heating in the reflector tank walls is believed to be less than 50 kw. A better approximation of this quantity will be made in the near future. Assuming the very pessimistic condition, for calculation purposes; that the heat is concentrated at the inner surface, the tank can safely receive $4.53 \text{ kw/ft}^2 \times 32.6 \text{ ft}^2 = 148 \text{ kw}$ and the cover

V. EXPERIMENTAL ENGINEERING (Cont'd)Thermal Stress - Reflector Tank

$1.77 \text{ kw/ft}^2 \times 3.14 \text{ ft}^2 = 5.55 \text{ kw}$. It therefore appears that excessive thermal stresses are improbable. The matter will be examined further when the heating and cooling details of the tank are better known.

Heat flow from the inner to outer surface of the reflector tank produces a thermal stress which must be considered. For purposes of calculation the reflector tank is taken to be a sphere, in which case the thermal stresses are tangential and radial. For the reflector tank the radial stress is negligible.

The tangential stress is a maximum at the inner or outer surface. Tangential stress at $r = a$ (inner surface) is given by (1)

$$\sigma_t = \frac{-\alpha E \Delta T}{2(1-\nu)} \frac{b(b-a)(a+2b)}{b^3-a^3} \quad (\text{compression})$$

Tangential stress at $r = b$ (outer surface) is given by (1)

$$\sigma_t = \frac{E T}{2(1-\nu)} \frac{a(b-a)(2a+b)}{b^3-a^3} \quad (\text{tension})$$

where σ_t = tangential stress, psi

α = coefficient of thermal expansion per $^{\circ}\text{F}$

E = Young's modulus, psi

ν = Poisson's ratio

a = inner radius, ft.

b = outer radius, ft.

ΔT = temperature drop ($^{\circ}\text{F}$)

- (1) Timoshenko, S : "Theory of Elasticity", Engineering Societies Monograph, McGraw-Hill Book Co., Inc., New York, 1934.

V. EXPERIMENTAL ENGINEERING (Cont'd)

Thermal Stress

The presently designed reflector tank has an inner radius of 19.5 in (1.63 ft) and an outer radius of 22.5 in (1.88 ft).

Substituting values gives at a

$$\sigma_t = -150 \Delta T$$

at b

$$\sigma_t = 124 \Delta T$$

For maximum stress conditions, all the heat is assumed to originate and flow from the inner surface to the outer surface.

$$\text{Then } \Delta T = \frac{q(b-a)}{\pi k (b+a)^2}$$

where k = coefficient of thermal conductivity,
BTU/hr °F ft²/ft

q = heat transferred, BTU/hr

and at a

$$\sigma_t = \frac{-150 q(b-a)}{\pi k (b+a)^2}$$

at b

$$\sigma_t = \frac{124 q(b-a)}{\pi k (b+a)^2}$$

For the reflector tank as presently designed, a heat transfer rate of 4.53 kw/ft² from inner to outer surface would be required to produce a thermal stress of 16,000 psi tension at the outer surface and a compression stress of 19,300 psi at the inner surface.

The stress in the reflector tank at 1000 psi internal pressure is approximately 3400 psi tension. At the inner surface the net stress would be 15,900 psi compression and at the outer surface 19,400 psi tension. These stresses would not be excessive and a heat flux of 4.53 kw/ft² is believed to be most pessimistic. Additional calculations to determine the actual heat flux from neutron and γ -ray adsorption will be made.

V. EXPERIMENTAL ENGINEERING (Cont'd)

Thermal Stress

For the cover plate the thermal stress with a temperature gradient thru the thickness is given by (2)

$$\text{stress} = \frac{E \alpha \Delta T}{2(1 - \nu)} \quad \text{compression on the hot face, tension on the cold face}$$

Substituting values gives

$$\text{stress} = 130 \Delta T$$

where ΔT = temperature difference, °F

For a flat round plate of two feet I.D. and eight inches thick, ΔT can be expressed in terms of heat transferred in BTU/hr as

$$\Delta T = 0.0081 q$$

where q = heat transferred, BTU/hr

$$\text{or stress} = 130 \times 0.0081 q = 1.05 q$$

For a stress of 20,000 psi at the inner and outer surface, the heat flux would have to be 1.77 kw/ft². Additional calculations will determine the actual flux. If it is too large, the thermal stress can be relieved by cooling coils on the inner surface.

F. Heat Exchangers

Quotations have been received from Andale Corporation and Ross Heater Company on stainless steel heat exchangers for steam generation. According to the latest corrosion data, these designs may have to be modified to allow zirconium tubing and tubesheets, so that the prices quoted are not directly applicable.

(2) Roark, R. J.: "Formulas for Stress and Strain", McGraw-Hill Book Co., Inc., 1943.

V. EXPERIMENTAL ENGINEERING (Cont'd)Heat Exchangers

The Ross design was found to introduce excessive thermal stresses in the tubes under operating conditions, and would have to be modified considerably to include suitable expansion joints. The price on the original stainless unit is \$1,625 f.o.b. Buffalo.

The Andale design provides a stuffing box expansion joint. The proposed packing is being tested in the X-10 pile for radiation stability. Materials considered are John Crane Style 6-AM and Johns-Manville Style No. 14 J-M Jewett packing. Both are graphite-asbestos plastics.

This latter exchanger also provides double tube-sheets to localize leakage of solution. The price of this unit is quoted as \$6,489 net.

VI. CORROSION AND METALLURGY

A. Summary

Much effort has been directed to the problem of preventing decomposition of uranyl sulfate in stainless steel systems at 250°C. The presence of 0.35M sulfuric acid is extremely detrimental corrosion-wise and apparently on solution stability. The addition of nitric acid, chromic acid, or sodium nitrate in acid-free uranyl sulfate solutions prevented reduction of the medium. Bureau of Mines zirconium continues to show good corrosion resistance to various uranyl sulfate media at 100° and 250°C. Tests are continuing with crystal bar zirconium and various forms of Bureau of Mines zirconium. A zirconium welding program has been started at Battelle. A list of zirconium requirements for the Homogeneous Reactor has been prepared. Numerous corrosion studies at low and high temperatures are continuing with various materials in uranyl sulfate. The elimination of sulfuric acid from the reactor medium has resulted in a great improvement of the corrosion resistance of stainless steels making their use for component parts of the reactor very possible.

B. Uranyl Sulfate Solution Stability Studies

As mentioned in the previous Technical Division Quarterly Progress Report, ORNL-527, heavy black insoluble products were observed on the bottoms of the stainless steel bombs used for corrosion tests at 250°C. It was also noted that many of the test specimens removed from the bombs had heavy black films and scales covering their surfaces. Chemical and X-ray diffraction analyses showed this sludge to be 83.4 percent uranium and was U_3O_8 . Traces of UO_2 and UO_3 were found also. Such heavy accumulation of insoluble products had not been observed during preliminary 24 hours tests, but when the testing time was increased to 4-7 days, the reduction of the sulfate was very pronounced. With free sulfuric acid present in the uranyl sulfate solution, strong odors of hydrogen sulfide were observed when the bombs were dismantled. This observation led to the general assumption that solution reduction was taking place at the elevated temperature through one or more mechanisms. The initial solution pH was 0.4-0.7 with 0.35M sulfuric acid present. Such an acid solution undoubtedly attacked the walls of the stainless steel bombs resulting in the formation of atomic hydrogen. This gas in turn may have reduced the weakly oxidizing sulfate solution to possibly SO_3 and finally to H_2S with a corresponding reduction of the uranyl sulfate to uranium oxides, predominantly U_3O_8 .

VI. CORROSION AND METALLURGY (Cont'd)

B. Uranyl Sulfate Solution Stability Studies

Nitric Acid solutions of 0.168M uranyl sulfate containing 0.35M sulfuric acid were made containing concentrations of nitric acid from 0.053 to 0.265M. Tests were operated for 70 hours in stainless steel bombs at 250°C and approximately 600 psi pressure. Solution volumes were 150 ml. Data are tabulated below.

<u>Nitric Acid Molarity</u>	<u>Solution Condition at End of Test</u>
0.053M	Dark green color; black residue
0.106M	Original pale yellow color; no ppt.
0.159M	Slightly yellow-green color; no ppt.
0.212M	Slightly yellow-green color; no ppt.
0.265M	Slightly yellow-green color; no ppt.

In cases where the solution retained its original color and condition, the stainless steel bomb walls remained clean with no apparent film build up or scale formation. Concentrations of nitric acid from 0.106M to 0.265M were sufficiently strong in oxidizing capacity to prevent the solution from being reduced.

Chromic Acid - Similar tests were made using chromic acid in concentrations of 0.066M to 0.330M. These tests were of 96 hours duration. The results are tabulated below.

<u>Chromic Acid Molarity</u>	<u>Solution Condition at End of Test</u>
0.066M	Pale green color; black ppt.
0.132M	Green-brown color; light black ppt.
0.198M	Yellow-brown color; no ppt.
0.264M	Yellow-brown color; no ppt.
0.330M	Yellow-brown color; no ppt.

Solutions containing 0.198M to 0.330M chromic acid showed no tendency to be reduced. Spectrographic analyses of the solutions showed that as the chromic acid concentration increased, the concentration of metallic ions, such as iron, manganese, nickel, and silicon, obtained from corrosion attack on the stainless steel bombs, decreased, indicating that even at 250°C chromic acid may possibly exert an inhibiting influence on the corrosion reaction.

VI. CORROSION AND METALLURGY (Cont'd)

B. Uranyl Sulfate Solution Stability Studies

Cupric Sulfate - Cupric sulfate was also used since it is often employed industrially to inhibit corrosion attack on stainless steels handling sulfuric acid solutions. Concentrations of 0.012M-0.084M were added to 0.168M uranyl sulfate containing 0.35M sulfuric acid. Tests were operated for 72 hours, and in all cases, were unsuccessful. Reduction of the uranyl sulfate occurred in every instance.

Sodium Nitrate - Sodium nitrate in concentrations of 0.055M-0.392M were added to acidified 0.168M uranyl sulfate solutions. Tests were conducted at 250°C for 96 hours. Results are listed below.

<u>Sodium Nitrate Molarity</u>	<u>Solution Condition at End of Test</u>
0.055M	Pale green color; black ppt.
0.118M	Original color; no ppt.
0.196M	Original color; no ppt.
0.392M	Original color; no ppt.

Spectrographic analyses of these solutions showed also that sodium nitrate exerted an inhibiting effect on corrosion of the stainless steel bombs. As the concentration of sodium nitrate increased, concentrations of metallic ions (chromium, copper, iron, manganese, nickel, and silicon) decreased.

Summarizing, these tests indicate that reduction of acidified uranyl sulfate solutions can be prevented by the addition of the following materials; 0.106M nitric acid, 0.198M chromic acid, and 0.118M sodium nitrate. The use of nitric acid or sodium nitrate for such purpose in the Homogeneous Reactor may not be practical since at this temperature, 250°C, the nitrates are decomposed and exist as oxides of nitrogen in the vapor phase. Present design plans for the reactor provide for rapid removal of gases formed by irradiation effects on the sulfate medium. The gaseous nitrogen oxides would undoubtedly be removed from the system along the oxygen and hydrogen gases, and thus may not be present long enough to add any beneficial influence to the solution instability problem. Further work on this problem is contemplated.

It was also suspected that perhaps the sulfate reduction was aided by a metal displacement process; i.e., contact of the solution with metals in the stainless steel bombs having a

VI. CORROSION AND METALLURGY (Cont'd)

B. Uranyl Sulfate Solution Stability Studies

higher position in the electromotive series than uranium and thus causing a displacement of the uranium. These materials could be manganese, chromium, aluminum, and possibly iron.

Previous tests at 250°C with uranyl sulfate contained in fused silica capsules or tubes had shown no evidences of solution decomposition. An attempt was made to supply further information on the metal displacement theory. A small stainless steel bomb (40 ml capacity) was completely plated on the inside with 2 mils of silver followed with 0.3 mil of gold plate. Twenty five ml of 0.168M uranyl sulfate containing no free sulfuric acid were placed in the bomb and heated at 250°C for 24 hours. At the end of the test, the solution was pale green as compared to its original yellow color, but there was no sign of any black insoluble precipitate. The gold plating in the vapor phase region was discolored black, however, and preliminary examination disclosed this black film to contain uranium. Spectrographic analysis of the solution showed strong concentrations of iron and copper and weak concentrations of nickel and chromium indicating that the plating was not completely non-porous, and solution or vapor had seeped through fine pin holes to contact the base metal, stainless steel, resulting in corrosion attack with the probable production of hydrogen, and reduction of uranyl sulfate.

Several tests were conducted to check the effect of nitric acid additions to the uranyl sulfate solution to prevent the precipitation of uranium oxides. Test solutions were 0.168M uranyl sulfate containing 0.35M sulfuric acid and 0.11M nitric acid. Volumes of 150 ml were placed in stainless steel bombs and exposed for 72 hours. Dense clouds of red nitric oxide fumes were encountered when the bombs were opened. Both solutions were pale yellow in color and contained a very slight, brown colored precipitate. Spectrographic analyses of the solutions and residues follow:

Element	Solution 1	Residue 1	Solution 2	Residue 2
Ag	-	T	-	VS
Ca	W	FT	W	FT
Cr	VW	VS	W	VW
Cu	VW	T	VW	T
Fe	W	S	M-	S
Mn	W	T	W	T
Mo	-	FT	-	VFT
Ni	W	M	W	M
Si	VW	VW	VW	VW
U	VS	-	VS	-

VI. CORROSION AND METALLURGY (Cont'd)

B. Uranyl Sulfate Solution Stability Studies

Silver was present in the residues due to the fact that silver gaskets were used for sealing the bombs. The above analyses show that the slight precipitates present in the solutions were evidently products of the corrosion reaction, and not decomposition products from the uranyl sulfate.

A test was run to determine the effect of hydrogen peroxide on the decomposition problems. A solution of 0.168M uranyl sulfate containing 0.35M sulfuric acid and 0.11M nitric acid was made 0.05M with hydrogen peroxide. There was no precipitation of uranyl peroxide at this hydrogen peroxide concentration. The test was operated for 24 hours at 250°C in a stainless steel bomb. At the completion of the test, the solution was pale green in color but was perfectly clear. There was no evidence of precipitation and there was no scaling in the bomb. Hydrogen peroxide, dissociating into water and nascent oxygen at these conditions, probably aided in stabilization of the uranyl sulfate solution against reduction.

As noted previously, uranyl sulfate solutions have not been reduced when contained in a fused silica liner at 250°C and up through the critical range, approximately 300°C. These results have been verified by other investigators. Tests are now in progress to determine whether or not, the presence of various metals will cause a reduction of uranyl sulfate solutions contained in a fused silica tube at 250°C. Preliminary tests with 0.168M uranyl sulfate with and without 0.35M sulfuric acid have been operated for 96 hours in a silica tube without visible signs of a precipitate.

The first metal placed in the acidified uranyl sulfate solution at 250°C was Bureau of Mines zirconium. At the end of the test, the solution had discolored slightly, and the surfaces of the zirconium were covered with a number of tiny black specks. Both solution and black tuberculations are being analyzed, spectrographically and chemically. The tests are continuing with samples of pure metals commonly encountered as impurities in zirconium. These tests will show the effect, if any, of such metals on the decomposition of uranyl sulfate solutions.

C. Zirconium Corrosion

Since zirconium continues to head a list of 65 metals and alloys with its excellent corrosion resistance to the uranyl sulfate medium, it will be discussed in detail. Corrosion data

VI. CORROSION AND METALLURGY (Cont'd)

C. Zirconium Corrosion

have been obtained predominantly with Bureau of Mines zirconium and this material compares favorable with the limited data obtained on crystal bar zirconium (iodide decomposition method). The experience of the Naval Reactor groups at ANL indicate that processing techniques may be important from a corrosion standpoint. All zirconium metal undergoing corrosion studies at ORNL is examined spectrographically, chemically, metallographically, by electron diffraction studies, and finally, by X-ray analyses. This exhaustive survey is being undertaken to further improve and substantiate existing zirconium information.

Efforts are being made to determine and identify the various impurities in zirconium. Small zirconium sample melts are being made using 2 percent by weight additions of iron, aluminum, calcium, magnesium, titanium, and carbon.

A test to determine the effects of irradiation on the corrosion and physical properties of Bureau of Mines zirconium in enriched uranyl sulfate solution (40 gm U/liter) at 250°C was started in the X-10 pile on February 6th. The uranyl sulfate contained no free sulfuric acid. Pressure on the bomb reached 950 psi within two hours and has remained relatively constant since the test was started. The test will continue until February 13th, after which time the apparatus will be dismantled. The zirconium sample and the solution will be checked for pertinent data.

The following corrosion data for zirconium will be separated into two categories, 100°C tests and 250°C tests. Weight losses and corrosion rates are based on defilmed weight changes unless otherwise stated. A suitable defilming method on zirconium for the purpose of these tests consists of immersing the specimen in 30 percent nitric acid by volume at 70-80°C for 30 minutes. The weight loss on the metal by this treatment is 1.3 mg/dm². All tests in the 100°C section have been operated for 1344 hours unless otherwise stated.

100°C Corrosion Tests

Numerous tests have been conducted with Bureau of Mines zirconium bars approximately one inch in diameter. These bars were prepared by taking an "as cast" round ingot, quartering on a band saw, forging at 750°C, and swaging through a 1.1 inch die. The swaging operation was conducted at 750°C; the

VI. CORROSION AND METALLURGY (Cont'd)C. Zirconium Corrosion

bars were air cooled, and oxides and flaws were removed by grinding. Chemical analyses of the bars used for corrosion tests appear below in percentages of various elements present.

<u>Element</u>	<u>Bar 138A</u>	<u>Bar 138B</u>
Al	0.080 %	0.260 %
Fe	0.058	0.071
Ti	0.120	0.110
Hf	2.260	2.130
Ca	Weak	Weak
Mg	Weak	Weak

Table VI-1 shows corrosion data compiled with Bar 138A. All samples were polished on No. 80 and No. 120 emery paper prior to test. Weight changes are reported in milligrams/square decimeter/month, (mdm).

TABLE VI-1

THE CORROSION OF B. M. ZIRCONIUM (BAR 138A)
IN URANYL SULFATE AT 100°C

<u>Uranyl Sulfate</u> <u>Molarity</u>	<u>Sulfuric Acid</u> <u>Molarity</u>	<u>Remarks</u>	<u>Wt. Change,</u> <u>mdm</u>	<u>Corrosion Rate,</u> <u>mil/yr.</u>
0.0168	None		-0.95	0.007
0.0168	None	Solution aerated	-0.32	0.002
0.168	None		-1.89	0.014
0.168	0.35		-35.60	0.267
0.168	0.35	0.005M H ₂ O ₂	-48.50	0.364

Corrosion attack increased progressively as the uranyl sulfate concentration increased, as sulfuric acid was present, and as hydrogen peroxide was added to the uranyl sulfate-sulfuric acid system. In no case, however, was the corrosion attack of any serious magnitude. Solution aeration was sufficient to maintain a slightly oxidizing condition which apparently enabled the metal to become more passive in the uranyl sulfate solution.

VI. CORROSION AND METALLURGY (Cont'd)C. Zirconium Corrosion

Table VI-2 shows corrosion data compiled with Bar 138B.

TABLE VI-2

THE CORROSION OF B. M. ZIRCONIUM (BAR 138B) IN
0.168M URANYL SULFATE AT 100°C

<u>Sulfuric Acid</u> <u>Molarity</u>		<u>Remarks</u>	<u>Wt. Change,</u> <u>mdm</u>	<u>Corrosion Rate,</u> <u>mil/yr.</u>
None			- 0.39	0.003
None	30 days exposure		- 8.76	0.066
None	60 "	"	- 5.84	0.044
None	90 "	"	- 0.97	0.007
None	120 "	"	+ 1.09	--
None	150 "	"	neg.	neg.
0.35	30 "	"	-60.60	0.455
0.35	60 "	"	-48.50	0.364
0.35	90 "	"	-31.90	0.239
0.35	120 "	"	-23.90	0.179
0.35	150 "	"	-22.30	0.167

Corrosion attack on these samples showed a gradual decrease with increased time of test. The maximum corrosion rate observed in the 0.35M sulfuric acid solution was approximately 0.5 mil/year which is considered excellent. In general, the corrosion resistance of Bar 138B did not appear quite as good as that of Bar 138A. This may possibly be attributed to the higher aluminum and iron concentrations in Bar 138B.

Several series of tests were run with 1/16 inch thick Bureau of Mines sheet zirconium containing approximately 1% hafnium and various percentages of iron and carbon. Analysis of this material is listed below.

<u>Heat No.</u>	<u>Carbon, %</u>	<u>Iron, %</u>
S-278	0.05	0.12
S-453	0.20	0.10
S-461	0.30	0.11
S-510	0.16	0.03
S-407	0.15	0.28
S-441	0.16	0.72

VI. CORROSION AND METALLURGY (Cont'd)C. Zirconium Corrosion

All samples, except S-510, were annealed in air at 790°C for one hour and cooled slowly. Heat S-510 was not annealed. Corrosion data are shown in Table VI-3.

TABLE VI-3

THE CORROSION OF B. M. ZIRCONIUM SHEET
IN 0.168M URANYL SULFATE AT 100°C

Heat No.	Sulfuric Acid Molarity	Remarks	Wt. Loss, mdm	Corrosion Rate, mil/yr.
278	None	Polished surface	0.79	0.006
453	None	" "	neg.	neg.
461	None	" "	1.28	0.010
510	None	" "	1.67	0.013
407	None	" "	neg.	neg.
441	None	" "	neg.	neg.
278	0.35	Polished surface	3.89	0.029
453	0.35	" "	13.25	0.099
461	0.35	" "	8.06	0.060
510	0.35	" "	6.23	0.047
407	0.35	" "	14.44	0.109
441	0.35	" "	4.67	0.035
278	0.35	Air annealed 1 hr. at 790°C	28.05	0.210
453	0.35	" " " "	51.50	0.387
461	0.35	" " " "	20.50	0.154
510	0.35	" " " "	38.60	0.289
407	0.35	" " " "	37.90	0.285
441	0.35	" " " "	17.78	0.133
278	0.35	Vacuum annealed 1 hr. at 790°C	13.65	0.103
453	0.35	" " " "	31.92	0.239
461	0.35	" " " "	28.30	0.212
510	0.35	" " " "	21.38	0.161
407	0.35	" " " "	31.30	0.235
441	0.35	" " " "	11.33	0.085
278	0.35	Vacuum annealed 1 hr. at 790°C; cooled in oxygen	7.85	0.059
453	0.35	" " " "	10.50	0.079
461	0.35	" " " "	10.00	0.075
510	0.35	" " " "	8.18	0.061
407	0.35	" " " "	8.41	0.063
441	0.35	" " " "	2.56	0.019

VI. CORROSION AND METALLURGY (Cont'd)C. Zirconium Corrosion

Little correlation of corrosion resistance versus amounts of carbon and iron present as impurities was obtained by these data. Of the three heat treatment methods tested, vacuum annealing for one hour at 790°C appeared to give the best corrosion resistance to the zirconium.

Several corrosion tests have been completed with crystal bar zirconium and foil zirconium. These data are included in Table VI-4.

TABLE VI-4

THE CORROSION OF CRYSTAL BAR AND FOIL ZIRCONIUM
IN 0.168M URANYL SULFATE AT 100°C

<u>Sulfuric Acid</u> <u>Molarity</u>	<u>Remarks</u>	<u>Wt. Change, Corrosion Rate,</u>	
		<u>mdm</u>	<u>mil/yr.</u>
None	Foil	neg.	neg.
0.35	Foil	0.23	0.002
0.35	Bar-machined surfaces	neg.	neg.
0.35	Bar-machined surfaces; solution contained 0.005M H ₂ O ₂	+1.83	-

These preliminary tests show the corrosion resistance of crystal bar zirconium to be better than that of Bureau of Mines zirconium under similar conditions of exposure. Further tests with crystal bar zirconium are planned.

250°C Corrosion Tests

Corrosion tests data on Bureau of Mines zirconium (Bar 138A) at 250°C in uranyl sulfate are shown in Table VI-5. Weight changes are reported in milligrams/square decimeter/day, (mdd.). All tests were made in stainless steel bombs and testing times were 24-120 hr. Samples were defilmed by the treatment described previously under 100°C tests.

VI. CORROSION AND METALLURGY (Cont'd)C. Zirconium CorrosionTABLE VI-5THE CORROSION OF B. M. ZIRCONIUM (BAR 138A)
IN 0.168M URANYL SULFATE AT 250°C

<u>Sulfuric Acid</u> <u>Molarity</u>	<u>Remarks</u>	<u>Wt. Change,</u> <u>md</u>	<u>Corrosion Rate,</u> <u>mil/yr.</u>
0.35	Solution contained 0.005M H ₂ O ₂	+0.29	--
None	Polished surfaces	+6.97*	--

* Arithmetic mean weight gain for six specimens

In all cases, the specimens showed a weight gain after test. It should be remembered that in most of these tests, solution decomposition occurred although this condition was not prevalent in tests operated for 24 hours and less. The films present on the specimens were usually extremely adherent and very uniform. Film colors ranged from light gray to dull black. X-ray diffraction studies indicated that the film was not an oxide type but contained traces of UO₂ and UO₃, along with more dense concentrations of U₃O₈.

High temperature corrosion data on Bureau of Mines zirconium (Bar 138A) are listed in Table VI-6. This material was tested in an "as received" condition and in three different heat treated forms as previously mentioned.

VI. CORROSION AND METALLURGY (Cont'd)C. Zirconium CorrosionTABLE VI-6

THE CORROSION OF B. M. ZIRCONIUM (BAR 138B)
IN 0.168M URANYL SULFATE AT 250°C

<u>Sulfuric Acid</u> <u>Molarity</u>	<u>Nitric Acid</u> <u>Molarity</u>	<u>Remarks</u>	<u>Wt. Change, mdd</u>	<u>Corrosion Rate, mil/year</u>
None	None	Polished surfaces	+65.80	---
0.35	None	Polished surfaces; three tests	+ 5.58	--
0.35	0.11	No treatment	+13.48	---
0.35	0.11	Polished; passivated in 30% HNO ₃ at 70°C for 30 min.	+15.45	---
0.35	None	No treatment	- 1.65	0.371
None	None	Air annealed 1 hour at 790°C	+ 2.96	---
0.35	None	Air annealed 1 hour at 790°C	-73.8	16.60
None	None	Vacuum annealed 1 hour at 790°C	+23.45	---
0.35	None	Vacuum annealed 1 hour at 790°C	+ 3.65	---
None	None	Vacuum annealed 1 hour at 790°C cooled in oxygen	- 0.47	0.106
0.35	None	Vacuum annealed 1 hour at 790°C; cooled in oxygen	- 0.37	0.082

VI. CORROSION AND METALLURGY (Cont'd)C. Zirconium Corrosion

Rather heavy film formation was evident on most of the specimens except the last two which were vacuum annealed and cooled in oxygen. Again, solution decomposition was prevalent except in those tests containing 0.11M nitric acid. The corrosion resistance of the air annealed specimen in the uranyl sulfate-sulfuric acid system was far more severe than in any other test. A corrosion rate of 16.6 mils/year was calculated.

The films were very adherent, uniform, and varied in color from dark gray to dull black. Heavy weight increases where solution decomposition took place may be attributed to the presence of uranium oxides on the metal surfaces.

Assuming the use of zirconium for the major component parts of the reactor, a heavy rate of film formation would not be desirable. For instance, excessive film build up on heat exchanger tubes could create severe heat transfer problems. The ideal situation would appear to be that in which a very minor corrosion attack existed, say 0.1 mil/year, as exhibited by the last two specimens in Table VI-6. Thus, there would be no major corrosion problem, and there would be no interference with heat transfer processes due to heavy film formation.

High temperature tests were run with Bureau of Mines sheet zirconium specimens containing different carbon and iron concentrations. These materials were described in previous paragraphs. The tests were operated at 250°C in 0.168M uranyl sulfate containing 0.35M sulfuric acid. Data are shown in Table VI-7.

TABLE VI-7

THE CORROSION OF B. M. ZIRCONIUM SHEET IN
0.168 URANYL SULFATE AT 250°C

<u>Heat No.</u>	<u>Sulfuric Acid Molarity</u>	<u>Remarks</u>	<u>Wt. Loss, mdd</u>	<u>Corrosion Rate, mil/year</u>
278	0.35	Surfaces polished	9.18	2.07
453	0.35	" "	9.28	2.09
461	0.35	" "	15.48	3.48
510	0.35	" "	24.25	5.46
407	0.35	" "	5.47	1.23
441	0.35	" "	6.63	1.49

VI. CORROSION AND METALLURGY (Cont'd)C. Zirconium Corrosion

The corrosion resistance of this sheet material was not nearly as good as that of the zirconium bars, 138A and 138B. Whereas most of the latter specimens showed weight gains, the sheet zirconium specimens showed definite weight losses. No apparent reason for this difference in behavior is known, unless it is the fact that the sheet zirconium specimens had previously been air annealed at 790°C for one hour. Corrosion data from other tests have shown air annealed zirconium to possess the poorest corrosion resistance of the various heat treating methods tested.

A corrosion test with crystal bar zirconium at 250°C in 0.168M uranyl sulfate containing 0.35M sulfuric acid resulted in a sample weight gain of 6.0 mdd.

Two long term zirconium corrosion tests were run with duplicate specimens obtained from Bar 138B. The tests were operated intermittently for four weeks at 250°C. Samples were inspected weekly and replaced in fresh test solution. The actual total testing time was 640 hours. Samples "A" were exposed in 0.168M uranyl sulfate containing 0.11M nitric acid for the entire test. Samples "B" were exposed to 0.168M uranyl sulfate containing the following:

<u>1st week:</u>	0.35M H ₂ SO ₄ + 0.11M HNO ₃
<u>2nd week:</u>	0.35M H ₂ SO ₄ + 0.11M HNO ₃
<u>3rd week:</u>	0.35M H ₂ SO ₄ + 0.22M HNO ₃
<u>4th week:</u>	0.11M HNO ₃

All samples were coated with a tight, light gray colored film. The average weight gain on samples "A" was +124.6 mdd; the average weight gain on samples "B" was +41.4 mdd. Samples "B" exhibited rather drastic dimensional changes. The original specimens were 2.5 cm in diameter and 0.45 cm thick. Final dimensions were 2.65 cm in diameter across both flat surfaces.

The diameter through the center of the sample (i.e., the diameter at 0.225 cm thickness) had decreased slightly so that the edges of the specimens had a bowed appearance. This effect was not evident on samples "A".

An "A" sample and a "B" sample were placed in a vise and fractured by tapping with a hammer. Sample "B" fractured with a very light tap while Sample "A" required as strong a tap to fracture as an unexposed zirconium specimen of similar dimensions and composition.

VI. CORROSION AND METALLURGY (Cont'd)

C. Zirconium Corrosion

The fractured structure of Sample B was very fibrous and contained numerous white products arranged in stringer fashion across the fractured areas. This sample appeared to have been completely embrittled by the test exposure. Sample A exhibited a very slight fibrous structure with no signs of white stringers as were present on Sample B. All samples have been submitted for microscopic and X-ray studies.

Two specimens of B. M. zirconium, Bar 138B, were exposed to solutions of concentrated phosphoric and sulfuric acids containing 0.168M uranyl sulfate. The phosphoric acid solution was maintained at 170°C; the sulfuric acid solution was kept at approximately 265°C. Tests were operated for 80 hours and the specimens were severely attacked. The corrosion rate on the zirconium exposed to concentrated phosphoric acid was 3.215 inches/year; corrosion attack on the sulfuric acid specimen was 1.250 inches/year.

D. Zirconium Welding

Work on the development of a satisfactory welding technique for one half inch thick zirconium plate has been delayed somewhat by proper authorization to Battelle Memorial Institute to undertake this problem. This delay has now been overcome.

The general program outline has reached agreement between ORNL and BMI, and actual welding tests on one half inch plate were started February 14. Helium atmospheres will be used rather than argon atmospheres for welding inasmuch as the former is more readily available in higher purity. Battelle has reported previously that using argon in welding good crystal bar zirconium, a weld was produced on which only a thin metal surface layer was adversely affected. This effect was reduced by vacuum annealing after the welding operation.

Samples of one half inch welded zirconium plate will be sent to ORNL for corrosion studies. Mechanical properties and corrosion studies also will be conducted at BMI. Bend tests, providing biaxial stressing, will be used to determine the tensile strength and ductility of the base plate and welded joints.

VI. CORROSION AND METALLURGY (Cont'd)E. Zirconium Requirements for the Pilot Model Homogeneous Reactor

These requirements are based on a system in which all uranyl sulphate solution at 250°C is contained in zirconium.

1) One Sphere

- a) To be formed in two halves and welded together. Preferred forming operation - drawing
- b) Dimensions
 - 1) Outside radius no less than $9 \frac{9}{16}$ in at any point.
 - 2) Inside radius no greater than $8 \frac{15}{16}$ in at any point. To finish sphere 18 in I.D. and 19 in O.D. with $\frac{1}{2}$ in wall thickness and no less than $\frac{1}{16}$ in having been removed from all surfaces.
- c) Minimum volume of metal prior to machining, 670 cu in
- d) Approximate weight of sphere before machining, 154 pounds minimum
- e) Estimated casting requirement - 150 lb ingot, for each hemisphere

2) Head on Sphere

- 1) Dimensions
4 in diameter x 6 in long
- 2) Weight of block approximately 18 lbs
- 3) Estimated casting requirements - one 40 lb casting.

3) Control Rod Tubes

- a) Dimensions
 - 1) 2.000 in O.D. x 1.500 in I.D. $\pm$ 0.005 in
 - 2) Length of each - 5 ft

VI. CORROSION AND METALLURGY (Cont'd)E. Zirconium Requirements for the Pilot Model Homogeneous Reactor3) Control Rod Tubes

- b) Total number of tubes - 6
- c) Weight of each tube - approximately 19 lbs
- d) Total weight of finished tubes - approximately 114 lbs
- e) Estimated casting requirements - one 40 lb ingot for each tube

4) Instrumentation Thimbles

- a) Dimensions
 - 1) 3 in nominal pipe - Schedule 160
 - 2) Length - 18 in each
- b) Total number of tubes - 6
- c) Weight of each tube approximately 17.5 lbs
- d) Total weight of finished tubes approximately 105 lbs
- e) Estimated casting requirement - Six 40 lb ingots

5) Heat Exchanger Tube Sheets

- a) Dimensions
 - 1) One plate - 10 inches in diameter x 1 1/2 in thick
 - 2) One plate - 7.5 inches in diameter x 1 1/2 in thick
- b) Finished weight of each plate
 - 1) 10 in plate approximately 28 lbs
 - 2) 7.5 in plate approximately 11 lbs

VI. CORROSION AND METALLURGY (Cont'd)E. Zirconium Requirements for the Pilot Model Homogeneous Reactor5) Heat Exchanger Tube Sheets

c) Estimated casting requirements

1) One 60 lb ingot

2) One 20 lb ingot

6) Liners for Heat Exchanger Headsa) To be formed from two pieces of sheet stock
16 inches in diameter x 1/8 in thick

b) Weight of two sheets - approximately 15.0 lbs

c) Casting requirements

One 30 lb ingot or two 15 lb ingots

7) Heat Exchanger Tubes

a) Dimensions

1/4 in O.D. tubing

20 gauge wall thickness

Length of each tube 5 to 11 ft

b) Total length of tubing - 1100 ft

c) Weight of metal per foot of finished tubing,
0.0852 lbsd) Total weight of finished tubing approximately
94 lbs8) Entrance and Exit Piping

a) Dimensions

1) 26 ft of nominal 1 1/2 in pipe, schedule 80

2) 3 1/2 ft of nominal 2 in pipe, schedule 80

3) 10 ft of nominal 1/2 in pipe, schedule 80

4) 4 ft of 0.5 in O.D. x 0.4 in I.D. tubing

VI. CORROSION AND METALLURGY (Cont'd)E. Zirconium Requirements for the Pilot Model Homogenous Reactor8) Entrance and Exit Piping

b) Finished weight of piping

- 1) 1 1/2 in pipe - approximately 78 lbs
- 2) 2 in pipe - approximately 14 lbs
- 3) 1/2 in pipe - approximately 9.3 lbs
- 4) 0.5 in O.D. tubing - approximately 2.2 lbs

c) Estimate of Casting Requirement

- 1) and 2) Six 30 lb ingots
- 3) and 4) One 15 lb ingot

9) Pipe Flanges

- a) 1 1/2 in inlet - one piece 4 in diameter x 1 1/4 in thick, weight approximately 4.5 lbs
- b) 1/2 in drain - one piece 2 in diameter x 2 in thick, weight 1.5 lbs
- c) 2 in exit and 2 in control thimbles
Seven pieces 5 1/4 in diameter x 2 in thick,
weight approximately 10 lbs each.
Total weight 70 lbs
- d) Instrumentation Thimbles
 - 1) Six pieces 7 in diameter x 2 1/2 in thick,
weight approximately 22 lbs each.
Total weight approximately 154 lbs
 - 2) Estimated casting requirements
Six 40 lb ingots

10) Pipe Joint Stock

- a) 1 1/2 in pipe connections
1 ft of 2 1/2 in diameter bar stock approximately
11.5 lbs

VI. CORROSION AND METALLURGY (Cont'd)E. Zirconium Requirements for the Pilot Model Homogeneous Reactor10) Pipe Joint Stock

- b) 1/2 in pipe connections
1 ft of 1 1/2 in diameter bar stock approximately
two lbs

11) Pressurizer Liner

- 1) Dimensions - 1 sheet 90 in long x 20 in wide
x 1/8 in thick
- 2) Weight - approximately 52 lbs
- 3) Estimated casting requirement - one 100 lb
ingot

12) Valve Stock

- 1 ft of 1 3/4 in diameter bar stock approximately
6.5 lbs

13) Welding Rod

- Five pounds of 1/8 in diameter welding rod, ap-
proximately 2000 ft. (This item is subject to doubt
as the welding experiments are just starting)

Pump Modification

The following is a listing of estimated zirconium requirements for modification of the Westinghouse centrifugal pump. These estimates are based on the only available drawing (ANL Drwg. No. BSK-1049). This drawing is for a 30 gpm pump and consequently all dimensions were increased by a factor of 20% to meet the requirements of the 100 gpm pump.

14) Shaft

- 1) To be machined from one rod 2 in in dia. x 20 in
long
- 2) Estimated weight of rod approximately 14 lbs
- 3) Estimated casting requirements - one 30 lb ingot

VI. CORROSION AND METALLURGY (Cont'd)E. Zirconium Requirements for the Pilot Model Homogeneous Reactor15) Impeller

- 1) To be formed from two plates
 - a) 8 in diameter x 2.2 in thick
 - b) 8 in diameter x 1.5 in thick
- 2) Weight of each plate
 - a) 2.2 in plate 25 lbs
 - b) 1.5 in plate 17 lbs
- 3) Estimated casting requirements
 - a) One 50 lb ingot
 - b) One 40 lb ingot

16) Inlet Nozzle

- 1) To be machined from one rod 4 in diameter x 6 in long
- 2) Weight - 17 lbs
- 3) Estimated casting requirement - one 30 lb ingot

17) Sealing Ring

- 1) To be machined from one rod 3.5 in diameter x 3.5 in long
- 2) Weight of rod approximately 8 lbs
- 3) Estimated casting requirement - one 15 lb ingot

18) Labyrinth Collar

- 1) To be machined from 2 in diameter x 2 1/2 in length, bar stock
- 2) Estimated weight approximately two lbs

VI. CORROSION AND METALLURGY (Cont'd)E. Zirconium Requirements for the Pilot Model Homogeneous Reactor19) Labyrinth Discs and Spacers

- 1) To be machined from bar stock 2 inches in diameter x 4 in long.
- 2) Estimated weight approximately 3 lbs

20) Pump Housing Liners

- 1) To be formed from two sheets 12 inches in diameter x 1/4 inch thick
- 2) Weight of each sheet approximately 7 lbs
- 3) Estimated casting requirements
 - a) One 30 lb ingot or
 - b) Two 15 lb ingots

VI. CORROSION AND METALLURGY (Cont'd)E. Zirconium Requirements for the Pilot Model Homogeneous ReactorSUMMARY SHEET FOR ZIRCONIUM REQUIREMENTS

These figures are based on the accepted rule of 50% metal loss in fabrication.

<u>Item</u>	<u>Finished Weight (lbs)</u>	<u>Casting Weight and Number</u>	
1	154	2 at	150
2	18		40
3	114	6 at	40
4	105	6 at	40
5 (1)	28		60
5 (2)	11		20
6	15.	1 at	30
		or 2 at	15
7	94	10 at	20
8 (1)	78	5 at	30
8 (2)	14		30
8 (3)	9.3		25
8 (4)	2.2		
9 (1)	4.5		12
9 (2)	1.5		
9 (3)	70	7 at	20
9 (4)	154	6 at	40
10 (1)	11.5		30
10 (2)	2		
11	52		100
12	5		10
13	5		10
14	14		30
15 (1)	25		50
15 (2)	17		40
16	17		30
17	8		15
18 & 19	5		10
20	14	1 at	30
		or 2 at	15
<u>Total</u>			<u>1882</u>
	979		

VI. CORROSION AND METALLURGY (Cont'd)

F. Other Metals and Alloys

Corrosion tests under various conditions of exposure in uranyl sulfate solutions have continued at 100°C and 250°C with approximately 35 metals and alloys. Twenty-eight materials have been eliminated from the corrosion program as showing unsatisfactory corrosion resistance at 250°C. These materials are:

Ni Resist	K Monel	414 S.S.
Hastelloy D	Inconel	431 S. S.
Chlorimet 2	Inconel X	Duriment 20
Hastelloy A	Monel	Silicon Bronze
Tophet C	Nickel	SAE 1045
Chromax 527	Tophet A	Stellite
Tophet D	K42B	K42B
63 S Aluminum	Beryllium	
2S Aluminum	Lead	
Hastelloy B	Molybdenum	

Many of the materials undergoing test have shown good corrosion resistance to various uranyl sulfate media at 100°C but have failed in tests at 250°C.

100°C Corrosion Tests

A summation of the corrosion results obtained thus far on different metals and alloys at 100°C in uranyl sulfate media is shown in Table VI-8. These tests were run for 1344 hours.

VI. CORROSION AND METALLURGY (Cont'd)F. Other Metals and Alloys

TABLE VI-8

THE CORROSION OF METALS AND ALLOYS IN 0.168M
URANYL SULFATE AT 100°C

<u>Material</u>	<u>No Sulfuric Acid</u>		<u>0.35M Sulfuric Acid</u>	
	<u>Wt. Loss, mdm.</u>	<u>Mil/yr.</u>	<u>Wt. Loss, mdm.</u>	<u>Mil/yr.</u>
Lead	17.3	0.07	468.5	1.99
Columbium	21.1	0.12	16.3	0.09
Durichlor	171.6	1.17	388.0	2.64
Duriron	47.6	0.32	351.0	2.39
430 S.S.	38.9	0.24	245.0	1.53
446 S.S.	12.2	0.08	18.8	0.12
321 S.S.	10.0	0.06	15.7	0.10
302 S.S.	85.9	0.52	12.5	0.08
304 S.S.	4.0	0.02	36.4	0.22
316 S.S.	8.2	0.05	21.2	0.13
347 S.S.	2.8	0.02	15.9	0.10
317 S.S.	3.9	0.02	20.3	0.12
310 S.S.	4.0	0.02	5.2	0.03
309 S.S.	1.8	0.01	9.0	0.06
Worthite	6.2	0.04	113.9	0.69
Durimet 20	1.4	<0.01	82,850.0	500.00
Carpenter 20	2.4	0.01	16.6	0.99
Chlorimet 3	373.0	2.08	1,690.0	9.40
Titanium	3.9	0.04	55.2	0.59
Hastelloy C	69.3	0.31	831.0	4.46
Inconel	34.5	0.20	1,132.0	6.40
Inconel X	8.6	0.05	1,812.0	10.40
Palladium	3.4	0.01	0.4	< 0.01
Illium G	5.4	0.03	neg.	neg.
Platinum	4.2	0.01	8.2	0.02
Ticonium III	7.1	0.04	25.1	0.15
Stellite	0.7	<0.01	19.5	0.11
Tantalum	neg.	neg.	neg.	neg.
Silver	255.2	1.17	2,192.0	10.00
Gold	5.0	0.01	3.1	< 0.01
Rhodium	3.9	0.02	0.4	< 0.01

VI. CORROSION AND METALLURGY (Cont'd)

F. Other Metals and Alloys

Recently, it was thought that the free sulfuric acid could be eliminated from the uranyl sulfate solution. The presence of the sulfuric acid was originally intended to prevent the precipitation of uranyl peroxide formed by contact with hydrogen peroxide produced by irradiation of the uranyl sulfate solution. The existence of stable hydrogen peroxide at 250°C is most unlikely and it is believed that no precipitation of uranyl peroxide will occur. The fact also remains that decomposition of UO_4 to UO_3 is nearly complete at 200°C. If UO_3 is formed, it is likely that it would redissolve in the acid reactor medium.

With the temporary elimination of sulfuric acid from the system, the reactor solution composition resolves to 0.168M uranyl sulfate plus a small concentration of an oxidant, such as nitric or chromic acid, to ensure solution stability at 250°C. The problem remains of reevaluating the corrosion resistance of materials for component parts of the reactor system exposed to temperatures below 250°C. This re-testing program is now in process.

250°C Corrosion Tests

Table VI-9 shows test results at 250°C for different metals exposed to 0.168M uranyl sulfate with and without free sulfuric acid. In many of the tests, where the testing time exceeded 24 hours, solution decomposition took place. This phase of the program was conducted without the presence of an oxidant in the solution.

VI. CORROSION AND METALLURGY (Cont'd)F. Other Metals and Alloys

TABLE VI-9

THE CORROSION OF METALS AND ALLOYS IN 0.168M
URANYL SULFATE AT 250°C

<u>Material</u>	<u>No Sulfuric Acid</u>		<u>0.35M Sulfuric Acid</u>	
	<u>Wt. Loss, mdd.</u>	<u>Mil/yr.</u>	<u>Wt. Loss, mdd.</u>	<u>Mil/yr.</u>
Lead	122.3	15.8	262.0	33.4
Columbium	‡1995.0	--	neg.	neg.
Durichlor	404.5	82.5	323.0	65.8
Duriron	+ 578.2	--	742.0	151.5
430 S.S.	854.5	159.5	1127.0	211.0
446 S.S.	--	--	82.0	15.3
321 S.S.	192.9	34.7	10.1	1.8
302 S.S.	+ 895.0	--	908.0	165.6
304 S.S.	+ 490.0	--	--	--
316 S.S.	557.5	100.5	637.5	114.7
347 S.S.	172.9	29.7	543.5	98.6
317 S.S.	187.3	33.7	214.0	38.5
310 S.S.	245.3	46.0	3640.0	652.0
309 S.S.	7.9	1.4	149.0	27.1
Worthite	145.5	26.0	--	--
Durimet 20	348.0	62.9	--	--
Carpenter 20	204.5	36.8	--	--
Chlorimet 3	‡ 56.7	--	--	--
Titanium	9.4	--	--	--
Hastelloy C	112.2	18.1	--	--
Inconel	1067.0	181.0	--	--
Inconel X	391.5	67.4	--	--
Palladium	10.1	1.2	--	--
Illium G	80.5	14.0	--	--
Platinum	‡ 0.4	--	--	--
Ticonium III	51.9	9.0	--	--
Stellite	--	--	1502.0	254.5
Tantalum	‡ 151.2	--	--	--
Gold	‡ 4.1	--	--	--
Rhodium	‡ 0.6	--	--	--
K42B	--	--	3267.5	611.0

VI. CORROSION AND METALLURGY (Cont'd)

F. Other Metals and Alloys

Approximately ten of the materials in the preceeding table showed a corrosion resistance of 25 mils/year or less which might be permissible for the construction of heavy component parts. However, a large number of these metals and alloys could not be successfully used because of physical properties, poor neutron economy, and high cost.

Additional corrosion tests have been completed on a few stainless steels exposed to uranyl sulfate containing 0.35M sulfuric acid and 0.11M nitric acid. Tests were operated at 250°C for 164 hours. Solution decomposition did not occur. Results are included in Table VI-10.

TABLE VI-10

THE CORROSION OF STAINLESS STEELS IN 0.168M
URANYL SULFATE CONTAINING 0.35M Sulfuric
ACID AND 0.11M NITRIC ACID AT 250°C

<u>Material</u>	<u>Weight Loss,</u> <u>mdd.</u>	<u>Corrosion Rate,</u> <u>mils/year</u>
321 S.S.	374.5	67.6
347 S.S.	140.7	25.5
309 S.S.	186.6	34.1

Note The above figures represent an average for four tests on each type of stainless steel.

No improvement in the corrosion resistance of these stainless steels was evident by the addition of nitric acid to the system. With the exception of 321 stainless, the corrosion rates were increased over rates obtained in the acidified uranyl sulfate without the nitric acid. The appearance of the specimens had improved, however, inasmuch as there were no heavy black film depositions on the surfaces as previously encountered when the solution decomposed.

VI. CORROSION AND METALLURGY (Cont'd)F. Other Metals and Alloys

A series of tests was run with duplicate specimens of annealed stainless steels exposed to 0.168M uranyl sulfate containing 0.35M sulfuric acid and 0.2M chromic acid in place of nitric acid as an oxidant. Stainless steel Types 304, 316, 347, and 317 were annealed at 1950°F and quenched in water; 309 stainless steel was annealed at 2000°F and water quenched. Type 410 stainless steel, included in the test, was not annealed. Annealed specimens were pickled to remove scale, and all specimens were passivated in 30 percent nitric acid at 160°F for 40 minutes and exposed in air for four hours prior to test. The corrosion tests were run at 250°C for 138 hours. Data are shown in Table VI-11.

TABLE VI-11

THE CORROSION OF ANNEALED-PASSIVATED STAINLESS STEELS
IN 0.168M URANYL SULFATE CONTAINING 0.35M SULFURIC
ACID AND 0.2M CHROMIC ACID AT 250°C

<u>Material</u>	<u>Weight Loss, mdd</u>	<u>Corrosion Rate, mil/year</u>
304 S.S.	22.6	4.1
316 S.S.	28.6	5.1
347 S.S.	21.0	3.8
317 S.S.	26.2	4.7
309 S.S.	23.1	4.2
410 S.S.*	843.5	157.8

*Not annealed

A very marked improvement in the corrosion resistance of these stainless steels was observed. The unannealed 410 stainless steel specimens showed an extremely high rate of corrosion attack, however. The reasons for the improved corrosion resistance of the first five types of stainless are twofold; 1) annealing with subsequent passivation treatment, and 2) the presence of chromic acid acting as a corrosion inhibitor.

A similar series of tests was conducted with annealed stainless steel specimens in 0.168M uranyl sulfate containing 0.35M sulfuric acid and 0.11M nitric acid in place of chromic

VI. CORROSION AND METALLURGY (Cont'd)F. Other Metals and Alloys

acid. Specimens were annealed and passivated as described previously and were run in duplicate at 250°C for 138 hours. Results appear below.

TABLE VI-12

THE CORROSION OF ANNEALED-PASSIVATED STAINLESS STEELS
IN 0.168M URANYL SULFATE CONTAINING 0.35M SULFURIC
ACID AND 0.11M NITRIC ACID AT 250°C

<u>Material</u>	<u>Weight Loss,</u> <u>mdd</u>	<u>Corrosion Rate,</u> <u>mils/year</u>
304 S.S.	247.2	45.1
316 S.S.	103.2	18.7
347 S.S.	164.8	30.3
317 S.S.	116.5	21.0
309 S.S.	41.1	7.4

These results were not as good as those obtained with chromic acid in the uranyl sulfate solution. Thus, these two series of tests indicate that with sulfuric acid present, corrosion attack on annealed stainless steel specimens is inhibited far greater with chromic acid than nitric acid. In both types of test solution decomposition was prevented. Corrosion rates on the stainless steels were reduced roughly by a factor of 6 with chromic acid present rather than nitric acid.

Numerous tests have been started to determine the effects of chromic and nitric acids in uranyl sulfate containing no free sulfuric acid. Preliminary results at 250°C are shown in Table VI-13. Tests were run for 117 hours.

VI. CORROSION AND METALLURGY (Cont'd)F. Other Metals and AlloysTABLE VI-13

THE CORROSION OF STAINLESS STEELS IN 0.168M
URANYL SULFATE CONTAINING 0.2M CHROMIC ACID
OR 0.11M NITRIC ACID AT 250°C

<u>Material</u>	<u>0.2M Chromic Acid</u>		<u>0.11M Nitric Acid</u>	
	<u>Wt. Loss, mdd.</u>	<u>Mils/yr.</u>	<u>Wt. Loss, mdd.</u>	<u>Mils/yr.</u>
Durichlor	"	"	3.26	0.67
309 S.S.	+18.84	"	"	"
410 S.S.	"	"	3.45	0.65
309 S.S.*	"	"	1.35	0.25

*These tests were run without uranyl sulfate. Distilled water was adjusted to a pH of 2.5 with sulfuric acid to simulate 0.168M uranyl sulfate solution and then the water was made 0.11M in nitric acid. All tests were run in quadruplicate and the results represent average calculations.

In the absence of free sulfuric acid, nitric and chromic acids acted equally well in minimizing corrosion attack. The 309 stainless steel specimens exposed to the chromic acid solutions showed a tendency towards a slight film formation. This film was dark colored, extremely adherent, and very uniform. Other specimens showed a similar appearance. There were no indications that the uranyl sulfate solutions had undergone decomposition. All solutions and the films on the specimens are being checked chemically and microscopically.

The last set of tests with 309 stainless steel listed in the preceding table was conducted in distilled water adjusted to a pH of 2.5 with sulfuric acid to simulate the pH of a 0.168M uranyl sulfate solution. Nitric acid was then added to the water. This test was made to determine if uranyl sulfate itself contributed to the corrosion reaction. Corrosion tests with 309 stainless steel in 0.168M uranyl sulfate containing 0.11M nitric acid have not been completed and, therefore, it is not possible to draw any conclusions at the present time. These results will be included in a later report.

VI. CORROSION AND METALLURGY (Cont'd)

F. Other Metals and Alloys

Hydrogen peroxide was added to 0.168M uranyl sulfate solution containing 0.35M sulfuric acid and 0.11M nitric acid and corrosion tests were run on stainless steels at 250°C. The hydrogen peroxide molarity was 0.05 initially and no signs of uranyl peroxide precipitation were observed in the solutions at the beginning of the tests. The tests were run for 113 hours in quadruplicate. The solutions were pale yellow in color and slightly turbid at the end of the test. Average results appear in Table VI-14.

TABLE VI-14

THE CORROSION OF STAINLESS STEELS IN 0.168M URANYL SULFATE
CONTAINING 0.35M SULFURIC ACID 0.11M NITRIC ACID, AND
0.05M HYDROGEN PEROXIDE AT 250°C

<u>Material</u>	<u>Weight Loss, mdd.</u>	<u>Corrosion Rate, mils/year</u>
316 S.S.	89.2	16.0
317 S.S.	165.6	29.81
309 S.S.*	3.0	0.56

*This test was run in a similar solution
but in the absence of 0.35M sulfuric acid.

The absence of sulfuric acid plus the presence of hydrogen peroxide resulted in an extremely low corrosion rate for 309 stainless steel, 0.56 mil/year. This rate, however, was twice as great as the rate obtained in the water (pH 2.5) plus 0.11M nitric acid solution. A slight improvement in the corrosion resistance of 316 stainless steel in the peroxide solution was observed as compared to its resistance in similar solutions without hydrogen peroxide. At this point, corrosion data are not sufficient to permit any definite conclusions as to whether or not the presence of hydrogen peroxide (initially stable) is beneficial to the corrosion resistance of various materials at 250°C.

VI. CORROSION AND METALLURGY (Cont'd)G. Miscellaneous Corrosion Data

Zirconium Couple Tests - Several low and high temperature corrosion tests with B. M. zirconium coupled to a dissimilar metal have been completed. These tests were run in 0.168M uranyl sulfate containing 0.35M sulfuric acid at 100°C and 250°C. The 100°C tests were operated for 1344 hours; the 250°C tests were run for 173 hours. The zirconium was coupled to Illium G and K42B. Results of the tests appear in Table VI-15.

TABLE VI-15

THE CORROSION OF B. M. ZIRCONIUM COUPLES IN 0.168M
URANYL SULFATE CONTAINING 0.35M SULFURIC ACID

<u>Material</u>	<u>100°C</u>		<u>250°C</u>	
	<u>Wt. Loss, mdm.</u>	<u>Mils/yr.</u>	<u>Wt. Loss, mdd.</u>	<u>Mils/yr.</u>
Zirconium	55.7	0.42	‡ 36.8	-
Illium G	94.3	0.55	307.5	52.4
Zirconium	229.0	1.60	‡ 26.2	-
K42B	73.5	0.45	2990.0	548.0

The surface area ratio of zirconium to Illium G was approximately 1:1.6 (cm²) in both the 100° and 250°C tests. In both tests, the Illium G was attacked preferentially with zirconium acting as the cathodic member of the bimetallic couple.

The zirconium - K42B surface area ratio was 1:4 in the 100°C test and zirconium was preferentially attacked with K42B acting as the cathodic metal. The zirconium - K42B area ratio was 3:1 in the 250°C test and in this test the K42B underwent severe preferential attack. The zirconium specimens in both high temperature tests showed slight weight gains.

Uranyl Sulfate - Hydrogen Peroxide System

Laboratory tests were conducted to determine the effect of sulfuric acid concentration on the prevention of uranyl peroxide precipitation from uranyl sulfate solutions containing hydrogen peroxide. The volume of 0.168M uranyl sulfate used for each test was 50 ml and all tests were run at room temperature. Sulfuric acid molarities were selected to cover the range of

VI. CORROSION AND METALLURGY (Cont'd)G. Miscellaneous Corrosion Data

0.20 - 0.35M. These solutions had various amounts of dilute hydrogen peroxide added and were permitted to stand for 16-18 hours before observation. The results are presented in the following tables.

1) 0.20 M Sulfuric Acid

<u>Hydrogen Peroxide Molarity</u>	<u>Solution Condition (after 16 hrs.)</u>
0.0026	no ppt.
0.0130	no ppt.
0.0260	light ppt.
0.0390	heavy ppt.
0.0520	" "
0.0650	" "
0.0780	" "
0.0910	" "

2) 0.25M Sulfuric Acid

<u>Hydrogen Peroxide Molarity</u>	<u>Solution Condition (after 18 hours)</u>
0.0022	no ppt.
0.0110	no ppt.
0.0220	light ppt.
0.0330	light ppt.
0.0440	heavy ppt.
0.0550	" "
0.0660	" "
0.0770	" "

3) 0.30M Sulfuric Acid

<u>Hydrogen Peroxide Molarity</u>	<u>Solution Condition (after 18 hours)</u>
0.0020	no ppt.
0.0100	no ppt.
0.0200	no ppt.
0.0300	light ppt.
0.0400	heavy ppt.
0.0500	" "
0.0600	" "
0.0700	" "

VI. CORROSION AND METALLURGY (Cont'd)G. Miscellaneous Corrosion Data4) 0.35M Sulfuric Acid

<u>Hydrogen Peroxide Molarity</u>	<u>Solution Condition (after 16 hours)</u>
0.0018	no ppt.
0.0090	no ppt.
0.0180	no ppt.
0.0270	trace
0.0360	very light ppt.
0.0450	very light ppt.
0.0540	slight ppt.
0.0630	slight ppt.

These results show definitely that increasing concentrations of sulfuric acid retard the rate at which uranyl peroxide precipitation will occur from 0.168M uranyl sulfate solutions containing hydrogen peroxide. They also show that as low as 0.2M sulfuric acid concentration will probably prevent precipitation from uranyl sulfate solutions containing as high as 0.010M hydrogen peroxide. Based on these results, it would appear that the 0.35M sulfuric acid concentration suggested for use in the reactor medium is slightly on the high side. The proper sulfuric acid concentration, if found necessary, will be dependent upon whether or not and how much hydrogen peroxide is formed during the reactor operation.

General - After repeated use of the small, 300 ml capacity, stainless steel bombs for corrosion tests at 250°C, it has been observed that the most serious corrosion attack takes place at the solution-vapor interface. At these points on the bomb walls, pitting attack has been prevalent with pits sometimes reaching a depth of nearly 30-35 mils. Such data should be taken into consideration in the design of a reactor in that any point at which exists a liquid-vapor junction, will probably be more susceptible to a pitting type of corrosion attack.

VII. MISCELLANEOUS

A. Site Considerations

As can be seen from Figure VII-1, several sites have been considered for the Homogeneous Reactor. The Laboratory in its feasibility report will recommend Site B as being the best and safest available within the Oak Ridge reservation. Site B is located toward the south and east in the valley adjacent to Bethel Valley (the valley in which Oak Ridge National Laboratory is located). This valley is completely devoid of habitation or facilities and has numerous good reactor sites, all of which are about 2 miles from any property not owned by the Atomic Energy Commission. Site B is approximately $4 \frac{3}{4}$ airline miles from K-25, 5 miles from Y-12 and $\frac{1}{2}$ mile from any important X-10 building. Crude cost estimates were made with respect to the cost of developing each of these sites to a common standard, in which it was found that there was not over \$17,000 difference in cost between sites and that the extra cost of developing Site B over locating the reactor within the X-10 fence was about \$25,000. It would appear that this is a relatively minor expenditure compared with the large sum in personnel safety inherent in this location. Plans for site development, more detailed cost estimates, building and utilities as well as the detailed Health Physics situation will be presented in the forthcoming feasibility report.

B. Schedule

Referring to the schedule on Page 70 of ORNL-527, the 1/10 scale (Model I) experiments were completed in January, 1950. Operation of the full scale, low pressure system (Model II) was started in December, 1949. Full scale, high pressure system (Model III) will eventually become a full scale mock-up of the pilot reactor. Many of the components will be tested prior to their incorporation into this system. The status of this work is as follows:

1. Sufficient data should be available from Model II to establish the design of the core hydraulic system by March 31, 1950. Stainless steel hemispheres have been ordered and should be ready for assembly by April 15.

VII. MISCELLANEOUS (Con't.)Schedule (Con't.)

2. A 30 GPM recirculation pump has been installed in a high pressure test loop. This system will be used to obtain data on the pump, pipe joints, pressurizer, flow meter, pressure gages and heat transfer.
3. Design of the dump and concentrating systems is 80% complete and the tanks have been ordered. Completion of the design is expected approximately March 15, and all critical equipment should be ordered by this date. Satisfactory operation of this system may be expected in May, 1950.
4. A high pressure pump has been ordered for feeding soup at 1 GPM into the core. Delivery of this pump is expected about April 1. If satisfactory a duplicate pump will be used for the reflector feed.
5. Fundamental information needed for the design of a recombiner should be available approximately April 1, from test equipment which is now being installed. Completion of a satisfactory recombiner may then be expected approximately July 1, 1950.
6. If the Model III model is to be operating in June it appears now that it will be necessary to substitute stainless steel for zirconium parts for the first test. As zirconium parts become available, they will be used to replace equivalent stainless components.
7. It appears that if the Homogeneous Reactor is to receive its zirconium immediately after the first Naval Reactor requests are satisfied, Model III will not be an all zirconium system until August.

Engineering design and a construction proposal for the site and reactor building is being prepared with the recommendation that the facility be available for starting the installation of the reactor and associated components by October 1.

Assuring the availability of appropriate approvals and funds, the scheduled date at which the reactor should be operating is in the period between March and June of 1951.

VII. MISCELLANEOUS (Cont'd)

Homogeneous Reactor Project Organization
(Includes Part Time Personnel)

Project Engineer - C. E. Winters	(1)	
Assistant Project Engineer - C. Secoy*	(6)	
<u>Physics</u> - J. M. Stein, Leader	(10)	
		R. R. Coveyou (5)
		L. C. Noderer (3)
<u>Chemistry</u> - C. Secoy*, Leader	(6)	
<u>Radiation Stability</u> - E. H. Taylor	(6)	
		E. J. Boyle (6)
<u>Phase Rule Studies</u> - W. L. Marshall	(6)	
		J. S. Gill (6)
<u>Slurries</u>	(8)	R. C. Lovelace
<u>Recombination</u>	(7)	
		G. Clewett (7)
		D. W. Kuhn (7)
		A. D. Ryon (7)
		A. A. Palko (7)
<u>Corrosion</u> - J. L. English, Leader	(2)	L. L. Fairchild
		H. L. Barker
		S. H. Wheeler (2)
<u>Bearings and Joints</u> - J. Reed	(2)	
<u>Zirconium Procurement and Welding</u> - A. R. Olsen	(2)	
<u>Design</u>		
<u>Mechanical</u>	(4)	C. Segaser
<u>Experimental Engineering</u> - C. B. Graham, Leader	(2)	R. Smith
		W. B. Krick
<u>Calculations - Flow Sheets</u> - I. Spiewak	(2)	C. Burchell
<u>Models and Bubble Problem</u> - J. Culver	(2)	
		R. Wilson (2)

Experimental Engineering - C. B. Graham, Leader (2)

Test Soup H. C. Savage (2)

Dump System R. Van Winkle (2)

Process Instrumentation C. A. Mossman (6)

Participating ORNL Groups

Reactor Engineering Division (1)

Engineering Research and Development
Department (2)

Reactor Physics Department (3)

Design Department (4)

Mathematics Panel (5)

ORNL Chemistry Division (6)

Y-12 Chemistry Division (7)

Chemical Technology Division (8)

Instrument Department (9)

Loanee from Westinghouse (10)

Cooperating Installations

Battelle Memorial Institute - Zirconium Welding Problem

Consultants

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Plant - High Pressure Design and Techniques

F. N. Peebles - University of Tennessee - Bubble Rise
Problem