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**HOMOGENEOUS REACTOR EXPERIMENT-
QUARTERLY PROGRESS REPORT
for Period Ending February 28, 1951**

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SUMMARY

HRE Reactor Physics and Engineering. Design of the HRE is essentially complete, and procurement of equipment is in the final stages

The model 30A pump and test loop were operated over 1000 hr with uranyl sulfate at 1000 psi and 250°C. The solution showed a greenish discoloration soon afterward and was found to have a lowered uranium concentration. When the loop was disassembled, the pump was found to have a cracked front bearing (exposing unpretreated surfaces), and operation was suspended until the bearing could be replaced.

The model 100A pump and test loop were operated about 50 hr with water and 1% nitric acid at 1000 psi and 250°C. A voluminous reddish-brown precipitate was encountered in a run using demineralized water. Analysis of the precipitate showed it to contain >10% Fe, >5% Ni, 1% Si, 1% Co, 1 to 2% Cr, 1 to 2% Mn, and traces of Ca, Mg, Al, and Cu. The source of the precipitate is not known. No further difficulty was encountered during additional washings and the pretreatment, and the system is now operating with UO_2SO_4 at 1000 psi and 250°C.

Results of tests to date on various bearing materials for the 30A and 100A pumps indicate that stellite No. 6 bushings with graphitar bearings should operate satisfactorily. Other materials are being tested. During these tests it was noted that thrust loads on the pump bearing surfaces were excessive, and considerable effort was devoted to eliminating the thrust load.

Valve tests have shown solid stellite No. 6 plugs and seats to be satisfactory. There is some evidence that stellite No. 6 welded over 347 stainless steel on the plug and seat may be satisfactory.

Studies of the HRE core-gas-removal system showed an oscillation to be taking place in the vortex during operation. This resulted in oscillations in flow rate and pressure. The system operates quietly until a critical gas flow is reached, but then a very pronounced oscillation appears. There is evidence that the use of a surge tank will eliminate oscillations. The use of a 50% higher capacity pump for the feed water to the letdown heat exchanger also contributed to stability.

Mixing studies using dye have shown that there are regions in the core where the solution is by-passed to some extent and where the dye may have a slightly longer than average residence time. However, these studies were carried out under the somewhat unfavorable conditions of low temperature, and the situation is expected to improve at 250°C, where viscosity is lower.

A safety interlock circuit has been completed. It functions to prevent any operation which might cause the reactor to go critical before the safety plates are up and the reflector level is high enough to make them effective.

Out-of-Pile Corrosion. Emphasis has been placed on the study of HNO_3 - and CrO_3 -formed films which impart passivity to stainless steels in uranyl sulfate solution at 250°C. The application of these films has made the use of 347 stainless steel satisfactory in 0.17 M uranyl sulfate at 250°C under controlled laboratory testing conditions.

Type 347 stainless steel has been exposed to uranyl sulfate at 250°C for 32 weeks with one single initial pretreatment, resulting corrosion rates averaged 0.1 mil/year and less on HNO_3 -treated specimens, and 0.1 to 0.8 mil/year on CrO_3 -treated samples. Pretreating times of 4 hr at 250°C have been found as effective as 100-hr pretreating times for HNO_3 -formed films. Pretreating temperatures of 290°C resulted in a slight improvement in the corrosion resistance of 347 stainless steel exposed to uranyl sulfate at 250°C.

Stainless steel pretreated with HNO_3 can be exposed to air for 3 days at room temperature without losing its passivity in subsequent exposure to uranyl sulfate. A 7-day exposure in air after pretreating results in a destruction of passivity. It was also determined that (1) a HNO_3 -treated surface immediately exposed to uranyl sulfate at 250°C for 3 days retained its passivity after a 7-day exposure at room temperature, and (2) a HNO_3 -treated surface after standing in air for 7 days at room temperature was restored to its original passive state on being heated in water at 250°C or on being heated sealed with air in a test bomb at 250°C prior to the introduction of uranyl sulfate. Thermal cycling from room temperature to 250°C resulted in no loss of passivity by HNO_3 -treated stainless steel.

Scratches on HNO_3 -treated surfaces were found to be self-healing after exposure to uranyl sulfate at 250°C. The critical ratio of scratch area to solution volume was determined to be 1 cm² to 150 ml of solution. Exceeding

this scratch area resulted in solution reduction and corrosion attack on the stainless steel. The effect on HNO_3 - and CrO_3 -formed films of room-temperature exposure to oxygen, hydrogen, and nitrogen was investigated in relation to maintenance of passivity in uranyl sulfate at 250°C . The only failure observed was that of a HNO_3 -treated surface exposed to hydrogen gas.

Velocity effects at room temperature on HNO_3 -formed films were negligible; untreated specimens showed weight losses whereas HNO_3 -treated samples did not. A discussion of the possible mechanisms of protective film formation at 250°C is included. The operation of a 347 stainless steel thermal convection loop is described. The corrosion resistance of stainless steels, Bureau of Mines zirconium, titanium, tantalum, and other materials in 0.17 M uranyl sulfate at 250°C is reported.

The addition of 550 ppm of trisodium phosphate to distilled water at 200°C has resulted in a great improvement of the corrosion resistance of SAE 1030 carbon steel, even in the presence of hydrogen peroxide. The results of corrosion studies with uranyl fluoride and uranyl nitrate systems at 100°C are reported.

In-Pile Studies. Analytical data currently available indicate that high chloride ion content in solutions exposed to pile radiation is conducive to solution-corrosion failure, and, conversely, low chloride ion content tends to keep the solution good throughout the run.

An experiment in which the uranium precipitated during a pile shutdown was continued, and it was found that reducing the temperature of the bomb from 250 to about 175°C caused the uranium to go back into solution. This is presumably due to the fact that the higher concentration of peroxide at the low temperature oxidized the precipitated uranium and restored it to a soluble form.

Results of in-pile runs are described, and the general improvement in the appearance of samples after exposure is noted. Out-of-pile tests confirmed the detrimental effect of chloride ions in the bombs and also showed the need for changes in the design of the bombs.

A method is being developed for detecting the start of breakdown of the pretreatment film. This consists in using two electrodes to form two cells, "passivated steel | 0.2 M UO_2SO_4 | passivated steel," which are then balanced against each other. Failure of the film causes a potential to develop between

the two cells, and by measurement of this potential the failure can be detected.

Studies of the precipitation of uranium by peroxide indicate that uranyl sulfate in the concentration range 10 to 40 g of uranium per liter can be exposed to a flux of about 5×10^{11} at temperatures above 100°C without fear of UO_4 precipitation.

Recombination of Hydrogen and Oxygen. Tests of catalytic recombiners indicate that an alumina-base catalyst having 0.3% platinum will be satisfactory for use in the small catalytic unit which supplements the primary flame recombiner in the HRE off-gas system, provided the bed temperature is not allowed to fall below 500°C . The pilot model flame recombiner has been operated under conditions of temperature, pressure, composition, and flow rates that are expected during operation of the HRE. Design specifications established from these tests are reported.

HRE Chemical Studies. The solubilities of BaSO_4 and $\text{Y}_2(\text{SO}_4)_3$ have been measured at temperatures above 250°C and are reported. Calculations indicate that BaSO_4 will start to precipitate in from 30 min to 15 days. The uncertainty results from the unknown solubility of the xenon parent of barium and from the unknown activity or effective concentration of the sulfate ion.

Current evaluation of the most feasible methods for direct measurement of the reactor solution favors the determination of density using either the electromagnetic densitometer or the "Princo Densitrol," or both, and the determination of uranium concentration by its effect on the Q of a suitable high-frequency coil.

Experimental Program for the HRE. An integrated program of experiments for the HRE is presented with a discussion of some of the principal factors to be considered in carrying it out. To ensure the maximum information from the tests, they are graded on a basis of reactor power at which each is to be performed, ranging from subcritical conditions to full-power operation. The subcritical experiments are final test-loop runs to ensure satisfactory operation of the composite system.

It is proposed that after completion of the critical experiments most of the others shall be carried out at moderate temperature and power levels with temperature, pressure, and power being adjusted so that the gas effect will

approximate full-power operation. In this way many of the desired data may be obtained before the reactor is subjected to the more severe stability and corrosion conditions of high power and temperature.

From the time soup is introduced into the system, the reactor will provide a continuous source of material for a program of chemical tests covering solution stability, corrosion, fission products, and processing studies.

Long-Range Studies. The $\text{UO}_2\text{SO}_4\text{-UO}_3\text{-H}_2\text{O}$ system has been studied at 25 and 100°C and data are reported. Data are also reported for the $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ and the $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ systems.

Some progress has been made toward preparing UO_3 -water slurries stabilized with bentonite; however, a stable slurry has not yet been achieved. Thixotropic slurries of thorium oxide and water stabilized with bentonite have been prepared, and their stability at 250°C and 1000 psi has been demonstrated for as long as 450 hr.

A glass model of a slurry-pumping system has been set up and used to pump BaSO_4 slurries in preparation for future studies of pumping of UO_3 slurries.

Investigations of possible homogeneous reactor fuel-processing methods indicate that ion exchange shows promise. Radiation stability measurements on Dowex 50 resin indicate that it may be expected to last only about 1 day under actual operating conditions.

1. HRE REACTOR PHYSICS
AND ENGINEERING

DESIGN PROGRESS

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A flow diagram of the HRE process as conceived at the time of writing of this report is shown in Fig. 1. The status of procurement of each item of equipment is indicated by shading. Most of the pipe and fittings are now on hand, and procurement has started on concrete blocks to be used in construction.

Since the time of the last quarterly report (ORNL-925) the following changes have been made in the design:

1. Feed pumping capacity in the reflector system has been increased from 1 to 3 gpm by addition of two Pulsafeeder heads. It is now possible to raise the reflector level from half full to full in approximately 20 min.
2. Silica gel absorbers have been replaced in the reflector and soup off-gas systems by cold traps for removal of moisture in effluent gas streams. Two cold traps which are to be operated at -40°F are arranged in parallel in each system. One trap in each system will be defrosting while the other is operating.
3. A small Pulsafeeder pump has been added to pump 1 gal/hr of condensate from the soup gas condenser into the motor end of the soup-circulating pump. This will purge the bearings so that they will be running in relatively clean water instead of soup.

Bellows Valve Operator. An experimental all-metal bellows-valve operator has been designed and built for testing. If it proves satisfactory it will be used in place of the diaphragm operator for all valves in the system subject to radiation damage. This includes the soup letdown valve and approximately thirteen other valves in the soup compartment.

Soup-Circulating Pump. An experimental modified form (Fig. 2) of the Westinghouse canned rotor pump has been designed and is being constructed as a possible alternate soup-circulating pump. It will operate with the shaft vertical and will have two mechanical shaft seals, one to separate 1000-psi

FIG. 2
SHAFT SEAL MODIFICATIONS FOR MODEL 100A PUMP

soup in the pump from 1050-psi water and the other to seal the water from high-pressure helium in the motor. Water will be circulated through the intermediate chamber at a rate of approximately 1 gal/hr. It is planned also to try the pump with sleeve type bearings instead of the ball bearings shown and with the motor chamber filled with oil at high pressure.

An alternate type of seal suggested by Dura Seal Company can be used in which the bellows is replaced by a metallic chevron packing.

PUMPS AND VALVES

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Soup-Recirculating Test Loops. The model 30A pump and test loop (previously operated for approximately 1000 hr with uranyl sulfate) have been operated for an additional 184 hr with uranyl sulfate at 1000 psi and 250°C. Samples taken at frequent intervals indicated no change in concentration or appearance of the soup up to 161 hr of continuous operation. At this time some of the soup volume was lost through a small leak, making a comparative concentration check impossible. However, the normal yellow color of the solution had changed to a yellow-green.

The system was filled with fresh soup and operated for an additional 23 hr. A sample taken at this time showed a decided green color and had a concentration of 19.8 g of uranium per liter. There was evidence of a small amount of oxide precipitation. Addition of nitric acid to the solution increased the U(VI) concentration to 28.8 g of uranium per liter, indicating that some reduction to U(IV) had taken place. The front bushing of the pump was found to be cracked, and operation of the system was suspended at this point until it could be replaced.

The precipitate of uranium oxide is now being removed from the system with a water solution of Na_2CO_3 followed by hot 10% HNO_3 . The cracked bushing has been replaced, and, after passivation with 1% nitric acid, operation of this system with uranyl sulfate will be continued.

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The 100A pump and test loop described in ORNL-925 were run about 50 hr at 1000 psi and 250°C using both water and 1% nitric acid. Most of this time was spent in checking the pump bearings and the automatic control equipment.

The test loop became pressurized with helium, and an immediate problem arose in preventing helium gas from collecting in the pump rotor cavity. In view of past experience it was deemed advisable to convert to a steam pressurizer. While waiting for the necessary equipment, the bearing tests described below were made after an orifice plate was inserted in the system to maintain the rated pump flow and head.

After one 4-hr test run using demineralized water, a large quantity of reddish-brown material was found suspended in the water; it did not settle out of a sample left standing for two weeks. The source of this material is not definitely known. All the usual precautions of degreasing, etching, and rinsing of the system had been taken prior to any operation. The test loop was made of 347 stainless steel with heliarc welding throughout with the exception of one O-ring flange and gasket. A visual examination of interior surfaces does not reveal any corrosion or erosion. Additional runs have not produced a recurrence of the phenomenon to this degree; however, runs with distilled water at 500 to 1000 psi and 150 to 250°C show evidence of small amounts of foreign material. Spectrographic analysis of the original reddish-brown material showed it to contain >10% Fe, >5% Ni, 1% Si, 1% Co, 1 to 2% Cr, 1 to 2% Mn, and traces of Ca, Mg, Al, and Cu. Further investigations are expected to reveal that freshly etched surfaces, until passivated, are subject to hot-water corrosion.

The steam pressurizer has now been installed and the entire system re-etched with 15% H_2SO_4 followed by a 10% HNO_3 —3% HF solution. An analysis of the last cold distilled-water rinse, which was flushed through with the pump off, showed less than 1 ppm of Cl^- and less than 2 ppm of F^- . Following this re-etching, hot distilled water was circulated through the system with the pump running and was found to be discolored on removal. A second hot-water rinse (approximately 150°C) was tried with very little improvement in discoloration. A 1% HNO_3 solution was added, and the system was run at 250°C for approximately 1 hr, after which discoloration of the solution was noted. A second 1% HNO_3 solution pumped at 1000 psi and 250°C appeared almost clear

when drained. The system was then passivated for 6 hr with the 1% HNO_3 . This solution was water clear on draining. Uranyl sulfate solution (30 g of uranium per liter) was added, and the system is now operating at 1000 psi and 250°C. Frequent samples will be removed and checked for concentration of uranium, Cl^- , and F^- . In addition, periodic analyses for Fe, Cr, and Ni will be made. This procedure will be used on all soup-recirculating loops.

An additional 100A pump and a 30A pump have been received and are to be set up and run in loops similar to those already in operation. Since the 30A pump is to operate eventually in the D_2O reflector system, it will be run only on distilled water with the original titanium carbide and graphitar No. 14 bearings and nickel labyrinths and gaskets. The new 100A pump, however, will be equipped with Haynes alloy 98M2 and graphitar No. 14 bearings. The present nickel labyrinths and gaskets will be replaced with tantalum.

Bearings for the Recirculating Pumps. The model 100A and 30A Westinghouse pumps, as received, are equipped with titanium carbide bushings and graphitar No. 14 bearings. The titanium carbide bushings in the 100A pump are unsatisfactory for operation in the soup system and will be replaced because the nickel binder is attacked in the HNO_3 passivation. The titanium carbide bushings will be retained in the model 30A pump which is to be used in the reflector (D_2O) system.

Replacement bushings of hardened 410 stainless steel have been tried in a model 100A and a model 30A pump with unsatisfactory results. After recent visits to Westinghouse Electric Corporation, it was concluded that bushing materials harder than the 410 stainless steel must be used. The Rockwell hardness of the titanium carbide is approximately C-70 as compared to approximately C-35 for the 410 stainless steel. Westinghouse has several pumps, of both the 30A and 100A types, with titanium carbide bushings and graphitar No. 14 bearings which have well over 2000 hr operating time on water with no measurable bearing wear.

In view of the above information a second set of bushings of stellite No. 6 was installed in a model 100A pump. After approximately 50 hr of operation with both water and 1% nitric acid no radial bearing wear was observed, but considerable wear occurred on the front bearing thrust surface. This condition was unexpected since Westinghouse checks and eliminates thrust

loads in these pumps prior to shipment.⁽¹⁾ Using their method of eliminating thrust, the pump rotor was corrected to a "floating" position between the thrust faces and is now ready for operation with soup after the usual pre-treatment of the system.

Although it is anticipated that the stellite No. 6 bushings will operate satisfactorily, bushings of Haynes alloy 98M2 have been procured with a Rockwell hardness of C-60 and C-65. These are now being installed in a 100A pump just received. This pump will be checked to eliminate rotor unbalance and thrust loads prior to any operation.⁽¹⁾ It will then be installed in a test loop now under construction.

In order that the new system will simulate the reactor system, it is being built with provision for clean water feed, at approximately 1 gal/hr, into the rear of the 100A rotor cavity. This would allow the bearings to operate in water and prevent any abrasive particles from entering them. Some additional advantages of this system are (1) removal of any gas that is formed in the pump cavity, thus eliminating the necessity of venting the pump; (2) elimination of the possibility of corrosion of the 0.040-in.-thick inconel barrier separating the rotor cavity and field coils; and (3) elimination of contact between soup and graphitar bearings.

As mentioned previously, the model 30A pump was found to have a cracked front bushing after 184 hr of operation although the rear bushing and bearing were still in excellent condition. The bushings in this pump were chrome-plated 410 stainless steel hardened to Rockwell C-38. Wear resistance was good and operation was very satisfactory even with the cracked bushing. The cracked bushing could have been caused by hydrogen embrittlement from the chrome-plating operation or by too much interference between shaft and bushing. Attempts to determine the exact cause are being made. This bushing has been replaced with one made of Haynes alloy 98M2, the rotor and impeller have been rebalanced, and the pump has been installed in the test loop.

Radial Bearing Load in 100A Pump. In investigations using the Westinghouse 100A totally enclosed pump, one of the problems is to reduce bearing wear to a practical minimum. This wear depends upon several variables, one of which is the radial load caused by the hydraulic unbalance in the centrifugal type pump rotor. The direction and magnitude of this load are unknown.

(1) *Axial Thrust in Westinghouse Totally Enclosed Centrifugal Pumps, Model 100A*, WAPD-EM-54, Westinghouse Electric Corp., Atomic Power Division, Pittsburgh, Pa., Jan. 11, 1951.

On January 30 an experiment was started in an effort to evaluate the magnitude of the radial unbalance. In the test apparatus a standard motor is used and the Westinghouse pump impeller, thermal spacer, and pump housing are used in conjunction with a bearing fitted with strain gauges. Use of these strain gauges is expected to permit determination of the radial bearing load characteristics as a function of pump capacity. The work is approximately 70% completed.

Soup-Feed Pumps (Pulsafeeders). A Lapp Pulsafeeder feed pump (with bolted head design) has been operated for more than 700 hr. This includes approximately 300 hr on water, approximately 400 hr on soup, and approximately 50 hr on 1% nitric acid. Operating conditions are 0.85 to 0.95 gpm at 1000 psi head with solution temperature in the pump head of 80 to 85°C. The 1000-psi pressure drop is across two air-operated Fulton-Sylphon valves in parallel, and the temperature above the valves is maintained at 115 to 120°C. These valves are removed and inspected periodically for erosion and/or corrosion of the plugs and seats. The soup in the Pulsafeeder system shows no change in concentration or appearance after the 400 hr of operating time. The interior surfaces of lines and valves show no change in surface finish or condition (except two valves as noted below). Operation of this system will be continued, and at some future date the bolted pumping head will be disassembled for inspection of the 0.020-in.-thick diaphragm.

A remote pumping head of all-welded construction to replace the bolted head in this Pulsafeeder has been received. A tap for leak detection has been incorporated in the design. In addition, a second 1-gpm Lapp Pulsafeeder, similar to the above except for all-welded heads and using a belt drive rather than a gear drive, has been received. This unit will be installed in the mock-up.

Valve Tests in the Feed-Pump Loop. To date three valves have been removed and inspected. The first valve contained a stellite No. 6 plug and a seat made by welding stellite No. 6 on the wearing surface of 347 stainless steel. Erosion of the 347 stainless steel outer portion of the seat was noted after 22 hr of operation with soup at 115 to 120°C. The stellite was undamaged. This valve had previously been etched with an acid ferric chloride solution and passivated with 1% HNO_3 . The cause of failure of the base metal in this valve is unknown. The materials in the seat are being studied by the Metallurgy Division.

A valve with a hardened 410 stainless steel seat and 347 stainless steel plug was installed next. After being etched with 15% H_2SO_4 and HNO_3 -HF and passivated for 4 hr with 1% HNO_3 , this valve was operated on soup at 115 to 120°C for 124 hr. The valve seat (410 stainless steel) showed objectionable corrosion.

Another valve having a stellite No. 6 plug and a stellite-faced 347 stainless steel seat identical with the previously described valve which corroded in 22 hr showed no corrosion or erosion after 160 hr of operation with a 1000-psi drop using soup at 115 to 120°C. As a check on these results, one more valve of similar construction is now being installed for testing.

A stellite No. 6 plug and stellite No. 25 seat have been installed in the Fulton-Sylphon valve for use in the Pulsafeeder system. This valve has been tested for 400 hr on soup but has not yet been removed for inspection. It has been found to leak approximately 25 cc/min against a 1100-psi head when the valve is closed. Static corrosion tests at 100°C indicate that stellite No. 25 will not be satisfactory, and therefore this valve will be removed in the near future and replaced by one using a more promising material.

Valve seats of solid stellite, types Nos. 1, 3, and 6, have been ordered and will be tested when received. The results mentioned above indicate that welded stellite No. 6 will be satisfactory if a suitable explanation can be found for the negative results in the first test, but that a solid stellite seat would be preferable.

HRE CORE-GAS-REMOVAL SYSTEM

J. S. Culver R. H. Wilson
C. D. Zerby

All previous tests on the gas-removal system in the mock-up have been run with a high-pressure gas-liquid separator. However, it was felt that a flow-sheet more closely resembling that of the reactor should be used in the next phase of the program, and to this end the entire system was modified as described below.

Apparatus. Water is run in the soup-circulating system with helium admitted in the inlet stream to simulate gas in the reactor. Gas flows are measured by a rotameter after the gas has passed through the dump tanks and the condenser, where the accompanying liquid stream is removed and the steam is condensed. In Fig. 3 it will be seen that the soup-circulating system and gas-removal circuit closely resemble the reactor flowsheet with the exception of the pressurizer. Since the steam pressurizer was not available, a system employing helium was substituted and so constructed that it would be essentially a constant-pressure device to control all expected fluctuations in pressurizer level. To accomplish this a standard helium cylinder was inverted and connected by copper tubing to the top of the pressurizer. Total gas volume in this arrangement is approximately 44 liters as compared to the normal steam-pressurizer gas volume of only 0.1 liter. Since the system operates at 1000 psi, this larger volume allows a maximum fluctuation of about 2.3 psi. Another feature of the present system is the provision of windows in the core tank to permit visual observation of the vortex in operation. Moving pictures of vortex oscillation have been successfully made and will be taken from time to time as developments warrant.

A weigh tank and load beam type of level indicator has been installed on the pressurizer. Satisfactory control of pressurizer level using this device to operate the letdown valve will require additional work, but it shows considerable promise.

Early experience with the letdown valve showed it to be seriously affected by the violent surges in the two-phase letdown stream. Installation of a valve positioner has virtually eliminated this problem, as demonstrated by a dial indicator clamped to the operator.

Much effort has been expended on developing a letdown system which will operate smoothly over all ranges of gas flow expected in the reactor. Based on 50 ev per ion pair, the rate of gas formation would be about 200 cc/sec of dry gas at reactor conditions or about 1000 cu ft/hr at standard conditions. A constant water stream of 0.673 gpm was removed with the gas.

Problems Encountered in the Letdown System. When the system was first operated it immediately became apparent that a periodic contraction of the vortex void was taking place. As soon as gas was admitted at flow rates

FIG. 3
FLOW SHEET FOR HRE MOCK-UP.

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comparable to those expected in the reactor, regular oscillations appeared in the vortex, gas rotameter, and pressure gauge above the letdown valve.

Several arrangements were tested, and from Table 1 it will be seen that in each case the system oscillated at some gas flow. It is interesting to note that the bore of the $\frac{1}{2}$ -in. tube and the annulus between the tube and $\frac{1}{2}$ -in. pipe have almost identical cross-sections, yet the annulus will pass over twice as much gas at a higher temperature before oscillation occurs. Comparison of hydraulic radii shows a value of 0.094 for the tube and only 0.031 for the annulus. As a result of these observations two smaller tubes, a $\frac{3}{8}$ -in. tube and a $\frac{1}{4}$ -in. tube, were tested to observe the effect of higher velocities. The $\frac{3}{8}$ -in. tube was shown to be inoperable at any gas flow, and the $\frac{1}{4}$ -in. tube was a poor second to the larger annulus.

The next tests were run with a heat exchanger made of a 20-ft length of $\frac{1}{4}$ -in. pipe inside of a piece of $\frac{1}{2}$ -in. pipe 19 ft 3 in. long. All subsequent tests have been made with the letdown stream of gas and water in the annulus of this exchanger. Its hydraulic radius is 0.021 in.

In Table 1 and Fig. 4 the effect of temperature is clearly shown. Data taken over the temperature range available, using building steam in the circulating stream heater, show that instability of the vortex occurs at lower gas flows as temperature increases. Values actually measured fall short of maximum design gas flow (approximately 1000 cfm), indicating the need for design of a letdown channel that will not oscillate, or for some device to suppress changes in vortex volume to allowable limits. The volume change based on estimated vortex size compared favorably with displacement of the pressurizer level. Various combinations of gas flow, geometry, and temperature gave values of from 10 to 150 cc for the volume change in the vortex.

Since the system as a whole could not be made to operate smoothly, a series of tests was run to test various components of the system independently. First, a hand valve was inserted in the letdown line as close to the reactor as possible, which is actually about 5 in. from the vortex (see Fig. 5). Although the frequency of oscillations was high (102 cycles/min) and the amplitude was only about 50 cc, the vortex continued to oscillate without any heat exchanger. However, closing the valve to the helium cylinder in the pressurizer stopped the oscillations.

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TABLE 1

Results of Tests* in Different Types of Letdown Channels

TYPE OF CHANNEL	CHANNEL FLOW AREA (sq in.)	LIQUID VELOCITY AT 1 gpm (ft/sec)	HYDRAULIC RADIUS (in.)	TEMPERATURE (°C)	MAX ALLOWABLE GAS FLOW WITHOUT OSCILLATION (cu ft/hr)
1/2-in. tube in 1/2-in. pipe, 100 ft long					
Tube	0.110	2.91	0.094	50	480
Annulus	0.108	2.96	0.031	162	1000
1/4-in. pipe, 30 ft long	0.1041	3.08	0.091	50	100
3/8-in. tube, 50 ft long	0.0605	5.3	0.069	145	0
1/4-in. tube, 50 ft long	0.0276	11.6	0.047	147	398
1/4-in. pipe in concentric 1/2-in. pipe, 20 ft long, annulus only	0.074	4.44	0.021	40 143 158 190 202	1220 950 715 580 505

*All these runs were made at an operating pressure of approximately 1000 psi.

Figure 5

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Figure 6

Figure 7

The next test was made with gas admitted to the letdown stream between the reactor and the heat exchanger as shown in Fig. 6. This test showed the system to oscillate with no vortex void and even with the Westinghouse circulating pump off. Here again isolating the helium cylinder in the pressurizer system stopped the oscillation.

In Fig. 8 data taken with this last system are compared with those taken in runs made under similar temperature conditions on the original equipment with a vortex void. The comparison seems to indicate that the presence or absence of a vortex void has little to do with the oscillation. These curves also indicate the nature of the phenomenon. The system operates quietly until the critical gas flow is reached, at which time a very pronounced oscillation appears. The frequency increases slightly with gas flow, but gas flow rates that are twice the calculated maximum requirement fail to stop the oscillation.

Two interesting tests being run as this report is written show the most promise of all attempts to remedy the situation. A small surge tank installed as shown in Fig. 7 was found virtually to eliminate oscillations at all gas flows. Some random fluctuations occur, but they have no definite pattern. The amplitude of the fluctuations is about 50 cc at double design gas flow rates. These tests are being run at 150°C.

The small triplex pump used for the 1-gpm feed in place of the Pulsafeeder was recently repacked and now delivers a full 1 gpm, an increase of about 50% over former tests. Under these conditions marked improvement in stability is observed, and, when the system is coupled with the small surge tank, no oscillation occurs over the full gas range available.

Plans for Future Testing. Since it is evident that temperature plays an important part in the behavior of the system, a new heater for the main (100-gpm) circulating system is being built and will be supplied with 750-psi steam from a 40-kw electric boiler, now being fabricated. This heater will allow 250°C operation with gas flowing, thereby producing reactor temperature conditions.

Work on vortex oscillation will continue until smooth operation can be assured under all reactor conditions.

MIXING IN THE HRE CORE

I. Spiewak and J. O. Bradfute

The work on mixing as reported in ORNL-794 presents a qualitative picture of the flow patterns encountered in the HRE. In order to make an accurate prediction of the temperature distribution of the operating reactor, more quantitative data are needed, and a program in which the transparent plastic sphere will be used has been undertaken to obtain data which can be used to define the operating characteristics clearly. The work is planned as follows:

1. A thorough qualitative investigation of the flow pattern at low temperature will be undertaken.
2. A quantitative study of flow at low temperature will be made.
3. The temperature of the water will be varied to enable a quantitative investigation of the effect of changing the properties of the liquid.

The first part of this program has been largely completed. Dyes which could be introduced at almost any point in the sphere by means of a 1/8-in. stainless steel probe were bled into the full-scale model running at 100 gpm. This probe was found to disturb the flow pattern somewhat, but the information obtained is considered to be reasonably accurate.

It was found that the entering water stream produced a turbulent region along the walls of the sphere. This region, about 3 in. wide at the equator and perhaps $\frac{1}{2}$ in. wide at the poles, has the characteristic rotation of the rest of the sphere, but there is a considerable component of velocity along the sphere walls by-passing the heart of the reactor. This is shown in Fig. 9.

At the central axis of the sphere there is a sharply defined region of constant angular velocity, B region, which has an overall diameter, as determined by probe measurements, of about 5.4 cm. It loses its sharp identity only at the top of the vessel, in the proximity of the water outlet pipe, where there are considerable turbulence and mixing. The B region contains an inner tubular-shaped column of water approximately 1.8 cm in diameter and an outer annulus. Solution appears to enter the outer annulus near the outlet and flow down almost to the south pole, turn around, and go up the inner tube.

FIG. 9
FLOW PATTERN IN THE HRE CORE

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The flow rate is about $6\frac{2}{3}$ gpm, which amounts to a residence time of about 2.5 sec in B region. In the vicinity of the outlet about 2 gpm appears to go out the gas vent, the remainder being swept out with the main stream. If the liquid flow is reduced to 1 gpm through the gas vent, no significant change can be observed. The above data indicate that B region will be adequately cooled.

Surrounding B region is another annular cylinder with an outside diameter of about 10.5 cm. This is a region of upward component of flow with a velocity of 18 in./sec. The throughput, about 45 gpm, flows uniformly from bottom to top. This stream appears to be supplied by the by-passed liquid from the lower hemisphere.

Between the outermost by-passing region and the central updraft, the solution rotates with less turbulence, apparently depending principally on mixing with the by-passing streams to remove dye. This will be referred to as "C region." A typical dye run would be observed as follows:

1. Potassium permanganate bled continuously into the inlet stream first colors the region near the walls of the globe.
2. The central updraft region darkens.
3. Dye mixes into the main body of liquid from outside to inside, the process producing a uniform color throughout in about a minute.
4. When the dye is turned off, initial lightening is observed near the walls and in the central axis. Dye persists in the main body of liquid, disappearing last from a torus in the lower hemisphere outside the central axis (C region). The entire process occupies about 2 min after the dye is shut off.

Some quantitative data have been obtained by bleeding permanganate and methyl red into the sphere and measuring the rate of change in concentration upon shutting off the dye. Samples may be obtained continuously with the probe and analyses made colorimetrically. Traverses of the cold sphere have been made along a radius at the equator, and the qualitative observations have been confirmed. It has been noted that the disappearance of dye in all cases has been exponential, indicating a mixing rather than a slug-flow phenomenon. These data are still incomplete, however,

It is planned to scan the effect of changing the flow rate and introduction of gas on the rate of dye disappearance. It is further planned to repeat these experiments at about 120°F to examine the effect of changing viscosity. Also, it is proposed to record temperature data at various points when hot and cold water are mixed in the sphere. It is hoped that from these data an accurate prediction of temperature distribution in the HRE core can be obtained.

Some inferences regarding HRE mixing may be drawn by applying theory to some of the existing qualitative information. The half-residence time (analogous to half-life) of liquid in the reactor may be defined as the time it would take for half the existing molecules in the reactor to find their way to the exit. This quantity is not the same for slug flow as for mixed flow because with mixing some molecules find their way out in a second, and some may take hours, although the probability of the latter is very low.

While slug-flow half-residence time is 4.0 sec in this reactor, for perfect mixing this quantity would be 5.4 sec. If dye in the worst portion disappears in 120 sec, the half-residence at that point is 15 sec, which is about three times longer than the average (using 9°C water).

However, it is recognized that mixing is a function of the Reynolds number. Because of the decreased viscosity at elevated temperature, operating Reynolds numbers will be about ten times those observed, so that mixing resistances should be an order of magnitude less. This will tend to reduce nonuniformities, and therefore experiments at higher temperatures are expected to produce more favorable information. Further improvement may be expected as a result of the centrifugal action on lighter (warmer) liquid and the effect of bubbles as they pass through the liquid.

CONTROL AND SIMULATOR

The safety interlock circuit design for the nuclear and process instrumentation has been completed. It is shown in Fig. 10. The essential functions may be briefly summarized as follows: No operation which might cause the reactor to go critical can be performed until the safety plates are up and the reflector level is high enough to make them effective. The reactor may then

MONITRONS
23 - STEAM
24 - D₂O OFF GAS
25 - SOUP CIRC. OIL
66 - VENTILATORS
68 - STACK GASES

SIZ - SOUP CIRC. PUMP				
CONTACT	JOG	STOP	RUN	START
1				X
2			X	X
3-	X			

MONITRONS
23 - STEAM
24 - D₂O OFF GAS
25 - SOUP CIRC. OIL
66 - VENTILATORS
68 - STACK GASES

be made critical with concentration variation alone or with concentration and rod control. Safety interlocks prevent improper operation of the pumps, provision being made through a "start-run" switch for special operation necessary at start-up. Serious faults in the reactor components will shut the reactor down while minor faults will give an alarm. The control plate drives may be tested in position when the reflector is down since the reactor cannot go critical under this condition.

Additional data have been obtained from the simulator described in ORNL-925. Typical results for a neutron lifetime of 1.5×10^{-4} sec are presented in Figs. 11 through 13. These summarize data obtained for combinations of delayed neutron groups ranging from all out to all in. When a delayed group was cut out, it was replaced by the corresponding prompt neutrons; thus the curves for all delayed groups out is the result which would be obtained if all neutrons were prompt.

CONSTRUCTION

The HRE building was essentially complete at the end of this quarter. Beneficial occupancy of the building was obtained on March 5, 1951, and installation of the reactor was started immediately.

Excavations for the foundation under the reactor shield and for the underground piping have been started. The only installation remaining to be done is that which pertains directly to the reactor, its controls, and its components.

Figure 14 shows the HRE building at the completion of the contractor's construction.

FIG. 11

6K STEP FUNCTION

FIG. 12

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FIG. 13

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FIG.14 HRE BUILDING

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2. CORROSION AND RADIATION STABILITY

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OUT-OF-PILE CORROSION

J. L. English and A. R. Olsen

Introduction. During the past quarter work has been concerned primarily with studies on the nature and characteristics of the protective film formed on stainless steel surfaces by treatment in dilute nitric or chromic acid at 250°C. With controlled laboratory conditions (stagnant and no irradiation) the pretreated films on stainless steels have successfully withstood corrosion attack by 0.17 M uranyl sulfate at 250°C for periods of six to eight months. Resulting corrosion rates have been almost negligible, 0.1 mil/year and less in most cases.

In order to determine the effect of fluid movement on the behavior of pretreated stainless steel surfaces, two large-scale dynamic test loops are being installed. These units will operate at temperatures of 100 and 150°C and at velocities up to 25 ft/sec with 0.17 M uranyl sulfate solution. They will be constructed entirely of stainless steel.

A more thorough knowledge of the operation of uranyl sulfate systems at 250°C will be obtained by the installation of six stainless steel thermal convection test loops. The capacity of these loops, one of which is now in operation, is 1100 ml and the solution velocity is expected to approach 4 ft/sec.

Detailed corrosion data on stainless steels, zirconium, titanium, and other metals and alloys were included in ORNL-925, *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950*. These data showed that 347 stainless steel and other types were perfectly satisfactory, in a pretreated condition, for containing 0.17 M uranyl sulfate at 250°C under the conditions of laboratory tests. Zirconium and titanium metals were shown to be excellent substitutes for stainless steel, especially in view of the fact that initial pretreatment in dilute nitric or chromic acid is not a prerequisite for use in uranyl sulfate at 250°C.

The results of corrosion studies during the past quarter are divided into several sections:

1. Film Studies on Pretreated Stainless Steels.
2. Corrosion Resistance of Stainless Steels.

3. Corrosion Resistance of Zirconium.
4. Corrosion Resistance of Reflector Materials.
5. Miscellaneous Corrosion Studies.
6. Uranyl Fluoride Corrosion Studies.
7. Uranyl Nitrate Corrosion Studies.

Film Studies on Pretreated Stainless Steel. Previous studies on 347 stainless steel pretreated in 1% HNO_3 or 2% CrO_3 at 250°C showed that:

1. The presence of heavy oxide layers or welding scale made the pretreatment ineffective for withstanding corrosion attack by uranyl sulfate at 250°C.
2. Pretreatment times of 4 to 24 hr in 1% HNO_3 at 250°C resulted in equally excellent corrosion behavior of 347 stainless steel in uranyl sulfate at 250°C; i.e., a pretreatment time of 24 hr afforded no greater protection than a 4-hr pretreatment time.
3. Heating surfaces pretreated with nitric or chromic acid in air at temperatures of 100 to 200°C for a period of 1 to 2 hr resulted in a destruction of the pretreatment film.
4. Exposure periods of 7 days in air at room temperature after pretreatment resulted in a loss of the protective influence of nitric acid-formed films during later exposure to uranyl sulfate at 250°C.
5. Exposure to air for periods of 7 days in contact with uranyl sulfate solution at room temperature resulted in no loss of the protective nature of nitric acid-pretreatment films.
6. The presence of 25 ppm of chloride ion in uranyl sulfate at 250°C destroyed the nitric acid-pretreatment film.
7. The presence of scratches on nitric-or chromic acid-pretreated surfaces resulted in no loss of passivity.
8. The nitric acid-pretreatment layer was found to be 5 to 7 μ in overall thickness; the layer formed over the substrate layer during corrosion testing did not, because of its porous nature, appear to be protective; the pretreatment layer has not been identified, but the principal constituent of the layer formed during corrosion testing was either Cr_2O_3 or a Fe_2O_3 .

Although the major portion of work on pretreated stainless steel surfaces has concerned the nitric acid pretreatment, the use of chromic acid pretreatments has met with equally good results. It has been established that chromates are decomposed by irradiation, but experimental evidence, microscopic examination, and the fact that CrO_3 is thermally decomposed at temperatures exceeding 196°C , have indicated that the film formed on stainless steel exposed to 2% CrO_3 at 250°C is a reduced chromium oxide. In this state of reduction, the effect of irradiation might be expected to be almost negligible on the film stability.

The nitric acid—pretreatment film, however, was judged the better film because it appears thinner, harder, and less porous than the chromic acid film, and in general more closely approaches the qualifications for an ideal protective film.

The film formed on conditioning stainless steel in 1% HNO_3 at 250°C has been found extremely stable under controlled conditions and its effect has been to make the stainless steel passive to 0.17 M uranyl sulfate at 250°C . Passive films, in general, are of a delicate nature, i.e., slight changes in operating conditions or mishandling of the film can result in destruction of the film and therefore corrosion attack on the metal. In uranyl sulfate solutions this corrosion attack is of medium intensity and is accompanied invariably by a reduction of U(VI) to U(IV). If reduction is permitted to continue, uranium oxides, predominantly U_3O_8 and some UO_2 , are formed. The following section of this report deals with a study of the two types of protective films with the ultimate objective of producing a more stabilized type of film which will not be subject to destruction by slight changes in exposure or operating conditions.

Single initial pretreatments on 347 stainless steel with 1% HNO_3 or 2% CrO_3 at 250°C have prevented corrosion attack by 0.17 M uranyl sulfate at 250°C for periods of 27 to 32 weeks. The tests, which involve weekly inspection of the samples, frequent chemical analysis of the solution, and weekly replacement of the uranyl sulfate, are continuing. Numerous tests of this type run during the past nine months show clearly that stainless steel surfaces can be made completely passive to uranyl sulfate at 250°C for indefinite periods. Corrosion rates on 347 stainless steel pretreated in 1%

HNO_3 generally average less than 0.1 mil/year; corrosion rates of 2% CrO_3 —pretreated 347 stainless steel tend to run between 0.1 and 0.8 mil/year, indicating that this type of film may be less completely effective than the nitric acid—pretreatment film.

Data obtained with nitric acid pretreatment on stainless steel show conclusively that the length of pretreatment time between 4 and 100 hr is not a critical factor in determining the life expectancy of these films in uranyl sulfate at 250°C. Tests using pretreating times of 4, 8, 12, 24, and 100 hr show no significant difference in effect on corrosion behavior of 347 stainless steel after exposure periods of 20 weeks or more in 0.17 M uranyl sulfate at 250°C. The corrosion rates are almost negligible, and the data indicate that the mechanism by which passivity of the stainless steel is obtained is realized during the first 4 hr of pretreatment. There is therefore no advantage in extending the pretreatment time past 4 hr. The data are summarized in Table 2.

TABLE 2

Effect of Length of Pretreatment Time on Corrosion Rates

PRETREATMENT TIME (hr)	EXPOSURE TIME AT 250°C (weeks)	CORROSION RATE (mil/year)
4	20	0.002
8	20	0.015
12	20	0.002
24	18	0.012
100	15	0.017

The effect of increasing the pretreatment temperature to 290°C rather than 250°C was studied, using 1% HNO_3 and 2% CrO_3 . The pretreatment time was 24 hr in each case, and the corrosion tests were run at 250°C in 0.17 M uranyl sulfate with weekly replacement. At the end of 8 weeks, the CrO_3 -treated specimen of 347 stainless steel exhibited a corrosion rate of 0.13 mil/year. During the first four weeks of the test, the original dull black pretreatment

film appeared to dissolve gradually from the surfaces of the specimen, leaving a highly lustrous, metallic-colored, and almost invisible film. This film was completely protective during the remaining four weeks of the test. The original weight increase of the specimen caused by the pretreatment was 106.9 mg/dm²/day. At the end of four weeks, the original layer had been completely removed and the specimen showed a slight weight loss; after eight weeks the weight loss was 0.73 mg/dm²/day, corresponding to a corrosion rate of 0.13 mil/year. The HNO₃-treated specimen was tested for ten weeks and the sample exhibited a weight gain of 0.42 mg/dm²/day at the end of the test. A very uniform dull black film covered all surfaces of the sample. Samples from the 290°C pretreatment tests will be examined microscopically for any differences between the structure or characteristics of these films and those formed at pretreatment temperatures of 250°C. A more detailed study of 290°C pretreatment temperatures will be conducted during the next quarter.

Nitric acid—pretreated type 347 stainless steel was allowed to stand in air at room temperature for periods of 48 and 72 hr and then for 12 weeks was placed in contact with 0.17 M uranyl sulfate at 250°C. The specimen which stood in air 48 hr showed a corrosion rate of 0.007 mil/year at the end of the 12 weeks; the film was lustrous and brown colored. The specimen exposed 72 hr to air exhibited a weight gain of 0.005 mg/dm²/day at the end of 12 weeks and was dull black. Although it has been determined that a nitric acid—pretreated surface will lose its passivity after standing in air for 7 days, these data indicate that an air exposure time up to 72 hr results in no decrease in the protection afforded by the pretreatment film.

Thermal cycling effects on nitric acid—pretreated surfaces were investigated. The test procedure consisted of pretreating a 347 stainless steel sample and bomb in 1% HNO₃ for 24 hr at 250°C, placing 0.17 M uranyl sulfate and sample in the test bomb, and alternately heating the bomb to 250°C for 1 day and cooling for 1 day. The solution and sample were inspected during each cooling period. After 10 days of alternate heating and cooling, the test specimen was dull black and showed a corrosion rate of 0.13 mil/year. No solution reduction was detected chemically, and it was concluded that thermal cycling had no effect on the passivity of nitric acid—pretreated stainless steel.

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Corrosion tests were run in which three type 347 stainless steel specimens which had been treated with 1% HNO_3 at 250°C for 24 hr were allowed to stand in contact with 0.17 M uranyl sulfate solution at room temperature for periods of 2, 3, and 7 days before being placed in uranyl sulfate at 250°C for 12 weeks. The uranyl sulfate solution was replaced weekly. All samples withstood corrosion attack satisfactorily with no loss of passivity or reduction of the uranyl sulfate solution. Corrosion rates at the end of 12 weeks ranged from 0.001 to 0.02 mil/year on the three specimens. Similar tests are now being carried out, using water and inert atmospheres to determine if the passivity may be retained at room temperature for indefinite periods in contact with these media.

Two tests were run to determine the stability of the HNO_3 -treated film after exposure to air at room temperature for periods of 7 to 14 days. The conventional HNO_3 pretreatment, 24 hr in 1% HNO_3 at 250°C, was employed on type 347 stainless steel specimens. The samples were then placed in 0.17 M uranyl sulfate in type 347 stainless steel bombs for 3 days at 250°C. At the end of this time, the solution was drained and the test bombs and samples were allowed to stand dry and exposed to air, one for 7 days and the other for 14 days. After the air exposures, both bombs and samples were re-exposed to 0.17 M uranyl sulfate at 250°C. The 7-day air-exposed bomb and sample have been in contact with uranyl sulfate for two weeks with negligible corrosion attack and no solution reduction. The 14-day air-exposed bomb and sample showed corrosion attack on the stainless steel and reduction of the uranyl sulfate solution at the end of one week. Although these data indicate that the uranyl sulfate run at 250°C immediately after the pretreatment imparts additional stability to the HNO_3 -formed film, additional studies will have to be made before any definite conclusions can be made.

Interesting results were obtained from other tests which were made in attempts to increase the stability of the HNO_3 -treated films. Samples of 347 stainless steel and test bombs were pretreated in 1% HNO_3 at 250°C for 24 hr and then allowed to stand exposed to air at room temperature for a period of 7 days. One test assembly was sealed and heated, empty, to 250°C for 24 hr; the other test unit was partially filled with distilled water, sealed, and heated for 24 hr at 250°C. The bombs were then filled with 0.17 M uranyl sulfate and kept at 250°C for 3 days. No reduction of the sulfate occurred. The bombs

were next permitted to stand empty and exposed to air at room temperature for two weeks, after which time they were run again with uranyl sulfate at 250°C for 10 days. A period of dry exposure to air at room temperature for 7 days followed, and the bombs were again run in uranyl sulfate at 250°C for 7 days. These tests were marked by the absence of uranyl ion reduction during the entire run. The corrosion rate, based on 20 days in 0.17 M uranyl sulfate at 250°C, was negligible on the water-treated specimen, but the air-treated sample showed a weight increase of 0.25 mg/dm²/day.

A preliminary conclusion from these data is that if for reasons other than actual reduction of the uranyl ion in a nitric acid—pretreated stainless steel system at 250°C it becomes necessary to interrupt reactor operation, the passivity of the pretreatment film could be restored by heating in air or water prior to introduction of uranyl sulfate into the system. This treatment, however, would be effective only if the pretreatment film remained undisturbed during previous operation in uranyl sulfate at 250°C.

A study was made of the effect on film stability in uranyl sulfate at 250°C of scratching pretreated stainless steel surfaces. The techniques employed were:

1. Type 347 stainless steel pretreated in either 1% HNO₃ or 2% CrO₃ for 24 hr at 250°C; deep single scratch made across face of specimen; specimens then exposed to 0.17 M uranyl sulfate at 250°C.
2. Type 347 stainless steel pretreated in either 1% HNO₃ or 2% CrO₃ for 24 hr at 250°C; exposed to 0.17 M uranyl sulfate at 250°C for one week; deep single scratch made across face of specimen; exposed to 0.17 M uranyl sulfate at 250°C.

There were no evidences in any tests of passivity breakdown, solution reduction, or corrosion attack. The scratched areas did not act as a focal point for intensified corrosion attack or reduction of the sulfate solution. The samples all had black lustrous surfaces, and, during exposure, the scratches changed from a metallic color to a light gray color. Samples showed slight weight gains of from 0.1 to 0.9 mg/dm²/day at the end of 4 to 7 weeks of exposure. The results of these tests indicate strongly that the protective film has self-healing properties. This self-healing phenomenon is perhaps related to the presence of small quantities of dissolved oxygen initially present in the uranyl sulfate test solution.

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In connection with the above scratch tests, a series of tests was run to determine if a critical ratio existed between the area of a scratched surface and the solution volume used in the test. Test specimens consisted of 316 stainless steel pretreated 24 hr in 1% HNO_3 at 250°C. After the pretreatment, the film was completely removed in accurately measured areas by scratching the specimen surfaces. The samples, each of which had a surface area of 34.1 cm^2 , were then exposed in 150 ml of 0.17 M uranyl sulfate at 250°C. Test data are summarized in Table 3.

TABLE 3

Ratio of Scratch Area to Total Area and Solution Volume

SPECIMEN	SCRATCH AREA (cm^2)	RATIO OF SCRATCH AREA TO TOTAL AREA ($\text{cm}^2:\text{cm}^2$)	RATIO OF SCRATCH AREA TO SOLUTION VOLUME ($\text{cm}^2:\text{ml}$)
1	0.09	1:380	1:1667
2	0.15	1:227	1:1000
3	0.25	1:137	1:600
4	0.50	1:68	1:300
5	1.00	1:34	1:150
6	1.50	1:23	1:100
7	2.00	1:17	1:75
8	3.00	1:11	1:50

Samples 1 through 5 have been exposed successfully to uranyl sulfate at 250°C for three to five weeks. The behavior of these samples has been identical to that of previously described* single-scratch tests, a slight darkening of the scratch areas being the only visible sign of change from the original appearance. Samples 6 through 8, however, showed corrosion attack and uranyl

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sulfate reduction at the end of one week. If a critical ratio of scratch area to solution volume exists, these data show it to occur at a value of 1 cm² to 150 ml of solution. These tests are being continued and samples have been submitted for optical examination of the films on the specimens.

Stainless steel surfaces, initially pretreated in 1% HNO₃ or 2% CrO₃ for 24 hr at 250°C, were exposed individually to oxygen, hydrogen, and nitrogen gases at room temperature for 24 hr immediately after the pretreatments. The purpose of these tests was to determine if exposure to the various gas atmospheres would prolong or shorten the life expectancy of the protective films on subsequent exposure in 0.17 M uranyl sulfate at 250°C. Data are listed in Table 4.

TABLE 4

Effect of Various Gases on Film Life Expectancy

PRETREATMENT ACID	ATMOSPHERE	URANYL SULFATE EXPOSURE (weeks)	CORROSION (mils/year)	SAMPLE APPEARANCE
HNO ₃	O ₂	10	0.02	Shiny gray metallic color
CrO ₃	O ₂	7	0.24	Gray metallic color
HNO ₃	H ₂	1	(+174.7 mg/dm ² /day)	Flaky black film
CrO ₃	H ₂	7	0.13	Gray metallic color
HNO ₃	N ₂	2	0.23	Gray metallic color
CrO ₃	N ₂	6	0.28	Lustrous metallic color

Previous work had shown that when hydrogen was introduced into the system or when treated surfaces were pre-exposed to hydrogen atmospheres, HNO₃-treated systems showed solution reduction and corrosion attack on the sample, but CrO₃-treated systems showed no solution reduction or sample corrosion attack.

In this work an unusual result occurred. The samples had a much better appearance than specimens of 347 stainless steel pretreated in HNO₃ or CrO₃.

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and then exposed directly to uranyl sulfate; that is, they had no visible film but were lustrous, metallic gray in color, and exceptionally clean-appearing. In previous tests the usual color of pretreated specimens after uranyl sulfate exposure ranged from dull black to shiny black.

The effect of gas exposures after pretreating will be studied further along two lines: (1) increasing life expectancy of films for continuous operation in uranyl sulfate at 250°C, and (2) stabilizing the pretreatment films for intermittent operation involving dry exposure to air at room temperatures.

In order to study the effects of velocity on film resistance at room temperature, specimens of HNO₃-treated and untreated 347 stainless steel were rotated at peripheral velocities of 2, 6, and 10 ft/sec. A definite increase in corrosion of the untreated specimens occurred as the velocity was increased from 2 to 10 ft/sec; changes in velocity of the treated samples had no effect on the corrosion behavior except to show that the weight gain at 10 ft/sec was not so great as the weight gain at 2 and 6 ft/sec. The data summarized in Table 5 indicate that the pretreatment film will be wear-resistant in the range of velocities encountered in the operation of the reactor experiment. Similar tests will be carried out at higher temperatures.

TABLE 5

Velocity Effects on Film Resistance

EXPOSURE TIME (weeks)	VELOCITY (ft/sec)	CORROSION OF UNTREATED SPECIMENS		CORROSION OF HNO ₃ -TREATED SPECIMENS	
		(mg/dm ² /day)	(mils/year)	(mg/dm ² /day)	(mils/year)
5	2	-0.04	0.007	+0.07	
5	6	-0.11	0.010	+0.08	
5	10	-0.24	0.040	+0.03	

Techniques other than the use of HNO₃ and CrO₃ which were used in the attempts to produce a film on 347 stainless steel that would successfully

resist corrosion attack by uranyl sulfate at 250°C are described below:

1. The test bomb and sample were first heated in air for 24 hr at 250°C to determine if additional protection was imparted to the HNO_3 treatment by first increasing the thickness of the natural oxide layer on the stainless steel. This was followed by heating to 250°C in 1% HNO_3 for 24 hr. After exposure for three weeks to 0.17 M uranyl sulfate at 250°C, the samples showed an average corrosion rate of 0.05 mil/year and were dull black in color. The test was therefore successful. Tests will also be run using this treatment to determine the behavior of the film in uranyl sulfate after exposure periods to air at room temperature.
2. The test bomb and sample were heated in air at 250°C for 24 hr and then exposed to uranyl sulfate at 250°C. Solution reduction occurred and the sample exhibited a large weight increase, 20.8 mg/dm²/day, owing to adhering deposits of uranium oxides. Similar tests will be run using oxygen, nitrogen, and other gases rather than air during the initial heating.
3. A corrosion-test specimen of 347 stainless steel which had previously been exposed for 12 weeks to uranyl sulfate at 250°C was placed back into the uranyl sulfate after exposure to air for 12 days. After 168 hr the solution deteriorated and the specimen showed a corrosion rate of 1.9 mils/year. From this information, it is apparent that even after long-time successful exposure to uranyl sulfate at 250°C, the protective film is not stabilized sufficiently to be protective after extended exposure to air at room temperature.
4. An attempt was made to pretreat a stainless steel bomb by exposing it to a concentrated uranyl sulfate solution, 204 g of uranium per liter, at 250°C for 24 hr. Precipitation of uranium oxides occurred, as was expected, during this run. The solution was removed and a 0.17 M uranyl sulfate solution was placed in the bomb for 24 hr at 250°C. Solution reduction took place and the sample exhibited a weight gain of 58.9 mg/dm²/day.
5. Samples of 347 stainless steel were electropolished in a mixture of phosphoric acid, glycerin, and water at 100°C and then pretreated in 1% HNO_3 and 2% CrO_3 for 24 hr at 250°C. Some of the pretreated samples were submitted for optical examination, and others were exposed to uranyl sulfate at 250°C. Solution reduction occurred in the test on CrO_3 -treated specimens, but in the test on HNO_3 -treated specimens there was no reduction after one week. The corrosion rate of the HNO_3 -pretreated specimen was 0.012 mil/year; the appearance of the sample was characterized by brilliant interference patterns and a highly lustrous surface.

A difference in surface condition may account for the complete difference in behavior of the HNO_3 - and CrO_3 -pretreatment films. These data also indicate that the mechanism of the two treatments may be different. Additional tests will be made to study this phenomenon further.

6. A sample of 347 stainless steel was pretreated in an equivolume mixture of 1% HNO_3 and 2% CrO_3 at 250°C for 24 hr. This specimen, unlike specimens normally encountered in either HNO_3 or CrO_3 pretreatment, was uniformly pink in color and highly lustrous. The sample was then placed in uranyl sulfate, where it has been at 250°C for two weeks without solution reduction or excessive corrosion. The pink color has remained unchanged although the sample has shown a weight gain of $1.1 \text{ mg}/\text{dm}^2/\text{day}$. This test and others like it are being continued.
7. Sodium nitrate, 0.1 M, has been found partially successful for pretreating type 347 stainless steel surfaces. Tests are in progress in which (1) the surfaces were pretreated in 0.1 M NaNO_3 for 24 hr at 250°C and (2) the uranyl sulfate solution was made 0.1 M in NaNO_3 . Corrosion rates after three weeks at 250°C in 0.17 M uranyl sulfate have averaged 0.07 mil/year.

The standard nitric acid—pretreatment film has been found completely resistant to highly concentrated solutions of uranyl sulfate at 250°C . After six weeks of operation, the corrosion rate in uranyl sulfate containing 104 g of uranium per liter is 0.05 mil/year; the corrosion rate in uranyl sulfate containing 204 g of uranium per liter is 0.08 mil/year.

A marked improvement in the corrosion behavior of 347 stainless steel in 0.1 M H_2SO_4 has been obtained by the use of the HNO_3 pretreatment. A pretreated specimen exposed to 0.1 M H_2SO_4 at 250°C for 168 hr showed a corrosion rate of 16.6 mils/year, a rate which is lower by a factor of several thousand than that normally encountered, and was covered with a smooth adherent green film. The sample was then exposed to 0.17 M uranyl sulfate at 250°C for 168 hr, during which solution reduction occurred. The corrosion rate of the sample in the uranyl sulfate was 1.7 mils/year. The specimen at this stage was coated with a hard and tenacious, completely uniform black film, although normally when solution reduction occurs the sample acquires a flaky and spotty black film.

A HNO_3 pretreatment followed by an exposure of one week in 0.17 M uranyl sulfate at 250°C has resulted in an even more pronounced improvement in

sulfuric acid resistance, the corrosion rate in 0.1 M H_2SO_4 for one week at 250°C being reduced to 5.3 mils/year as compared to 16.6 mils/year obtained above. These studies will be continued.

In summarizing the work during the past quarter, new information may be added to previously mentioned data on the pretreatment of type 347 stainless steel surfaces for protection against uranyl sulfate at 250°C. These new data are as follows

1. Pretreatment at 290°C instead of 250°C with either 1% HNO_3 or 2% CrO_3 in general appeared to afford slightly better corrosion resistance to uranyl sulfate at 250°C.
2. Thermal cycling of HNO_3 -treated stainless steel in uranyl sulfate from room temperature to 250°C resulted in no loss of passivity.
3. Undisturbed HNO_3 -treated films, which normally lose their passivity after extended exposure to air at room temperatures, were shown to keep their passivity in uranyl sulfate at 250°C after exposures of one to two weeks in air at room temperature when (a) heated in water for 24 hr at 250°C, or (b) heated with the bomb sealed and dry at 250°C for 24 hr prior to the introduction of sulfate.
4. The stability of a HNO_3 -treated film was increased by a short run in uranyl sulfate at 250°C after the pretreatment. This film retained its passivity in uranyl sulfate after an exposure of 7 days to air at room temperature.
5. The HNO_3 - and CrO_3 -treated films have been found, by the use of scratch techniques, to be self-healing.
6. A critical ratio of scratch area on a HNO_3 -treated surface to uranyl sulfate solution volume was determined to be 1:150, i.e., 1 cm^2 of scratched area to 150 ml of solution.
7. Exposure of HNO_3 - and CrO_3 -treated surfaces to oxygen and nitrogen at room temperature resulted in no loss in passivity to uranyl sulfate at 250°C. Hydrogen gas exposure destroyed the passivity of HNO_3 -treated surfaces but not of CrO_3 -treated surfaces.
8. The wear resistance of HNO_3 -treated surfaces to velocities of 2 to 10 ft/sec in uranyl sulfate at room temperature was superior to the wear resistance of untreated specimens.

9. Sodium nitrate was used successfully to make stainless steel passive to uranyl sulfate at 250°C. Pretreatments using mixtures of HNO_3 and CrO_3 indicate great promise.
10. The HNO_3 -treated bombs have been used successfully to contain heavily concentrated uranyl sulfate solutions (104 to 204 g of uranium per liter) at 250°C.
11. The HNO_3 -treated film has improved the resistance of 347 stainless steel to 0.1 M H_2SO_4 at 250°C.

Sufficient data have not been obtained thus far to establish definitely the exact mechanism of formation of the protective films. In the case of the nitric acid pretreatment, the film is undoubtedly produced by an interaction between the thermal decomposition products of nitric acid and the natural oxide layer always present on stainless steel surfaces. It has been definitely established that this film, and not a film formed during exposure to uranyl sulfate at 250°C, is the film that causes initial passivation of the stainless steel.

One explanation of the mechanism of formation of the nitric acid film is that the thermal decomposition products of nitric acid, possibly NO and O_2 , react with the metal surfaces by satisfying residual valences. Since molecules such as NO and O_2 are considered to have residual valences also, the saturation of the residual valences on the metal by these molecules results in an extremely strong type of bonding, much stronger than that due to physical adsorption by Van der Waals' forces. This bonding then leads to passivation of the stainless steel.

Results of film studies, which are described elsewhere* in this report, have shown diffuse electron-diffraction patterns which indicate the presence of a hydrous oxide. The fact that pretreated specimens lose their passivity after exposure to air at room temperature for periods exceeding 7 days indicates that the film may be losing water of crystallization formed in it at 250°C. This is further substantiated by the data which showed that passivity could be restored to an undisturbed pretreatment film exposed to air for 7 days or more by heating in water at 250°C. However, the fact that similar results were obtained by merely heating the undisturbed film at 250°C in a sealed test bomb indicates that perhaps an additional mechanism is present.

Nitric acid—pretreated films have been found to be magnetic, which would indicate the existence of α Fe_2O_3 or Fe_3O_4 . Actually, the temperature of

*Section on electron microscope studies.

pretreating, 250°C, may be considered on the low side of high-temperature oxidation so that transition products may be partially responsible for the passive effects obtained. In many cases corrosion or reaction products formed at elevated temperatures are different, either in form or degree of hydration, from those formed at room temperature, and the exact temperature of transition from one form to the other is not known. Electron diffraction studies by Hickman and Gullrasser on 18-8 stainless steel in the temperature range of 300 to 500°C have shown that the oxide formed at 300°C is Fe_3O_4 .

Much work remains to be done on the study of pretreatment films and their characteristics. A concentrated effort will be made during the coming quarter to increase the knowledge of these films.

Corrosion Resistance of Stainless Steels. One of the six thermal convection loops described in the last quarterly report (ORNL-925) has operated for a period of 17 days at 250°C in 0.17 M uranyl sulfate. No indication of solution reduction has occurred during this run although a precipitation did occur the first time an attempt was made to run the system with uranyl sulfate. This failure was caused by unavoidable interruption of operation and a resulting deviation from the planned procedure for testing. A brief log of operations follows:

1. The system was degreased and etched in 15% H_2SO_4 for 20 min, followed by 20 min in 20% HNO_3 —3% HF solution. Etching was done at room temperature. The system was thoroughly rinsed with demineralized water after each operation.
2. The system was pretreated 8.7 hr with 1% HNO_3 at 250°C.
3. 1050 ml of 0.17 M UO_2SO_4 was placed in the system and heating was started. Heating was interrupted by (1) control thermocouple failure, (2) leak development in helium pressurizing system, and, finally, (3) burnout of heater. These failures caused a 3-day delay after the initial pretreatment, and the uranyl sulfate concentration decreased from 40 to 10.4 g of uranium per liter during subsequent operation at 250°C for 4 hr.
4. The system was re-etched in the same manner as in the initial etching operation, which included a soaking period in 5% Na_2CO_3 for 20 min followed by thorough rinsing with demineralized water.
5. Additional removal of precipitated uranium oxides was accomplished by means of two 20-min exposures to 10% HNO_3 at 130 to

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140°C. These combined treatments removed a total of 24.8 g of uranium per liter. This value, plus values of 3.4 and 3.6 g of uranium per liter from the sulfuric and nitric—hydrofluoric acid treatments, plus the residual solution content of 10.4 g of uranium per liter gives a total of 42.2 g of uranium per liter, which is reasonably close to the original content of 42.0 g of uranium in 1050 ml of solution.

6. The system was treated for 20 hr in 1% HNO_3 at 250°C.
7. 1050 ml of uranyl sulfate solution, 39.1 g of uranium per liter, was placed in system and heated to 250°C.
8. The unit was operated at 250°C for 404 hr. This testing time was interrupted by one 3-day period at room temperature and one 1-day period at room temperature, during which times the solution remained in the test loop. Samples were withdrawn every other day for analysis, which involved a shutdown period of 2 hr. The results of U(VI) analyses during the test are shown in Table 6.

TABLE 6

Results of U(VI) Analyses

OPERATION (hr)	U(VI) CONTENT (g/liter)
0	39.1
67	43.0
113	43.1
159	43.0
229	51.6
275	39.4
328	39.5
364	39.8
404	40.0

An increase in uranium concentration was observed during the first 229 hr. During this period a gradual leak developed in the sample withdrawal valve. This leak resulted in crystallization of uranyl sulfate inside the

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outlet pipe which was flushed into the next sample withdrawn. A new sample withdrawal method was devised which eliminated this problem as evidenced by the consistent analyses, starting with the 275-hr exposure time. The slight discrepancy in values for the last four samples with the original content of 39.1 g of uranium per liter may be attributed to the $\pm 2\%$ accuracy in the colorimetric method for uranium analysis. Analyses for U(VI) and U(IV) are made on the solutions as withdrawn from the system.

The five other thermal loops are rapidly approaching the completion stage and will be placed in operation in several days.

Types 347 and 410 stainless steel have been exposed to 0.17 M uranyl sulfate containing 1% HNO_3 at 250°C for 38 and 32 weeks, respectively. These samples were not initially pretreated, but nitric acid was added to the test solution weekly. The corrosion rate of 347 stainless steel was 0.15 mil/year; the 410 stainless specimen showed a weight gain of 0.35 mg/dm²/day. Both samples were in excellent condition at the end of the tests.

Specimens of 347 stainless steel were pretreated in 1% HNO_3 for 24 hr at 250°C and then exposed in the vapor phase above 0.17 M uranyl sulfate solution at 250°C. After 10 weeks the corrosion rate of the specimen was 0.2 mil/year and the sample had a dull black uniform film; no indication of any significant increase in corrosion attack as a result of vapor exposure was observed.

Numerous heliarc-welded samples of various stainless steels have been subjected to either HNO_3 or CrO_3 acid pretreatments and exposed to uranyl sulfate at 250°C. The results of these tests have been excellent, as shown in Table 7. The samples all exhibited glossy black surfaces when the initial treatment consisted of polishing but were dull black in color when the initial treatment consisted of etching. There were no signs of intergranular corrosion on the heat-affected zones around the weld.

Stainless steel specimens were heliarc welded with no additional heat treatment, and, after metallurgical polishing and etching, were examined for

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TABLE 7

Results of Acid Pretreatment of Heliarc-Welded Stainless Steels

TYPE OF STAINLESS STEEL	INITIAL TREATMENT	PRETREATMENT	EXPOSURE (weeks)	WEIGHT CHANGE (mg/dm ² /day)	CORROSION RATE (mils/year)
309	Polished	1% HNO ₃	12	-0.03	0.005
316	Etched	1% HNO ₃	15	+0.002	
316	Polished	2% CrO ₃	12	-0.83	0.15
347	Etched	1% HNO ₃	7	-0.64	0.12
347	Etched	2% CrO ₃	4	-0.42	0.08

signs of intergranular corrosion attack after exposure to 0.17 M uranyl sulfate at 250°C. The sample histories appear below:

No. 639: Type 309 Cb stainless steel; heliarc welded; polished on Nos. 80 and 120 emery paper to remove outer weld layer; pretreated 24 hr in 1% HNO₃ at 250°C; exposed 14 weeks to 0.17 M uranyl sulfate at 250°C; corrosion rate, 0.005 mil/year; no solution reduction during test.

No. 640: Type 347 stainless steel; heliarc welded; polished on Nos. 80 and 120 emery paper to remove outer weld layer; pretreated 24 hr in 1% HNO₃ at 250°C; exposed five weeks to 0.17 M uranyl sulfate at 250°C; solution reduction occurred during fifth week of test owing to test bomb failure; corrosion rate increased from 0.05 to 1.1 mils/year during the fifth week of test.

No. 641: Type 316 stainless steel; heliarc welded; polished on Nos. 80 and 120 emery paper to remove outer weld layer; pretreated 24 hr in 2% CrO₃ at 250°C; exposed 12 weeks to 0.17 M uranyl sulfate at 250°C; corrosion rate, 0.15 mil/year; no solution reduction detected during test.

No. 642: Type 309 Cb stainless steel; heliarc welded; polished on Nos. 80 and 120 emery paper to remove outer weld layer; pretreated 24 hr at 250°C in 2% CrO₃; exposed three weeks

to 0.17 M uranyl sulfate at 250°C; solution reduction occurred for unexplained reasons during third week of test; sample weight gain, 8.4 mg/dm²/day.

No. 759: Type 347 stainless steel; heliarc welded; etched 10 min in saturated FeCl₃-HCl solution to remove weld scale; pre-treated 24 hr in 1% HNO₃ at 250°C; exposed seven weeks to 0.17 M uranyl sulfate at 250°C; corrosion rate, 0.12 mil/year; no solution reduction detected during test.

Photographs of the five specimens were taken on their removal from the test solution. The samples were metallurgically polished and etched in chrome regia (HCl+CrO₃) to develop the weld structure. Photographs were taken on the etched sides, showing a cross-sectional view of the weld area. The specimens were then examined with a 30× microscope. Figures 16 through 20 show the condition of the specimens before and after polishing and etching. Figure 15 is a photograph of the condition of a 347 stainless steel specimen after the heliarc-welding operation. This specimen was not exposed to uranyl sulfate.

Intergranular corrosion attack was not visible on any of the specimens as removed from the test solution. Examination under a microscope showed all polished and etched surfaces to have clean-appearing, characteristic butt-welded microstructures. The appearance of these structures was identical to that of a heliarc-welded specimen of 347 stainless steel which was not exposed to uranyl sulfate at 250°C. No signs of intergranular corrosion attack were observed. One specimen, No. 640, type 347 stainless steel, which had been exposed for one week at 250°C after solution reduction occurred, did show a very slight indication of possible intergranular corrosion on a few isolated areas immediately adjacent to the weld metal. This sample will be examined at higher magnification for further indication of the existence of intergranular corrosion, as will the other four specimens.

The cause of intergranular corrosion attack in stainless steels has generally been attributed to the depletion of chromium in areas near grain boundaries. This depletion results from a combination of chromium with the carbon in stainless steel to form chromium carbides which collect along the grain boundaries. The carbides are dissolved by corrosive media, which process greatly lowers the physical properties of the stainless steel, often resulting in complete failure. The susceptibility of stainless steels can

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Initial sample condition (Mag 2X)

Polished and etched in chrome regia (Mag 2X)

Enlarged cross-sectional view of weld area,
polished and etched in chrome regia (Mag 3X)

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FIG.15 Photographs of Type 347 Stainless Steel Heliarc Welded Test
Specimen before Exposure to 0.17M Uranyl Sulfate at 250°C

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Top View of Specimen As Removed from
Test Solution (Mag 2X)

Side View of Specimen As Removed from
Test Solution (Mag 2X)

Cross-sectional View of Weld Area after
Polishing and Etching (Mag 2X)

Enlarged View of Weld Area after Polishing
and Etching (Mag 6X)

FIG. 16 Photographs of Type 309Cb Stainless Steel Heliarc
Welded Test Specimen after 14 Weeks Exposure in
0.17M Uranyl Sulfate at 250°C

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Top View of Specimen as Removed from
Test Solution (Mag 2X)

Side View of Specimen as Removed from
Test Solution (Mag 2X)

Cross-sectional View of Weld Area after
Polishing and Etching (Mag 3X)

Enlarged View of Weld Area after Polishing
and Etching (Mag 6X)

FIG. 17 Photographs of Type 347 Stainless Steel Heliarc
Welded Test Specimen after 5 Weeks Exposure in
0.17M Uranyl Sulfate Solution at 250°C (No.640)

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Top View of Specimen As Removed from
Test Solution (Mag 2X)

Side View of Specimen As Removed from
Test Solution (Mag 2X)

Cross-sectional View of Weld Area after
Polishing and Etching (Mag 3X)

Enlarged View of Weld Area after Polishing
and Etching (Mag 6X)

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FIG. 18 Photographs of Type 316 Stainless Steel Heliarc
Welded Test Specimen after 12 Weeks Exposure in
0.17M Uranyl Sulfate Solution at 250°C (No. 641)

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Top View of Specimen as Removed from
Test Solution (Mag 2X)

Side View of Specimen as Removed from
Test Solution (Mag 2X)

Cross-sectional View of Weld Area after
Polishing and Etching (Mag 2X)

Enlarged View of Weld Area after Polishing
and Etching (Mag 6X)

FIG. 19 Photographs of Type 309Cb Stainless Steel Heliarc
Welded Test Specimen after 3 Weeks Exposure in
0.17M Uranyl Sulfate Solution at 250°C (No.642)

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Top View of Specimen as Removed from
Test Solution (Mag 2X)

Side View of Specimen as Removed from
Test Solution (Mag 2X)

Cross-sectional View of Weld Area after
Polishing and Etching (Mag 3X)

Enlarged View of Weld Area after Polishing
and Etching (Mag 8X)

FIG. 20 Photographs of Type 347 Stainless Steel Heliarc
Welded Test Specimen after 7 Weeks Exposure in
0.17M Uranyl Sulfate Solution at 250°C (No.759)

be minimized by:

1. Reannealing of welds at 1900 to 2000°F followed by rapid cooling through the sensitization range, 650 to 1500°F; this treatment redissolves precipitated carbides caused by welding operations.
2. Using stabilized grades of stainless steels, i.e., steels containing either columbium or titanium, which have greater tendencies than chromium to form carbides; when these metals are present there is no loss of corrosion resistance by depletion of chromium near grain boundaries; columbium and titanium carbides are more resistant to corrosive media than is chromium carbide.
3. Using the extra-low-carbon grades of stainless steel which contain a maximum of 0.03% carbon as compared to 0.08% carbon generally found in the normal grades of stainless steel.

For the HRE program, initial studies with stainless steel welds have shown the absence of intergranular corrosion attack on various stainless steels exposed to uranyl sulfate at 250°C. A more detailed investigation into this subject will be undertaken in the immediate future. As a precautionary measure, it may be advantageous to subject representative samples of stainless steel used in reactor construction to recommended standard laboratory tests for susceptibility to intergranular corrosion before the materials are actually used in the field.

Corrosion Resistance of Zirconium. It has previously been reported* that resistance-melted Bureau of Mines zirconium had comparable corrosion resistance to pretreated 347 stainless steel in 0.17 M uranyl sulfate at 250°C. Corrosion rates ranged from 0.07 to 0.17 mil/year after 25 to 32 weeks of exposure. In many cases, slight weight gains, less than 1.0 mg/dm²/day, were reported. The great advantage to the use of zirconium, aside from its desirable nuclear properties, is that no initial pretreatment in nitric or chromic acid is required to prevent corrosion attack and solution reduction. Zirconium metal can be used satisfactorily, assuming good metal purity, without the danger of reduction of the uranyl ion in uranyl sulfate at 250°C.

Samples of Bureau of Mines zirconium, butt-welded to titanium metal, have shown good corrosion resistance after 21 weeks of exposure to 0.17 M uranyl sulfate at 250°C. The average weight loss of these samples was 4.1 mg/dm²/day. No evidence of weld corrosion due to dissimilar metal effect has been observed.

*See p. 2a for list of previous quarterly reports.

Crystal bar zirconium has shown slightly better corrosion resistance to uranyl sulfate at 250°C than Bureau of Mines zirconium tested to date. Corrosion rates for crystal bar zirconium after 24 weeks in 0.17 M uranyl sulfate averaged 0.03 mil/year and less. This material, in general, retains its original metallic luster during the test whereas Bureau of Mines zirconium becomes covered with an adherent light-gray film.

A zirconium-tin alloy has shown negligible corrosion attack after 168 hr in 0.17 M uranyl sulfate at 250°C.

Corrosion Resistance of Reflector Materials. Studies with SAE 1030 carbon steel in distilled water containing small concentrations of hydrogen peroxide at temperatures of 100 and 200°C have shown corrosion attack to be severe at 100°C and somewhat less severe at 200°C. Samples were characterized by voluminous corrosion product formation (especially at the lower temperature), roughened surfaces, and pitting attack. At 200°C, the temperature of primary interest, initial corrosion rates averaged 7 to 10 mils/year at the end of one week; these rates decreased to 2 to 3 mils/year by the end of 18 weeks. The hydrogen peroxide concentration was 0.005 M.

In these tests a consideration of corrosion rates based on uniform corrosion attack does not present the entire corrosion situation. Of greater significance is the formation and continued development of pitting or localized corrosion attack. This localized attack was found to be prevalent on dissimilar metal couples in distilled water containing 0.0005 M hydrogen peroxide at 200°C. Contact couples of 347 stainless steel and SAE 1030 carbon steel showed an intense localized corrosion attack on the carbon steel. This type of attack is accelerated by the presence of oxygen since oxygen is an active depolarizer and permits corrosion to proceed at an unimpeded rate.

In normal practice for the operation of steam boilers, the use of highly alkaline water (pH 10 to 12) in which the dissolved oxygen content has been reduced to 0.03 ppm and less by mechanical deaeration or chemical scavenging of the feed water has proved highly successful for minimizing corrosion attack in the boiler. Conditions in the HRE are entirely different from boiler operation, however, since oxygen is continually present in the reflector from the formation and decomposition of D_2O_2 by irradiation effects. The rate of D_2O_2 production within the reflector could be reduced slightly by keeping the

oxygen concentration of the incoming feed water as low as possible. Concentration of dissolved oxygen is one of the factors that determine the amount of peroxide formation in water subjected to irradiation. Oxygen may be removed, before entry of the feed water into the reflector, by deaeration or by adding sodium sulfite. The use of the sulfite method would necessitate periodic removal of the subsequently formed sulfate anion to eliminate effects of the sulfate on the carbon steel.

The presence of oxygen from the decomposition of D_2O_2 will have a pronounced effect on the extent of corrosion. Oxygen, even in alkaline water, is a depolarizer and promotes corrosion attack, as demonstrated by laboratory tests. High-resistance water, made alkaline to a pH of 10.5 by the addition of sodium hydroxide, and containing 0.005 M hydrogen peroxide, was placed in a test bomb with samples of 1030 carbon steel which were insulated from the test bomb assembly, and the system was heated to 200°C. At the end of one week the corrosion rate was 5 mils/year. This rate is undoubtedly low since peroxide was added just once at the start of the test. With the depletion of oxygen by the corrosion reaction, corrosion itself is retarded. At the end of 12 weeks the corrosion rate was 2 mils/year. These samples were improved in appearance as compared with specimens run under similar tests using pH 5.5 water. The surfaces were roughened, however, and showed pitting tendencies.

Galvanic corrosion studies with SAE 1030 carbon steel and 347 stainless steel were made in distilled water containing 0.0005 and 0.005 M hydrogen peroxide at 200°C. The initial pH of the water was 5.0; the final averaged 7.1. In every test the carbon steel was attacked preferentially, and the intensity of this attack was directly proportional to the peroxide concentration. Pitting attack was more intense at the higher peroxide concentration, and corrosion rates increased from 4.8 to 8.2 mils/year as the hydrogen peroxide concentration increased from 0.0005 to 0.005 M.

The use of trisodium phosphate as a corrosion inhibitor for carbon steel in distilled water containing hydrogen peroxide at 200°C was studied. The choice of this material was based on (1) its successful use in industrial steam boiler operation, and (2) its stability under irradiation. Initial tests were made using a 0.01 N Na_3PO_4 solution (550 ppm) in distilled water.

In Table 8 results of single and couple tests are shown and are compared to results obtained in the absence of this inhibitor.

TABLE 8

Results of Using Trisodium Phosphate as a Corrosion Inhibitor

MATERIAL	EXPOSURE (weeks)	H ₂ O ₂ (molarity)	INITIAL pH	FINAL pH	Na ₃ PO ₄ (ppm)	WEIGHT CHANGE (mg/dm ² /day)	CORROSION RATE (mils/year)
1030 carbon steel	16		5.1	6.5		-11.3	2.1
1030 carbon steel	16		10.2	8.0		-7.3	1.3
1030 carbon steel	14		11.7	10.1		+0.1	
1030 carbon steel	6		11.4	10.2	550	-0.07	0.01
1030 carbon steel	16	0.005	5.1	7.2		-6.1	1.1
1030 carbon steel	11	0.005	10.2	7.4		-7.5	1.4
1030 carbon steel	6	0.0005	11.4	10.1	550	-0.2	0.04
347 stainless steel	6	0.0005	4.5	4.6		-0.08	0.01
347 stainless steel	6	0.005	4.5	4.6		-0.06	0.01
1030 carbon steel } 347 stainless steel }	6	0.0005	4.5	5.1		-20.2 +0.4	3.7
1030 carbon steel } 347 stainless steel }	6	0.005	4.5	6.3		-27.5 +0.5	5.0
1030 carbon steel } 347 stainless steel }	6		11.4	10.1	550	+0.6 +1.0	
1030 carbon steel } 347 stainless steel }	6	0.0005	11.4	10.1	550	+0.3 +0.7	

The marked improvement in corrosion behavior of SAE 1030 carbon steel brought about by the presence of trisodium phosphate is readily seen. This improvement occurred on single and on galvanic couple specimens in contact with 347 stainless steel. The presence of hydrogen peroxide in the water did not make any noticeable difference in the corrosion of the carbon steel when

the phosphate inhibitor was present. All specimens of 1030 steel were free of pitting attack and scaly corrosion products.

Additional tests employing trisodium phosphate will encompass (1) lower concentrations of the inhibitor to reduce the water pH to 10.5; and (2) larger scale tests using a thermal convection test loop to obtain solution movement.

A suggested procedure for the initial operation of a new boiler is:

1. A thorough degreasing operation using dilute caustic soda solution.
2. An etching in inhibited acid solution to remove excessive scale.
3. A boiling-out operation using dilute trisodium phosphate solution.

Idle boilers are extremely susceptible to pitting corrosion unless precautionary steps are taken. One of the following precautions may be used:

1. Drain the boiler while hot (80 to 90°C) and dry by forced air circulation, taking measures to ensure that the boiler remains dry until placed back into operation.
2. Completely fill the boiler with alkaline water containing approximately 100 ppm of sodium sulfite and seal from the atmosphere.

Miscellaneous Corrosion Studies. Titanium and Tantalum. These materials were previously reported as showing excellent corrosion resistance to uranyl sulfate at 250°C. No pretreatment in either HNO_3 or CrO_3 was necessary to enhance their corrosion resistance, and the metals did not exhibit any tendency to cause solution reduction. At the end of 19 weeks in 0.17 M uranyl sulfate at 250°C, both specimens gained weight slightly, 0.16 mg/dm²/day for titanium and 0.21 mg/dm²/day for tantalum. Additional corrosion studies will be made with these materials.

Durimet 20. This alloy, containing 29 Ni, 19 Cr, 3 Mo, and 4 Cu, has shown excellent promise for use in intermediate-temperature operations up to 150°C. After 14 weeks in 0.17 M uranyl sulfate at 150°C, the corrosion of the alloy was 0.07 mil/year. No initial pretreatment is required for operation up to 150°C.

410 Stainless Steel. 410 stainless steel of Rockwell hardness C-42 was pretreated in 1% HNO_3 at 250°C for 24 hr and exposed for 15 weeks in 0.17 M

uranyl sulfate at 150°C. The sample remained a metallic gray color and gained in weight 0.38 mg/dm²/day. This material cannot be used at 150°C without an initial pretreatment in HNO₃ or CrO₃.

Elgiloy. Elgiloy, an alloy containing 20 Cr, 40 Co, 15.5 Ni, 15 Fe, and 2 Mo, was developed by the Elgin National Watch Co. for use primarily as watch mainsprings. In thin sections this material can be hardened to a Rockwell hardness of C-60 to C-65. Samples were exposed to 0.17 M uranyl sulfate at 150 and 250°C. No pretreatments in HNO₃ or CrO₃ were used. After two weeks at 150°C, the corrosion rate was 1.6 mils/year and the sample retained its original metallic luster. No solution reduction was detected. At 250°C, solution reduction occurred and the resulting corrosion of the metal was 26.5 mils/year. Although the alloy shows good resistance at temperatures of 150°C and less, the presence in the uranyl sulfate solution of cobalt resulting from corrosion is objectionable.

Titanium Carbide. This material, used as bearings in the Westinghouse induction pump, was tested in 0.17 M uranyl sulfate at 150°C. Corrosion attack was intense and solution reduction occurred. The material was also found completely unsatisfactory in 1% HNO₃ at 100°C.

Uranyl Fluoride Corrosion Studies. A series of exploratory tests have been completed using UO₂F₂ solution containing 30 g of uranium per liter at 100°C. The results of these studies on metals and alloys are listed in Table 9 in order of decreasing corrosion resistance. For specimens showing heavy weight gains, the gains were attributed to a deposit of reduced uranium compounds on the surfaces.

TABLE 9
Results of Corrosion Tests Using Uranyl Fluoride

MATERIAL	EXPOSURE (weeks)	WEIGHT CHANGE (mg/dm ² /day)	CORROSION RATE (mils/year)	SAMPLE APPEARANCE
Titanium	12	+0.012		Original condition
Gold	12	+0.020		Original condition
Tantalum	12	+0.028		Original condition
347 stainless steel	12	+0.030		Original condition
Platinum	12	+0.85		Slight darkening
Hastelloy C	11	-0.19	0.03	Original condition
316 stainless steel	12	-0.39	0.07	Original condition
Ticonium III	12	-0.57	0.10	Original condition
Silver	12	-3.50	0.50	Original condition
Inconel	12	-3.20	0.54	Dull gray color
Hastelloy D	6	-4.0	0.73	Original condition
Monel	8	-45.1	7.65	Gray-black film
Hastelloy A	7	+13.5		Etched black surface
BM zirconium	8	+104.8		Gray-black scale
Hastelloy B	5	+121.5		Blistered; black scale
Nickel	2	+582.2		Green-black scale Heavy flaky scale

Corrosion tests at elevated temperatures will be conducted on the materials showing good corrosion resistance at 100°C.

Uranyl Nitrate Corrosion Studies. A few corrosion studies using uranyl nitrate solution containing 40 g of uranium per liter have been made with various materials at 100°C. These results arranged in decreasing order of corrosion resistance are shown in Table 10.

TABLE 10

Results of Corrosion Tests Using Uranyl Nitrate

MATERIAL	EXPOSURE (weeks)	WEIGHT CHANGE (mg/dm ² /day)	CORROSION RATE (mils/year)	SAMPLE APPEARANCE
CB zirconium*	6	0.0	0.0	Original condition
Durimet 20	6	-0.03	0.005	Original condition
Carpenter 20	6	-0.08	0.014	Original condition
309 stainless steel	6	-0.09	0.015	Original condition
321 stainless steel	6	-0.10	0.017	Dark colored film
347 stainless steel	6	-0.12	0.021	Dark colored film
BM zirconium	6	-0.10	0.022	Light gray color
Worthite	6	-0.14	0.025	Original condition
316 ELC stainless steel	6	-0.28	0.049	Black colored film
410 stainless steel	6	-2.49	0.467	Dull gray color

*Crystal bar zirconium.

Additional tests will be run at higher temperatures using these and other materials which exhibit good corrosion resistance at 100°C.

Optical and Electron Microscope Surface and Film Studies. During this period a number of samples were examined, and observations were made which may prove valuable in contemplated future experiments. These observations deal chiefly with:

1. The physical structure and composition of the substrate films formed on 347 stainless steel after the following treatments:
(a) polishing one sample on Nos. 80 and 120 paper, pretreating

24 hr in 1% HNO_3 at 250°C, exposing for one week to 0.17 M uranyl sulfate, scratching 1/8 in. across the sample face, and exposing to 0.17 M uranyl sulfate for three additional weeks at 250°C; (b) polishing another sample on Nos. 80 and 120 paper, pretreating 24 hr in 2% CrO_3 at 250°C, scratching 1/8 in. across the sample face, and exposing to 0.17 M uranyl sulfate for three weeks at 250°C.

2. The replica studies of the submicroscopic structure of films formed on electropolished 347 stainless steel after passivation in (a) 1% HNO_3 , and (b) in 2% CrO_3 .
3. The replica studies of scratched and unscratched areas on a sample pretreated 24 hr in 1% HNO_3 at 250°C and then exposed to uranyl sulfate for seven weeks at 250°C.

These will be discussed in the order in which they have been listed.

All electron microscope studies were made, where possible, on the stripped film removed in an electrolyte consisting of a 20% solution of 34% hydrobromic acid in methanol, using a current density of 2 amp/sq cm at 20 volts with the sample as anode. This was followed by successive washes in methanol. Where the stripped film was found to be too thick for transmission examination, negative replica techniques were used.

1. *Samples 1004 and 1005.* Sample 1004 was polished on Nos. 80 and 120 paper, pretreated 24 hr in 1% HNO_3 at 250°C, exposed for one week to 0.17 M uranyl sulfate, scratched, and run in 0.17 M uranyl sulfate for three additional weeks at 250°C. Sample 1005 was polished on Nos. 80 and 120 paper, pretreated 24 hr in 2% CrO_3 at 250°C, scratched, and exposed to 0.17 M uranyl sulfate for 504 hr at 250°C.

It was noted during the film stripping on these samples that what appeared to be a two-layer film existed. These layers separated in the methanol wash. One, the substrate layer, on both samples was very thin, nearly transparent, and opalescent-white to straw-yellow in color by transmitted light. The outer layer on sample 1004 appeared ruby red to reddish black, and the outer layer on sample 1005 was translucent and amber to light yellowish brown by transmitted light. Preliminary surface examination with the optical microscope failed to show any of the outer encrustation previously identified as U_3O_8 which appeared on samples heretofore examined.

Stripped films were collected on 200-mesh electron-microscope screens. Micrographs and electron diffraction patterns were taken of the substrate films. The outer layers proved to be too thick for electron microscope examination.

Figures 21 and 22 show the nature of the structure of the thin substrate films formed on the two samples. It will be observed that whereas comparatively large crystallites appear to exist in the substrate film on sample 1004, the film on sample 1005 is practically structureless. This is borne out by the electron diffraction patterns accompanying the micrographs. A sharp line pattern was obtained with sample 1004, denoting large crystals, and a diffused line pattern with 1005, denoting an extremely small crystal structure nearly amorphous in nature. Comparison diffraction patterns seem to indicate that the substrate film on sample 1004 is primarily α Fe_2O_3 and that the film on sample 1005 is possibly Cr_2O_3 . Both may contain some Fe and Cr in varying amounts.

2. *Samples 1030 and 1031.* Sample 1030 was polished in H_3PO_4 -glycerin at 110°C and pretreated in 1% HNO_3 at 250°C for 24 hr. Sample 1031 was polished in H_3PO_4 -glycerin at 110°C and pretreated in 2% CrO_3 at 250°C for 24 hr. Preliminary examination of these two samples showed a marked difference, although second- and third-order interference colors were apparent on both. The surface of sample 1030 appeared to have a fairly homogeneous structure, whereas the surface of sample 1005 was marked by what seemed to be large humps or mounds. Stripped films were found to be too thick for electron microscope transmission examination; therefore negative-replica techniques were resorted to.

Micrographs of the surfaces, as illustrated in Figs. 23 and 24, sample 1030, and in Figs. 25 and 26, sample 1031, show the major part of these films to be composed of extremely small crystallites of less than 0.2μ in size. However, it will be observed that the surface of the sample passivated in CrO_3 is broken up by what seems to be extremely large crystalline-appearing material of an as yet unknown composition.

3. *Sample 1010.* This sample was polished, then pretreated 24 hr in 1% HNO_3 at 250°C , scratched $1/8$ in. across the face of the specimen, and then exposed to 0.17 M uranyl sulfate for 1176 hr at 250°C . Negative replicas of both

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Plate No. EM 942
Sample NO. 1004

FIG. 21

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84

Plate NO. EM 929
Sample No. 1005

FIG. 22

575

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UNCLASSIFIED

85

E.M. Plate No. 959

FIG. 23

E.M. Plate No. 960

FIG. 24

E.M. Plate No. 961

FIG. 25

E. M. Plate No. 962

FIG. 26

Films on Electro-polished stainless steel # 347,
Samples No. 1030 & 1031.

935 076

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scratched and unscratched areas were made prior to the film-stripping operation, inasmuch as examination in the optical microscope indicated that the film which had formed would be too thick for transmission work in the electron microscope.

It was observed that although the film on unscratched areas came off quite readily in the stripping bath, the film on the scratched area was not removed. The insert in Fig. 27 shows the scratched area with the film intact after a prolonged period in the electrolyte solution. Note the extensive attack in surrounding unscratched areas where the film was removed.

Electron micrographs of the negative replicas indicate that the film formed on the scratched areas is much more uniform than on surrounding areas. This can readily be seen in Fig. 27, scratched area, and in Fig. 28, unscratched area. The crystallites appearing in the scratched area seem to be considerably larger than those observed in the unscratched area, although the form seems to be much the same. The distribution and uniformity of the film formed on scratched areas is also better. Machine striations can readily be seen on the micrograph of the unscratched area whereas, on the scratched area, they are practically nonexistent. Shadowed areas appearing on the micrograph of the scratched surface may be the site of either machine striations or the original scratches.

IN-PILE STUDIES

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Analytical Data for Previous Experiments. The analytical chemistry of irradiated UO_2SO_4 solutions is difficult because of the high radioactivities involved and because the proper handling facilities are not yet available. These difficulties can be circumvented by using a minimum of solution for analysis and by allowing extended cooling times; however, the long time interval between removal from the pile and chemical analysis is undesirable

EM 924
Scratched Area
Sample No. 1010
5000 X

Insert ME 700
Shows film remain-
ing on Sample 1010
on scratched area.

FIG 27

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88

E M 923
Unscratched Area
Sample No. 101C
5000 X

72

FIG. 28

81

515

DECLASSIFIED

because chemical changes may take place during this period. It is possible to minimize chemical changes by keeping the bomb frozen until time for analysis, usually about four to six weeks after removal of the sample from the pile.

Data on the volumes of solutions used in the chemical analyses and on the accuracy which can be expected are given in Table 11.

TABLE 11

Accuracy of Chemical Analyses Used on Uranium Solutions

ANALYSIS	VOLUME USED (λ)	METHOD	LIMITS OF DETECTION (ppm)	EXPECTED ACCURACY
Gross uranium analysis	5-20 200 100	Colorimetric Microvolumetric Density*		$\pm 5-10\%$ $\pm 3\%$
U(IV)	500	Polarographic	5	$\pm 20\%$
pH	200	pH meter		± 0.05 units
Fe (acid)	100	Colorimetric	10	$\pm 10\%$
Fe (base)	1000	Colorimetric	10	$\pm 10\%$
Cr	100	Colorimetric	5	$\pm 5\%$
Cl ⁻	1000	Volumetric	5	$\pm 10\%$
S**	500	Polarographic	5	$\pm 10\%$

*The density method of analysis seems to be accurate to within $\pm 12\%$ when compared with the microvolumetric method for six cases.

**The sulfur analysis picks up any sulfur compounds which are easily reducible with aluminum strips.

The analytical results to date, which cover most of the runs listed in Table 17, ORNL-925, p. 175, are presented in Tables 12, 13, and 14. The previous designations of good, bad, and inconclusive are not changed. The analytical data bear out the conclusion reached in out-of-pile tests and discussed elsewhere that high chloride content is conducive to solution-corrosion failure, and, conversely, low chloride content means that the solution has a good chance of remaining good throughout the run.

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TABLE 12

Analytical Data for Experiments Designated "Good"^(a)

GROUP ^(a)	EXPT. NO.	STARTING U (mg)	FINAL U ^(b) (mg)	U(IV) (ppm)	pH	Fe (ppm)	Cr (ppm)	Cl ⁻ (ppm)	S ^(c) (ppm)
A	290a	187	187 ± 3%						
	291a	197	197 ± 3%						
	306	233	290 ± 3% C = 295 ± 5% D = 235		2.05	74		7	
	307	220	242 ± 3% C = 251 ± 5% D = 222	30	2.55	34		<2	<5
B	298	195	111 ± 5%	31	3.30	58	69	<2	28
	299	226	243 ± 5%		3.05				
C	292a	192	192 ± 3%						
	303	180	215 ± 5%	19	4.15	18	<1	4	<5
	308	166	172 ± 3% C = 173 ± 5% D = 159	43	2.36	37		7	<5
D	309		Not opened						
E	304	181	158 ± 5%	25	4.00	<10	<1	5	<1
H	292b	223	232 ± 5% ^(d)	72	1.65	<10		14	3
I	301	188	196 ± 3% C = 200 ± 5% D = 161		3.55	64	8	<2	

(a) Group designations are given in ORNL-925, p. 175.

(b) C = colorimetric method; D = density method.

(c) Any sulfur which is reducible with aluminum strips.

(d) Uranium in wash not included.

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TABLE 13

Analytical Data for Experiments Designated "Inconclusive"^(a)

GROUP ^(a)	EXPT. NO.	STARTING U (mg)	FINAL U (mg)	U(IV) (ppm)	pH	Fe (ppm)	Cl ⁻ (ppm)	S (ppm)
A	297 ^(b)	264	46 ± 5% ^(c)	17				
E	302 ^(d)	No results yet						
F	296 ^(e)	No results yet						
	290b	282	6 ± 5% ^(c)	<5	4.82	<10	24	3
	291b	167	3 ± 5% ^(c)	<5	4.10	<10	23	2
H	294	282	10 ± 5% Wash only					
	295 ^(e)	227	D ^(f) = 0		6.0		60	

(a) Group designations are given in ORNL-925, p.

(b) Wash water yellow.

(c) Uranium in wash not included.

(d) Wash liquid yellow; copious precipitation; irradiated sample bad.

(e) No uranium in solution in bomb after irradiation.

(f) D = density method.

TABLE 14

Analytical Data for Experiments Designated "Bad"^(a)

GROUP ^(a)	EXPT. NO.	STARTING U (mg)	FINAL U ^(b) (mg)	pH	Fe (ppm)	Cr (ppm)	Cl ⁻ (ppm)
D	300	219	126 ± 10%	2.00			
G	305	290	237 ± 3% C = 261 ± 5% D = 252	3.70	26	13	<2

(a) Group designations are given in ORNL-925, p.

(b) C = colorimetric method; D = density method.

Effect of Low-Temperature Irradiation — Discussion of Experiment 305.

During experiment 305 the solution definitely went bad at the first regular Monday shutdown of the pile. The failure was shown by the pressure, temperature, and flux data. The fact that the failure occurred during a shutdown strongly indicates that radiation is beneficial rather than detrimental. This line of thought is strengthened by the fact that other failures have also occurred at or during shutdowns. There seems to be something present during irradiation which keeps the uranium in solution but which is lacking during shutdowns at elevated temperature. This "something" may be hydrogen peroxide. Hydrogen peroxide which forms along the fission tracks is rapidly decomposed at 250°C but will last much longer and consequently build up to higher concentrations when the temperature is lowered.

It is known from laboratory tests that dilute H_2O_2 will bring U_3O_8 into solution in dilute H_2SO_4 solutions when refluxed at 100°C. After the failure of experiment 305, the temperature was allowed to drop to pile ambient overnight. During this time the pressure increased to about 4000 psi. The temperature was then raised for about a day and the bomb was removed from the pile. When the solution was analyzed it was found that about 90% of the uranium was in solution. It is quite likely that during the bombardment at reduced temperature the H_2O_2 present oxidized the U_3O_8 back to the soluble hexavalent uranyl ion.

This experiment suggests that when the correct conditions are present it will be very difficult if not impossible to have the solution go bad. If it is possible to bring U_3O_8 back into solution with a given set of conditions, it should be even easier to keep the uranium in solution with these same conditions. Thus it appears that temperatures in the region 100 to 160°C will give more stable conditions for UO_2SO_4 —stainless steel systems than temperatures in the region of 270°C. It is possible that the temperature need be lowered only during pile shutdowns, as the only trouble seems to occur during the absence of neutrons. The following conclusions are drawn from this experiment:

1. If the uranyl sulfate should be lost from solution during operation of the HRE (by reduction to U_3O_8), it may be brought back into solution by injection of a dilute solution of hydrogen peroxide into the reaction stream, or by operation at reasonable fluxes but at low temperature. This means that if corrosion or other causes for reduction of uranium begin to show up during

operation of the HRE at 250°C, it may be possible to operate safely at some lower temperature at which the equilibrium concentration of peroxide is high enough to provide oxidizing conditions sufficient to balance any reduction tendencies present.

2. For in-pile corrosion tests where it is desired to demonstrate long life and low corrosion in the presence of radiation, it will be desirable to lower the temperature whenever the neutron flux is absent or below a certain minimum value. Automatic apparatus has been designed and constructed to turn off the bomb heaters whenever the pile goes down and turn them back on at a specified time interval after the pile goes up.
3. Automatic operation at low temperature in the absence of flux may result in protection even against the effects of known amounts of added halide ions such as chloride or iodide. For eventual operation of large-scale homogeneous reactors with large burn-up fuel it might be important to be able to counteract the effect of fission product iodine on the stainless steel surfaces.
4. Since it has previously been shown that unpassivated stainless steel is resistant to corrosion by UO_2SO_4 at 100°C in the absence of radiation, it might be possible to utilize unpassivated stainless steel throughout a reactor by operating at a temperature somewhere between 100 and 250°C where the beneficial effects of radiation outweigh the harmful effects of high temperature.

In-Pile Corrosion Specimens. The following is a description of the type and extent of the corrosion of type 347 stainless steel samples after exposure to UO_2SO_4 solutions under irradiation in the X-10 pile. The tests are listed according to run number and include all those returned to the Corrosion Group during the last three months.

Pretreatment (General). The stainless steel samples, all type 347, were etched 10 min in ferric chloride solution to remove weld scale and clean the surface. They were then rinsed thoroughly in demineralized water under tap pressure, rinsed in alcohol, and dried.

Medium (General). 40 g of uranium per liter as UO_2SO_4 , 93% enrichment.

Run 295. Pretreated 24 hr in 2% chromic acid at 250°C and exposed 13 days in hole 12 at 290°C; designated inconclusive from pressure curve. Surface condition: strong corrosion attack evident although weight loss was only 1.0 mg/dm²/day; all surfaces covered with a loose brown rust.

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Run 299. Pretreated 24 hr in 1% nitric acid at 290°C and exposed 12 days in hole 12 at 250°C; designated good from pressure curve. Surface condition: surface of sample did not indicate severe corrosion attack; sample coated with smooth, dull, dark brown coat. Weight change: -15.2 mg/dm²/day.

Run 300. Pretreated 24 hr in 2% chromic acid at 290°C and exposed 12 days in hole 12 at 250°C; designated bad from pressure curve. Surface condition: sample covered with a loose, blistered, black scale which showed brown where chipped; yellow powdery precipitate on approximately 5% of the area. Weight change: +9.5 mg/dm²/day.

Run 301. Pretreated 24 hr in 2% chromic acid at 290°C and exposed 28 days in hole 60 at 290°C; designated good from pressure curve. Surface condition: sample was metallic bronze to brown over three-fourths of surface; band approximately 3/8 in. wide near center of sample had a rough, blistered, rust-colored appearance. Weight change: -11.2 mg/dm²/day.

Run 303. Pretreated 24 hr in 2% chromic acid at 250°C and exposed 14 days in hole 12 at 250°C; designated good from pressure curve. Surface condition: appearance of sample essentially good, showing the dull black of the pretreatment except for a reddish brown streak along the length of the sample and one small chipped area. Weight change: +6.3 mg/dm²/day.

Run 304. Pretreatment consisted of only the general etch and cleaning procedure; exposure was for 14 days in hole 12 at 250°C; designated good from pressure curve. Surface condition: sample covered with reddish-brown scale which appeared adherent on the lower three-fourths of the sample but was loosely attached on the upper quarter where chipping had occurred. Weight change: -5.0 mg/dm²/day.

Run 305. Pretreated 24 hr in 1% nitric acid at 290°C and exposed 7 days in hole 60 at 290°C; designated bad from pressure curve. Surface condition: surface had dull, mottled brown and black appearance with the brown areas definitely rusty. Weight change: -144.1 mg/dm²/day.

Run 306. Pretreated 24 hr in 1% nitric acid at 250°C and exposed 42 days in hole 12 at 250°C; designated good from pressure curve. Surface condition: this is by far the best sample the Corrosion Group has seen so far; surface covered with tight, smooth, black coating as after pretreatment; only a thin white line around specimen near the water level marred the appearance. Weight change: -6.8 mg/dm²/day.

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Run 307.: Pretreated 24 hr in 1% nitric acid at 250°C and exposed 42 days in hole 12 at 250°C; designated good from pressure curve. Surface condition: apparently little change in appearance from that of pretreated condition; dull, brownish-black coating, tight and smooth on top one-fourth of specimen and somewhat roughened and lighter in color below; change from one surface type to the other was sharp and distinct. Weight change: $-9.9 \text{ mg/dm}^2/\text{day}$.

Run 308.: Pretreated 24 hr in 2% chromic acid at 250°C and exposed in hole 12 for 42 days at 250°C; designated good from pressure curve. Surface condition: dull, black film of pretreatment covered upper one-fourth of the sample and remained in spots below; rest of surface covered with a bronze-colored film of semi-metallic luster. Weight change: $8.2 \text{ mg/dm}^2/\text{day}$.

Discussion. The marked improvement in the appearance of samples after irradiation-corrosion testing is encouraging. The constant recurrence of a sharp line of some description indicates, however, that a liquid level phenomenon is pronounced. The fact that this line in the case of Run 306 was just a line leads to the conclusion that this phenomenon may be of little if any importance in the case of a satisfactorily pretreated sample. Efforts are being made to arrange the tests so as to ensure total immersion during both the testing and the cooling periods to avoid such surface level effects.

Studies of Nonradiation Factors. Consideration of the results reported in Table 17 of ORNL-925 and those of a similar nature obtained since that time suggested the following:

1. None of the combinations of pretreatment type, pretreatment temperature, and test temperature which were explored was found to give consistently bad results in the presence of pile radiation.
2. If radiation were deleterious to some particular combination of other conditions, all results for that combination should have been bad. This was not found to be the case.
3. Hence, the inconsistencies noted might well have been due to deleterious nonradiation factors occasionally present.

In order to test this inference it was decided to carry out tests on complete assemblies (bomb-fitting-tubing) at the chosen temperature but in the absence of radiation. Such tests would be true "controls" or "blanks," more strictly comparable with in-pile tests than the flat plate specimens in large

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bombs which had characterized the engineering-corrosion tests previously conducted in the absence of radiation. The first such test, on an assembly which had actually been prepared for radiation, indicated that the inference was correct; all the uranium was lost from solution after only 8 days at 200°C. Furthermore, a check analysis of the solution at the conclusion of the test established the presence of 10 ppm of Cl^- .

At this point results from analyses of solutions after irradiation became available, confirming high chloride ion concentrations in many instances.

To establish with more certainty the presence or absence of chloride ion in the bombs as received, additional passivated bombs were ordered from the engineering corrosion section. Analyses of the water inside the bombs as received and analyses of the water inside the bombs after successive hot washes (heating to 250 to 300°C with distilled water) established definitely the presence of high concentrations of chloride ions, particularly in the bombs which had been passivated with nitric acid. Results are given in Table 15.

TABLE 15
Effect of Chloride Ion on Solution Stability

EXPT. NO	CHLORIDE (ppm)			URANIUM LOSS ON HEATING (%)		Cl ⁻ IN HEATED URANIUM SOLUTION (ppm)	COMMENTS
	COLD RINSE	HOT RINSE	CUMULATIVE	WITH PLUG	WITH FITTING		
Nitrate							
312	6	8, 2	16	32			Platinum strip on thermocouple well
313		3, 1	4	0	100		
316	7	6, 1	14				
317	1	<2, <1	<4				
320	2	16, <1	<19				
321	7	12, <1	20				
Chromate							
311					100	10	Platinum strip on thermocouple well
314	0	<2	2	0	100		Platinum strip on thermocouple well; 200 g of uranium per liter
315 a		3 *	3	0	100	<5	
318	<1		<1	0	100	7	
319	<1		<1	0	100	7	
322	1		1	0	100	<5	
323	1		1	0	100	?	

*50 ppm Cr^{+6} .

Bombs from which the chloride had been removed, as indicated by analyses on cold and/or hot rinses, have been loaded with enriched uranyl sulfate solution (in one case 218 g of uranium per liter), plugged, and heated for several days at 200 to 300°C. In only one case, as shown by the table, was uranium lost from solution. This exception showed a history of 16 ppm of chloride removed from the bomb before the uranium was added.

Bombs which retained their uranium content in solution after heating were reassembled with fittings (which had been rinsed with acetone, alcohol, and distilled water) as if for irradiation tests and then reheated for several days in the absence of radiation. Two of the fittings were wound with a platinum spiral at the upper end of the thermocouple well (for contemplated in-pile use to catalyze recombination of hydrogen and oxygen, thus permitting operation at 250°C with pressures less than 5000 psi). In every case, with or without platinum ribbon, the solution was completely decomposed and the uranium was reduced to a black layer on all exposed surfaces. Intense pitting with exposure of bare metal was noted on the thermocouple wells which had been wound with platinum. High concentrations of ferrous iron were found in some solutions.

It seems reasonable at this point to draw four tentative conclusions:

1. The rinsing procedure was inadequate to remove chloride ions remaining after the etch treatment. Some of our failures in the pile have undoubtedly been due to this. The bomb has been redesigned to eliminate the sliding fit which produced a deep, thin, annular crevice around the top.
2. Some defect in the pressure fitting must be suspected (electrolytic coupling involving the passivated thermocouple well and the unpassivated portion of the fitting, damage to the thermocouple well caused by the heat-treatment during silver-soldering, or inadequate rinsing of the pressure fitting).
3. Platinum strips around the thermocouple well should be eliminated unless it can be shown that they do not contribute to solution decomposition. This will call for temperatures of 290°C in future in-pile experiments if pressures of less than 5000 psi are to be maintained.
4. The known successful runs with bombs exposed to pile radiation become more striking when considered in the light of the probable fate of these tests if they had been conducted in the absence of

radiation. Of particular significance are successful in-pile tests with unpassivated 347 stainless steel when out-of-pile tests are known to lead consistently to failure. All the evidence indicates that radiation is helpful in maintaining the stainless steel in a state of passivity toward uranyl sulfate.

Potentiometric Corrosion Studies. An electrochemical investigation of the corrosion properties of 347 stainless steel has been initiated. To date the studies have been confined to potential measurements of steel specimens which have received either nitric or chromic acid pretreatment. All steel specimens used have been pretreated in a manner described in previous HRE quarterly reports (see page 2a for ORNL numbers).

It has been found that when 347 stainless steel is given either a nitric or chromic acid pretreatment it behaves like a noble metal. In a uranyl sulfate solution containing 30 g of uranium per liter the pretreated steel has a potential 0.5 volt more positive than the saturated calomel electrode (S.C.E.). In this respect the difference between chromic acid— and nitric acid—passivated steel is not detectable. An untreated 347 stainless steel under the same conditions has a potential approximately equal to the S.C.E.

When a passivated steel surface is scratched below the liquid level, the potential of the cell "passivated steel | 0.2 M UO_2SO_4 | S.C.E." changes instantly so that the potential of the cell is approximately zero. However, there is a tendency toward self-healing even in a uranyl sulfate solution, and the potential of the cell approaches its original value after a period of time. The presence of a small amount of nitric acid increases the rate of self-healing; a very small amount of dichromate brings about extremely rapid healing.

At room temperature the pretreated steel retains its passivity for at least 5 days in a uranyl sulfate solution containing as much as 0.1 M potassium chloride. At 100°C under the same conditions the passivity is destroyed within a few minutes.

Future experiments are to be carried out at a high temperature (about 250°C). Under these conditions there are no suitable reference electrodes available; hence an attempt will be made to utilize the cell "passivated steel | 0.2 M UO_2SO_4 | passivated steel." When the two electrodes are identical the

potential of the cell should be zero. If one electrode loses its passivity there will be a change in cell potential, and by determining the cell polarity it will be possible to determine which electrode has become active. If both electrodes should lose their passivity at the same time and to the same extent, there will be no detectable difference in cell potential, and hence the proposed cell will be useless. However, experiments at 100°C have indicated that it is highly unlikely that two separate pieces of steel will lose their passivity at exactly the same time.

At present a high-temperature bomb that will allow an electrically insulated lead to be introduced inside the bomb is being constructed. With this assembly it is hoped that some information concerning the resistance of the pretreated steel when exposed to uranyl sulfate solutions at high temperatures can be obtained. An attempt will then be made to correlate changes in the composition of the solution with changes in potential of the cell "passivated steel | 0.2 M UO_2SO_4 | passivated steel."

Peroxide Precipitation Studies. The start-up procedure for the HRE would be greatly affected if uranium peroxide were to precipitate before equilibrium conditions could be attained in the reactor. For this reason experiments were conducted to determine what effect on the precipitation of uranium peroxide in pile-bombarded solutions would be contributed by the variables temperature, acidity, concentration, and flux.

Portions of enriched uranyl sulfate solutions of the appropriate concentration and acidity were pipetted into quartz (vitreosil) ampoules. These samples were sealed off after degassing on a vacuum line (10^{-3} to 10^{-4} mm Hg). The ampoules were exposed in the pile for periods of at least 15 min each at four different flux positions. In the initial series of experiments the following limits were employed for the variables examined: temperature, 100 to 250°C; concentration, 10 to 40 g of uranium per liter; acidity, pH ~2.5 (that of uranyl sulfate solutions in this concentration range) to 2 N excess sulfuric acid; and flux, from the 0.2 position to the full flux obtainable in the vertical hole 12 of the ORNL pile (about 5×10^{11}). As far as could be determined, the effect of flux was negligible in this range, and all subsequent experiments were therefore run at the highest flux position.

Small precipitates were obtained in the acid samples in the high-temperature range. These precipitates did not increase in volume as the temperature

was lowered; analyses showed that the precipitates were silica, formed by attack on the walls of the ampoules at high temperatures (200 to 250°C); the amount of precipitate present appeared to be roughly proportional to the excess acid present in the sample. The results of this series of experiments can be summarized as follows: enriched (93%) uranyl sulfate solutions in the concentration range 10 to 40 g of uranium per liter can be exposed to a flux of about 5×10^{11} at temperatures of 100°C or higher without fear of uranium peroxide precipitation.

Another series of experiments was conducted in which no excess acid was present in the solutions. The following results may be noted: (1) natural uranyl sulfate solutions containing 120 and 200 g of uranium per liter showed no evidence of uranium peroxide precipitation at 100 and 150°C; (2) verification of the results of the first series of experiments was obtained by 4-hr bombardments of samples of solution containing 30 and 40 g of uranium per liter. Uranium peroxide precipitation was noted, however, in one run in which the samples were placed in the pile at 25°C and heated up gradually to 90°C (near pile ambient temperature) over a period of an hour.

A series of runs was made with solutions containing 120 g of uranium per liter, using two different enrichments, 18 and 93%. The lower enrichment gives a flux density comparable to that obtained above with the 40 g of uranium per liter samples with 93% enrichment. The higher enrichment was used in order to obtain a very high flux density for long-range studies; since the flux in the ORNL pile is low compared with estimated figures for the HRE and large-scale long-range reactors, the only way to obtain high flux densities is to step up the uranium concentration at this high enrichment. The 18% enriched samples exposed at 175 and 200°C for 30 min showed very small precipitates, which on analysis proved to be silica. The highly enriched samples also showed precipitates up to 200°C, and traces of uranium were found in the precipitates. One sample exposed at 250°C showed no precipitation. This last series of experiments will be duplicated, using longer bombardments to verify the results.

It should be noted that, except for one case, in those samples which gave UO_4 precipitates analyses showed that less than 20% of the uranium had precipitated. The one exception, as noted in Table 16, was the sample which fell into the liner of hole 12 and remained there for 4 hr at an undetermined temperature, probably less than 100°C.

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TABLE 16

Observations on Peroxide Precipitation

SAMPLE	URANIUM CONCENTRATION ^(a) (g/liter)	ACIDITY	TEMPERATURE (°C)	TIME IN PILE	SiO ₂ PPT	UO ₄ ^(b) PPT
Batches 1-9 (16 samples)	10 - 40	from pH ~2.5 to 2 N H ₂ SO ₄	100-250	>30 min	Ppt'd at 200 and 250°C in acid sam- ples	
	20	pH ~2.5	(?)(c)	~4 hr		Large; ¾ ppt'd
Batch 10	30 40 120	All subsequent samples had no excess acid present, i.e., pH ~2.5	25 - 90, heated up gradually	50 min		Small Medium Medium
Batch 11	10 30 40 120		125	30 min		Small
Batch 12	30 40 120		150	30 min	Trace Trace Trace	Small
Batch 13	30 40		100	30 min		
Batch 13A	30 40		100	30 min		
Batch 14	40 40 D ^(d)		90-108 Avg. 100	57 min		
Batch 15	120 (-17%)(a) 120 120 (-17%)(a) 120		175 200	30 min 30 min	Small Small Small Small	Small Trace
Batch 16	120 120 D 200 D 120 D 200 D		250 150 100	40 min 30 min 30 min		

(a) All samples are 93% enriched, unless otherwise noted, as in case of 17% samples.

(b) Size of precipitate estimated visually; even those marked "medium" had less than 20% of uranium precipitated.

(c) Ampoule fell down into liner in hole 12.

(d) Samples marked "D" are natural uranium.

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LITR Experiments. Progress has been made toward the irradiation of HRE samples in a vertical shim rod hole of the LITR. Equipment and instruments have been fabricated and partially installed at the site.

In order to obtain a higher flux at the sample, better heat transfer from the bomb, and greater strength for the higher pressures which are expected, the short bomb of 1 in. O.D. which is used in the graphite pile is being replaced, for the LITR, by a longer bomb of 5/8 in. O.D. and with thicker walls. These bombs are being tested for deformation at 300°C and 10,000 psi, which are the most severe experimental conditions anticipated.

The present equipment provides for temperature control by means of variable flow of air over the fins of a magnesium sleeve which fits snugly around the stainless steel bomb. Laboratory scale tests of this method of heat removal from the bomb showed it to be more than adequate for the 100 watts of fission heating which would be produced by a 5-ml sample of 40 g per liter solution of U^{235} at 10^{13} flux. A furnace is also provided in the present equipment so that the temperature can be maintained at lower flux. Air flow control is preferred to variable heating in a furnace since a system of lower heat capacity and shorter time lags is thereby made possible.

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3. RECOMBINATION OF HYDROGEN AND OXYGEN

INTRODUCTION

During the past quarter emphasis has been placed on obtaining the data needed to complete the design of the HRE recombiner system and on rearranging the pilot plant equipment to permit simulating the conditions expected in operation of that system.

LABORATORY-SCALE STUDIES

H. M. McLeod, Jr.	F. L. Daley
D. W. Kuhn	A. A. Palko
A. D. Ryon	K. O. Johnsson

Catalytic Recombination. The results of tests carried out for the purpose of determining the effect of variables on the efficiency of conversion of $H_2 + \frac{1}{2}O_2$ to water in the presence of platinum-on-charcoal catalyst were presented in a previous report (ORNL-925). These results showed that with a catalyst bed temperature above $350^\circ C$, the carbon base of the catalyst was attacked and that when recombination was carried out employing a catalyst poisoned with I_2 , the efficiency of the conversion reaction was less, even at $350^\circ C$, than that obtained with a nonpoisoned catalyst. Because of these limitations it appeared desirable to carry out the necessary tests with a platinum-on-alumina catalyst to permit comparison of the two catalyst bases. For this purpose an alumina base catalyst was purchased from the J. Bishop & Company Platinum Works, Malvern, Pennsylvania which was in the form of cylindrical pellets, $1/8$ by $1/8$ in., with a platinum content of 0.3%.

Recombination with Nonpoisoned Catalyst. To obtain a comparison of the efficiency of the alumina base catalyst with that of Product 43, tests were carried out employing about 30 g of catalyst contained in a 5-in. length of 0.75-in.-diameter pyrex tube and about 200 g contained in a 4.5-in. length of standard 2-in. pipe (316 stainless steel). The gas composition was varied from 0.5 to 21% electrolytic gas and the combined flow rate from 12.4 to about 74 liters/min. Under these conditions the catalyst bed temperature varied from about 175 to $900^\circ C$ with essentially complete recombination in every test. The results indicate that the Bishop catalyst was as effective in promoting recombination as was Product 43 (platinum on charcoal).

Recombination with Catalyst Poisoned with Iodine. A study of the effect of iodine on the efficiency of the conversion reaction in the presence of Bishop catalyst was carried out in tests in which about 30 g of catalyst was contained in the 0.75-in.-diameter pyrex glass tube as previously described. The first series of tests was made employing catalyst bed temperatures of 200 and 500°C, which were obtained by holding the composition of the gaseous mixture at about 3 and 6% electrolytic gas, respectively. Other conditions were a total gas flow rate of about 10 liters/min and an iodine flow of about 50 mg/hr. The results showed that the efficiency of the conversion reaction was only about 5% at 200°C and above 96% at 500°C.

A second series of tests was carried out employing catalyst bed temperatures of about 500 and 200°C with other conditions the same as those of the first series except that the catalyst used had previously been poisoned with iodine and no iodine was added during the tests. The results showed that the efficiency of the conversion reaction at 500°C was about 97%. When the bed temperature was reduced to 200°C the efficiency did not decrease.

It was concluded that the Bishop catalyst would be satisfactory for use in the small catalytic unit which supplements the primary flame recombiner in the HRE off-gas system provided the bed temperature is not permitted to fall below 500°C.

High-Pressure Catalytic Recombination. The possibility of carrying out recombination of hydrogen and oxygen at the temperature and pressure of the HRE soup system has been under consideration since the project was initiated. To investigate the feasibility of recombining the gases under these conditions, five runs were made in which hydrogen and oxygen were admitted to a catalytic recombiner containing steam at pressures varying from 280 to 520 psia. The electrolytic gas flow rate was varied from about 200 to 420 cc/min. The reaction was carried out in a section of 1½-in. standard stainless steel pipe with about 35 g of Product 43 catalyst in a bed about 2 in. deep located in the topmost portion of the pipe. In each test the reaction started immediately upon admission of the gas, and no pressure build-up was shown. These results indicate the desirability of continuing the studies.

In-Pile Test. In order to get a direct evaluation of the effect of radiation on catalyst materials, an in-pile test was conducted in which Product 43 was suspended over a uranyl sulfate solution. The assembly utilized was similar to that described in the previous report (ORNL-925).

The catalyst (about 50 mg) was supported on a perforated plate in the vapor space above the solution. Since this prevented insertion of the usual thermocouple into the liquid, an upper thermocouple measured the vapor temperature and a second thermocouple was introduced through the bottom of the bomb into the liquid. A split furnace was used for heating so that the temperatures of the vapor and the liquid could be controlled independently. Hydrogen and oxygen formed in this bomb should be recombined to water in contact with the catalyst and should then reflux to the soup.

The unit was placed in the graphite pile (hole 12) at full flux on December 20, 1950 with a liquid temperature of 250°C. The power to the furnaces was controlled so that the vapor temperature was maintained at 3 to 7°C above that of the liquid to reduce the possibility of flooding the catalyst.

During in-pile testing of bombs used for corrosion studies there was usually a pressure build-up during the first day or two to about 4000 psi above the steam pressure, at which point it remained, probably owing to recombination on the walls of the vessel. In this test the pressure increase was very gradual; the pressure was only about 200 psi above that of steam at the end of the first week.

Several attempts were made to flood the catalyst with water by lowering the temperature of the vapor by 15 to 20°C below that of the liquid. If successful, this should have permitted the pressure to rise in a manner similar to that in the bombs without catalyst. Since the pressure continued its gradual rise, it was assumed that local hot spots on the catalyst prevented complete flooding.

The bomb remained in the pile for a total of 25 days, at the end of which time the pressure was 400 psi above that of steam. The assembly is now cooling, and analysis will be made of the solution, the residual gas, and of the catalyst pieces.

PILOT-SCALE TESTS OF THE FLAME RECOMBINER

H. M. McLeod, Jr.
Don Phillips

M. J. Fortenberry
T. S. Mackey

The feasibility studies of the combustion type recombiner were concluded and the results reported in Y-706; the important results of these studies were

also given in past HRE quarterly reports (ORNL-826 and 925). Subsequently the existing pilot plant equipment was rearranged to permit operation of the flame recombiner under the conditions of temperature, pressure, composition, and flow rates that are expected during operation of the HRE. A flow diagram of the pilot plant is shown in Fig. 29.

Description of the Pilot Plant. Stoichiometric gas ($H_2 + \frac{1}{2}O_2$) and steam at flow rates of 17 and 70 cfm (N.T.P.), respectively, were mixed and passed through a condenser in which most of the steam was condensed. The gas and remaining steam as well as the condensate passed to a receiver which also served the purpose of a primary liquid-vapor separator. The liquid level in this receiver was maintained at the desired height by means of a level control which operated a pump. The pump discharged into a portable tank, and the quantity of condensate was measured at intervals. After leaving the receiver the gas, saturated with water vapor, passed through the burner orifice into the combustion chamber, where it was burned in contact with a spark. The burner orifice contained 147 openings, 1/32 in. in diameter. A second spark plug was located upstream from the orifice to permit creating a flashback at any time desired during operation. Condensate and unrecombined gases left the burner chamber and passed to a second receiver similar in all respects to that previously described. From the receiver the unrecombined gases passed through an auxiliary condenser to an ejector at a rate sufficient to maintain about 9 psia in the receiver. An auxiliary line was provided to facilitate adjusting the gas flows during start-ups; as soon as the flows were adjusted to the desired rates, the auxiliary line was closed and the ejector line opened. Cooling water was separately metered to the various points of use, and its inlet and outlet temperatures were measured. The temperature and pressure at other important points in the system were also recorded.

Flashback Quenching. In rearranging the equipment to permit operation of the pilot plant under conditions simulating those expected during operation of the HRE, provisions were included for automatically quenching flashbacks by the method previously tested on a small scale (ORNL-925). The method consisted in adding additional steam to the steam-gas mixture leaving the dump tanks in quantity sufficient to provide a noncombustible mixture between the dump tank and a condenser in which most of the steam was condensed and recycled back to the dump tank.

FIG. 29
EQUIPMENT LAYOUT & FLOW DIAGRAM — RECOMBINER PILOT PLANT
(Gas flow rates based on 70°F & 1 atm.)

The pilot plant equipment for effecting quenching consisted of: (1) a tubular condenser (347 stainless steel) containing forty-four 0.75-in.-diameter tubes, 6 ft in length, which provided a total condensing surface of about 50 sq ft; (2) a condensate pot fabricated from a 24-in. section of standard 6-in. pipe (316 stainless steel); and (3) a commercial manometer type level control for maintaining the desired liquid level automatically. The burner chamber cover plate, which contained the burner orifice, was located outside the barrier during the flashback tests to permit observation of the orifice and spark plug as well as the flame.

In carrying out the tests, measured quantities of hydrogen and oxygen were mixed and passed through a loop formed of 1/2-in. copper tubing, then into a heat exchanger in which the gases were mixed with metered steam, and finally into a condenser, in which most of the steam was condensed and removed; the remaining gases then passed to the burner orifice where they were ignited and burned in contact with a spark. A second spark plug was located upstream from the burner orifice to ignite the mixture behind the orifice at any time desired. The gas and steam flows were maintained at the desired rate for about 10 min prior to a flashback test. After flashing, the flame either was quenched in the condenser and reignited at the burner or it penetrated back to the point of admixture of hydrogen and oxygen and burned out the copper tubing loop. The flow of gas ($H_2 + \frac{1}{2}O_2$) was maintained at 17 and 9 cfm, while that of steam was varied to determine the maximum percentage of gas entering the condenser which would successfully quench flashbacks.

During the first series of tests the composition that was effective in quenching flashbacks at maximum gas flow varied from about 20 to 31% electrolytic gas. Since steam was introduced into the gas stream at a point only 18 in. upstream from the condenser, it appeared likely that the noncombustible blanket maintained in the system was too shallow; consequently the point of mixing the steam and gases was moved upstream to provide an additional 6 ft of depth. The second series gave consistent results over a period covering several days; with gas flow rates of 17 cfm the maximum percentage of gas at the condenser inlet which would effectively quench the flashback was about 28% while with a gas flow rate of about 9 cfm the value was about 21%. These compositions will be checked again under the conditions of simulated HRE operation in the immediate future.

Testing of the HRE Flame Recombiner. In the HRE flowsheet a condenser has been provided to condense all the steam leaving the small catalytic unit which supplements the primary flame recombiner. To design this condenser it was necessary to know approximately both the quantity of gas passing from the flame recombiner to the catalytic unit and its temperature under the condition of maximum gas flow. Consequently the HRE flame recombiner was connected into the system and operated with 17 cfm combined gas and about 70 cfm steam entering the condenser. The quantity of cooling water entering the burner chamber jacket was varied from about 7 to 21 gpm and its temperature from 45 to 75°F.

Results showed that the maximum quantity of uncondensed steam leaving the burner chamber was about 20 lb per hour and the maximum temperature was about 880°F; these values were obtained when the temperature of the cooling water to the burner chamber was maintained at 75°F at a flow rate of 21 gpm. The quantity of condensate from the burner chamber under these conditions was about 18 lb per hour. With the cooling water at 45°F (ambient), the quantity of condensate was about 30 lb per hour while that of uncondensed steam was about 6 lb per hour and its temperature was only about 520°F. Since these conditions represent the extreme, it was concluded that the second condenser should be designed to condense about 20 lb of superheated steam which would have an inlet temperature of about 840°F.

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4. HRE CHEMICAL STUDIES

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SOLUBILITY OF FISSION PRODUCT SULFATES

B. Zemel

The determination of the solubilities of the fission product sulfates is continuing along the lines previously described (ORNL-925, pp. 251-260).

The solubilities are determined by equilibrating the solution, with the sulfate precipitate in type 347 stainless steel bombs at a fixed temperature and analyzing by the tracer technique. The solubilities of BaSO_4 and of $\text{Y}_2(\text{SO}_4)_3$ were determined over the range of 120 to 400°C; the values are given in Figs. 30 and 31.

The concentrations of $\text{Y}_2(\text{SO}_4)_3$ were determined by evaporating and counting an aliquot. Those of BaSO_4 were determined primarily by precipitating the barium as the chloride in HCl-ether reagent, using four precipitations as described in report CN-2815, and counting the BaCl_2 immediately after the last precipitation. This value was then corrected for yield, and for growth of La and decay of Ba. This more involved procedure was made necessary by the existence of the 40-hr La^{140} daughter and by apparent contamination with other activities.

The solubility of BaSO_4 in water was found to be about 6 μg per 100 g of solution at 250°C, showing that BaSO_4 has the same type of temperature dependence as SrSO_4 and the other alkaline earth sulfates.

The solubility of $\text{Y}_2(\text{SO}_4)_3$ at 250°C was found to be about 0.01 mg per 100 g of solution, which is probably fairly typical of that of the other rare earth sulfates.

TABLE 17
Solubility Values

BaSO_4		$\text{Y}_2(\text{SO}_4)_3$	
TEMPERATURE (°C)	AMOUNT DISSOLVED ($\mu\text{g}/100$ g solution)	TEMPERATURE (°C)	AMOUNT DISSOLVED (mg/100 g solution)
150	60.4	190	10.1
180	26.5	200	0.9
220	11.25	218	0.01
250	5.25	230	0.01
250	6.2	230	1.75
262	4.6	230	1.5
290	2.3	240	0.28
291	1.4	240	1.12
		240	1.38
		285	0.01
		320	0.12
		325	0.06
		340	0.24
		385	0.01

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113

DWG. 10481

106

500 194

UNCLASSIFIED

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114

DWG. 10300

FIG. 31

65 105

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BARIUM SULFATE PRECIPITATION AND XENON CONCENTRATION IN THE HRE

O. E. Myers and M. H. Lietzke

The following calculation indicates that barium sulfate will begin to precipitate from the HRE solution after full-power operation for a few hours. This may pose a serious problem, the more so because BaSO_4 is notorious as a scavenger. The figures are based on recent work by M. H. Lietzke and R. W. Stoughton (ORNL-970) and B. Zemel (this report) on the behavior of fission product and uranyl sulfates at high temperatures.

The following simplifying assumptions were made: No xenon or barium atoms are initially present in the 70 liters of solution. Full power of 1000 kw is achieved instantaneously. No barium is formed directly; except from Cs^{136} and Cs^{142} in 0.01 and 3.5% yield, it must derive from decay of radio-xenon. A total of 480 cc of gas will be formed in the reaction vessel per second ($\text{H}_2 + \text{O}_2$ at 420 psi and steam at 580 psi), which will serve to sweep out a portion of the xenon produced before it has decayed. All cesium and barium atoms produced in the gas phase are removed. Neutron capture by xenon, cesium, and barium isotopes considered will be negligible. No barium with mass ≤ 134 or ≥ 146 need be considered. For Ba^{143} , Ba^{144} , and Ba^{145} the decay constant is chosen as 0.23 sec^{-1} .

Other necessary assumptions materially affect the calculation. It has been assumed that the solubility of xenon in the HRE solution at 250°C is equal to its solubility at room temperature. For other gases the solubility passes through a minimum below 200°C and at 250°C is within a factor of 2 or 3 of the room temperature value. Further, the assumption is made that xenon will at all times maintain its equilibrium vapor pressure. Whether this is valid is difficult to estimate. Perhaps the poorest assumption made here concerns the thermodynamic sulfate ion activity; this will be considered later.

The following symbols refer to a single isobaric system

N = number of barium atoms present at time t

N' = number of xenon atoms present at time t

N'' = number of cesium atoms present at time t

λ = barium decay constant

λ' = xenon decay constant

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λ'' = cesium decay constant

r = xenon removal constant, $r = \lambda' + \sigma\phi + s$

σ = xenon cross-section for neutron capture

ϕ = neutron flux

s = sweeping constant for xenon (fraction swept out per second)

t = time after sudden full-power operation has begun

y = fission yield

F = rate of fission (1 g/day = 2.96×10^{16} atoms/sec)

Rate of Sweeping Out of Xenon. The ratio of the number of xenon atoms in the gas phase in equilibrium with an equal volume of aqueous solution to the number of xenon atoms in solution is sensibly constant at a given temperature. At 17°C the solubility is 28.4 cc per 100 g of H₂O and the value of the ratio is 3.5. From the above assumed conditions 1/40 of the xenon in solution would be swept out in each second.

$$\frac{s}{0.48} \frac{1-s}{70} = 3.5; \quad s = 1/40 \approx 0.0246$$

Rate of Barium Formation from Radioxenon. The rate of barium build-up is equal to the rate of cesium decay less the rate of barium decay:

$$dN/dt = \lambda''N'' - \lambda N \quad (1)$$

To find N'' , the rate of cesium build-up is given by the rate of xenon decay less the rate of cesium decay:

$$dN''/dt = \lambda'N' - \lambda''N'' \quad (2)$$

N' may be found by integrating

$$dN'/dt = Fy - \lambda'N' - sN' = Fy - rN' \quad (3)$$

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For $N' = 0$ at $t = 0$,

$$N' = \frac{Fy}{r} (1 - e^{-rt}) \quad (4)$$

Substitution into Eq (2) gives

$$\frac{dN''}{dt} = \frac{\lambda' Fy}{r} (1 - e^{-rt}) - \lambda'' N'' \quad (5)$$

Integration of Eq. (5) with $N'' = \text{zero}$ at zero time gives

$$N'' = \frac{\lambda' Fy}{r - \lambda''} \left[\frac{1 - e^{-\lambda'' t}}{\lambda''} - \frac{1 - e^{-rt}}{r} \right] \quad (6)$$

Equation (6) may be substituted into Eq. (1) and integrated for $N = \text{zero}$ at zero time:

$$\frac{dN}{dt} = \frac{\lambda' \lambda'' Fy}{r - \lambda''} \left[\frac{1 - e^{-\lambda'' t}}{\lambda''} - \frac{1 - e^{-rt}}{r} \right] - \lambda N \quad (7)$$

$$N = \frac{\lambda' Fy}{r\lambda(\lambda - \lambda'')(\lambda - r)(r - \lambda'')} [r\lambda''(r - \lambda'')(1 - e^{-\lambda t}) + r\lambda(\lambda - r)(1 - e^{-\lambda'' t}) + \lambda\lambda''(\lambda'' - \lambda)(1 - e^{-rt})] \quad (8)$$

If stable barium is formed (mass 135, 137, 138), $\lambda = 0$, and equation (8) becomes:

$$N = \frac{\lambda' Fy}{r^2 \lambda'' (r - \lambda'')} [r \lambda'' (r - \lambda'') t - r^2 (1 - e^{-\lambda'' t}) + \lambda'^2 (1 - e^{-r t})] \quad (9)$$

Rate of Barium Build-up from Radiocesium. If there is no xenon precursor (mass 136, 142) Eq. (2) becomes

$$dN''/dt = Fy - \lambda'' N'' \quad (10)$$

For $N'' = 0$ at $t = 0$,

$$N'' = \frac{Fy}{\lambda''} (1 - e^{-\lambda'' t}) \quad (11)$$

and Eq. (1) simplifies to

$$dN/dt = Fy(1 - e^{-\lambda'' t}) - \lambda N \quad (12)$$

which gives on integration

$$N = \frac{\lambda'' Fy}{\lambda - \lambda''} \left[\frac{1 - e^{-\lambda'' t}}{\lambda''} - \frac{1 - e^{-\lambda t}}{\lambda} \right] \quad (13)$$

for $N = 0$ at $t = 0$.

If stable barium is formed (mass 136), Eq. (13) reduces to

$$N = \frac{Fy}{\lambda''} [\lambda'' t - 1 + e^{-\lambda'' t}] \quad (14)$$

TABLE 18

Total Number of Barium Atoms Present in the HRE at Any Time

CHAIN*	λ' (sec ⁻¹)	λ'' (sec ⁻¹)	λ (sec ⁻¹)	Y (%)	$10^{15} F_y$ (atoms/sec)	$r = \lambda' + s$	$\frac{t}{\text{Eq.}}$	$\frac{10 \text{ sec}}{10^{15} N}$	$\frac{10^2 \text{ sec}}{10^{16} N}$	$\frac{10^3 \text{ sec}}{10^{18} N}$	$\frac{10^4 \text{ sec}}{10^{19} N}$	$\frac{10^5 \text{ sec}}{10^{20} N}$	$\frac{10^6 \text{ sec}}{10^{21} N}$	$\frac{10^7 \text{ sec}}{10^{21} N}$
135	$2.1 (10)^{-5}$	$2.2 (10)^{-14}$	0	5.9	1.75	0.0246	9							
136	0	$6.2 (10)^{-7}$	0	0.01	0.003		14						0.0078	0.025
137	$3.4 (10)^{-3}$	$6.7 (10)^{-10}$	0	6.2	1.84	0.0280	9							
138	$6.8 (10)^{-4}$	$3.6 (10)^{-4}$	0	6.2	1.84	0.0253	9			0.008	0.036	0.048	0.049	0.49
139	$1.7 (10)^{-2}$	$1.3 (10)^{-3}$	$1.36 (10)^{-4}$	6.3	1.86	0.0416	8			0.31	0.38	0.054	0.0054	0.0054
140	$4.3 (10)^{-2}$	$1.05 (10)^{-2}$	$6.3 (10)^{-7}$	6.1	1.80	0.0676	8	1.4	3.4	1.0	1.1	1.1	0.84	1.8
141	0.23	(0.023)	$6.4 (10)^{-4}$	5.7	1.69	0.2546	8		0.080	0.084	0.11	0.024	0.0024	0.0024
142		5 to 12 (10) ⁻³	$1.9 (10)^{-3}$	5.6	1.66		13	0.7 to 1.2	3.4 to 6.5	0.7	0.089	0.0089	0.00089	0.00089
143	~0.69	(0.023)	>0.023	5.4	1.60	~0.715	8	0.08	0.008					
144	~0.69	(0.023)	(0.023)	5.3	1.57	~0.715	8	0.08	0.008					
145	0.87	(0.023)	(0.023)	4.7	1.40	0.895	8	0.09	0.009					
Total								~2.7	~8.4	2.1	1.7	1.2	0.9	2.3

*Small equilibrium amounts of Xe¹³³ will be present also.

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TABLE 19

Total Number of Radioxenon Atoms Present in the HRE at Any Time

CHAIN*	$10^{15}F_y$	r	$10^{16}F_y/r$	$t = 1 \text{ sec}$	$t = 10 \text{ sec}$	$t = 100 \text{ sec}$	$t > 500 \text{ sec}$
				$10^{15}N'$	$10^{16}N'$	$10^{17}N'$	$10^{17}N'$
135	1.75	0.0246	7.12	0.9	0.9	0.52	0.71
136							
137	1.84	0.0280	6.57	1.1	1.0	0.53	0.66
138	1.84	0.0253	7.27	1.0	0.9	0.54	0.73
139	1.86	0.0416	4.47	1.3	1.2	0.43	0.45
140	1.80	0.0676	2.66	1.4	1.2	0.27	0.27
141	1.69	0.2546	0.66	1.4	0.60	0.066	0.066
142							
143	1.60	~0.715	0.22	1.1	0.22	0.022	0.022
144	1.57	~0.715	0.22	1.1	0.22	0.022	0.022
145	1.40	0.895	0.16	0.94	0.16	0.016	0.016
Total	15.4			10.2	6.4	2.4	3.0

*Small equilibrium amounts of Xe^{133} will be present also.

On the basis of the above values, one can expect that the opacity of Xe^{135} will amount to about one-fifth that of the sulfur present.

Barium Sulfate Precipitation. B. Zemel has observed that the solubility of BaSO_4 in water at 250°C is $50 \mu\text{g/liter}$, $K_{sp} = 4.6 \times 10^{-14}$. Lietzke and Stoughton found the sulfate ion activity in $0.13 f \text{ UO}_2\text{SO}_4$ to be 1.4×10^{-9} . If one assumes this to be correct, it is found that the sulfate will begin to precipitate when the barium concentration in the reactor reaches 1.4×10^{21} atoms/liter. This value is indicated on the graph (Fig. 32) by the horizontal line which intersects the curve of barium growth at an abscissa of 25 days.

However, 0.7×10^{-9} mole of uranium per liter per second undergoes fission, leaving an equivalent excess of free sulfate ion. If this factor alone were to determine the sulfate ion activity growth, the second "solubility limit" line of the graph would apply, and barium sulfate would begin to precipitate after about 18 min.

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The low sulfate activity in UO_2SO_4 solutions at high temperature is probably accounted for largely by the formation of $\text{UO}_2(\text{SO}_4)_2^{--}$ ions; neither the constant for this complex at 250°C nor the behavior of barium ion in such a system is known. The logarithmic mean of the two precipitation limits occurs at 14 hr.

Probable Limits of Error. Uncertainty in the determination of the barium concentration is caused primarily by poor knowledge of the rate of sweeping of xenon. The fraction of equilibrium vapor pressure achieved will depend on the average bubble size; for an average bubble path of 30 cm it may be shown that the total volume swept per second is

$$V \approx 12/r \quad \text{liters}$$

where r is the bubble radius in centimeters. It is not unreasonable to suppose that evaporation will proceed halfway to equilibrium if the total volume is swept each second. Then if r is 0.1 mm or less the equilibrium approximation is valid. Other errors may be introduced by the following factors:

1. Xenon solubility is assumed to be within a factor of 3 of the chosen value.
2. Sulfate activity is assumed to be within a factor of 10 of the mean value for the two cases considered.
3. No other assumption involves large uncertainties.

Barium sulfate will begin to precipitate after 30 min to 25 days.

ANALYTICAL CHEMICAL CONTROL

W. H. Davenport and R. H. Powell

Current evaluation of the most feasible methods for direct measurement of the reactor solution favors the determination of density using either the electromagnetic densitometer or the Princo Densitrol, or both, and the determination of uranium concentration by its effect upon the Q of a suitable high-frequency coil.⁽¹⁾ The rate of development of these methods has slowed considerably owing to the difficulty in obtaining the special materials and apparatus required for reactor conditions.

(1) *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950, ORNL-925 (Jan. 30, 1951).*

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The investigation of the effect of radiation on Alnico magnets was concluded.

Radiation experiments were started on glasses reported to have high optical stability under pile radiation conditions, with the hope that such glasses might be used for optical measurements of the reactor solution. Chemical stability of these glasses will be investigated if the radiation properties of the glasses are satisfactory.

Electromagnetic Densitometer. The stainless steel float previously tested at 1000 psi and room temperatures was tested in a bomb at HRE temperatures and pressures. The bomb collapsed at a point believed to be 285°C and 1000 psi. Microphotographs at the rupture point of the collapsed float⁽²⁾ indicated that possible structural weaknesses accompany the welding operation. A new float was fabricated from the same stock of 309 stainless steel; this float contained 0.3 g of distilled water purposely added to pressurize it at higher temperatures. To date this float has been simultaneously pressure tested and heat tested to 1330 psi and 305°C without visible structural damage. It is planned to use it experimentally for current purposes and subsequently determine the collapsing strength for higher temperatures and pressures. The ultimate float will be constructed of 347 stainless steel.

The magnetic coil has been temperature tested to 305°C without detectable damage to the electrical circuit.

Two microformers for position detection of the float have been received. They were constructed by Schaevitz Engineering Company, using Lava forms and Seroc coils.

No further work has been done on the radiation detection methods.

The idea of using a magnetic device to detect float position had been abandoned; however, the study of the effect of radiation upon Alnico magnets was completed. The results, based on the deflection of a magnetic dip needle, showed no detectable loss of magnetism in magnets which had been exposed to a total of 5 months of irradiation in the X-10 pile at a temperature of 150°C.

Princo Densitrol. Three of these commercially available instruments have been ordered from Precision Thermometer and Instrument Company, and specifications for HRE use have been incorporated in the design. The sampling

(2) Willmarth, T. E., private communications.

chambers and connecting pipe are 347 stainless steel. Glass insulation will be used on the wiring. Hydrometer floats have been requested in stainless steel and in pyrex. Duplicate floats have been requested for in-pile radiation and corrosion tests.

Under normal operating conditions the Princo Densitrol will measure densities within $\pm 3\%$ of the total range or within 0.0002 g/cc units, whichever is the greater. The instruments especially constructed for the HRE will meet the added requirements of temperature and pressure and are designed to meet the requirements for radiation and corrosion stability. The last two effects must be tested, however.

Q Coil. Platinum coils which had been embedded in compressed Lava Grade A⁽³⁾ powder were taken to the American Lava Corporation to be glazed, if possible. The American Lava Corporation spent several weeks testing various glazes before concluding that, owing to differences in the thermal coefficients of expansion of the ceramic and the glazes, a satisfactory glaze could not be applied to this particular grade of Lava. They suggested that Lava Grade M be used as a substitute and also supplied a glaze which they have been using successfully on natural Lava Grade M. The Research Shops have embedded copper coils in compressed Lava Grade M powder and fired the ceramic in a hydrogen atmosphere. Radiographs of the cylinders indicated that the coils remained intact. The cylinders will be machined and glazed. The bare copper leads will have to be protected when the glaze is fired since tests have shown that the glaze cannot be fired in a hydrogen atmosphere.

Electronic equipment which will be used to measure the Q automatically has been designed and is now being fabricated in the Instrument shops.

Radiation Protected Glasses. Gamma and neutron absorbing glasses have been cut and polished for optical measurements before and after irradiation. A glass having chemical and optical stability in HRE solutions is being sought.

(3) ORNL-925, *op. cit.*

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5. EXPERIMENTAL PROGRAM FOR THE HRE

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INTRODUCTION

An integrated program of experimentation for the HRE will help ensure adequate instrumentation and controls and provide a guide for obtaining a maximum of information as the HRE goes through successive stages. Experiments best performed at a given power level can be carried out in an orderly fashion, and thus possible faults in design reasoning may be detected and corrected before operation has proceeded to the point of no return or, at least, of costly return. The planned experiments should provide data to answer or help answer the questions raised in considering the feasibility of this reactor and future reactors of this type. These data will afford checks on the reasoning and design factors used in planning the HRE and will lend support to the extension of these to other reactors of the same general class.

The design values of the HRE have been based on an operating goal of 1000 kw at 250°C and 1000 psi. However, a large part of the information which can be obtained under these conditions can also be obtained by operation at lower power, temperature, and pressure. In fact, so many of these data may be obtained under these less severe conditions, if the reactor experiments are performed at the lower values and for some reason it is impractical to go on to the final level, the HRE can still be considered highly successful. It seems reasonable to assume that many problems, such as chemical stability, corrosion, and valve erosion, will be less severe at lower operating levels than at the ultimate values; it is therefore proposed that all the experiments possible be performed at these levels before going to higher levels for any experiment. The exact values of temperature and pressure to be used should be decided at the time the reactor goes critical in light of our knowledge then. The power level may then be adjusted to give operating conditions similar to those which would prevail under full power at 250°C and 1000 psi. These factors will be discussed in connection with the individual experiments. The temperature coefficient of reactivity decreases with decrease of temperature so the reactor cannot withstand as large k surge at 150 as at 250°C. The coefficient should still be adequate, but extra care in introducing reactivity changes is necessary.

The various experiments may be grouped into general categories coinciding with the steps in the construction and operation of the HRE. These are component tests, subcritical tests, critical experiment, low-flux experiments, and high-flux experiments.

The experiments suggested for each of these steps will be discussed in some detail. It should be understood that there is considerable interrelation between many of the experiments, and that as the actual tests proceed modifications may be necessary. In addition to these formal tests careful observation of the general operation of the system as a whole and of its components will yield useful data on the general feasibility of the reactor as a practical unit in the atomic energy program.

COMPONENT TESTS

It is assumed that the necessary testing of the components has been done; therefore these tests will not be discussed here.

SUBCRITICAL TESTS

In a sense, tests at this stage are component tests, but the integrated assembly offers an opportunity to observe the behavior of some of the controls when all the interconnecting functions are in the system. Possible erratic behavior can then be corrected before changes are complicated by radioactive materials.

Process Control Response. The functioning of many of the process controls may be tested with only water in the system. Neutron and gas effects will not be present, but response times and possible oscillating conditions may be checked. Data of value from this test will be:

1. Level-time curves from the level recorder or, if necessary, an oscillograph.
2. Pressure-time curves for core when pressurizer temperature is varied and when pumps are started and stopped.
3. Pressure-time curves for reflector space for conditions outlined above.
4. Time characteristics of dump systems.
5. Response of controls for various operating pressures.

Concentration Calibration. The operating indicator of concentration is a weight instrument weighing the amount of water held in the condensate tanks.

The total amounts of water and uranium in the system is known from charging data, but a calibration of the condensate weight against chemical analysis of solution samples will indicate the accuracy to be expected from this method of concentration measurement. At each calibration point the circulation system should operate for sufficient time to ensure equilibrium conditions.

Soup Stability. Perhaps the most important subcritical test is to assure the chemical stability of the soup before neutrons are introduced. In this respect the reactor will serve as the final "test loop." When the reflector is down the reactor cannot go critical and the soup may be circulated as desired. Of course, these tests will not be run for times comparable with those used in the regular test loops, but it is hoped that techniques will be developed for forecasting stability from short-time runs.

The temperatures at which the test is run should be determined by the knowledge of the stability problem at the time. Since it is proposed that many of the experiments be performed well below 250°C, it may be desirable to limit the temperature here to a lower value. Temperature may be readily controlled by introducing steam from the house boiler or the 40-kw reactor boiler into the main heat exchanger. The minimum pressure will be determined by the excess pressure required for the circulating pump.

Close check on the soup condition during this test is essential. Since test loop experiments are still in progress, it is too early to outline just what analyses should be made, but certainly all procedures which may be developed by the time of this test should be utilized.

CRITICAL EXPERIMENT

The critical experiment for the HRE will differ somewhat from the usual reactor critical experiment in that increments of fuel will be added by increasing the concentration rather than by adding successive fuel elements. The experiment must be performed at constant reflector level. To ensure this condition the reflector pumps should not be operated while determining counts. The soup temperature should be maintained constant by heating with building steam. It is necessary to operate the circulating system for a sufficiently long time between concentration changes to ensure the attainment of solution equilibrium before measurements are made. The variation of counting rate

with time after an incremental concentration change will give an indication of the degree to which solution is held at semistagnant points in the system. This effect should be negligibly small.

The temperature and pressure at which this experiment and successive experiments at increasing power levels are to be carried out need to be established. The question should be reviewed at the time of this experiment and the values set then. Unless the picture changes appreciably, it will probably be wise to perform the critical experiment at 150°C, or lower if possible. Other experiments at power values up to several kilowatts should be done before trying to operate at 250°C and 1000 psi. The circulating pump requires an excess pressure in the system to prevent cavitation, and this will place a lower limit on the pressure to be used. The presently accepted value for this excess pressure is 200 psi, but further pump tests may prove this to be high although it is unlikely that it can be less than 50 psi. If 200 psi is correct, the system pressure at 150°C needs to be approximately 270 psia and the pressurizer temperature 209°C.

With these precautions the actual experiment is performed by increasing concentration in steps and obtaining and plotting inverse counts against uranium mass. Mass is obtained from the calibrated condensate weight instrument and counts from the customary fission chambers. By taking counts with the shim rod down and then up, the horizontal displacement of the two curves will give a "mass equivalence" for the rod at this flux distribution.

LOW-FLUX EXPERIMENTS

Temperature Coefficient. The temperature coefficient of reactivity as used in the feasibility study is expressed as $\delta k/^\circ\text{C}$. The measurement of temperature is rather straightforward, but of necessity must be measured at reasonable distances from the core. Provisions are made for measuring temperature in the inlet and outlet soup pipes, the desired core temperature being some kind of an average between these two values. It is obvious that the temperature in the core cannot be determined with any great degree of accuracy. The δk which appears in the temperature coefficient is a very convenient concept when dealing with computations of neutron economy, but in a complex reactor experiment its meaning is best translated into some other unit of more

practical significance. The material multiplication constant may be expressed as

$$k = \eta \frac{\Sigma_a}{\Sigma_t}$$

where Σ_a is the macroscopic absorption cross-section of the uranium and Σ_t is the macroscopic cross-section of the solution of UO_2SO_4 in water. Since these quantities may be easily expressed in terms of ratio of mass of uranium to that of water, our basic unit of reactivity in the reactor will be considered as grams of uranium per kilogram of water, i.e., g U/kg H_2O . This is a thoroughly practical unit and is independent of temperature and pressure.

In measuring the temperature coefficient, or what might be considered an adequate indication of temperature coefficient, we can deal entirely with states of equilibrium. In order to avoid the effect of gas coefficient, this experiment should be performed at low flux levels.

With the reactor operating at an average core temperature of probably around 150°C , the actual value to be based on the considerations discussed in connection with the critical experiments, a small change in concentration should be allowed to become adjusted and the inlet and outlet temperatures then measured. Another small change of this size should be made and the temperatures noted, the process continuing until the maximum allowable temperature or power is reached. A plot of these data may be interpreted with reasonable accuracy in terms of the temperature coefficient used in calculations. It is desirable that this experiment be performed over as large a range of average reflector temperatures as is consistent with the conditions of the experiment.

Control Plate Calibration. The shim and regulating plates may be calibrated in two ways. If the basic unit of reactivity is considered to be g U/kg H_2O , as discussed above, the plate calibration may be obtained by moving the plate a known distance and bringing the reactor back to the same temperature by varying the concentration. This is a rather slow procedure since the solution concentration and temperature must be allowed to reach equilibrium for each concentration increment.

If it is assumed that the temperature coefficient is an adequate indication of reactivity conditions, this coefficient may be used as a transfer

standard and the plate calibration procedure shortened. With a constant concentration the rod position may be changed in steps, the temperature at inlet and outlet obtained, and from this information the equivalent $g\text{ U/kg H}_2\text{O}$ of the rod increment determined from the results of the previous experiment.

The reflector temperature should be maintained constant during the calibration. This experiment should be performed for at least two reflector levels, the first that of a completely filled reflector and the second that corresponding to the core just covered with D_2O .

Since k may be expressed in terms of $g\text{ U/kg H}_2\text{O}$, the calibrations may be converted to conventional calibration form if desired.

Reflector Level Calibration. This calibration is carried out in the same way as that of the control plates. The level is controlled by adjusting the set-point of the level controller. The level will not be known as accurately as the control plate position, but, since the reflector can serve as a rough shim only, this is not of great importance. Surface turbulence may be an important factor, especially when the reflector level is low. Temperature fluctuations will serve as a measure of this turbulence effect, and for calibration purposes a mean value may be used.

Reflector Temperature Effect. The reflector temperature enters into the overall temperature coefficient of the reactor and some measure of its effect is desirable. The measurement can be made by making changes in the average reflector temperature (determined by the controlled flow of water in the D_2O heat exchanger) and observing the concentration change required to keep the temperature difference between the core and reflector constant. Since this experiment is performed at low power, the principal heat extraction is due to the core-reflector temperature differential. Keeping this constant keeps heat extraction constant and eliminates gas effect complications. At higher powers the heat extraction may be maintained constant by keeping the core inlet-outlet temperature difference as well as the core-reflector temperature difference constant. The interpretation of these data should be made in conjunction with the core temperature coefficient.

Safety Plate Calibration. If the feasibility study is correct, the safety plates are superfluous. Since they have been included in the design and since there may be a possibility of needing them when raising the power of the reactor, this is a good point at which to check their effectiveness.

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The check may be made by observing the change in average temperature of the core at constant concentration for the two extreme positions of the plates. The safety interlocks on the system prevent start up except when the safety plates are completely withdrawn, and the experiment is performed by first bringing the reactor up to the desired operating condition and obtaining data for the plates withdrawn. They are then run down and the automatic dump of the reflector is blocked with the manual control. In this way the data for the extreme positions of the plates may be obtained without blocking out any of the safety interlocks. While temporary operation with the plates down was foreseen in the safety circuits and the manual override of the reflector dump was provided to allow such operation, it is an abnormal condition and the experiment should not be performed until considerable operating experience with the reactor has been obtained. As a safety measure the shim plates should be withdrawn to serve as safety plates for this experiment.

The safety plate calibration should be repeated for several values of reflector level.

Transient Behavior. A time record of the values of n , $\log n$, $(d \log n)/dt$, core pressure, and pressurizer level under transient conditions will aid in interpreting similar records taken under power conditions later. These low-power data will not include gas effects but will include temperature and delayed neutron effects. The desired transient conditions are discussed in the preceding section. Critical observation of all instruments under any transient condition is assumed.

HIGH-FLUX EXPERIMENTS

"High flux" in this section is interpreted to mean any flux above that necessary for a few watts. In line with the discussion given in the introduction, these experiments should all be performed at relatively low power values, perhaps starting at about 10 kw, before increasing the power. Then each experiment should be repeated at increased power steps, with properly adjusted temperature and pressure conditions, until rated conditions are reached. In this way, if some fault should develop and necessitate shutdown of the reactor, valuable data on all the experiments will have been obtained. If the reactor performs as expected the series of experiments at increasing power levels will be very helpful in forecasting the behavior at each successive power step and hence increasing the safety of the project.

Power level may be adjusted by the control plates, the concentration, or reflector level. In the early stages of the program one of the first two is preferable as it is desirable to use a full reflector to increase the effectiveness of the safety plates. Preliminary experimentation will indicate which is the simpler. At a later stage more complete performance data on concentration as the principal control will be needed.

Feasibility of Decontamination. The feasibility of decontaminating surfaces in contact with the soup and hence the magnitude of the maintenance problem can be determined before the reactor is operated at even moderately high power levels. The reactor should be run at nominal power to determine this feasibility before going on to the other high-flux experiments.

Heat Extraction and Power Calibration. The usual methods for determining reactor power are by flux distribution measurements and by determining the amount of heat removed by the coolant.

Because of the construction of the HRE foil, activation measurements of flux are not feasible. A possible method of getting the flux distribution would be to insert a silver wire along the core diameter where the distribution is desired. After operation this wire could be removed; then, by cutting it into short sections and determining the activity of these sections, the flux distribution could be obtained. This method is open to at least two objections. First, it has been found that probe wires in the plastic spheres used in circulation experiments disturb the flow so that the silver wire would probably upset the flow pattern appreciably. In the second place, the only way such test wires can be inserted and removed is by removal of the top flange. It is questionable whether the results which might be obtained are worth the effort in this case.

This leaves the second alternative of obtaining power by heat-extraction measurements. The heat removed from the core by the circulating soup could be obtained from inlet and outlet temperatures and the rate of flow. There is no suitable flow instrument in the soup line, and a precalibration of the pump is therefore the only way to get the flow. The pump calibration would probably not hold accurately.

The heat removed from the soup in the main heat exchanger may be obtained from boiler feed-water temperature and steam pressure and flow measurements. Suitable instruments are provided for determining these quantities. Of course,

there are heat losses in other parts of the system. Loss to the reflector may be obtained from flow and temperatures of the cooling water. Perhaps the best way to handle this is to let all this heat go into boiler feed water heating so that it will be included in the heat balance of the main boiler. If this does not prove feasible, a temporary flow meter may be installed in the D₂O cooler line to give the flow and thus enable this loss to be obtained directly.

The air circulating through the shield will remove a large part of the radiation heat in the shield as well as most of the stray losses from the soup system. Hence the temperatures and flow of this cooling air will provide data for computing most of the losses. This air-removed heat may be corrected for electrical energy supplied to various motors and heaters in the shield.

It is thus possible to obtain a fairly accurate figure for the overall heat extraction and hence the power level of the reactor. This should be correlated with the nuclear instrument readings to obtain a power calibration of these instruments.

The results of this experiment are not dependent upon the gas conditions; therefore the balance between power, temperature, and pressure which will give full-power gas volumes is not necessary. The accuracy of the results will be lower at lower power levels, but it seems advisable to start the tests at the lowest value consistent with the range of the instrument provided. The temperature and pressure to be used will be determined by the considerations already mentioned.

Gas Volume. Calculations indicate that several cubic feet per minute of gas will be generated at rated power by decomposition of the water by fission fragment bombardment. By reducing the excess pressure the same gas volume can be produced at a correspondingly lower power. Thus, since the rated excess pressure is 440 psi, the same gas volume would be obtained at 100 kw and 44 psi. It is realized that 44 psi excess pressure is lower than the minimum currently specified for the pumps. The excess pressure should be set at the minimum allowable value, and the gas volume determined at each power level should be used in these experiments. It is understood, of course, that these determinations are interlaced with other experiments at each power level so that all experiments are performed at each step before advancing to the next one.

The gas going to the recombiner is a mixture of hydrogen, oxygen, and steam. From readings of the condenser temperature and pressure and the pressure drop across the orifice in the gas line, the volume of dry gas may be determined. The measurements should be made under steady conditions to avoid the effect of transient factors on the volume of gas being extracted.

Gas Coefficient. The gas coefficient relates the reactivity and gas volume and may be determined in a manner somewhat similar to that used for the temperature coefficient. To avoid temperature coefficient effects the average core temperature should be held constant. A small change in fuel concentration (or in calibrated rod position) of about the same order of magnitude as that used for temperature coefficient measurements should be made and the heat extraction adjusted to obtain the desired average temperature. The inlet and outlet temperatures, the steam pressure and rate, and the nuclear power level should be recorded. This procedure is followed over as wide a range of power change as possible.

The data obtainable from this experiment are in the form of power versus fuel concentration for various temperatures and may be interpreted as the product of gas coefficient of reactivity and volume of gas present. The volume of gas is known from the results of the earlier experiment, so the gas coefficient is readily obtained.

Gas Time Delay. The effect of the gas coefficient on the transient behavior of the reactor depends on the time delay of the gas evolution. If the delay is zero the gas effect is similar to that of the temperature and the behavior is readily forecast. If there is a delay in the evolution of the gas after a reactivity change, the transient behavior is complicated. For reliable design of future reactors of this type information concerning the time delay is of prime importance, even if it is no more accurate than an order of magnitude.

Operation at less than rated power, even if the same volume of gas is produced, may not give results in this experiment equivalent to those which would be obtained under rated conditions. However, the time delay should decrease with increasing power density, so results obtained at reduced power will be pessimistic and hence on the safe side.

With steady-state gas and temperature effects known, valuable data on delay effects may be obtained from time records of n , $\log n$, and $(d \log n)/dt$

as the reactivity is changed. These quantities are recorded by a suitable oscillograph as concentrated solution is pumped into the core. Similar oscillograms obtained under transient conditions induced by any means will aid in estimating the delay effect. Possible means of inducing these transients include stopping and starting the circulating pump, sudden changes in steam rate, control plate withdrawal, and the concentration increase mentioned above.

Comparison of the transient curves with curves taken on the simulator for known time delays will aid in interpreting the data.

If experience indicates that the pressurizer level is steady under normal operation, an oscillogram of this level as the reactivity is varied may be used to give an approximate indication of gas delay.

Transient Characteristics. The feasibility of a homogeneous enriched reactor as a power producer depends upon the dynamic stability which is indicated in the feasibility study. Besides the gas effect discussed above, the general transient behavior of the reactor is very important. Data of primary importance include the variation of power (both extracted and nuclear), temperature, core pressure, and reflector pressure as functions of time. These may be obtained by oscillographic recording of the appropriate function as a transient is initiated. A major difficulty in obtaining such data is that of producing a sudden change in k (corresponding to bubble collapse, for example). The methods proposed above are probably the closest approach that may be realized.

The core pressure is quite important and is a variable which cannot be measured directly. The pressure-sensing element cannot be connected directly to the core. The next best location is probably in the liquid outlet line as close to the core as possible, but even here the damping action of the pressurizer chamber will be felt.

The transient behavior of the reactor under scram conditions is more easily determined. The various quantities listed are recorded as the rod magnets are released. The time scale should be correlated with the time of initiation of the scram signal.

Loss of Delayed Neutrons. The delayed neutrons have an important effect on the control of a reactor. The HRE offers an excellent means of varying

the contribution of these neutrons by varying the soup circulation rate. The transient response of the reactor as outlined in the preceding section should be obtained for several flow rates. The pump drive is an induction motor, and the speed may be controlled by varying the applied frequency, the reactor generator speed being regulated to obtain this variable frequency. From the pump calibration, the actual flow rate is obtained and hence the loss of delayed neutrons computed.

Power Demand Control. The feasibility study predicts that the HRE will be inherently stable under varying power demands. Consequently the reactor should behave as a power-demand controlled boiler insofar as the power generation is concerned. This is readily checked under actual operation, and, in fact, the results of the heat extraction and power calibration experiment may be interpreted to yield this information as far as heat extraction is concerned. The response of the overall system to fluctuations in power demand are obtained by operating with the generator connected to the TVA system. Changes in governor adjustment will then alter the power fed into the line. Oscillograms of the nuclear power, electrical power output, core temperature, and core pressure will indicate the stability of the reactor under these conditions. The time scale should be correlated with the time of initiating the governor change.

Concentration Control. If experience has not already indicated the feasibility of using concentration as a control without recourse to conventional rods or plates, a performance test should be made to determine whether or not this can be done. Such a test is quite simple, involving a general study of the system as the concentration is changed in steps.

Engineering Survey. All the data suggested above help in a study of the general operation of the system. In addition to a critical study of these data and observation of the general functioning of the equipment, a more detailed heat balance of the system and its components is desirable. This requires temperatures and flow rates at all possible points.

Poison Effects. After the reactor has operated at appreciable power for some time, a redetermination of the critical mass will indicate the importance of residual poisons. Some of the fission products are gaseous and are removed with the hydrogen and oxygen; others will probably precipitate and settle in the dump tanks. Those either in solution or suspended in the circulating soup will cause a change in the critical mass.

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CHEMICAL ASPECTS

Corrosion. The rate and nature of corrosion and erosion attack on various parts of the reactor system must be studied thoroughly. Nearly continuous or at least frequent chemical analysis of the soup for all possible products of corrosion is mandatory. A flange-connected section is provided in the soup-circulating system so that specimens may be introduced for corrosion testing. Extreme care must be taken to avoid couple effects due to dissimilar metals and to limit the tests to those materials which have been shown by previous experiments to behave in a satisfactory manner.

Soup Stability. A thorough and frequent chemical analysis of the soup should prove adequate to indicate any chemical trends. Determinations which appear at this time to be required include:

1. Total soluble uranium.
2. Soluble uranium other than hexavalent.
3. Sulfur in any form other than sulfate.
4. pH.
5. Iron, chromium, and nickel in solution.
6. Presence and identification of any suspended solids either in the liquid samples or collected on the filter in the pile circuit.

Present plans to provide a facility for the removal of liquid samples from the reactor for routine analysis should be adequate.

Decomposition Gases. Since the hydrogen-oxygen production rate is determined by gas flow measurements, an analysis of gas samples obtained at the charcoal adsorbers will give the measure of the total gas composition.

Fission Gases. A means of collecting, storing, and removing fission gas samples is being provided by the charcoal adsorber system. Chemical and radiochemical study of such samples should be made as soon as feasible after the reactor is put in operation.

Other Fission Products. The chemical and physical states of other-than-volatile fission products should be made a matter of study as soon as possible.

Liquid samples from the reactor should provide suitable source material. Such studies would fit in with, and perhaps should be a part of a program on recovery processes.

No changes in reactor design will be required to make available to members of the Laboratory samples of the liquid and gaseous products of the reactor. It would seem that these should provide excellent source material for both fundamental and applied chemical research. It is to be expected that members of the Laboratory, especially in the Chemistry and Chemical Technology Divisions, will take advantage of the possibilities offered. Since no changes in reactor design or operation are involved, suggestions for possible research with these materials will not be given here.

MODIFICATION OF THE REACTOR AND/OR THE CHEMICAL SYSTEM

After studies such as those indicated above have advanced to a point of diminishing returns, possible modifications in the reactor should be considered. For example, changes in the pump, the valves, the geometry of the centrifugal gas separator, or the design of the pressurizer may seem advisable. A switch to uranyl fluoride, uranyl nitrate, or some other fuel medium may appear feasible and desirable; the substitution of a zirconium core tank should be made sooner or later. Two criteria appear to be necessary before such changes should be permitted. First, simulated out-of-pile tests must show the new design or material to perform adequately and, second, the proposed change must offer real promise of improvement, or in some manner justify the cost and effort of making the change.

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6. LONG-RANGE STUDIES
(Experimental)

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THE URANYL SULFATE--URANIUM TRIOXIDE--WATER SYSTEM

W. L. Marshall and J. S. Gill

A fundamental study is in progress on the uranyl sulfate--uranium trioxide--water system at 25 and 100°C. The purpose of this work was to determine the aqueous solubility relations of the two components and the constitution of the solid phases.

A preliminary investigation of this system from 25 to 310°C by a synthetic method is discussed fully elsewhere.^(1 3) However, scattering of the data and the limitation of the experiments to dilute solutions (10 to 40 g of uranium per liter) warranted the present investigation.

Experimental An analytical method is being used in the current experiments. Uranyl sulfate solutions of varying concentrations are shaken with excess solid uranium trioxide in a thermostat for 60 hr. Equilibrium conditions are reached within this time. The solution and solid phases are sampled and analyzed gravimetrically for sulfate and uranium by precipitation and a subsequent ignition of barium sulfate and ammonium diuranate, respectively.⁽⁴⁾

Results. The experimental data concerning the solution phases at 25 and 100°C are given in Table 20 and are shown graphically in Fig. 34. These data show the mole ratio variation (in the presence of excess solid) of total uranium to sulfate ion up to at least 45 wt. % uranyl sulfate.

The solid phase analytical data have been interpreted by Schreinemakers' "wet residue" method⁽⁵⁾ and show these phases to be hydrated uranium trioxide up to 35% UO_2SO_4 at 25°C and at least up to 45% UO_2SO_4 at 100°C. These solid phase data will be given in a future report.

The extremely low solubility temperature coefficient of the hydrated uranium trioxide phase indicates no significant reaction with aqueous uranyl sulfate in this concentration and temperature range, but rather a complexing phenomenon.

In Fig. 33 the most reliable mole ratio of UO_3/SO_4 at 250°C and 40 g of total uranium per liter has been combined with the present data to show the

- (1) *Homogeneous Reactor Experiment Report for the Quarter Ending February 28, 1950*, ORNL-630, pp. 49ff. (Apr. 21, 1950).
- (2) *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL-685, pp. 32ff. (June 16, 1950).
- (3) *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1950*, section on phase rule studies (now in preparation)
- (4) Scott, W., *Standard Methods of Chemical Analysis*, Vol. I. pp. 127 and 1022, 5 ed, Van Nostrand, New York, 1939.
- (5) Schreinemakers, F. A. H., "Graphische Ableitungen aus den Lösungs-Isothermen eines Doppelsalzes und seiner Komponenten und mögliche Formen der Umwandlungskurve", *Z. phys. Chem.* 11, 75, especially p. 81 (1893).

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FIG. 34
MOLE RATIO SOLUBILITIES OF UO_3
IN AQUEOUS UO_2SO_4 AT 25° AND 100° C

FIG. 33
THE MOLE RATIO $\frac{UO_3}{SO_4}$ SOLUBILITY
VARIATION WITH TEMPERATURE
(40 g U PER LITER)

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ratio variation with temperature. It is thus evident that reactor solution temperatures must be kept somewhat below 250°C if the addition of uranium trioxide is to reduce appreciably the effective absorption cross-section of sulfur or to inhibit corrosion.

TABLE 20

**Solubility Relations of Uranium Trioxide in
Aqueous Uranyl Sulfate at 25 and 100°C**

AT 25°C		AT 100°C	
UO ₂ SO ₄ (wt. %)	MOLE RATIO UO ₃ /SO ₄ ⁺⁺	UO ₂ SO ₄ (wt. %)	MOLE RATIO UO ₃ /SO ₄ ⁺⁺
5.76	1.54	5.46	1.28
12.55	1.55	11.37	1.30
15.71	1.45	15.66	1.33
22.05	1.38	21.35	1.26
24.87	1.47	24.78	1.35
29.06	1.44	29.18	1.35
33.21	1.39	32.89	1.36
37.25	1.38	37.26	1.35
45.87	1.32	44.14	1.37

**AQUEOUS URANYL NITRATE AND URANYL NITRATE—NITRIC ACID—WATER
SOLUTIONS ABOVE 100°C**

W. L. Marshall and J. S. Gill

Introduction. Results of a preliminary investigation of the thermal stability of aqueous uranyl nitrate solutions above 100°C are given elsewhere.⁽⁶⁾ In the work reported here the exploratory study was extended to include other concentrations as well as solutions containing free nitric acid.

(6) Marshall, W. L., "The Uranyl Nitrate—Water System," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1949*, ORNL-499, p. 36 (Dec. 6, 1949).

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Experimental. Aqueous uranyl nitrate and uranyl nitrate—nitric acid—water solutions of appropriate concentrations were made from Mallinckrodt c.p. uranyl nitrate and Baker and Adamson c.p. nitric acid.

The subsequent experimental procedure, which was that previously described by Secoy,⁽⁷⁾ consisted in filling 10-cm lengths of silica capillary tubing (sealed at one end) to one-third volume with a given solution, removing all dissolved gases, then sealing the open end. These tubes were rocked in a cylindrical heating unit. The temperature was raised slowly, and observations were made through a slit in the heating unit.

Temperature was recorded with an iron-constantan thermocouple.

Results and Discussion. The experimental observations concerning thermal stability of aqueous uranyl nitrate—nitric acid solutions are given in Table 21. The data represent phenomena occurring upon raising slowly the temperature of a given solution from 25°C to the maximum value over a 5- to 6-hr period. Solution flow in the tubing was observable only above 305 to 310°C.

The appearance of a yellow product in the so-called "dry" end of the tube was apparent below this flow temperature in the designated runs.

The color of the vapor phase appearing between 280 and 310°C became progressively darker from a faint yellow-brown to a deep red-brown at the higher temperatures (340 to 370°C). The solution of necessity became proportionately colored. Upon lowering the temperature, the reverse phenomena occurred, although the vapor phase did not become colorless until a given tube had cooled to about 250°C.

Direct precipitation at 340°C of a yellow solid phase from solution was observable only in the 1.90 M $\text{UO}_2(\text{NO}_3)_2$ solution. A similar precipitate might also have been observed in other solutions if the higher temperatures had been attained.

The estimated 1- to 3-mg yellow precipitate appearing after final observation at room temperature represented approximately 2 to 6% of the total UO_3 in solution. This remaining solid would not redissolve, possibly owing to incompleteness of mixing in the small-bore tubing.

Conclusions. The apparent conclusion to this investigation is that aqueous uranyl nitrate solutions are hydrolytically unstable at elevated

(7) Secoy, C. H., *The System Uranyl Sulfate—Water, Temperature-Concentration Relationships Above 250°C*, ORNL-98 (July 7, 1948).

temperatures and thus produce uranium trioxide and oxides of nitrogen. However, in a closed system, uranium trioxide is sufficiently soluble in the acid medium to remain in solution until the apparent equilibrium shifts far enough with increasing temperature in the direction of uranium trioxide precipitation. Addition of nitric acid is sufficient to prevent this precipitation by shifting the equilibrium concentration of uranium trioxide in the reverse direction.

The nitric acid concentrations given in Table 21 fix within approximate limits the amounts of acid necessary to prevent precipitation at temperatures above 300°C.

It is apparent, then, from an inspection of the data in Table 21 that a uranyl nitrate—water system or a uranyl nitrate—nitric acid—water system could be thermally feasible at 250°C for a homogeneous reactor solution. However, additional thermal experimentation is necessary if serious consideration is to be given these systems.

URANIUM TRIOXIDE—BENTONITE SLURRIES

L. E. Morse

Bentonite-stabilized slurries of uranium trioxide have been demonstrated to be stable at 250°C and 1000 psi pressure for a period as long as 330 hr. It is now planned to determine the effect of radiation on the stability of this slurry. If the radiation does not have a significant effect on the slurry stability, it is felt that this slurry may be useful in a homogeneous type reactor.

In this study the criterion for the stability of the slurry has been to cool the slurry to room temperature and then allow it to stand in a graduated cylinder for a period of time, determining the solids concentration in the solution as a function of the solution depth. In addition, the ease of resuspending the solids and the tendency of the slurry to cake were observed. It was felt that a slurry was satisfactory if it settled to less than 50% of its original volume in 24 to 48 hr and could be readily resuspended. Other factors that were observed were an increase in the iron content of the slurry and the presence of reduced uranium after heating. It was originally believed

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TABLE 21

**Thermal Stability Characteristics of Uranyl Nitrate—Water and
Uranyl Nitrate—Nitric Acid—Water Solutions**

RUN NUMBER	UO ₂ (NO ₃) ₂ (M)	HNO ₃ (M)	TEMPERATURE OF "DRY" SOLID FORMATION (°C)	TEMPERATURE OF VAPOR PHASE COLORATION (°C)	TEMPERATURE OF DIRECT PRECIPITATION FROM SOLUTION (°C)	HIGHEST TEMPERATURE (°C)	OBSERVATIONS .. AFTER RUN
1	0.171	0	290	None observed	None observed	344 (explosion)	
2	0.90	0	300	305	None observed	336 (explosion)	
3	0.90	0.05	310	310	None observed	325	Est. 1 to 3 mg of yellow precipitate
4	0.90	0.10	305	300	None observed	325	Est. 1 to 3 mg of yellow precipitate
5	0.90	0.20	None observed	300	None observed	325	No observable change
6	0.90	0.20	None observed	300	None observed	371 (explosion)	
7	1.90 (sat'd. at 22°C)	0	270	290	340	376	Est. 1 to 3 mg of yellow precipitate
8	1.80	0.03	330	290	None observed	378	Est. 1 to 3 mg of yellow precipitate
9	1.80	0.42	None observed	280	None observed	350 (explosion)	
10	1.80	0.42	None observed	290	None observed	351	No observable change

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that the corrosion of the type 347 stainless steel bomb was responsible for the breaking of the stable uranium suspension. However, when the tests were repeated in sealed quartz tubes, unstable slurries again resulted when the tubes were heated for periods longer than 330 hr. The oxidation state of uranium was then examined and it was found that 28 to 45% reduction of the original uranium trioxide had occurred (see Table 22). Studies were initiated to determine the mechanism of the reduction of uranium, but no significant results have been obtained. Further work on this problem is proposed.

URANYL PHOSPHATE SLURRIES

L. E. Morse

Preliminary studies of a uranyl phosphate slurry indicated that it was relatively stable in water at high temperature. When formed under proper conditions, the uranyl phosphate was present as a bulky precipitate of long needles occupying 45% of the total volume of a 40 g U/liter slurry. Uranyl phosphate which was ground in a ball mill and screened through a 170-mesh screen settled rapidly from a water slurry to about 15% of the total volume.

It is planned to continue this work, investigating the effect of the addition of phosphoric acid and its sodium salts as stabilizers for the uranyl phosphate, since it is known that several of the various phosphates act as dispersants for suspended solids. A second investigation using mixtures of uranyl phosphate and uranium trioxide is also planned since, if such combinations are practical, they will represent an improvement with respect to neutron economy.

THORIUM OXIDE—BENTONITE SLURRIES

T. C. Runion

Development work has been initiated with the objective of obtaining a stable thorium slurry which might be used as a breeding blanket for homogeneous type reactors. For this purpose, a slurry containing approximately 1000 g of thorium per liter is desired. This slurry must be stable under conditions

TABLE 22

Thermal Stability of Uranium Trioxide—Water Slurries Stabilized with Bentonite

Composition: Uranium - 40 g as anhydrous uranium trioxide
 Bentonite - 1000 ml of suspension containing 12 to 15 g
 of electrolyzed bentonite. Average particle size below 25 m μ

Temperature: Heating cycle - 250°C
 Sedimentation cycle - 20°C

VESSEL	HEATING TIME (hr)	SETTLING TIME (hr)	URANIUM CONCENTRATION (g/liter)				IRON CONCENTRATION (g/liter)		REDUCED URANIUM (%)
			SETTLED SLURRY			WELL-MIXED			
			TOP	MIDDLE	BOTTOM		BEFORE	AFTER	
347 stainless steel	330	48	1.2	50.7	56.3		0.29 ^(b)	0.48	
	562	24 ^(a)	10.0	54.8	61.8	35.7	0.25 ^(b)	0.83	28.4 ^(c)
Quartz	768	24	0.4	2.0	107	35.0	0.08	0.16	44.5
	34 ^(d)	24	1.9	45.0		37.0	0.08	0.14	44.9

(a) On longer standing the uranium oxide continued to settle out with caking.

(b) The method of preparation of the slurry resulted in the introduction of a large amount of iron.

(c) This value is probably low since the slurry was stored in contact with air for several months before analysis

(d) 17 hr at 400°C + 17 hr at 250°C.

similar to those for the uranium slurry, namely, 250°C and 1000 psi pressure, and in neutron fluxes of 10^{11} to 10^{13} .

In preliminary studies, a slurry composed of 1000 g of thorium per liter as thorium oxide and 30 g of bentonite per liter (Montmorillonite clay) was found to form a thixotropic slurry which was stable after being heated 450 hr at 250°C and 1000 psi pressure in a sealed quartz tube. The study of this problem is to be continued using synthetic bentonite.

SYNTHESIS OF MONTMORILLONITE

T. C. Runion

The naturally occurring Montmorillonite clays are composed of aluminum oxide, silicon dioxide, and magnesium dioxide in the mole ratio of 1:4:2. They also contain iron, sodium, and other materials with high thermal-neutron absorption cross-sections which are not easily removed. In addition, the reproducibility of any commercially available bentonite is in doubt. Consequently, the possibility of synthesizing Montmorillonite in the laboratory was of interest.

The synthesis was carried out along the lines recommended by Blanck and Linck.⁽⁸⁾ Al_2O_3 , SiO_2 , and MgO in water are the essential components in the mole ratio of 1:4:2. The reaction was carried out in an autoclave at about 300°C at the equilibrium vapor pressure of water (about 1200 psi).

X-ray studies of the prepared material showed that with at least 1 mole of magnesium per mole of aluminum and 4 moles of silicon, Montmorillonite is obtained. One run in which a Mg/Al ratio of 0.5 was used resulted in a high yield of kaolin.

A slurry of thorium prepared with the synthesized bentonite has properties very similar to those of one prepared with the naturally occurring material.

An effort was made to obtain a high degree of purity for the Al_2O_3 and SiO_2 used in the reaction mixture although the necessity for this is open to question. The physical form (i.e., degree of dehydration of the salts) was apparently more important. The SiO_2 was added as silicic acid, which had been prepared by passing Na_2SiO_3 through the acid form of a cation resin (Dowex 50).

(8) Blanck, E., and Linck, G., *Chemie der Erde*, Vol. 10, Part 2, Verlag von Gustav Fischer, Jena, 1936.

The Al_2O_3 was added as a standardized slurry of $\text{Al}(\text{OH})_3$, which had been precipitated from $\text{Al}(\text{NO}_3)_3$ with NH_4OH and washed repeatedly. USP MgO was used with no further purification.

The autoclave used in the experiments was a standard 1-liter model, obtained from Autoclave Engineers, with a built-in propeller type agitator and sampling well. The agitator shaft was lubricated with white mineral oil (viscosity about 100 cp), and considerable difficulty was experienced in preventing contamination of the product from oil leaking through the packing around the agitator shaft. Plans are underway to provide a different method of lubrication using a silicone grease and standard grease fittings.

The next immediate effort will be devoted to preparing ThO_2 slurries stabilized with synthetic bentonite and checking the stability of such slurries to elevated temperatures and pressures in order to determine the relative effectiveness of natural and synthetic bentonite.

It is also planned to determine the stability of the slurries to radiation as soon as experimental holes in the pile are available for such purposes.

SLURRY PUMPING STUDIES

A. S. Kitzes

A glass model of a possible slurry type reactor has been constructed and operated using barytes (density 4.2) fines as the solid material. The experiment was set up primarily to demonstrate the principles involved in such a system.

The reactor is a 5-liter spherical flask with two horizontal discharge openings 180° apart. The inlet is tangent to the bottom of the flask and perpendicular to the discharge openings. The slurry is pumped by a 10-gpm 50-ft-head pump from the reactor flask through a liquid cyclone separator, where a separation of the coarse and fine material is effected. The coarse material is removed from the bottom of the cyclone separator by means of a jet activated by the overflow from the top of the separator being pumped through the jet. Through the action of the jet, the coarse and fine material are recombined prior to being pumped back into the reactor.

UO₃ (equivalent to a uranium concentration of 100 g/liter) will be circulated in this system as soon as a satisfactory pump can be provided. At present, barytes (BaSO₄) equivalent to a uranium concentration of 100 g/liter is being circulated.

Probable advantages of the system include the following:

1. No need for a stable slurry.
2. Minimal erosion of the heat transfer tubes and pump because the overflow from the separator which contains only the finely divided material would be pumped through these units.

Future Program. The following studies are planned:

1. Erosion studies using UO₃ of different particle sizes to determine erosion rates as a function of particle size.
2. Determination of the capabilities and operating characteristics of a liquid cyclone separator. Practically no literature or information is available on the subject.
3. Investigation of the homogeneity of particles in the reactor sphere.
4. Determination of pumping and stability characteristics of UO₃ slurries, both bentonite stabilized and unstabilized, at elevated temperatures by pumping through a similar system at 150°C.

FUEL PROCESSING

I. R. Higgins

There are two major phases to the homogeneous fuel processing program; the first concerns the Homogeneous Reactor Experiment (HRE) and the second concerns processes for future homogeneous reactors. For the HRE Process phase, minor alterations of the existing Purex Process will be sufficient to recover and decontaminate the fissionable material in solvent extraction equipment located at ORNL. For future homogeneous reactors, a processing technique which will reduce the processing cost significantly is probably feasible. The general procedure will be to remove the plutonium and fission products from the homogeneous reactor fuel without altering the fuel composition. This process will allow the fuel to be returned directly to the

reactor and reduce the fuel inventory for the reactor. Study is now in progress on an ion-exchange procedure for the extraction of plutonium and fission products from a uranyl sulfate solution. A second procedure involving electrochemical precipitation is under consideration.

The ion-exchange study was concerned with the study of ion-exchange resin stability under β irradiation and with the development of a procedure applicable to the HRE.

Since the fuel is to be processed after a short cooling period, to keep the fuel inventory low, the radiation stability of the organic ion exchangers employed is of major concern. According to radiation energy absorbed from a Co^{60} gamma source, Dowex 50 loses about half its capacity after absorption of 2 to 3 kwh per kilogram of resin (see Table 23). Assuming for the HRE a processing cycle which allows 1 day of cooling and a 1% fission product build-up in the reactor (5% increase in inventory), about 1 lb of resin will be used per day to adsorb 1 g of fission products.

TABLE 23

**Capacity Loss of Dowex 50 Resin on Absorption of
Radiation Energy From Co^{60} Gamma Rays**

SAMPLE	RADIATION ENERGY ABSORBED (kwh/kg of resin)	RESIN CAPACITY REMAINING (%)
1, exposed to air	0.7	74
	0.9	65
	1.3	56
1, sealed in tube	2.0	56
	3.0	41
2, sealed in tube	0.6	93
	2.2	69

New interest is taken in the phenolic ion exchangers since they have been found, on the initial test, to be as stable to radiation as Dowex 50. The

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phenolic resins have, in general, about one-third the capacity of the styrene resins and are not so chemically stable to oxidizing conditions. However, they yield their holdup uranium much faster. In a processing cycle where speed and low uranium loss is vital, the phenolic resins may compete with the higher capacity Dowex 50.

Greensand, a natural aluminum iron silicate mineral, and Decalso, a synthetic aluminum silicate, were studied. They each exhibited unusual affinity for zirconium, niobium, and cesium and their holdup uranium was only 2 to 5% of that for Dowex 50. However, about twenty times as much adsorber was needed as for Dowex 50 before rare earth breakthrough occurred. The uranium could neither be selectively eluted from the adsorbed rare earths nor removed completely. Their best foreseen application is in cases where they can be used for a long period of time to adsorb fission products for which they have a high affinity, where no elution step is contemplated, and where any uranium loss can be ignored.

Scouting tests have been run on some of the natural and synthetic aluminum silicate ion exchangers on the assumption that, being inorganic, they are more stable to radiation. However, these elution and separation characteristics are so inferior to those of the organic exchangers that they are not being considered at the present.

The present process development is aimed at achieving fission product removal to a concentration equal to 1% of that of the fissionable material and to providing chemical processing with very low uranium losses. As the process is now visualized, 5% of the reactor charge will be withdrawn per day, cooled for 1 day, and passed through a fuller's earth bed for the removal of zirconium, niobium, and cesium. The solution will then pass to a Dowex 50 cation-exchange column where all the remaining fission products with the exception of ruthenium, molybdenum, and tellurium will be removed. These last-mentioned elements are then removed by passage of the fuel solution through a Dowex A-1 anion-exchange column. Present indications are that the approximate size of these columns will be about 1 liter for a reactor about the size of the HRE. Radiation stability measurements on ion-exchange resins indicate that the life of the cation exchangers will be about 1 day. Studies during the last quarter have emphasized investigation of the radiation stability of the resin and a comparison of various ion exchangers.

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