CIVILIAN POWER REACTOR PROGRAM

PART III

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Book 3

Status Report on Aqueous Homogeneous Reactors as of 1959

UNITED STATES ATOMIC ENERGY COMMISSION

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Published : 1960

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PREFACE

Thermal Breeder Reactor Program—Aqueous Homogeneous Reactors is a report on the technical status of aqueous homogeneous power-breeder reactors. It was prepared at the request of the U.S. Atomic Energy Commission as background information for the Civilian Power Reactor Program. The report is to be included by the Commission in a compilation of reports which describe the technologies of all the types of power reactors now being developed.

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SUMMARY

THERMAL BREEDER REACTOR PROGRAM—AQUEOUS HOMOGENEOUS REACTORS

1. Objective

The primary objective of the program is to develop a thermal breeder power reactor which is based on the thorium-U^{233} cycle and has a high conversion ratio and a low inventory of fissionable and fertile materials.

2. Description

Two-region circulating-fuel reactors are considered to be the most promising aqueous homogeneous thermal breeder power reactors. The preferred type has a dilute (less than 0.03 *m*) solution of uranyl sulfate, predominantly fissionable uranium, in D_2O in the core and a concentrated slurry of thorium oxide in D_2O in the blanket. Preference is based on the greater potential of the solution-core reactor for combining high conversion ratio and high specific power to achieve an efficient breeder. Fuel solution and slurry are circulated through the reactor and steam generators, where non-radioactive steam is produced to drive a turbogenerator. The reactor plants feature remote maintenance of primary systems and auxiliaries. "On-site" processing appears to be desirable for large power stations.

3. Technical Status

Aqueous homogeneous reactors depend on the development of a complete new technology. Equipment for pressurized-water reactors forms the basis for some homogeneous-reactor equipment, but the fuels are completely different from those used in any other type of reactor. The properties of the fuels and circulating them through the reactor plant impose unique requirements on materials, components, maintenance, and plant design. Fuels, materials, fuel processing, and the engineering and operation of reactor experiments have been emphasized in the development program. Although the technology has not yet reached the stage of construction of large power reactors, the following status has been attained.

Physics

The physical and nuclear characteristics and the adjustment of fuel concentrations in homogeneous reactors are sufficiently simple that critical experiments have been limited to startup experiments on Homogeneous Reactor Experiment No. 1 (HRE–1), Homogeneous Reactor Experiment No. 2 (HRE–2), and the small research reactors. Reactor statics calculations are made by use of two-group methods in which the constants are based on data obtained from other programs. Agreement between calculated and measured critical concentrations has been good in small reactor experiments and should be even better as the size increases.

Neutron balances and breeding ratios have been calculated by both modified two-group and multigroup methods. An important uncertainty in the calculations has been in the value of η, the number of neutrons emitted per neutron absorbed in the fuel. The best value, based on recent careful measurements, is about 2.3. This should allow a breeding gain of 0.1 and doubling times of 15 years or less in the target reactors.

Effectiveness of the negative temperature coefficient in controlling the reactor has been demonstrated in HRE–1 and HRE–2. It has been concluded that control rods are not required in the reactors. The kinetics of a variety of reactors have been investigated by calculation, and experiments have been done in HRE–1, HRE–2, and in the "water-boiler" reactors. Criteria have been established for stability against divergent oscillations in power produced by the interaction of the nuclear and mechanical systems of a circulating-fuel reactor. Methods have been developed for calculating the power, temperature, and pressure behavior of a circulating-fuel reactor in relation to a step increase or rate of increase of reactivity. The kinetics studies have been used to establish criteria for design of reactor pressurizer and pressure-relief systems.

Fuels and Materials

Investigation of fuels and materials both in- and out-of-pile, including the development of equipment for those studies, has constituted one-third to one-half of the research and development program. Studies of potential fuels have led to selection of uranyl sulfate solutions and thoria slurries as being the most promising. Most of the criteria have been established for use of stainless steel as the general container material and Zircaloy–2 as the core-tank material. Titanium has been established as a potentially superior container material.

Solution Fuels.—Solubility relationships have been investigated for uranyl sulfate in both H_2O and D_2O. The studies are being continued to establish details of the phase diagrams for the five-component reactor core fuel, UO_3–CuO–NiO–SO_3–$D_2O(H_2O)$, in the region 0 to 0.04 *m* in UO_3, CuO, and NiO and 0 to 0.20 *m* in SO_3. Copper is present in the fuel to catalyze the recombination of radiolytic gas, and nickel is a soluble corrosion product.

Hydrolysis occurs at high temperature and the hydrolysis products separate from the bulk solution as precipitates, which may or may not contain appreciable uranium (depending on the concentration region), or as a heavy liquid phase which is enriched in all metal constituents. Dilute solutions in which the molar ratio $\frac{U_2O_5^{++}+Cu^{++}+Ni^{++}}{HSO_4^-}$ is 0.5 are stable against precipitation of solids to at least 300° C and the second-liquid-phase temperature is above 320° C. The temperature at which instability occurs is raised by adding sulfuric acid to decrease the ratio. There is little difference between the solubilities in H_2O and in D_2O.

Decomposition of the water is the only observed effect of reactor radiations on dilute uranyl sulfate solutions. At low temperature D_2 and D_2O_2 are produced, and uranyl peroxide precipitates from solutions at lower densities above 1 kw/liter at 100° C. At power-reactor temperatures, peroxide decomposes very rapidly and the products are radiolytic gas, D_2 and O_2. Copper sulfate is an effective catalyst for recombining the gases in solution to reduce the hazard and the problems of handling large quantities of gas. Concentrated solutions have been irradiated at the power densities that would be produced in large reactors, but facilities have not been available for doing this with the dilute fuels.

Thorium Oxide Suspensions.—In the absence of a suitable thorium solution, suspensions or slurries of thorium oxide in water are being developed as reactor fuels.

The slurries are non-Newtonian fluids, and their properties depend on both the characteristics of the particles and the environment. Properties such as suspension density, thermal conductivity, and specific heat are known over the complete range of temperature and pressure. Some information has been obtained concerning the electrokinetic and ion exchange properties of thoria, permitting a better understanding of the effects of ionic contaminants on the physical properties of the slurries.

Flow studies have established that the yield stress increases with increasing concentration and decreasing size of particles of a given shape. Current production material must be larger than 2 to 3μ to obtain the desired <0.1-lb/ft^2 yield stress in blanket slurries. Slurries must be kept in turbulent flow to maintain homogeneity. Velocities of 2 to 8 ft/sec are necessary to obtain fully turbulent flow in pipes. Heat transfer and fluid flow behavior of slurries in turbulent flow are those of a Newtonian fluid with the same physical properties.

A qualitative understanding has been developed of the mechanism of deposition of slurry solids in hard cakes in engineering systems. Early difficulties with caking were eliminated by changes in the processes for manufacturing thoria.

Irradiation of slurries for a few hundred hours at power densities below 10 kw/liter, representative of the average power density in a blanket system, has shown no obvious effect on slurry properties. Longer tests at higher power densities are required to provide definitive data.

Deuterium and oxygen are produced by irradiation of slurries also. Molybdenum oxide and palladium catalysts are being tested out-of-pile and have recombined the gases satisfactorily in-pile at power densities of about 10 kw/liter. Considerable additional work is required to establish their suitability for use in a reactor.

Corrosion.—Corrosion of stainless steel, Zircaloy-2, and titanium in uranyl sulfate fuel solutions has been studied extensively. It has been established that ASA type 347 stainless steel is a satisfactory material for containing the dilute fuel solutions in the heat-removal and auxiliary systems of a homogeneous reactor if (1) the excess acid is less than 0.02 *m* or possibly 0.03 *m*, (2) the velocity is less than 25 ft/sec, (3) the temperature is below 150° C or above 250° C but below the boiling point, (4) there is enough oxygen in solution to stabilize the uranyl ion, and (5) the chloride concentration is less than 2 ppm.

Below 150° C the corrosion rate is less than 2 mpy (mils per year) and independent of velocity. Above 250° C and with flows below a critical velocity the metal corrodes less than 1 mil in forming a protective film, and then there is essentially no corrosion as long as the film is intact. Above the critical velocity the film does not form or once formed is eventually removed and rates of 100 mpy are common. The intermediate temperature range is a transition region in which heavy scales form, which are only partially protective. Corrosion rates are 5 to 50 mpy. The rates and their dependence on velocity increase with rising temperature; critical velocities are low. Very few parts of a homogeneous reactor operate continuously in the intermediate temperature range. Stainless steel is used if the velocity is low and a short service life is acceptable, but titanium is the preferred material for those parts.

Increasing the acidity lowers the critical velocity and increases the corrosiveness of the fuel. Oxygen depletion results in reduction of the uranyl ion, hydrolytic precipitation of the reduced uranium at high temperature, and an increase in acidity. A concentration of 50 ppm of dissolved oxygen is sufficient, but 500 ppm is maintained in engineering systems to provide against depletion in crevices and stagnant regions. Boiling depletes the fuel of oxygen. Chloride concentrations must be kept low to prevent stress-corrosion cracking of the austenitic stainless steel.

Experience in in-pile loops and in HRE–1 and HRE–2 indicates that fission-product radiation in the fuel circulating systems and the auxiliaries has no important effect on corrosion. A few hours of high corrosion, tentatively attributed to oxygen depletion, during the first low-power operation of HRE–2 has been followed by several thousand hours at rates less than 0.5 mpy.

No important difference has been found between type 347 SS and other austenitic stainless steels. Titanium and zirconium are not corroded appreciably by uranyl sulfate solution fuels at much higher acidity, flow velocity, and temperature than can be used with stainless steels. Corrosion of zirconium is very severe in fuel solutions which are contaminated by small amounts of fluoride.

Corrosion in slurry systems is a combination of corrosion by water and erosion by slurry particles. Austenitic stainless steels appear to be satisfactory container materials for oxygenated slurries at velocities as high as 20 ft/sec and at all temperatures and slurry concentrations of interest if the design of the equipment and size or shape of the slurry particles are properly controlled. Careful design to prevent flow separation is important. Irregularly shaped particles with sharp corners must be smaller than 5μ. The upper limit on size of spherical particles is not known.

Stress-corrosion cracking has been troublesome in some parts of slurry systems. The tolerable chloride concentration has not been established. Inconel and low-alloy steels which are highly resistant to chloride-induced cracking are promising substitutes for stainless steel. Zircaloy-2 and titanium are highly resistant to stress-corrosion cracking and to corrosion and erosion by oxygenated slurries under severe flow conditions. Hydriding of Zircaloy has been experienced with hydrogenated slurries when exposed to highly turbulent flow of mixtures of slurry and vapor.

Zircaloy–2 is presently the only material which is sufficiently good in corrosion resistance, mechanical properties, and low neutron-absorption cross section to be useful for the core tank of a breeder. Exposure to fissioning solutions has been shown to increase markedly the corrosion rates of Zircaloy–2 and other materials. Corrosion rates of 11 mpy at 250° C and 40 mpy at 300° C have been estimated for the core tank of the target breeder in fuel solution. The estimates are based on the correlation of results of many tests over wide ranges of conditions; facilities are not available for performing tests with dilute fuel solutions at the high power densities of a large breeder. Tests have shown that zirconium-niobium alloys may be more corrosion-resistant than Zircaloy–2.

Preliminary tests in autoclaves indicate that corrosion of Zircaloy–2 is increased by exposure in fissioning slurries. The effect appears to be less important than that found with solution fuels.

Procedures were developed for fabricating the core tank of HRE–2, the first zirconium pressure vessel of appreciable size, and fabrication methods are being improved. Physical properties of Zircaloy plate for use in larger vessels have been improved considerably by the development of new manufacturing schedules. The metallurgy of zirconium-niobium alloys is being investigated in the development of high-strength alloys of improved corrosion resistance. Both zirconium and titanium have been ignited by exposure of oxide-free surfaces to vapors which contain oxygen at partial pressures greater than 50 to several hundred psi, depending on test conditions. The metals could not be ignited in and were quenched by oxygenated water.

Chemical Processing

Core and blanket fuels must be processed on short cycles to achieve high breeding gain and low inventory in the reactor. Development of economical methods for manufacturing and short-cycle processing of the fuels is the objective of the processing work.

Krypton, xenon, and iodine are removed from the core fuel continuously by boiling a portion that is circulated between the reactor high-pressure and low-pressure systems. Iodine can be separated from the vapor by reaction with silver in a packed column or absorption in water in a distillation column. The vapor is then condensed, and the gases that are left are adsorbed on carbon until they decay. Processes involving silver and carbon beds have been demonstrated on HRE–2; efficiency of the iodine removal process is still being determined there.

Most of the fission and corrosion products have been shown to be only slightly soluble in fuel solutions under reactor conditions, and a method based on hydroclones (hydraulic cyclone separators) was developed for removing the solids. A hydroclone plant has been operated in conjunction with HRE–2. The low solubility of fission and corrosion products has been demonstrated, but only about 10 percent of the solids have been removed by the hydroclone. Most of the solids deposited on pipe walls and separated in regions of low flow in the reactor systems. Means are being sought for increasing the effectiveness of the hydroclone plant. Nickel and manganese, from the corrosion of stainless steel, and fission-produced cesium will not precipitate from fuel solution until concentrations have been reached which could result in fuel instability or significant loss of neutrons. It is expected that the processing rate will be determined by the rate of buildup of corrosion products. The amount of uranium processed daily should be so small that the solution can be combined with the blanket slurry and processed in the Thorex plant. Uranyl peroxide precipitation and electrolytic methods for processing larger amounts of solutions rapidly in D_2O have been demonstrated in the laboratory. In HRE–2 the first batch of fuel required processing after a few hundred hours; the second has been used for more than 5,000 hours.

Methods are being sought for rapid removal of uranium and fission products from thoria without destroying the slurry particles, but at present it is necessary to convert the oxide to a solution of thorium nitrate in H_2O and process by solvent extraction in a Thorex plant. Simple methods which should be easily adaptable to remote handling have been developed for converting the uranyl nitrate product to uranyl sulfate in D_2O.

Thoria is presently produced from thorium nitrate in a pilot plant by precipitating thorium oxalate, decomposing the oxalate in a furnace at 300° C, firing the resulting oxide in the range of 800 to 1,600° C, and dispersing the dry product in water. Cubes or platelets with average size controlled in the range 1 to 5 μ are produced. Uranium has been incorporated in the thoria in U/Th ratios from 0.005 to 0.33 in the development of slurry fuels for the core of the alternative breeder. Methods of making spherical particles and of converting the nitrate directly to oxide are being developed. The processes must be adapted to remote handling for recycling long-irradiated thoria.

Engineering Development

Solution Fuel Systems.—Except for the reactor core tank, equipment for 5- to 10-Mwt reactor experiments which utilize solution fuels at 250° to 300° C and 2,000 psia has been developed and demonstrated to be satisfactory on HRE–2. Equipment and instruments were developed or modified to be completely leaktight and to provide life expectancies from about 4,000 hours to several years. Most of the critical equipment handles highly radioactive fluids and operates in a sealed tank at temperatures to 140° F at ½ atm pressure and is flooded with water for maintenance.

Included in the development were modified canned-motor pumps, diaphragm-type high-pressure feed pumps, bellows-sealed valves, level-indicating instruments, a variety of heat exchangers, recombiners, samplers, weighed storage tanks, electrically heated pressurizers, steam generators, and the reactor vessel. Carbon steel shells, stainless-clad carbon-steel tube sheets, and stainless steel tubes were used in the 5-Mw steam generators. The reactor vessel is a 5-foot-diameter stainless-clad carbon steel sphere with a 4.4-inch-thick wall. It contains a Zircaloy core tank with special flanges for joining zirconium to stainless steel and is surrounded by a blast shield to contain the vessel in the event of a brittle failure of the pressure vessel.

Studies of core hydrodynamics are being emphasized in the development to overcome difficulties experienced in HRE–2 and to provide satisfactory core designs for large power breeders. Other work on large reactors has been limited to preliminary efforts on pumps and heat exchangers.

Slurry Fuel Systems.—The development of HRE–2 scale equipment for slurry reactors is less advanced. Slurries have been circulated in many loop tests under a variety of conditions. Two tests were for 3,800 hours each. Severe wear of Graphitar-Stellite bearings and stainless steel impellers in the circulating pumps was experienced in those tests. An improved pump with aluminum oxide bearings and a Zircaloy impeller has operated for 2,800 hours with no significant wear. No completely satisfactory solution has been found for the problem of erosion of throttling valves and check valves in high-pressure feed pumps. Improvements have been made in the hydrodynamic design of reactor vessels for slurries, but not enough testing has been done to establish whether a satisfactory design has been achieved.

Preliminary work has been done on some components for large slurry systems.

Maintenance.—Methods and tools for maintaining reactor experiments by removal and replacement of components have been developed and demonstrated to be satisfactory on HRE–2. Some operations are done by use of long-handled tools with the equipment submerged in water for shielding. Others are accomplished by operating the tools through special shields. Ring-joint flanges have been perfected for joining equipment and provided with means for detecting leaks and preventing the escape of radioactivity.

Whether these methods can be used on large reactors has not been determined. Considerable work has been done on development of remote cutting and welding and on repair of components in place for large reactor plants.

4. Current Design Parameters

The technology is not yet sufficiently developed to construct a central-station powerplant. Considerable development must be done on large components and maintenance. The feasibility of operating the fuels at the power densities of a large reactor must be demonstrated. Design parameters proposed for the first large plant are listed below:

a. Steam conditions—400 psia, 445° F.
b. Reactor coolant outlet temperature—550° F.
c. Reactor coolant pressure—1,750 psi.
d. Fuel material, core—6 g U/liter uranyl sulfate solution.
    blanket—1,000 g Th/liter thorium oxide slurry.
e. Core-tank material—Zircaloy-2.
f. Maximum core-tank temperature—500° F.
g. Average power density, core—75 kw/liter.
    entire core system—14 kw/liter.
    entire blanket system—2.5 kw/liter.
h. Average specific power, reactor and processing plant:
    fissionable material—1,800 kw/kg.
    fertile material—6,800 kw/metric ton.
i. Conversion ratio, steady state—1.10.
j. Doubling time, steady state—15 years.

5. Operating Experience

Operating experience on aqueous homogeneous reactors has been obtained with HRE–1 and HRE–2. Both reactors employed uranyl sulfate solution in the core and D_2O in the blanket. No reactors have been operated with slurry fuels in core or blanket.

Homogeneous Reactor Experiment (HRE–1)

In 1950 construction of Homogeneous Reactor Experiment (HRE–1) was undertaken to investigate the nuclear and chemical characteristics of a circulating-fuel reactor at temperature and power sufficiently high for production of electricity from the thermal energy released. The reactor was designed to deliver 1,000 kw of heat from fuel solution at 482° F and 1,000 psia, yielding, after heat exchange, steam at a saturation pressure of about 200 psia. Fuel was a solution of uranyl sulfate in H_2O. The reactor core was an 18-inch diameter stainless steel sphere, reflected with D_2O.

The reactor was operated for about 24 months beginning in April 1952. Liquid was circulated for about 4,500 hours; the reactor was critical a total of 1,950 hours and operated above 100 kw for 720 hours. The maximum power attained was 1,600 kw, and a total of 600 Mw-hr of heat was produced. HRE–1 was dismantled in the spring of 1954 to be replaced by HRE–2.

Operation of the reactor demonstrated:

(1) nuclear and chemical stability at average power densities as high as 32 kw/liter,

(2) safe handling of the highly radioactive fuels at high pressure and temperature,

(3) effectiveness of the negative temperature coefficient in regulating the normal reactivity fluctuations and in controlling power surges that result from large rapid additions of reactivity, making regulating and safety rods unnecessary,

(4) control by control of fuel concentration and release of steam to turbine, making shim rods unnecessary,

(5) safe handling of radiolytic gas and use of copper as a homogeneous catalyst to recombine the gas.

Although the reactor was not designed for maintenance, the fuel circulating pump and feed pump were replaced several times, and some other work was done in radiation fields as high as 2,000 r/hr by use of improvised shielding and long-handled tools and without exposure of personnel beyond accepted tolerances. The work was difficult and even simple operations took a long time. At the end of the operation the reactor was partially decontaminated, and the reactor and shield were dismantled by similar methods.

Homogeneous Reactor Test (HRE-2)

During operation of HRE-1 it became evident that a second reactor experiment should be run before attempting to construct a full-scale homogeneous power reactor. HRE-2 was built to provide a facility for investigating the engineering problems of operating and maintaining fluid-fuel reactors and the longer term effects of operation on fuels and materials. Basic design criteria were: a 32-inch-diameter core contained in Zircaloy-2 and reflected by a D_2O blanket to permit operation at 250 to 300° C with a 10-g-U-per-liter solution of uranyl sulfate in D_2O as the fuel. Cost considerations led to the specification of 5,000 kw (thermal) for the power. Although the average specific power in the core was only 17 kw/liter, this was considered acceptable since operability at 30 kw/liter had been demonstrated in HRE-1.

The reactor was designed to operate at 2,000 psia. Equipment and systems were designed to take advantage of experience with HRE-1 and to test ideas that were being proposed for power reactors. Maintenance and containment were primary considerations in the design. Primary equipment and auxiliaries were housed in a steel tank which is welded closed and maintained at ½ atm abs when the reactor is operating. Provision was made for submerging the equipment in water to provide shielding so that most operations could be done with simple long-handled tools. Special shields and tools were provided so that some operations could be done dry.

First nuclear operation was in December 1957. Between then and Aug. 1, 1959, fluids were circulated for a total of 5,750 hours, 3,420 hours critical, in generating 5,720 Mw-hr of heat, and operation is continuing. A maximum power of 6.3 Mw was reached during the first week of high-power operation. A hole was melted in the core tank after 30 minutes at 6.3 Mw. Subsequent operation has been with fuel in core and blanket at power levels as high as 5.3 Mw but mostly at 3.5 Mw and below in investigation of fuel instability.

Experience with HRE-2 has shown that mechanical components can be developed which will permit long uninterrupted operation of a complete reactor system. Since the core-tank incident the reactor has been operated in four tests of 800 to 1,100 hours duration. Maintenance was required between tests, but in no instance was a test terminated by an equipment failure.

The ability to construct completely leaktight systems by care in fabrication and inspection and to keep the systems tight and the highly radioactive fluids contained have been demonstrated in 1½ years of operation.

Satisfactory maintenance of the reactor equipment has been accomplished by simple equipment and methods, and information is being obtained that forms a basis for development of maintenance for large reactors.

Continuous removal of krypton, xenon, and iodine is being effected in the reactor system.

Major difficulties experienced with HRE-2 have resulted from an unsatisfactory hydrodynamic design of the core coupled with the high-temperature instability of the fuel. In addition to the hole in the core tank, damage to corrosion assemblies, thermocouples, and diffuser screens in the core has provided evidence of severe overheating of some metal surfaces. This experience has led to renewed emphasis on core design and hydrodynamics studies in the development programs.

The hydroclone plant has operated satisfactorily but has removed only 10 to 20 percent of the fission- and corrosion-product solids which have been produced.

Determination of fuel inventory and analysis of abnormal behavior have been difficult. Additional and improved instruments for measuring flows and fuel concentrations are required to obtain completely satisfactory process control.

6. Economics

The technology has not been developed sufficiently to support completely realistic estimates of cost. Estimated total power costs based on the most complete design studies which have been made are 11.2 and 13.3 mills/kw-hr for 150-Mwe plants and 9.1 to 10.5 mills/kw-hr for 333-Mwe plants. The plants represent several types of reactors but are more sensitive to estimates of the requirements of a large plant and to assumptions concerning the status of development than to the type of reactor. The 13.3 mills/kw-hr for an early 150-Mwe plant based on a one-region slurry reactor was obtained from the most thorough study of reactor plant and maintenance.

Part I

PROGRAM OBJECTIVES AND HISTORY

1. OBJECTIVES

Development of high-performance power-breeder reactors based on the thorium-U^{233} cycle is the objective of the aqueous homogeneous reactor program. High conversion ratio and low inventories of fissionable and fertile materials necessary to the achievement of the high material efficiency required in a large nuclear power economy are important features of the target reactors. The present program encompasses all phases of development of a complete power-breeder system and would terminate in the demonstration of a successful power-breeder prototype plant or in an earlier determination that the reactors are not technologically feasible. Commercial development would be done by industry and would depend on an appraisal of economic potential based on experience with the prototype.

The program includes:

(1) development of reactor fuels and compatible constructional materials,

(2) development of economical methods for manufacturing and for processing the reactor fuels,

(3) development of the processes and equipment required to build, operate, and maintain the reactors and special processing plants,

(4) determination of the feasibility of the reactor systems, equipment, and associated processing plants by operation of reactor experiments and a prototype.

2. HISTORY

Homogeneous reactors were considered first for producing plutonium by the Manhattan Project in 1942–44. Initially the need for large amounts of D_2O or enriched uranium, then engineering problems, and finally the successful operation of the Hanford reactors prevented their serious development as production reactors. Work was discontinued by late in 1944.

The first homogeneous reactors were the Los Alamos water-boiler experiments: LOPO, a zero-power critical experiment fueled with uranyl sulfate dissolved in ordinary water (first operated in May 1944); HYPO, a 5-kw modification of LOPO, with uranium in the form of uranyl nitrate (operation began in December 1944); and SUPO, a further modification and improvement, which allowed operation at 45 kw (final modifications completed in March 1951). The work on water boilers at Los Alamos led to the design of power-reactor versions as possible package power reactors for remote locations. Construction of these reactors, known as Los Alamos Power Reactor Experiments No. 1 and No. 2 (LAPRE–1 and LAPRE–2), started in early 1955. Both experiments were fueled with solutions of enriched uranium oxide in concentrated phosphoric acid. The first experiment reached criticality in March 1956 and was operated at 20 kilowatts for about 5 hours. At that time serious corrosion difficulties were encountered, and the reactor was shut down and dismantled. The corroded parts were replaced, and operations were resumed in October 1956; however, similar corrosion difficulties caused the experiment to be terminated. Construction of LAPRE–2 was completed in 1958, and the reactor was operated intermittently at power levels up to 800 kw of heat in early 1959.

The first serious effort to develop homogeneous reactors for thermal breeding and the production of power was started at the Oak Ridge National Laboratory in 1949, when it was agreed that work should be directed toward the design of a small power reactor experiment. The ORNL Homogeneous Reactor Project was formed in 1950 to develop and build the two-region circulating-fuel Homogeneous Reactor Experiment (HRE–1) to obtain information about the physics, engineering, and chemistry of aqueous homogeneous systems when operated at temperatures high enough for producing power. The reactor, fueled with a solution of uranyl sulfate in distilled water, was designed to operate with a full-power heat release of 1,000 kw and a maximum fuel-solution temperature of 250° C (482° F). During a 24-month period, starting in April 1952, the reactor was operated intermittently and attained a maximum power level of 1,600 kw. In the spring of 1954 the reactor was shut down and dismantled to make room for the Homogeneous Reactor Test (HRE–2), having successfully demonstrated the short-term nuclear and chemical stability of a moderately high-power-density circulating-fuel reactor. Details of the design and operation of HRE–1 are presented in Section 11.1 of this report.

During the period of construction and operation of HRE–1, it became evident from the reactor program and from the associated development program that a second homogeneous reactor experiment should be constructed. The main reason for this decision was that HRE–1 did not demonstrate the engineering features of a homogeneous reactor required for continuous operation of a nuclear power plant. Therefore a second two-region circulating-fuel experimental reactor (Homogeneous Reactor Test, HRE–2), also fueled with uranyl sulfate in heavy water, was constructed on the HRE–1 site. Its purpose was to test the reliability of materials and equipment for long-term continuous operation of a homogeneous reactor, remote-maintenance procedures, and methods for the continuous removal of fission products and insoluble corrosion products. The reactor was brought to criticality on December 27, 1957, and reached full-power operation at 5 Mw on April 4, 1958. Shortly thereafter, a hole developed in the core tank which permitted fuel solution to leak into the D_2O blanket. After consideration of the nuclear behavior of the reactor with fuel in both the core and blanket, operation was resumed under these conditions in May 1958 and is continuing. HRE–2 is described in Section 11.2 of this report.

During the period of construction and operation of HRE–1 and HRE–2, design and development work was also done at ORNL on a variety of aqueous homogeneous reactors: plutonium producers, converters based on the uranium-plutonium fuel cycle, and special-purpose mobile and research reactors, in addition to the main effort on thorium breeders. Moreover, in spite of the formidable development program associated with the construction of a full-scale homogeneous reactor power plant, industrial groups proposed building homogeneous reactors as part of the power demonstration program in cooperation with the Atomic Energy Commission.

The Pennsylvania Advanced Reactor Project (established by the Pennsylvania Power and Light Co. and the Westinghouse Electric Corp. in 1955) studied the technical and economic feasibility of a large aqueous homogeneous reactor plant for central-service application having an electrical output of at least 150,000 kw. The Project completed two reactor-plant reference designs, prepared equipment layouts and cost estimates for the two plants, and undertook an extensive technological development program. The proposed reactor was a one-region power reactor fueled with a slurry of mixed thorium-uranium oxides in heavy water. However, from results of the development program it was concluded, in December 1958, that construction of a large-scale plant should be preceded by a prototype, and work on the Project was terminated.

In January 1956 the Foster Wheeler and Worthington Corps. proposed the construction of a one-region U^{235} aqueous homogeneous burner reactor. Plans were for a reactor and associated oil-fired superheater with a net electrical capacity of 10,000 kw for the Wolverine Electric Cooperative, Hersey, Mich. In May 1958 the Atomic Energy Commission announced that the plans had been canceled owing to large increases in the estimated cost of the plant.

Work on aqueous homogeneous reactors at ORNL is continuing, with exclusive attention being given to the development of thermal power breeders based on the thorium-U^{233} fuel cycle.

Part II

DESCRIPTION OF POWER-BREEDER STATION

3. GENERAL CHARACTERISTICS OF TWO-REGION POWER BREEDERS

A two-region circulating-fuel reactor is believed to be the most promising type of aqueous homogeneous power breeder. The reactor contains a core in which most of the power is generated and a blanket surrounding the core to absorb leakage neutrons. Fuels are solutions of uranium compounds, and suspensions of mixtures of uranium and thorium compounds in heavy water. The ratio of D_2O to fissionable and fertile material is large enough so that the neutron spectrum is thermal.

A one-region reactor which has a significant breeding gain is so large, to reduce the neutron leakage, as to seriously prejudice the present estimates of engineering and economic potential. Reactors in which the heat is removed by boiling and others in which core and blanket fuels are present as solids fluidized by the heavy water have received some study. As the technology develops, alternatives such as these may prove superior to the circulating-fuel reactors. At present, however, they do not appear to offer determinative advantages in technology, feasibility, or economic potential over the circulating-solution and slurry reactors.

Two types of two-region circulating-fuel reactors—one with a solution core and a slurry blanket, the other with a slurry core and a slurry blanket—are attractive as power breeders. A reactor in which the core fuel is a dilute uranyl sulfate solution (less than 6 g of U per liter) and the blanket is a concentrated thorium oxide slurry ($\sim$1,000 g of Th per liter) is the preferred two-region breeder. It offers the best possibility of combining high specific power and high conversion ratio to obtain efficient breeding. Estimates indicate that the inventory of fissionable material in the reactor and processing plants can be kept below 2 kg per MwE and that the conversion ratio could be as high as 1.10, with a resulting doubling time of 10 to 15 years. Neutron losses to a zirconium-alloy core tank and to parasitic absorbers in the core fuel solution are kept acceptably low by maintaining a fissionable-material concentration of about 2 g/liter. With this concentration, the critical diameter of the core is about 5 feet if it is spherical, or 4 feet if it is cylindrical and long. The average power density in the core may be limited to 100 kw/liter or less, and the total heat that can be produced in one reactor core may be 500 Mw or less. Two or three reactors operating in parallel would be required to provide steam for turbogenerators in the 200- to 300-Mw range.

The most promising alternative to the solution-core breeder is one that employs a 200- to 300-g/liter thorium oxide–uranium oxide slurry in the core and a 1,000-g/liter thoria slurry in the blanket. Poisoning the fuel with thorium permits both the concentration of fissionable material and the critical volume to be varied over a wide range. The total amount of power that can be extracted from one core may then be limited only by structural considerations, and only one reactor would be required for each large turbogenerator. When thorium is included in the core fuel, a limit is imposed on the reactor flux and specific power in kilowatts per gram of fissionable material by the flux-dependent losses which result from absorption of neutrons in Pa^{233}. In a typical reactor and processing plant the total inventory of fissionable material would be 3 to 5 kg per

MwE, the conversion ratio could be as high as 1.10, and the doubling time would be 20 to 40 years.

A 333–MwE power plant based on two-region breeder reactors is described here. General design characteristics are those which would be proposed for a first large breeder plant. The size is intermediate between the probable size of a first commercial plant and the size of an optimum power-breeder station, but is one that was used by the Fluid Fuel Reactors Task Force in January and February 1959 and is being used in the Ten-Year Plan studies as a reasonable size for comparison of power reactors.

4. SOLUTION-CORE SLURRY-BLANKET POWER BREEDER

4.1 REACTOR PLANT

A 333–MwE plant based on two-region solution-core power breeders contains three reactors, each producing 380 Mwt. The three reactors are operated separately but share buildings, control rooms, waste, ventilation, maintenance, and many other facilities. Steam from all three reactors is piped to one 333–Mw turbogenerator. The flowsheet for one reactor system is presented in Figure 4.1.

Each reactor vessel consists of a 4-foot-diameter by 12-foot-long cylindrical core operated at 320 Mwt (75 kw/liter average, 50 kw/liter maximum in fluid adjacent to the core-tank wall) surrounded by a 2-foot-thick blanket which is operated at 60 Mwt (2.7 kw/liter). The core tank is made of Zircaloy-2, or a more corrosion-resistant zirconium alloy, with an effective wall thickness of ½ inch. The pressure vessel has a 6-inch-thick wall of carbon steel clad with stainless steel.

Under steady-state conditions the core fluid is a D_2O solution 0.025 *m* in UO_2SO_4 (5 g of U per liter at 275° C—1.9 g U^{233}, 1.4 g U^{234}, 0.2 g U^{235}, and 1.4 g U^{236}), 0.025 *m* in $CuSO_4$, 0.005 *m* in $NiSO_4$, and 0.025 *m* in D_2SO_4. Copper sulfate is present to recombine radiolytic gas, nickel is a soluble corrosion product, and the excess acid is added to reduce the tendency for the constituents to separate from solution by hydrolysis. The blanket contains a 1,000-g-Th-per-liter slurry of thorium oxide in D_2O (11 vol % solids). The steady-state concentration of U^{233} and Pa^{233} in the thoria is 2.5 to 4.5 g per kg of Th, depending on the importance of processing cost relative to short doubling time. Molybdenum oxide (0.02 *m*) or palladium (0.002 *m*) is incorporated in the slurry to catalyze the recombination of radiolytic gas produced in the blanket. Total inventories in each reactor plant are estimated to be 110 kg of $U^{233}+Pa^{233}+U^{235}$, 24 metric tons of thorium, and 53 metric tons of D_2O. The conversion ratio is calculated to be 1.09.

Fuel solution is pumped through the zirconium-alloy core tank of the reactor at a rate of 30,000 gpm, entering at 250° C (482° F) and leaving at 290° C (554° F). After leaving the core it divides into two parallel circuits. In each circuit, 15,000 gpm of fuel solution is circulated through a 160-Mw steam generator and is returned to the reactor by a canned-motor circulating pump. The steam generator is of the natural-circulation type with separate 4-foot-diameter by 35-foot-long horizontal steam drum and steam generator sections which are joined by vertical risers and downcomers. Fuel is cooled from 290 to 250° C in passing through 2,200 ½-inch-diameter tubes. Steam is delivered from the drum at 400 psia and 445° F. The canned-motor pump is a 700-hp unit rated at 150 feet of head.

The entire core circulating system is pressurized by boiling D_2O in a surge chamber which is attached to the piping at the reactor vessel. The pressurizer temperature is maintained in the range 325 to 335° C (617–635° F) to control the pressure between 1,750 and 2,000 psia. Nuclear control is accomplished by controlling the fuel concentration and by the negative temperature coefficient. Power level is controlled by regulating the release of steam to the turbogenerators.

Under normal operating conditions 100 gpm of fuel at 290° C is passed through a hydroclone system to remove suspended fission- and corrosion-product precipitates and is dis-

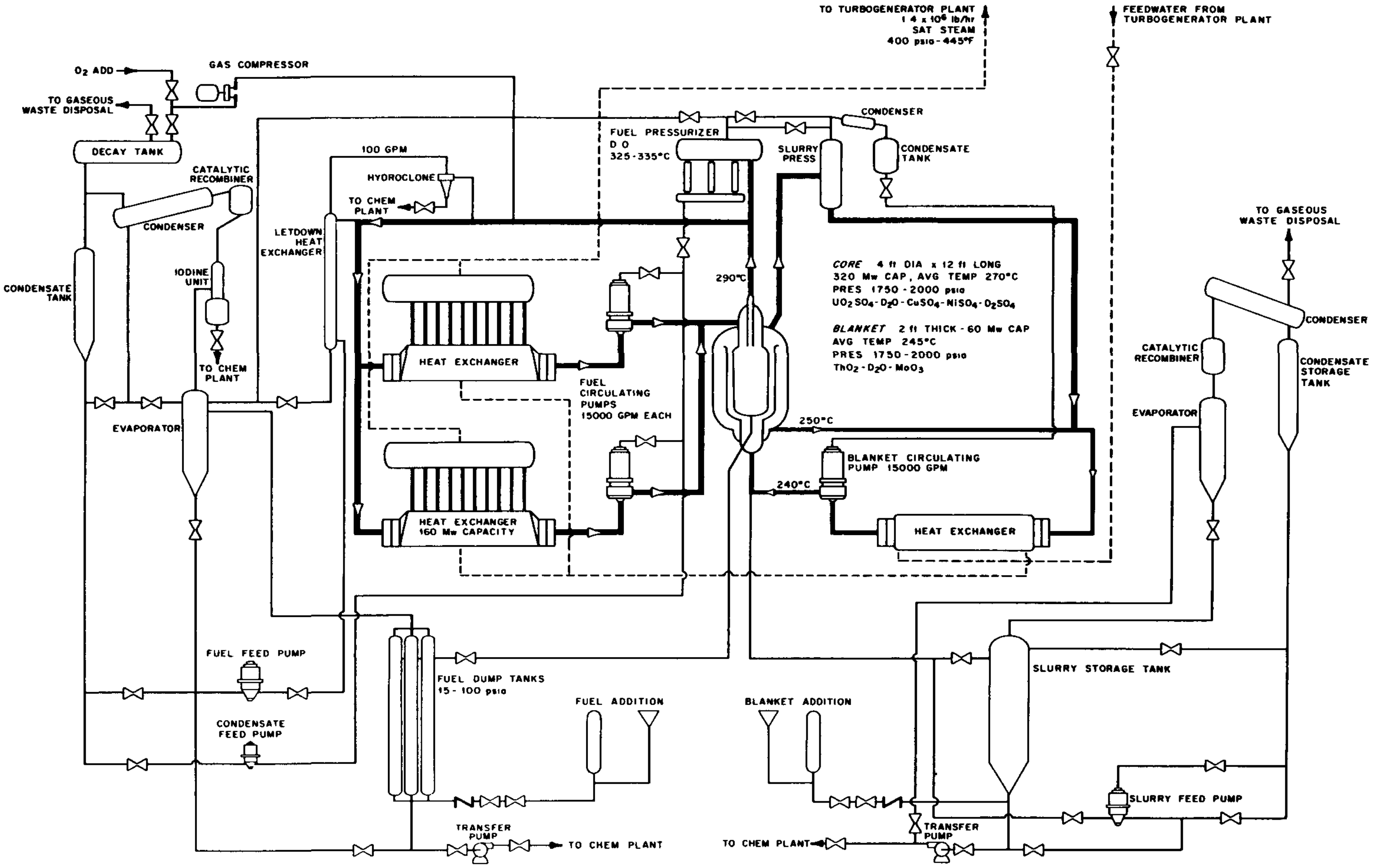

FIGURE 4.1—Flow diagram of two-region solution-core slurry-blanket reactor.

charged through a counter-current heat exchanger into a low-pressure system that operates at 15 to 100 psia. There heavy water is evaporated from the fuel at a rate of 10 gpm, carrying with it the radiolytic gas, excess oxygen, fission-product gases, and iodine that are dissolved in the fuel. Iodine is stripped from the vapor by partial condensation of the D_2O and concentrated in a small reboiler; Xe^{135} is removed through the precursor I^{135}. Deuterium is recombined with part of the oxygen in a catalytic recombiner, and the heavy water is separated from oxygen and fission-product gases in a condenser.

Fuel solution is returned directly from the low-pressure system to the high-pressure circulating system. Condensate is returned partly to the pressurizer and partly to the fuel circulating pumps as purge for the bearings and rotor cavity. Oxygen and fission-product gases are passed through decay tanks after which most of the gas is recycled to the high-pressure system, but a part is discharged from the plant to the waste system.

Although the letdown and low-pressure system has been discussed above in connection with the removal of fission products and the production of condensate, it has several other intermittent functions. Fuel is added to the reactor through the low-pressure equipment. The fuel concentration, and by this means the operating temperature, of the reactor is regulated by control of the return of fuel and condensate to the high-pressure system. When the reactor is shut down, the fuel is contained in the storage tanks.

The thoria slurry which fills the reactor blanket is circulated through the pressure vessel at a rate of 15,000 gpm. It enters at 240° C (464° F) and leaves at 250° C (482° F). The high flow rate is required to keep the slurry suspended homogeneously. Temperatures are kept low to help cool the core tank and to reduce the neutron leakage. Because only 15 percent of the power is generated in the blanket, the heat can be used efficiently at the lower temperature for heating the feed water to the saturation temperature before it enters the steam generators.

Slurry from the blanket is circulated through a heat exchanger which contains 600 1-inch-diameter, 35-foot-long tubes in a 4-foot-diameter shell. Circulation is maintained by a 15,000-gpm canned-motor pump similar to that used in the core system except that it delivers only 75 feet of head when circulating the heavy slurry. The blanket is pressurized by heating the slurry in a pressurizer attached to the slurry circulating system. Condensate is produced in the pressurizer to purge the bearings and rotor cavity of the pump. The blanket pressurizer is interconnected with the core pressurizer through pressure-regulating valves to limit the difference in pressure across the core tank.

A low-pressure system is provided for the blanket, but there is not continuous circulation between the high-pressure and low-pressure systems. The low-pressure system contains storage tanks for slurry and condensate, evaporators, recombiners, condensers, and feed pumps. The equipment is used primarily for storing slurry and adjusting concentrations, for feeding material to the reactor, and for withdrawing material for processing. Gases released from the system are processed in the general plant facility.

With the exception of the reactor vessel the major material of construction of the entire reactor system is type 347 stainless steel. Titanium and zirconium are used for special parts of equipment where exceptional resistant to corrosion or abrasion is required.

Reactor primary and radioactive auxiliary systems are installed in cells which consist of an inner metal liner, the concrete biological shield, and an outer metal shell assembled as an integral structure. Access to equipment is through removable sections at the top of the cells. The sections are keyed into girders which support the removable shield plugs in two layers. A metal diaphragm is installed between the layers and welded into the girders, so that the cell is completely sealed and can be maintained at ½ atm abs. pressure during operation. Penetrations for instrument and service lines terminate in galleries along the cell walls. Control rooms are located adjacent to the service galleries.

Cells and operating galleries for the three reactors in the powerplant are contained in a single canyon-type structure approximately 300 feet long and 125 feet wide. The cells are about 60 feet deep, and the crane bay rises to about 40 feet above the cells. The canyon is equipped with a shielded-cab crane for maintenance operations and communicates directly with the radioactive maintenance facilities.

4.2 TURBOGENERATOR PLANT

The turbogenerator plant has few unusual features. Steam from each steam generator passes through delay drums where it is monitored for radioactivity and where it can be contained in the event of a serious fuel leak. Then the combined steam from the three reactors flows directly to a 333–Mw turbogenerator set, the largest which has not yet been designed for low-pressure saturated steam. The turbogenerator unit will have an 1,800–rpm tandem compounded double flow, non-reheat type turbine, direct connected to a conductor-cooled type generator. Extraction steam will be employed for three stages of feed-water heating. The plant will contain all the conventional auxiliaries. Output of the generator will be delivered to step-up transformers to obtain the distribution line voltage.

4.3 SUPPORTING FACILITIES

In addition to the reactor and turbogenerator plants, the power station contains many supporting facilities. They include general administrative services, plant stores, maintenance shops, pumping station, and water-treatment plant, which are common to all types of power stations and which will not be discussed here. Also, there are facilities for maintaining radioactive equipment and for disposing of radioactive gaseous, liquid, and solid wastes; and there is a plant for manufacturing and reprocessing reactor fuels.

4.3.1 Maintenance Plant

Maintenance problems of the homogeneous reactor are similar to those encountered in the fuel processing plants at Hanford and Savannah River except that the activity levels are higher in the powerplant and the major equipment is larger and built for much higher pressure. Work must be done remotely with special tools, there must be strict control of contamination, and facilities must be provided for storing, decontaminating, and repairing highly radioactive components and tools.

The primary maintenance tool for the reactor plant is the shielded-cab crane, and the primary maintenance area is the canyon above the reactor cells. The crane is used to manipulate the many special tools and to handle reactor equipment in and out of the cells. The canyon communicates directly with a pool 60 feet long, 20 feet wide, and 30 feet deep. The pool is large enough for temporary storage of heat exchangers and reactor vessels. All equipment removed from the reactor cells is partially decontaminated and may be partially disassembled in the pool and in an adjacent decontamination area.

A portion of one end of the pool projects into a hot shop wherein items that have been partially decontaminated, but which are still too radioactive for direct maintenance, can be reclaimed. The hot shop is approximately 60 feet long, 20 feet wide, and 20 feet high and is surrounded by 5-foot-thick concrete walls for biological shielding. It is equipped with a 10-ton overhead crane with an auxiliary hook for light equipment, a heavy-duty overhead manipulator, and wall-mounted manipulators for light and intermediate service. Windows penetrate the shielding walls at appropriate places, and at two of the observation points small master-slave manipulators are provided to facilitate maintenance of a more delicate nature than could be handled by the heavy-duty manipulators. A turntable is provided to facilitate work on large, heavy items.

In addition to the hot shop, the maintenance building contains a mockup shop with jigs and fixtures that are used for fabricating new piping and equipment for the reactor, a shop for work on slightly radio active equipment, and the general maintenance shops.

4.3.2 Fuel Processing Plant

In order to obtain an efficient breeder, material is withdrawn from several places in the reactor for reprocessing. Solids and some uranyl sulfate solution are removed from the core high-pressure system through the underflow receiver on the hydroclone for separation of soluble and insoluble corrosion and fission products from the uranium. Concentrate is withdrawn from the reboiler in the iodine separation unit of the core low-pressure system for removal of iodine. Slurry is withdrawn through the blanket low-pressure system for separation of U^{233} and fission and corrosion products. Material from the three sources is combined and cooled for about 10 days; then the D_2O is recovered by evaporation. D_2O recovery can be carried out in shipping containers, and the residue can be sent to a central facility for reprocessing. However, it is believed that power breeder stations ultimately will be large enough so that on-site processing will be economical; so it is assumed that a plant having the capacity to process 500 kg of thorium and 2 kg of fissionable material per day is a part of the 333–MwE station.

In the processing plant, residues from the D_2O recovery step are dissolved in nitric acid and stored for about 150 days; then they are processed through two full cycles of Thorex solvent extraction in heavily shielded cells. The thorium and U^{233} are recovered essentially free of fission-product activity but containing isotopic contaminants that present difficult handling problems. The fuel solution is reconstituted by precipitating the uranium from uranyl nitrate solution as UO_4, firing to anhydrous UO_3, and redissolving in D_2SO_4 solution. This is carried out rapidly enough to avoid serious radiation problems from the daughters of U^{233}.

Preparation of pure thorium oxide for the reactor blanket involves precipitating thorium oxalate from the thorium nitrate product solution of Thorex and decomposing this material to anhydrous oxide by firing above 800° C. A particle size of 2 to 3 μ is obtained, by control of conditions under which the oxalate is precipitated, to provide a slurry of satisfactory engineering properties. As a final step, the oxide is slurried in D_2O to a concentration suitable for addition to the reactor low-pressure system. Preparation of the thorium oxide must be carried out behind shielding.

Chemical and radiochemical analytical laboratories necessary for operation of the entire power station are included in the reprocessing plant.

4.3.3 Waste Disposal Plant

Radioactive wastes from the power station include fission-product gases saturated with D_2O; contaminated ventilating air; liquid wastes from the reactor, the decontamination facilities, and the Thorex plant; and solids primarily from the maintenance plant. Fission-product gases are passed through cold traps for drying and D_2O recovery; then they are discharged into beds of activated carbon, where krypton, xenon, and iodine are retained until all but the Kr^{85} has decayed. They are released from the plant to the atmosphere through a 250-foot stack. Ventilating air from contaminated areas of the plant is filtered and discharged through the same stack. Radioactive solids are packaged and stored by burial or in caves at the site; depending on the plant location, this may be temporary or permanent storage.

More elaborate facilities are required for handling the liquid wastes. Wastes that involve a considerable quantity of fissionable material are discharged into a 2,500-gallon critically safe storage tank. They are transferred from this tank to an evaporator, where they are concentrated, and the concentrate is sent to the Thorex plant. Wastes that do not involve large quantities of fissionable material are stored in four 60,000-gallon storage tanks until they are concentrated in evaporator. The condensate is collected in tanks, is sampled, and is discharged to ion-exchange units as makeup for the maintenance pool or to a storage pond for return to the environment if the activity level is low. It is recycled if the activity level is too high. Depending on the plant location, bottoms from the evaporators are discharged to permanent storage tanks or to facilities for packaging for shipment to a central storage site.

5. SLURRY-CORE SLURRY-BLANKET POWER BREEDER

A 333-MwE power plant based on the two-region slurry-core alternative to the solution-core reactor contains one reactor operated at a power of 1,140 MwT to provide the steam for a 333-Mw turbogenerator. The reactor consists of a core 7 feet in diameter by 21 feet long, operated at 1,060 Mw (40 kw/liter); the core is surrounded by a 2-foot-thick blanket which is operated at 80 Mw. Under steady-state conditions of a thoria-heavy-water slurry containing 200 g of Th and 14.3 g of U per liter (6.9 g U^{233}, 4.8 g U^{234}, 0.6 g U^{235}, and 2.0 g U^{236}) is circulated through the core at a rate of 90,000 gpm. It enters at 256° C (493° F) and leaves at 300° C (572°F). Radiolytic gas is recombined in the slurry by a catalyst such as palladium.

Inventories in the reactor plant are estimated to be about 900 kg $U^{233}+Pa^{233}+U^{235}$, 65 metric tons of thorium, and 145 metric tons of D_2O. The conversion ratio is calculated to be 1.07 to 1.10, depending on the efficiency of removal of Xe^{135}.

Slurry from the reactor core is circulated at a rate of 15,000 gpm through each of six parallel steam-generator and pumping circuits. Steam is produced in the steam generators at 400 psia and 445° F, as with the solution-core reactor. The reactor is pressurized by heating slurry in a pressurizer attached to the circulating systems. Steam is condensed in the pressurizer to provide purge for the circulating pumps.

The blanket slurry and the blanket high-pressure system are similar to those for the two-region solution-core reactor. Because this blanket is larger, the slurry (1,000 g of Th per liter) is circulated at a rate of 30,000 gpm to obtain adequate mixing. Two parallel pumping circuits are provided, but only one contains a heat exchanger; the 80 Mw of blanket heat is used for feed-water heating. Core and blanket pressurizers are interconnected to prevent the pressure difference across the core tank from becoming excessive.

Although they are not in continuous use, low-pressure systems must be provided for the core and blanket. They consist of storage tanks, recombiners and condensers, evaporators, and feed pumps. Gas-handling equipment is shared by the core and blanket systems. Slurry is charged into the low-pressure systems for feed to the reactor, and it is removed through the low-pressure systems for processing.

The reactor vessel is made of carbon steel clad with stainless steel and contains a zirconium-alloy core tank. Type 347 stainless steel is the major material of construction for other equipment and for the piping. Titanium and zirconium are used for internal parts in places where exceptional abrasion resistance is important.

The power station includes the turbogenerator plant and all the supporting facilities that are discussed for the solution-core slurry-blanket breeder station.

Part III

WORK DONE

6. INTRODUCTION

Development of aqueous homogeneous reactors has required the establishment of new technology in many areas and the expansion of existing technology to new and difficult fields in others. At the inception of the work nothing was known about the behavior of aqueous solutions and slurries of uranium and thorium salts, about container materials for the fuels, or about the effects of radiation on fuels and materials at temperatures appreciably about 100° C.

Engineering of high-pressure, high-temperature systems to meet the leaktightness, reliability, and maintenance requirements for handling the highly radioactive homogeneous reactor fuels had never been attempted. Whether a circulating-fuel reactor would have adequate nuclear stability was in serious question; therefore, the development has involved extensive work on fuels, materials, and all phases of reactor engineering. Fuel reprocessing has been included in the program in search of new processes that would take full advantage of the fluid nature of the fuel to achieve rapid continuous removal of fission and corrosion products.

Important progress has been made in the development program. Experimental work, both in- and out-of-pile, has led to the selection of uranyl sulfate solutions and thoria suspensions as the most promising fuels. All but one or two alternatives have been eliminated. A considerable knowledge has been obtained of the uranyl sulfate fuels in container materials. Satisfactory equipment and maintenance methods have been developed for handling solution fuels on reactor experiment scale. HRE–1 and HRE–2 have been built and operated. Nuclear stability has been demonstrated, and promising solutions have been found for many of the engineering problems. It should soon be possible to decide on the technological feasibility of the solution fuel system for the core of a power-breeder reactor.

The technology of suspension fuels is less advanced. Slurries are being made which show promise of being satisfactory for core and blanket applications, but little quantitative information has been obtained about their behavior in-pile. Equipment for handling slurries has about reached the stage of development where it should be satisfactory for a reactor experiment. Much additional work will have to be done in all areas before a prototype plant can be built with the expectation of successful operation.

7. FUELS AND MATERIALS

Fuels and materials work for aqueous fluid-fuel reactors is among the most interesting and challenging in modern technology. The conditions of interest involve considerable departures from areas for which data and techniques for obtaining data were available. The problems have an interdependence on many variables, both physical and economic. New factors are introduced by the fact that the radiations which are a result of the nuclear reactions significantly alter the chemistry of the fuels and the corrosion and physical behavior of materials exposed to them. In many cases those variables uniquely associated with the reactor environment are most important, necessitating extensive in-pile testing of fuels and materials before adequate specifications can be given. Consequently, there must be comprehensive research and development on (1) chemistry and properties of solution and suspension fuels, (2) corrosion and erosion of materials by the fuels, and (3) metallurgy of commercial metals and the new metals, zirconium and titanium. Facilities ranging from conventional laboratory apparatus to complex in-pile loops are involved in extensive experimental investigations.

7.1 CHEMISTRY OF AQUEOUS POWER-BREEDER FUEL AND BREEDER BLANKET SOLUTIONS

Many uranium and several thorium salts have been considered for possible use as components of aqueous fuel and breeder-blanket solutions. These include uranyl sulfate, nitrate, fluoride, chromate, phosphate, lithium uranyl carbonate, thorium nitrate, and thorium phosphate. Solubility relationships, radiation stability, corrosiveness, and neutron adsorption have been important factors in the selection of a suitable fuel. Uranyl sulfate has generally been considered to be the most promising fuel solute and was used in the two experimental power reactors, HRE–1 and HRE–2. Experience gained with uranyl sulfate and the changing needs of the program have led to intensification of the solubility studies and inclusion of additional chemical components in the system. The effects of radiation have been found to be substantial, and these have given rise to studies of the various reactions which are consequences of the presence of the fission-fragment radiation in such solutions.

7.1.1 UO_2SO_4-Based Materials

Review of Studies

In the main, two types of studies have been performed to elucidate the chemistry of fuel solutions, these being solubility and reaction studies.

Solubility Studies.—Uranyl sulfate was originally studied as if it were a binary system, UO_2SO_4-H_2O. Two experimental methods were used to obtain the necessary heterogeneous equilibrium information under carefully controlled conditions in laboratory studies.

In the *synthetic* method, a mixture of known weights of uranyl sulfate and water was sealed in a silica or glass capillary tube which was then heated in an appropriate air or fused-salt bath with agitation to keep the mixture in equilibrium; continuous visual observation of the contents permitted the temperatures to be established at which significant phase changes occurred. From the knowledge of the composition of the synthetic mixture, the solubility of such a composition could be established for a particular temperature at which solid or second liquid phases disappeared. From the results of many such experiments the effects of composition and temperature on solubility could be determined.

In the *analytical* method, after discovering that the system should be treated as a three-component system, an excess of one component (usually UO_3) was provided in a mixture which was sealed in a metal autoclave and heated, with agitation, to a desired temperature; sampling the solution in equilibrium with the solid and subsequent analysis of the solution sample permitted the composition of a saturated solution to be determined; quenching of the autoclave and subsequent examination of the solid confirmed the existence of the suspected solid phase. In a modification of this technique a two-part autoclave was used, with a sintered-metal filter disc separating the two regions; after establishing a saturated solution in one region, the autoclave was turned upside down and the lower end was cooled so that the difference in vapor pressure would cause the liquid to be driven through the filter disc and thus separated mechanically from the solid with which it was in equilibrium. The results of such studies were generally confirmed by the operation of engineering experimental equipment such as circulating loops for corrosion studies, in which various solutions were demonstrated to be stable over periods of time for as long as one year while at elevated temperatures and in rapid circulation.

Considerable information has been obtained about the three-component system, UO_3–SO_3–$H_2O(D_2O)$, and concerning the effect of adding various other components on phase stability. Phase diagrams were established at temperatures of 25, 100, 175, and 250° C. covering concentration regions of interest. From these it was possible to predict accurately the results of the various changes in temperature and concentration which were required for experimental engineering or reactor operation.

Solubility relationships in the five-component system, UO_3–CuO–NiO–SO_3–D_2O, were studied because cupric sulfate was added to the fuel solution in HRE–2 as an internal catalyst for the recombination of D_2 and O_2 and nickel enters the solution as a soluble product of the corrosion of stainless steel. Work on this system is still in progress, particularly at temperatures of 200–350° C. and at sulfate concentrations below 0.1 *m*. It is not possible, in three dimensions, to represent the phase diagram of a five-component system over a range of temperature, but by selecting a particular temperature and sulfate concentration, the number of remaining variables is small enough to permit the construction of a three-dimensional model showing the locations of the various phase boundaries, invariant points, binary lines, and liquid-liquid miscibility gaps. Such models, constructed from the many experimental results already available, have served both as a guide to the selection of reactor fuel compositions and as a basis for the selection of further areas for experimentation.

The solubility of fission products in water and in UO_2SO_4–H_2O solutions has been measured in the same manner as described for the measurement of fuel-component solubilities. Much use has been made of the visual observation method and the filter-bomb techniques. The solubility of $La_2(SO_4)_2$, $Y_2(SO_4)_3$, $BaSO_4$, $SrSO_4$, Cs_2SO_4, and Ag_2SO_4, both individually and combined, were determined in H_2O, 0.126 *m*, and 1.26 *m* UO_2SO_4 solutions from 100 to 325° C. Later extensive investigations by the visual observation method were made on fission-product solubilities in low concentration UO_2SO_4–H_2O and UO_2SO_4–D_2O solutions. In these latter investigations the fission-product compounds included the above salts as well as ruthenium, neodymium, and others.

Reaction Studies.—Several chemical reactions have been demonstrated to be of importance in the operation of homogeneous reactors; almost without exception they have their origin in the driving force created by the energy released in the fission process itself and released via the radiolytic decomposition of the heavy water of the fuel solution. Radiation chemistry studies were first made by exposing water and uranyl sulfate solutions, sealed in quartz ampoules, to pure gamma radiation sources. Similar exposures were then made to thermalized neutrons; when U^{235} solutions were used, fissioning was induced in the solution. Tests were performed covering wide ranges of the variables believed or found to be important. These included radiation intensity, uranium enrichment, uranium concentration, acidity, temperature, choice of anionic species, added cationic species, dissolved gas concentrations, etc. These tests were extended by analogous studies in small stainless steel, titanium, and zirconium autoclaves exposed to radiation in the ORNL Graphite Reactor and the Low Intensity Test Reactor (LITR). Ultimately the studies were confirmed by tests in the course of the operation of HRE–1 and HRE–2.

The production of D_2, O_2, and D_2O_2 by radiolytic decomposition in the reactor resulted in several laboratory kinetic studies.

The recombination of D_2 and O_2 *in situ* by catalysis with cupric ion was studied in small titanium bombs over a wide range of temperatures, D_2 and O_2 pressures and pressure ratios, and in a variety of uranium, acid, and cupric ion concentrations. The results of these laboratory studies were confirmed by in-pile tests and the operating data from HRE–2.

The rates of decomposition of peroxide in uranyl sulfate solutions made up in H_2O or in D_2O have been studied between 50–100° C. in the absence and in the presence of added catalysts.

Results of Studies

Solubility Studies.— The solubility relationships in aqueous systems based on uranyl sulfate have been developed, in general, to the point that for given temperature limits and uranium concentrations the remaining composition of the system can be specified so as to ensure the absence of a phase separation.

Study of the uranyl sulfate–water system revealed the presence of an interesting liquid-liquid miscibility gap, a phenomenon well known in organic systems but seldom found in aqueous systems. Upon heating a solution of stoichiometric uranyl sulfate to a temperature above 290° C. under the pressure of its saturated vapor, with the exact temperature dependent upon the uranium concentration and rising rapidly as the concentration decreases below 0.5 molal, the homogeneous solution suddenly separates into two liquid phases (unless hydrolytic precipitation of uranium occurs, with very dilute solutions, before the temperature of two-liquid phase separation is reached). One of these phases is more concentrated in uranium and the other less concentrated than the initial solution; the relationship between temperature and concentration was found to be such that a small elevation of the temperature above the phase separation temperature is sufficient to force the separation of a very concentrated uranium solution from a quite dilute solution. Analysis of the two phases in equilibrium revealed that the light phase is relatively more acidic that the heavy or concentrated phase. This alone was sufficient information to indicate that UO_2SO_4–H_2O mixtures could not properly be represented as a binary system but would have to be represented as the three-component system, UO_3–SO_3–H_2O, in order to account for the observed facts. It was quickly established that raising the SO_3 concentration (the excess acidity) would elevate the temperature of phase separation. For example, a solution containing initially 10 wt percent uranium and a sulfate: uranium molar ratio of 2.95 remained a single liquid phase to a temperature of 525° C., the limit of the test.

The many detailed results of the investigations of solid-liquid and liquid-liquid equilibria appear to support the following conclusions:

1. In moderately dilute aqueous solutions at 250 to 350° C, sulfate is present predominantly as the HSO_4^- ion. Data supporting the existence of HSO_4^- instead of $SO_4^=$ ion at higher temperatures were obtained in solubility studies of $NiSO_4$, $3CuO \cdot SO_3 \cdot 2H_2O$, Li_2SO_4, and $MgSO_4$ in H_2SO_4–H_2O mixtures from 150 to 300° C.

2. Uranyl ion, (UO_2^{++}), appears to be dimerized to $U_2O_5^{++}$. The uranium species in solution expressed as a stoichiometric com-

pound would then be $U_2O_5(HSO_4)_2$. Study of $UO_3 \cdot H_2O$ solubility in H_2SO_4–H_2O supports this belief.

3. Combining conclusions (1) and (2), a solubility limitation rule was obtained which states that solutions having a molar ratio $\frac{U_2O_5^{++} + Cu^{++} + Ni^{++}}{HSO_4^-}$ greater than 0.5 at 300° C will approach or exceed the solubility limit at that temperature. This solubility rule is used as a criterion of phase stability for the current reactor fuels. Experimentally, the actual solubility ratio has been found to be higher than 0.5 and can approach a value of 0.6 when the total concentration of anion expressed as HSO_4^- is between 0.05 and 0.2 *m*. If, however, the concentration of nickel ions in solution should become excessively high, e.g., equivalent to more than 33 percent of the total cations in solution, the solubility ratio drops below 0.5.

4. The tie-line compositional relationships in the liquid-liquid regions of the sytem UO_3–SO_3–H_2O and the corresponding D_2O system have been established. The heavy-liquid phase from solutions which initially contained stoichiometric UO_2SO_4 approximates a stoichiometric composition, $UO_2SO_4 \cdot 5H_2O$, at 350° C. The light-liquid phase in equilibrium with heavy phase at this temperature is about 0.04 *m* UO_2SO_4, and 0.04 *m* free H_2SO_4.

5. When the temperature of solutions of compositions at or near the HRE–2 fuel composition is increased, the first phase to separate is a second liquid phase rather than a solid. For the current HRE–2 fuel (0.025 *m* UO_2^{++}, 0.013 *m* Cu^{++}, 0.006 *m* Ni^{++}, 0.06 *m* total $SO_4^{=}$) the temperature is 332° C. No solid phases appeared in the system at temperatures up to 500° C, and the heavy liquid phase, the only phase remaining above 374° C, was clear yellow.

6. In experiments designed to show the effect of a temperature difference between solutions in vapor-pressure equilibrium in the system UO_3–SO_3–H_2O, it was found that a ΔT of 20 to 30° C. between heavy and light liquid phases would cause a saturating solid phase to appear in the heavy liquid phase. Therefore, under ΔT conditions in a reactor in which a heavy liquid phase forms due to an elevated temperature and it is at least 20 to 30° C. higher in temperature than the light liquid phase, solids could subsequently appear. The solids $UO_3 \cdot H_2O$ and UO_2SO_4 have been shown to be stable to 800° C. in the presence of high-pressure water vapor.

7. For fuel compositions similar to that listed in (5) above, there was very little difference in solubility between H_2O and D_2O solutions.

8. Data obtained on the five-component system UO_3–CuO–NiO–SO_3–$H_2O(D_2O)$ at 300° C permit fuel compositions to be selected so that, if precipitation occurs due to the decrease of free H_2SO_4 or increase of Ni^{++} in solution, the solid phases can be limited to non-uranium compounds such as $NiSO_4 \cdot H_2O$ or $3CuO \cdot 2H_2O$. A new compound of uranium and copper oxides, $CuO \cdot 3UO_3$, was discovered in the course of investigation of this system.

The results of the solubility studies of fission products showed a considerable increase in solubility for fission-product salts in UO_2SO_4–$H_2O(D_2O)$ solutions as compared to their solubility in water. If the particular fission product hydrolyzed and, to a large extent, precipitated from solution, then the complexing capacity of UO_2SO_4 in H_2O solution was small. Salts such as $Y_2(SO_4)_3$, $La_2(SO_4)_3$, $BaSO_4$, $SrSO_4$, and Cs_2SO_4 were stable as sulfates at high temperature in UO_2SO_4 solutions, whereas ruthenium hydrolytically precipitated and showed very low solubility in UO_2SO_4–H_2O solutions in the 200–330° C. temperature range. Quantitative solubility data are available for most of these systems at temperatures to and above 300° C and at several concentrations of UO_2SO_4–H_2O solution. Solubility of fission products in 0.02 *m* UO_2SO_4, 0.005 m H_2SO_4, are given in Section 8.1.1.

Reaction Studies.—The studies of reactions induced by the fission process revealed that D_2 and D_2O_2 were the primary products of the decomposition of D_2O, with yields of approximately 1.7 molecules (of each) per 100 ev of fission energy absorbed by the solution. The subsequent decomposition of D_2O_2 to D_2O plus $\frac{1}{2}$ O_2 gives an over-all decomposition of D_2O into its elements $D_2+\frac{1}{2} O_2$; the resulting gas mixture is known as radiolytic gas which is equivalent to the term "knallgas" for the similar mixture formed upon electrolysis of water. Increasing the uranium sulfate concentration decreased the yields of D_2 and D_2O_2 from 1.7 for 0.02 *m* uranium to 0.5 for 3.4 *m* uranium solutions.

The decomposition of peroxide in uranium sulfate solutions was found to proceed at a rate proportional to the peroxide concentration, i.e., a first-order process. This rate is much faster than the decomposition of peroxide in pure water. It represents the decomposition of dissolved uranyl peroxide, formed by the equilibrium reaction

$$UO_2^{++}+H_2O_2=UO_4+2H^+.$$

In dilute reactor fuel solutions essentially all the peroxide appears as UO_4. Catalysts for the decomposition of peroxide were found; a combination of Cu(II) and Fe(II or III) appeared to be synergistic. Rate constants at 100° C were as large as 5 x 10^5 liters/mole/minute for Fe(II) promoted by Cu(II).

Studies of the radiation-induced decomposition of water in fissioning uranyl sulfate solutions at 250–300° C led to the discovery that hydrogen (or deuterium) and oxygen were recombined to water when dissolved in such solutions. The rate was found to be proportional to the hydrogen partial pressure and, presumably, to the dissolved-hydrogen concentration. The uranyl ion, or some U(VI) species, appeared to catalyze the reaction, but better catalysts were discovered. Cu(II) salts, in particular, are extremely effective. For copper, the essential chemistry of the over-all reaction includes, as the slow or rate-determining step, a reaction between dissolved hydrogen and dissolved copper salt which consumes dissolved hydrogen and produces some unestablished reduced copper species. Its rate may be expressed as

$$\frac{-d[H_2]}{dt}=k_{cu}[Cu^{++}][H_2].$$

It is followed by a rapid regeneration of the cupric ion or species through oxidation by dissolved oxygen, uranyl ion, or any other oxidizing agent which may be present. In the presence of a 2 : 1 ratio of $H_2 : O_2$, uranium solutions are maintained in the hexavalent state, but the exhaustion of oxygen will lead to the reduction of uranium. The kinetics of the reaction have been studied, and representative values for k_{cu} have been calculated on the basis that the solubility of hydrogen is the same as that reported for water. For a solution containing 5 g of U per liter and 25 mole percent excess sulfuric acid, reported values were:

T (°*C*)	k_{cu} (M^{-1} min^{-1})
250	147
275	382
295	845

Recent studies with heavy-water solutions containing 0.042 *m* uranium, corresponding to the fuel solution then in use in HRE–2, confirmed earlier reports that D_2 reacts more slowly than H_2 and established firm rate constants for these solutions at 250, 275, and 300° C. A subsequent evaluation of HRE–2 operating data and in-pile corrosion-loop data gave recombination rate constants which bracketed those of the laboratory study (which had been made under conditions more easily controlled).

Systematic surveys were made in hopes of finding catalysts even more active than copper. None has yet been found, but silver salts appeared to have substantial activity, coupled with a lower activation energy and a second-order dependence on the silver concentration.

In a sealed system containing enriched uranyl sulfate solution, exposure to a neutron flux causes fissioning which decomposes water; this action causes an increase in hydrogen pressure which, at constant power density, proceeds at a constant rate; i.e.,

$$\frac{dP_{H_2}}{dt}=K_1\,(\text{power density}),$$

When the recombination reaction is superimposed on this decomposition reaction, the following differential equation represents the situation:

$$\frac{dP_{H_2}}{dt}=\underset{\text{(decomposition)}}{K_1\,(P.D.)}\qquad\underset{\text{(recombination)}}{-k_2P_{H_2}}.$$

This representation was tested by in-pile autoclave experiments which confirmed both the decomposition rates expected and the recombination rates expected on the basis of the separate experiments. These decomposition and recombination rates were further confirmed, within the engineering limitation present, by tests made during the operation of HRE–1 and HRE–2. The use of copper dissolved in the reactor fuel for the complete recombination of radiolytic gas has been successfully demonstrated in HRE–1 and HRE–2.

Significance of Studies to Homogeneous-Reactor Design

Solubility Studies.—The solubility studies have, of course, fundamental significance for homogeneous-reactor design in that they provide the temperature-composition-pressure limitations within which the fuel solution must be maintained to preserve homogeneity. Furthermore, they make it possible to predict what new phases may appear if these limits are exceeded in various ways. From such knowledge the designer can establish operating conditions and margins of safety with respect to phase stability.

Fission-product solubility data have been applied to the design of HRE–2 and will be of importance in the design of future aqueous homogeneous reactors. Fission products which hydrolytically precipitate from fuel solution are removed by hydroclones in the fuel system. Fission products not precipitating are removed by chemical reprocessing of the fuel solution. The quantitative solubility data provide limits to concentration buildup which are of importance in establishing the rate of reprocessing the fuel solution.

Reaction Studies.—The reaction studies first provided an indication of the magnitude of the gas-production problem—about 10 cfm (STP) of radiolytic gas per magawatt.

In the earlier stages of the development of homogeneous-reactor technology, it was planned that this radiolytic gas would be allowed to collect, would be reduced in pressure, diluted with steam for safety, and, finally, burned in a flame recombiner just after removing the excess steam. This plan worked quite satisfactorily for handling the 10.3 scfm produced in the 1,000-kw HRE–1. The copper-catalyzed homogeneous recombination provided a mechanism by which the radiolytic gas would be removed *in situ* as rapidly as it was being generated. This enables the designer to avoid most of the hazard previously associated with the safe handling of large quantities of explosive gas. Again, temperature and composition information were provided which could be used in the choice of conditions giving a desired reaction rate.

The studies of peroxide formation and decomposition have provided a basis for extrapolation to useful reactor operating conditions. The decomposition reaction has not yet been measured above 100° C; on the basis of the established temperature dependence below 100° C, it would seem that reactor operation at 250–300° C would involve extremely low steady-state concentration of peroxide. So far it has not been established conclusively that harmful concentrations of peroxide exist under such conditions, although a number of anomalous results are as yet unexplained. At temperatures below 100° C the decomposition information has been valuable to the designer in avoiding the precipitation of the relatively insoluble $UO_4\cdot 2D_2O$ or $UO_4\cdot 4D_2O$ in storage tanks and stagnant pipelines exposed to beta- and gamma-ray-induced decomposition of the water to H_2O_2.

7.1.2 Alternate Materials

Review of Studies

Solubility Studies.—Many aqueous uranium solutions in addition to the UO_2SO_4–H_2O system have been investigated for possible use as alternate fuel systems. In addition, a search has been made for thorium solutions which would be suitable for a homogeneous-reactor breeder solution.

The methods for investigation of alternate systems were similar to those used for UO_2SO_4–H_2O solutions. These methods included the visual observation, the filter bomb, and the direct sampling techniques. In studying carbonate-CO_2 equilibria, the vapor phase, of necessity, was an important part of the over-all system. In order to make these studies, liquid CO_2 contained in a special high-pressure vessel, was heated and transferred to the equilibration vessel which contained water and excess solid components. The total pressure was measured by means of Bourdon gages, the vessel containing the system components was rocked at temperature, and aliquots of the solution phase were withdrawn for analysis. The solubility of the alkali metal oxide—uranium carbonate complex as a function of temperature and CO_2 pressure was determined.

The laboratory investigation of aqueous plutonium solutions as alternate fuels was hampered by the high toxicity of plutonium. Semimicro visual observation techniques were developed for investigating plutonium solutions in gloved boxes.

Alternate fuel systems investigated and the ranges of investigation follow:

1. The solubility and thermal stability of $UO_2(NO_3)_2$ in H_2O and HNO_3–H_2O has been studied by the visual observation method from 60 to 374° C, and by the direct sampling technique from 135 to 300° C.
2. The system UO_3–HF–H_2O has been investigated from 25 to 374° C.
3. The solubility and stability of UO_2CrO_4 and $UO_2Cr_2O_7$ in H_2O has been explored to 400° C.
4. The system UO_3–H_3PO_4–H_2O has been studied at this Laboratory to 300° C and at Los Alamos Scientific Laboratory to 450° C.
5. The solubility of lithium uranyl carbonates in CO_2–H_2O solution has been investigated at 250° C as a function of lithium carbonate and CO_2 concentration.
6. The solubility of PuO_2^{++} ion in HNO_3-H_2O, H_2SO_4–H_2O, and H_3PO_4–H_2O solutions from 100 to 300° C has been explored. Attempts have been made to stabilize hexavalent plutonium in aqueous solution at high temperature by the use of O_2 pressure.
7. Thorium nitrate solubility and thermal stability in H_2O and in HNO_3–H_2O solutions have been investigated from 60 to 374° C.
8. The system ThO_2–H_3PO_4–H_2O has been explored from room temperature to 400° C at concentrations of thorium approaching 1,200 grams per liter.
9. The effect on phase stability of adding LiF to UO_2F_2–H_2O, and the addition of Li_2SO_4, $BeSO_4$, or $MgSO_4$ to UO_2SO_4–H_2O solutions has been studied.

Reaction Studies.—The rates of radiolytic hydrogen gas production have been investigated in solutions of UO_2F_2, $UO_2(NO_3)_2$, and $U(SO_4)_2$ at various concentrations of uranium.

The rates of nitrogen gas evolution in irradiated solutions of $Th(NO_3)_4$ and of $UO_2(NO_3)_2$ have been determined as a function of concentration.

Preliminary experiments have been started at temperatures below 200° C with solutions of $UO_2(NO_3)_2$ to investigate copper as a homogeneous catalyst in nitrate systems for hydrogen-oxygen recombination.

Results of Studies

Solubility Studies.—The accomplishments in the solubility studies of various alternate systems follow:

1. The solubility of $UO_2(NO_3)_2$ in H_2O solution has been found to be greater than 70 wt percent $UO_2(NO_3)_2$ up to 300° C. At low concentrations and at temperatures above 250° C hydrolysis of $UO_2(NO_3)_2$ produces $UO_3 \cdot H_2O$. Addition of a small excess of HNO_3 prevents hydrolysis at 300° C. Uranyl nitrate in water solution decomposes thermally at the higher temperatures to produce equilibrium vapor pressures of nitrogen oxides.
2. The solubility of UO_3 in HF–H_2O solution at high temperature is in the same order of magnitude as the solubility of UO_3 in $HNO_3 \cdot H_2O$. However, a two-liquid phase region is present

in this system; the lower limit of this liquid-liquid immiscibility is 313° C. Hydrolytic precipitation occurs in dilute solutions at high temperature. The solid formed is a solid solution of $UO_3 \cdot H_2O$ and $UO_2F_2 \cdot H_2O$; hydrolysis occurs to a greater extent than in the corresponding UO_3–H_2SO_4–H_2O system, thereby necessitating a greater amount of HF compared to H_2SO_4 to stabilize the solutions.

3. The solubility of UO_2CrO_4 and $UO_2Cr_2O_7$ in H_2O are in the same order of magnitude as $UO_2(NO_3)_2$ in H_2O. However, UO_2CrO_4 hydrolytically precipitates in the 100° to 125° C temperature range, depending upon concentration; and, although $UO_2Cr_2O_7$ is stable to concentrations of 60 wt percent and is even soluble to above 450° C in the supercritical fluid, when hexavalent chromium is exposed to radiation it is rapidly reduced to trivalent chromium which hydrolytically precipitates at high temperature.

4. Solutions of H_3PO_4, as much as 2 molal, in hexavalent uranium are phase stable to temperatures above 400° C. In fact, investigators at Los Alamos have shown that UO_3 in H_3PO_4–H_2O is soluble in the supercritical fluid above 400° C analogously to $UO_2Cr_2O_7$–H_2O solutions. A molar ratio, $PO_4/UO_3 = 6$, is necessary to solubilize UO_3 at 200–350° C in the high concentration range.

5. Lithium uranyl carbonate is soluble at high temperature in Li_2CO_3–CO_2–H_2O under a CO_2 pressure. At 250° C and 1,000 psi CO_2 pressure, 0.1 m uranium in soluble; the Li/U molar ratio=6.

6. Tetravalent plutonium in HNO_3–H_2O, H_2SO_4–H_2O, or H_3PO_4–H_2O solutions hydrolytically precipitates at elevated temperature, although the data indicate that high concentrations of acid would solubilize this species. Hexavalent plutonium, although highly soluble in acid solutions, is unstable and reduces to tetravalent plutonium. Questionable partial success in stabilizing Pu(VI) has been attained using O_2 or using HNO_3–H_2O as the solvent.

7. Thorium nitrate is soluble in H_2O from 25 to above 300° C to approximately the same extent as $UO_2(NO_3)_2$. However, as in the case of $UO_2(NO_3)_2$, it is thermally and hydrolytically unstable. An excess of HNO_3 to produce an NO_3/Th ratio of 6.65 will prevent hydrolysis in 1 to 2 m $Th(NO_3)_4$ solutions to 300° C; however, the concentrations of nitrogen oxides in the vapor are considerable.

8. Solutions containing up to 1,200 g of thorium per liter in concentrated H_3PO_4 are phase stable to temperatures above 400° C. In these solutions the mole ratio H_3PO_4/Th is 5:1. This material is a gel at temperatures below 150° C. In order to obtain liquid ThO_2–H_3PO_4–H_2O solutions at room temperatures which are stable to 400° C, the H_3PO_4/Th ratio must be increased to 10 and the thorium concentration is correspondingly reduced to 300 g per liter.

9. The addition of LiF or NaF to UO_2F_2–H_2O solutions and Li_2SO_4, $BeSO_4$, or $MgSO_4$ to UO_2SO_4–H_2O solutions have produced phase-stable solutions in the 200–300° C temperature range. Beryllium sulfate and Li_2SO_4 elevate the two-liquid-phase lower boundary.

Reaction Studies.—Apparently there is no significant difference in the rates of hydrogen generation per 100 kv of energy absorbed in solution of UO_2F_2, $UO_2(NO_3)_2$, and $U(SO_4)_2$ as compared with solutions of UO_2SO_4.

The rate of nitrogen gas evolution in solutions of $Th(NO_3)_4$ and $UO_2(NO_3)_2$ was found to decrease markedly with decreasing solute concentration and appeared to extrapolate to zero at 0.80 m NO_3.

The preliminary values for k_{cu} in solutions of $UO_2(NO_3)_2$ appear to be roughly 25 percent as large as the corresponding constants in solutions of UO_2SO_4. Extrapolation to reactor temperature indicates that the difference may decrease at higher temperatures.

Significance of Studies to Homogeneous-Reactor Design

Solubility Studies.—It is necessary to have considerable knowledge of the solubility and stability of alternate fuel and breeder solutes in order to provide assurance that the presently preferred fuel system (UO_3–SO_3–D_2O) and blanket system (ThO_2 suspension in D_2O) are the best ones available for homogeneous-reactor operation. It is possible that additional information may be found concerning alternate systems which would make one of the alternates more promising for homogeneous-reactor use than the present fuel or breeder-blanket system.

1. Uranyl nitrate is considered to be a promising alternate fuel solute. $UO_2(NO_3)_2$–$H_2O(D_2O)$ solutions do not form a second liquid layer at elevated temperatures as do UO_2SO_4–$H_2O(D_2O)$ solutions, and it is possible that the excess nitric acid required to prevent hydrolysis of $UO_2(NO_3)_2$ solutions at high temperature may be less corrosive than the H_2SO_4 added to stabilize UO_2SO_4 solutions. However, nitrogen oxides have a greater tendency to go into the vapor phase at high temperatures than does SO_3, and it is necessary to consider the effect of high-temperature steam containing nitrogen oxides on reactor-container materials as well as the extent of solution corrosion. The data presently available on uranyl nitrate solutions appear to justify further consideration of their use as an alternate fuel system.

2. Solubility relationships in the system UO_3–HF–$H_2O(D_2O)$ system are similar to those in the system UO_3–SO_3–$H_2O(D_2O)$ and the same problems exist: i.e., two-liquid phase separation at high temperatures and hydrolytic precipitation of uranium in solutions of low acidity. Consequently, there appears to be little advantage from a phase-stability standpoint in using UO_2F_2 as the fuel solute instead of UO_2SO_4. The principal drawback to its use is the corrosiveness of fluoride-containing solutions to zirconium alloys.

3. Presently available data on UO_2CrO_4- and $UO_2Cr_2O_7$-containing solutions do not indicate that these solutes are likely to be attractive for use as fuel components. It is known that hexavalent chromium is readily reduced to trivalent chromium in a radiation field and that trivalent chromium solutions undergo hydrolysis at high temperatures, precipitating the chromium from solution.

4. Moderately high concentrations of phosphoric acid are required to hold UO_2 of UO_3 in solution at high temperature, and the corrosiveness of such solutions to promising materials of reactor construction constitutes one of the principal deterrents to the use of phosphate solutions in homogeneous reactors.

5. The limited data available on the system UO_3–Li_2O–CO_2–H_2O indicate that a high CO_2 pressure will be required to hold UO_2CO_3 in solution at high temperatures. However, the availability of high-purity Li^7 and the low corrosiveness of such solutions to materials of construction such as stainless and even carbon steels, seems to warrant further consideration of these solutions as an alternate fuel system.

6. The data obtained to date on plutonium in nitric, sulfuric, and phosphoric acid solutions indicate that the use of plutonium as the fissionable species in solutions of this type is not attractive due to the reduction of Pu(VI) to Pu(IV), which hydrolytically precipitates.

7. Thorium nitrate is quite soluble at high temperatures and is stable in the presence of an excess of nitric acid. However, the high cost of the N^{15} isotope, the radiation effect on nitrate ions, and the problems resulting from the high concentration of nitrogen oxides in the vapor phase over concentrated nitrate solutions at high temperature make the use of thorium nitrate solutions for breeder blankets appear unattractive at the present time.

8. The corrosiveness of phosphoric acid solutions at high temperatures and the high cross section of the phosphorus atoms present in the amount required to solubilize thorium combine to make thorium phosphate solutions appear unpromising for breeder-blanket use.

9. The addition $BeSO_4$ and Li_2SO_4 to UO_3–SO_3–H_2O solutions elevates the temperature at which the second liquid phase appears, but since second-liquid-phase formation is not likely to be a problem in very dilute uranyl sulfate solutions, there seems to be little incentive for the use of additives of this type to the fuel system, insofar as phase stability is concerned.

Reaction Studies.—The radiolytic studies in alternate systems provide an indication that the magnitude of the gas production problem with solutions of UO_2F_2, $UO_2(NO_3)_2$, and $U(SO_4)_2$ is about the same as with solutions of UO_2SO_4.

The expected low rates of N_2 evolution (under radiation) in HRE–2 fuel concentration ranges indicate that little or no free nitrogen gas would be produced with low nitrate concentrations, and the HNO_3 concentration in solution required for phase stability could be maintained by an equilibrium gas pressure of nitrogen oxides over the solution.

If the preliminary values of k_{cu} are typical for $UO_2(NO_3)_2$ systems, a reactor using a nitrate fuel solution must be operated at a temperature 20° C. higher than the equivalent UO_2SO_4 system in order to obtain the same hydrogen recombination efficiency.

7.2 AQUEOUS THORIUM OXIDE SUSPENSIONS

7.2.1 General Characteristics of Thorium Oxide Suspensions

A solution or sol of a thorium salt is the preferred fuel for the blanket of a homogeneous reactor. However, none have been found which are stable to temperature and radiation and satisfactory in nuclear and chemical respects. In the absence of a suitable solution or sol, effort has been devoted to the development of a suspension fuel with thorium oxide as the fuel compound.

The principal problems in the application of ThO_2 suspensions to homogeneous reactor systems arises from the fact that the homogeneous suspensions possess non-Newtonian flow characteristics and that the solids may separate from the liquid. The degree of non-Newtonian character of the suspension affects the reactor design largely through the velocity required to ensure turbulent flow: the more non-Newtonian, the higher the velocity required. The tendency for the solid to separate from the liquid affects the design not only from the point of view of the minimum velocity to prevent settling in the reactor vessel and associated horizontal and inclined piping but also from the requirement that the system should be designed to eliminate rapid changes in direction of the suspension, which would tend to separate solids centrifugally. Therefore it is necessary to provide basic information on suspension characteristics in order to ensure satisfactory performance of system components.

The properties of homogeneous suspensions of thorium oxide in water are, in some cases, simply functions of the properties of the pure materials. Examples are the density, specific heat, and thermal conductivity. These particular properties of a suspension can be calculated for any concentration and temperature if data for the pure material are available. However, other properties, such as settling rate and viscosity, are functions of particle size and shape as well as concentration. Furthermore, as the ThO_2 particle size is reduced toward colloidal dimensions, physico-chemical forces become significant. Under these circumstances, not only does the presence or absence and the concentration of electrolytes become important, but also the rate of shear (or velocity gradient) may exert a profound influence on such physical properties as the viscosity.

The object of the studies of the physical and engineering characteristics of ThO_2 suspensions is to relate the easily measured hindered-settling and laminar-flow properties to the more important turbulent-flow characteristics such as heat and momentum transfer and transport velocity. In addition, studies are being made to determine the relative importance of the particle characteristics, such as size and shape, on the laminar-flow physical properties.

Because of the complex nature of the behavior of semicolloidal suspensions, it is often necessary to make simplifying assumptions based on the nature of the particular solution sought in order to obtain useful results. An example might be the choice of a flow model for use in heat and momentum transfer studies. In this case the controlling processes occur in the high-shear-rate regions near the wall, and the specific flow model chosen should fit the data over the high-shear-rate region. However, great care should be used in applying these high-shear-rate models in studies of low-shear-rate phenomena such as flow separation and stagnation, or turbulent diffusion at large distances from shear surfaces.

7.2.2 Intrinsic Physical Properties

Intrinsic suspension properties are those properties, such as density, which are functions of properties of the pure materials alone. In all cases these calculated properties are free from restrictions due to presence of electrolyte, rate of shear, etc.; and some, such as the viscosity, represent minimum values below which the property value can never be reduced.

Suspension Density

The density of ThO_2 is 10.03 g/cc. The density of a suspension is the sum of the products of pure component density and the volume fraction of that component. For a concentration of 1,000 g Th/liter at 280° C, the volume fraction solids at room temperature is 0.145 and the corresponding suspension density is 2.31 g/cc; at 250° C, the volume fraction solids and suspension density are 0.114 and 2.03 g/cc, respectively.

Suspension Heat Capacity

The heat capacity of pure ThO_2 is

$$C_p = 16.45 + 0.02346\ T - 2.124 \times 10^5/T^2, \quad (1)$$

where C_p = cal/(g-mole) (°K) and T = degrees Kelvin. The heat capacity of a suspension is the sum of the heat capacities on a weight basis of the liquid and the solid at the bulk mean suspension temperature, each multiplied by its respective weight fraction in the suspension. For a ThO_2 suspension of 0.145 volume fraction solids at room temperature, the specific heat is 0.408 Btu/(lb) (°F), compared to a value of 1.00 Btu/(lb) (°F) for water.

Suspension Thermal Conductivity

The thermal conductivity of ThO_2 suspensions has been shown to follow the empirical relationship:

$$\left(\frac{k_s - k_o}{k_s + k_o}\right) = 1.13\,\phi\left(\frac{k_p - k_o}{k_p + 2k_o}\right), \quad (2)$$

where ϕ = volume fraction solids for volume faction solids up to 0.14 and temperatures up to 70° C. Equation 2 is believed to be satisfactory for use at volume fraction solids up to 0.20 and temperatures up to 300° C based on the good correlation obtained for materials having widely different thermal conductivities. Since the termal conductivity of water has a maximum value in the vicinity of 130° C, ThO_2 suspensions show a similar maximum, the room-temperature value for 0.145 volume fraction solids increasing from 0.528 to 0.574 Btu/(hr) (ft) (°F) at 130° C and then decreasing to 0.485 Btu/(hr) (ft) (°F) at 280° C.

Suspension Viscosity

The viscosity of suspensions of spherical non-interacting particles is a function only of volume fraction solids. A typical relation between the suspension viscosity, μ_s, and the viscosity of the suspending medium, μ_o, is

$$\mu_s = \mu_o\,[1 + 2.5\,\phi + 7.17\,\phi^2 + 16.2\,\phi^3]. \quad (3)$$

As the particle size is reduced, the colloidal forces between particles becomes important and the viscosity is increased and becomes dependent on the rate of shear, i.e., non-Newtonian. Under these circumstances, Equation 3 represents the minimum value below which the viscosity can never be reduced. For a volume fraction solids of 0.145, the ratio of suspension viscosity to suspending medium viscosity is 1.562.

Suspension Settling Rate

Single spherical particles of ThO_2 less than 10 microns in diameter settle in water with a velocity given by Stokes' law (Eq. 4) for water temperatures covering the complete range of interest:

$$U_o = \frac{g_L D_p^2 (\rho_p - \rho_o)}{18\mu}, \tag{4}$$

where U_o=single-particle settling rate,
D_p=particle diameter,
ρ_p=particle density,
ρ_o=fluid density,
μ=fluid viscosity.

The presence of additional particles decreases the settling rate, with the decrease being a function only of volume fraction solids, provided that the particle size is sufficiently large to minimize colloidal forces. A typical relation between the suspension settling rate, U_s, and the single-particle settling rate, U_o, is

$$U_s = (1-\phi)^{4.65} U_o.$$

For a volume fraction solids of 0.145, the ratio of hindered settling to Stokes' law velocity is 0.482.

7.2.3 Extrinsic Physical Properties

Reduction of the ThO_2 particle diameter below 5 to 10 microns results in increased relative importance of the physico-chemical forces responsible for the distinctive behavior of colloidal materials. Although not truly colloidal, suspensions in which the particle size is 0.1 to 10 microns are often observed to be flocculated. In a flocculated suspension the particles stick together in the form of loose irregular clusters or flocs in which the original particles can still be recognized. Under these circumstances, small additions of electrolyte as well as the rate of deformation may markedly affect those physical properties, such as viscosity and settling rate, which are dependent on floc structure. As yet, there is no relation which gives a general description of the effect of electrolytes on the suspension physical properties. However, fundamental studies of the surface chemistry of aqueous ThO_2 suspensions suggests qualitative explanations of the observed hindered-settling and flow behavior in terms of the amount and nature of ions adsorbed on the surface of the particles.

The adsorption of ions at the solid-liquid interface is often interpreted in terms of a double-layer structure which has a characteristic electrokinetic zeta potential. Flocculated suspensions of ThO_2 are observed to have zeta potentials between +30 and −30 mv; whereas deflocculated suspensions may have zeta potentials from +30 to +80 mv in acidic media or −30 to −60 mv in basic media. The zeta potential of ThO_2 powder in double-distilled carbonate-free water is from +18 to +24 mv; hence it would be expected to be flocculated. Good correlation has been observed in studies in which the zeta potentials, settling rate, and effective viscosities of ThO_2 suspensions have been measured as a function of pH (i.e., concentration of hydrogen ion), with maxima being observed in the hindered-settling rate and the apparent viscosity which corresponded to the minimum in the absolute value of the zeta potential. Examination of the electrokinetic and ion adsorption properties of ThO_2 after irradiation to an nvt of 3.7 x 10^{18} neutrons/cm^2 showed that the neutron radiation reduced the positive zeta potential by a factor of 2 in pure water; consequently, irradiated ThO_2 possessed significantly different ion adsorption characteristics when in contact with acids. However, in contact with neutral salts and bases the ion adsorption properties did not appear to be markedly affected by neutron irradiation.

Infrared spectroscopy gives more detailed information on the types of chemical bonds between adsorbed species and ThO_2 surfaces. Systematic studies of the adsorption of carbonate, sulfate, and silicate indicate a very complex adsorption process as a function of temperature, with the existence of two or more adsorption sites being postulated to explain the results. Additional information is being obtained by measuring heats of adsorption, studying effects of pH, and by making equilibrium adsorption measurements. The combined results will allow the determination of the reaction mechanism and will permit prediction of the effect of temperature on the adsorption characteristics of ThO_2 surfaces, and hence on the effect of additives on ThO_2 suspension properties at elevated temperatures.

The quantitative evaluation of the effect of floc structure on the engineering characteristics of ThO_2 suspensions is being approached through measurement of the laminar-flow properties of the suspension. The hindered-settling characteristics of flocculated ThO_2 suspensions are also being studied, and in addition to yielding design information, a better understanding of floc structure is being achieved.

Laminar-Flow Characteristics of Flocculated ThO_2 Suspensions

A large class of materials have a constant viscosity under laminar-flow conditions. These are called Newtonian fluids. However, flocculated ThO_2 suspensions do not have a constant viscosity under laminar-flow conditions and hence are classified as non-Newtonian materials. It is convenient to describe their flow behavior in terms of the rate of shear in the system. Under steady flow conditions in a circular conduit, the rate of shear is highest at the wall and decreases to zero at the center line. At any given radial position, the rate of shear is also a function of the velocity; the higher the velocity, the higher the rate of shear. Since the viscosity is not a constant in non-Newtonian systems, it will be called the apparent or effective viscosity and it will be understood that this viscosity is a point value that holds for a particular radial position and velocity. ThO_2 suspensions have not been observed to have significant time-dependent properties.

At low rates of shear, the effective viscosity of ThO_2 suspensions is high and often does not vary appreciably as the rate of shear is decreased. At intermediate rates of shear, the effective viscosity changes rapidly with shear rate, decreasing as the shear rate is increased. At high rates of shear, the effective viscosity is again almost constant, approaching a limiting value. This limiting value is always greater than that of the suspending medium. The complicated variation of viscosity with shear rate means that a complicated expression having at least three different coefficients must be used to describe the flow rates of ThO_2 suspensions.

Numerous laminar-flow data have been taken with suspensions prepared from a wide variety of ThO_2 powders. However, an immediate difficulty in attempting to correlate the data is that no general relation is available which adequately describes the data over the complete shear-rate range of interest. Many mathematical models have been proposed, and although some have a more theoretical basis than others, none are completely satisfactory for general application. This means that when a particular flow model is chosen for its suitability for a given situation, great care should be used in applying this model, and constants determined for use with it, to different situations.

A flow model suitable for use in correlating data where processes occurring at high shear rates are controlling, i.e., heat and momentum transfer at pipe walls, is the Bingham plastic model. This model has the following desirable features:

1. It fits the data sufficiently well at high shear rates that accurate effective viscosities and laminar velocity gradients at the wall can be calculated from the experimentally determined flow parameters.
2. It extrapolates to give a limiting value of the viscosity at high rates of shear that is always greater than the viscosity of the suspending medium.

Two parameters that characterize the Bingham plastic model are the yield stress, τ_y, and the coefficient of rigidity, η. The coefficient of rigidity is the limiting value of the viscosity at high rates of shear, whereas the effective viscosity is a function of tube diameter and mean velocity as well as the two physical constants. Although knowledge of the coefficient of rigidity is important for design purposes, the yield stress is the more significant of the two parameters since it is the major variable controlling the velocity for the onset of turbulent flow. This is shown in Figure 7.1. A yield stress less than 0.1 lb/sq. ft. and a coefficient of rigid-

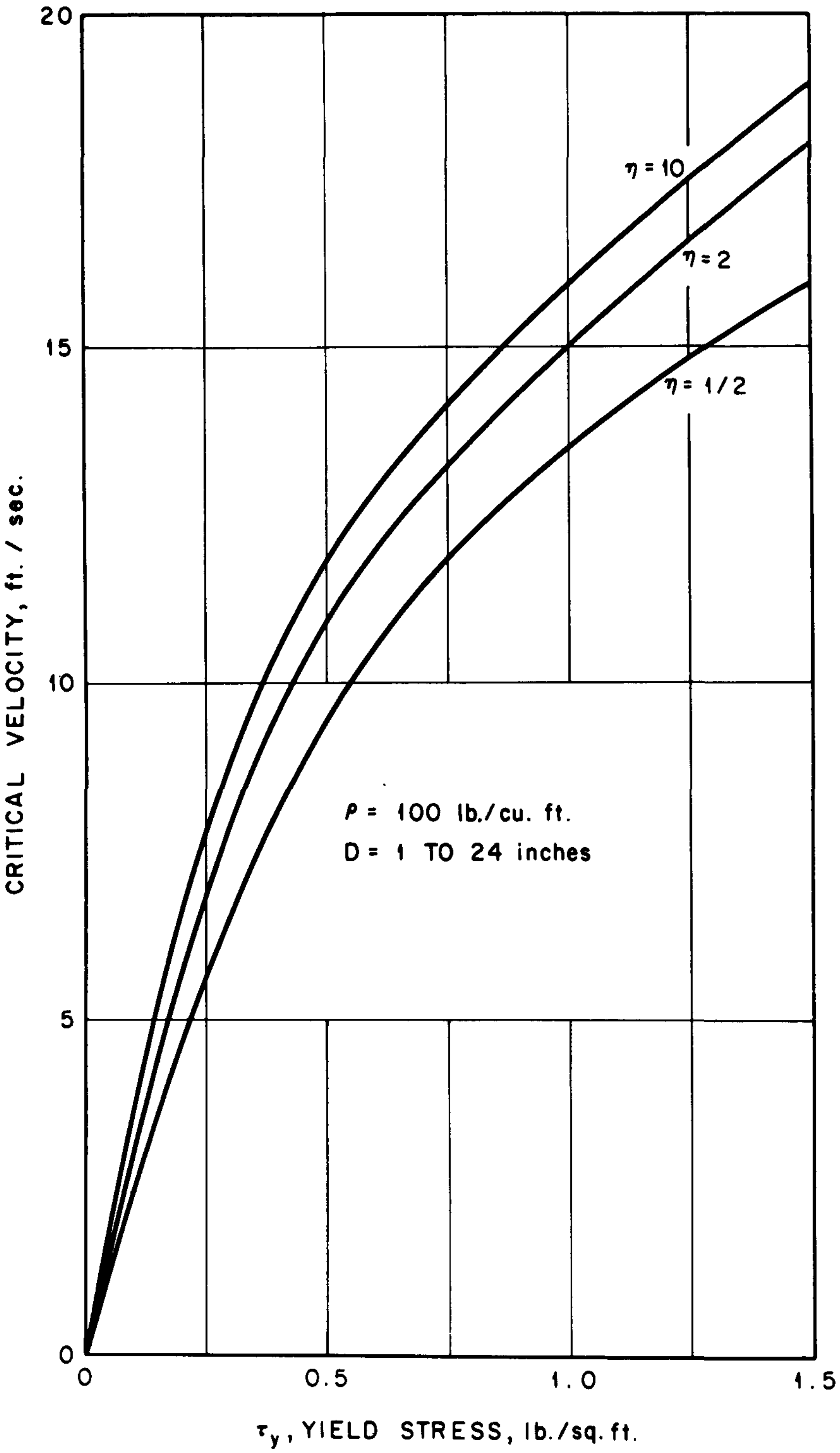

FIGURE 7.1—Effect of slurry physical properties on velocity for onset of turbulence.

ity less than about 4 centipoises have been established as goals in the slurry development program so that flow behavior will approach that of Newtonian fluids and will not seriously affect equipment design.

Data taken with ThO_2 suspensions with ThO_2 powders having mean particle diameters from 0.2 to 13 microns show that, on the average, the yeild stress is proportional to the third power of the volume fraction solids. The yield stress is also inversely proportional to the 1.4 power of the particle diameter. The effect of particle diameter on yield stress at constant volume fraction solids is shown in Figure 7.2. The data from this figure show that the yield stress is given by the expression:

$$\tau_y = \left(1.8^{+1.8}_{-.08}\right) \times 10^2 \phi 3 / D_p{}^{1.4}, \qquad (6)$$

where τ_y=lb/sq ft,
ϕ=volume fraction solids,
D_p=microns.

The uncertainty in the numerical constant is attributed to unresolved factors such as electrolyte effects, surface activity as determined by the temperature at which the material was calcined, and the shape of the ThO_2 particles. In limited tests at room temperature, the addition of 0.13 mole fraction uranium appeared to at least double the yield stress, compared to the value expected for pure ThO_2. For a typical blanket slurry concentration of 0.145 volume fraction solids, the relations given above indicate a minimum mean particle size of 3 to 4 microns to achieve a yield stress of less than 0.1 lb./sq. ft. at room temperature.

The logarithm of the ratio of the coefficient of rigidity to the viscosity of the suspending medium is proportional to the volume fraction solids, and the constant of proportionality varies from 10 to 25 depending on the particular oxide.

Preliminary data taken at temperatures up to 300° C. show that the yield stress is almost independent of temperature; whereas the coefficient of rigidity decreases with temperature, although not to the same extent as the viscosity of water.

Hindered-Settling Characteristics of Flocculated ThO_2 Suspensions

The hindered-settling rate of nonflocculated particles is a function of the volume fraction solids, the particle and liquid density difference, the square of the particle diameter, and the liquid viscosity as given by the combination of Equation 4 (Stokes' law) and Equation 5. In principle, the same is true for a flocculated system, except that the floc properties (i.e., floc diameter and density) are usually unknown. However, if the relations describing the settling of nonflocculated particles are accepted, then the floc density and diameter can be inferred from systematic sets of experiments, the floc diameter being larger and the floc density being smaller than the single-particle values.

Extensive hindered-settling tests have shown that the dilute flocculated-suspension settling rate is 10 to 50 times greater than the single-particle settling rate. Thus the decrease in floc density (tending to decrease settling rate) is more than compensated for by the increase in floc diameter. At the same time, the ratio of the settling rate at a concentration of 0.145 volume fraction solids to the single-floc settling rate is in the range 0.003 to 0.02, compared to the value of 0.482 quoted above for nonflocculated suspension. Clearly, the flocs are large in diameter and of low density so that the effective volume fraction solids (i.e., the volume occupied by the ThO_2 particles and the fluid immobilized by the particles in the floc) is quite large. Typical values of floc density are 1.6 to 4 g/cc with a diameter of about 40 microns. ThO_2 calcined at the higher temperatures produces a suspension having the larger floc densities. Recent experimental studies of the surface charge show very good qualitative agreement between theory and experiment and indicate that electrokinetic measurements can indeed serve as a guide to those factors which are important in determining floc structure.

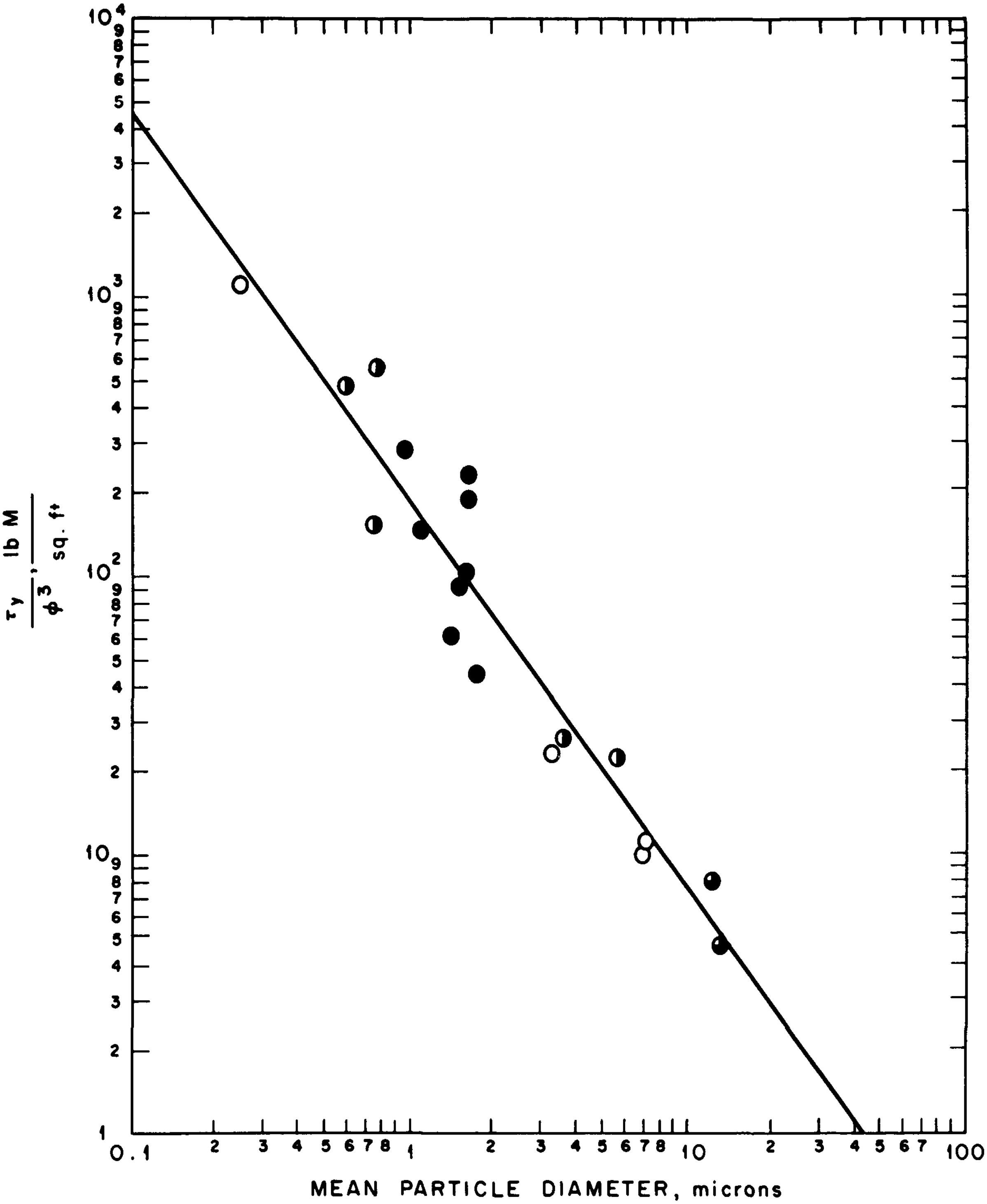

FIGURE 7.2—Effect of ThO_2 particle diameter on yield stress of ThO_2 slurry.

Studies of the effect of small quantities of silicate and sulfate on the hindered-settling rate with temperatures up to 300° C show a pattern of results that are consistent with the series of tests in which the surface properties were measured. In addition, the tests at elevated temperatures show that sulfate retains some effectiveness at temperatures up to 250° C, whereas the silicate appears to be ineffective above 250° C. These results are in accord with basic theoretical and experimental studies of ThO_2 surface chemistry.

Hindered-settling tests of ThO_2 in inclined cylindrical containers show that the settling rate goes through a maximum as the angle with the vertical is varied from 0 to 90 degrees. The maximum settling-rate increase observed was a factor of 4, and this occurred at an angle of 50 degrees with the vertical. These results are in good agreement with semitheoretical predictions.

Increasing the temperature results in an increase in hindered-settling rate for ThO_2 suspensions. Typical results are shown in Figure 7.3. For ThO_2 suspensions with mean particle size greater than 2.4 microns, the settling rate is inversely proportional to the viscosity of the suspending medium for temperatures up to 300° C. This indicates that the floc size is essentially independent of temperature in this range. In addition, the product of the square of the floc diameter and the density difference of the floc and the suspending medium was observed to be directly proportional to the true mean particle diameter.

As a flocculated suspension settles, the flocs approach and finally rest upon each other, and a pronounced decrease in the settling rate is observed. The suspension is then said to be in compaction. The concentration at which a suspension goes into compaction is a function of the container diameter, the suspension concentration, and yield stress. A suspension having a yield stress of 0.1 lb/sq ft and a volume fraction solids of 0.145 would be in compaction in vertical containers having diameters less than 1.5 inches.

Settled-bed densities are observed to be between 1.5 and 4 g/cc and to increase in density about 0.03 (g/cc)/(cm depth) for bed depths up to 1 foot in thickness. Settled beds formed at different temperatures appear to decrease in density as the temperature is increased. The ratio of settled bed concentration at 200° C to that at room temperature was found to be 0.62 ±0.06 for suspensions prepared from a variety of different ThO_2 powders. These suspensions varied in settled-bed concentration at room temperature by a factor of 2.5. The ratio apparently is a function of particle size, approaching unity as the particle size increases.

Hindered-settling experiments carried out in centrifuges show a lower settling rate than would be predicted from Stokes' law using floc diameters determined from conventional settling-rate studies. This indicates that the floc size is a function of shear rate, decreasing as the shear rate is increased.

7.2.4 Caking Phenomena Observed with Flocculated ThO_2 Suspensions

Development of reliable methods for preventing deposition of thoria in the form of hard cakes on pipe walls and in circulating pumps is one of the important problems of slurry technology. A cake may be defined as an accumulation of particles on part of the surface of the system in so dense and rigid a form that it cannot be deformed without fracture. In one case, a 1/4- to 3/8-inch layer of ThO_2 cake was built up on essentially all parts of a 3-inch 200-gpm circulating system. The density of the cake was about 5.5, and it resembled chalk in strength and consistency. A second manifestation of the caking tendency is the formation of spherical particles 15 to 100 microns in diameter during circulation of the slurry in high-temperature circulating loops, starting with unpumped ThO_2 2 to 5 microns in diameter. It is believed that a necessary step preceding sphere and cake formation is the degradation of the 2- to 5-micron particles

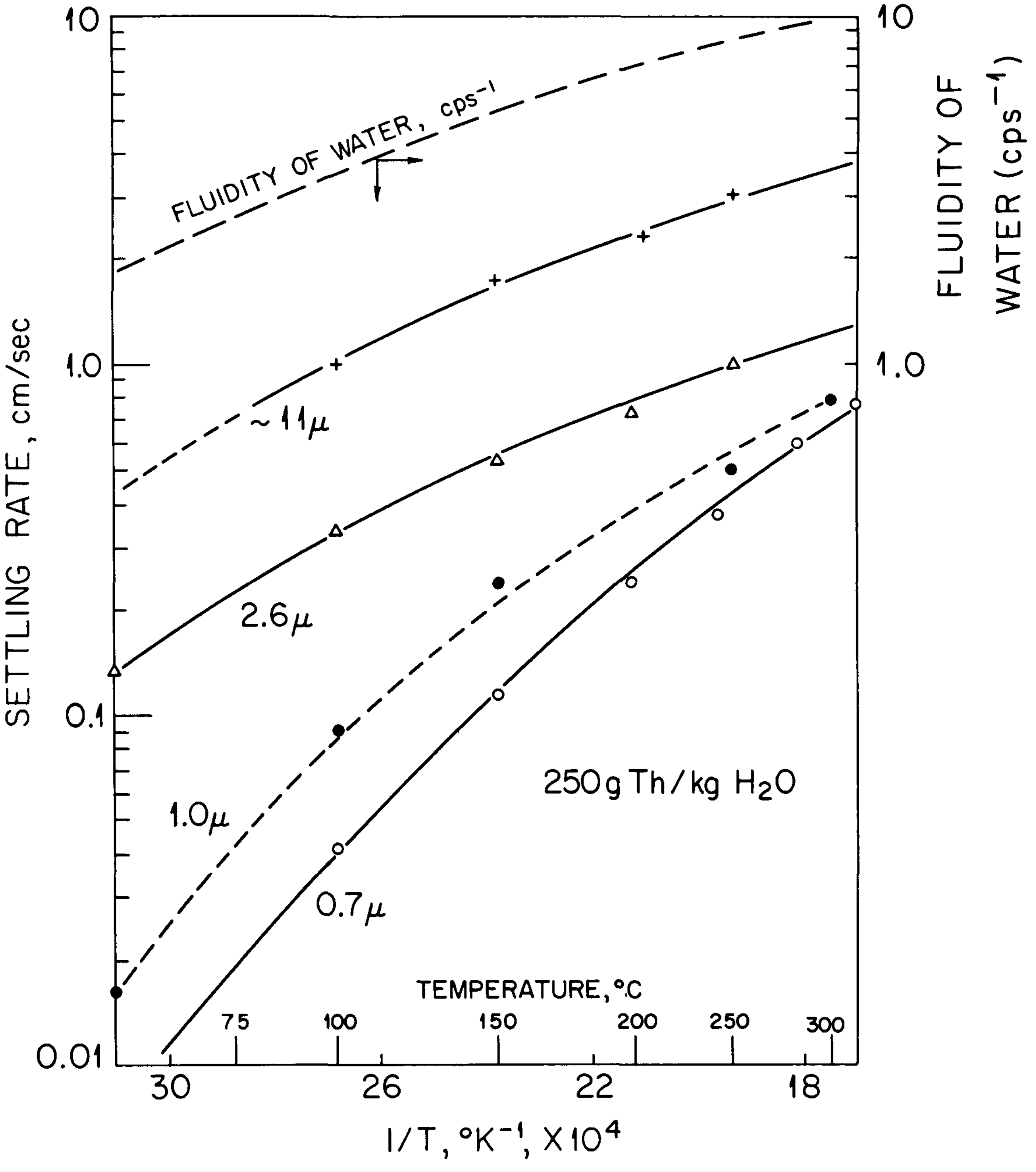

FIGURE 7.3—Temperature-particle size effects on the settling rate of thorium oxide slurries: 250 g Th/kg H_2O.

into 50 to 100 Angstrom particles which then agglomerate. Direct evidence is indicated on electron micrographs showing extremely fine particles remaining on the collodion film mount after a "sphere" of ThO_2 was removed. Since the original observation of cake and sphere formation, the manufacturing procedure for the ThO_2 powder has been modified by raising the calcination temperature from 850 to 1,600° C. to increase the particle integrity, and no instances of cake or sphere formation have been observed since the change in manufacturing procedure except during special tests designed to study the caking phenomena.

Qualitative theoretical considerations indicate that the density and strength of a cake deposited on pipe walls is a function of the shear stress at the wall, the net attraction between ThO_2 particle surface, the degree to which particles have been reduced in size, and the shape of the particles. The importance of the wall shear stress on the formation of cakes has been demonstrated, and some information is available on the importance of the net attraction between ThO_2 particle surfaces. Evidence is inadequate to allow prediction of whether a known caking oxide will deposit on the metal loop surfaces or will form spheres. There are some indications that the zeta potential of the metal surface is an important factor in the determination of the cake location.

7.2.5 Engineering Characteristics of ThO_2 Suspensions

Conventional correlations of the engineering characteristics of Newtonian materials relate observed pressure drops and heat-transfer coefficients to intrinsic material properties and system characteristics in order to develop useful generalizations. Obviously, the task is more complicated with flocculated ThO_2 suspensions because of the peculiar laminar-flow characteristics as well as the tendency for the material to segregate. Nevertheless, this approach was selected since it would eliminate the complications attendant on attempts to include specific electrolyte effects and would relate the engineering characteristics to the relatively easily measured laminar-flow characteristics, the hindered-settling rate, and the intrinsic suspension properties. Thus the relations developed would be independent of particular methods of ThO_2 preparation.

Particular problems that have been studied include laminar and nonlaminar fluid flow and heat transfer, nucleate boiling with ThO_2 suspensions, and ThO_2 suspension transport characteristics.

Suspension Flow Characteristics

Laminar Flow.—The determination of the pressure drop for laminar flow of suspensions involves the use of the variable effective viscosity, which may be quite large at low flow rates but which continually decreases as the flow rate is increased. Since the usual method of evaluating the effective viscosity is by making pressure-drop–flow-rate measurements, the calculation of the pressure drop for different tube lengths and diameters is easily done using the experimental data with no recourse to a particular flow model being necessary. Practical problems associated with laminary flow of ThO_2 suspensions occur with small-diameter tubes in which pronounced wall effects have been observed or with large-diameter tubes in which the suspension is not in compaction. Wall effects are observed in tubes less than 0.080 to 0.100 inch in diameter. On the other hand, a suspension with a concentration of 0.145 volume fraction solids and a yield stress of 0.1 lb/sq ft is no longer in compaction if the tube diameter is greater than 3/4 inch. However, present reactor concepts do not envisage laminar flow at any point in the system.

Turbulent Flow.—Turbulent-flow friction factors have been measured for many different slurries. The limiting viscosity at high rates of shear was shown to be the best viscosity term to use in the Reynolds-number-friction-factor correlation, giving no evidence of a tube-diameter effect for diameters in the range 0.124 to 1.030 inches. In all cases the friction factors were less than the values for Newtonian fluids and in most cases appeared to approach the Newtonian smooth-tube line at the highest flow rate. The deviations from the Newtonian behavior increased in an orderly fashion as the non-Newtonian characteristics were increased, and empirical correlations have been developed which give a good fit to the data. The data were correlated by the following relation:

$$f = B N_{Re}^{-b}, \tag{7}$$

$$B = 0.079\left(\frac{\mu}{\eta}\right)^{0.48}, \tag{8}$$

$$b = 0.25\left(\frac{\mu}{\eta}\right)^{0.15}, \tag{9}$$

where f = Fanning friction factor,
$N_{Re} = DV\rho/\eta$ = Reynolds number,
D = tube diameter,
V = mean flow velocity,
ρ = slurry density,
η = slurry coefficient of rigidity,
μ = viscosity of suspending medium.

Non-Newtonian materials which can be fitted by a Bingham plastic relation show a strong dependence of critical velocity (the velocity at the onset of turbulence) on the yield stress, with the critical velocity being almost independent of the tube diameter and the coefficient of rigidity. For a yield stress of 0.001 lb/sq ft, the critical velocity is about 0.9 ft/sec; and for a yield stress of 0.5 lb/sq ft, the critical velocity is about 10 ft/sec. Since it is necessary to operate slurry systems under turbulent-flow conditions to prevent dropout and to achieve desirable heat-transfer characteristics, the design of systems to operate with high-yield-stress suspensions presents many different problems.

Suspension Heat Transfer

Laminar Flow.—The Bingham plastic model has been used to obtain an approximate expression for the laminar-flow velocity gradient at the tube wall. This expression was then substituted into Leveque's laminar heat-transfer solution for the case of constant wall temperature with uniform fluid temperature at the entrance of the tube. The final relation was

$$\frac{hD}{k} = 1.615\left(\frac{V\rho D^2}{kL}\right)^{1/3}\left(1+\frac{g_c\tau_y D}{24\eta V}\right)^{1/3}. \tag{10}$$

Laminar-flow heat-transfer data taken with ThO_2 suspensions having yield stresses of 0.075 to 0.5 lb/sq ft were in good agreement with the theoretical equation.

Analytic solutions to the Graetz-Nusselt problem have been presented using the Bingham plastic flow model. Solutions were also given for the case of heat generation within the suspension with arbitrary heat generation term and for the thermal entry region as well as for far downstream. Analyses are also available which give temperature distributions as well as Nusselt numbers for laminar flow of Bingham plastics in round tubes.

Turbulent Flow.—Heat-transfer and pressure-drop measurements have been made using non-Newtonian aqueous thorium oxide suspensions with concentrations up to 0.10 volume fraction solids. The limiting viscosity at very high shear rates gives a unique correlation of turbulent data for tube diameters from 0.124 to 1.030 inches; whereas the use of the effective viscosity (i.e., the viscosity evaluated at the point value of the wall shear stress corresponding to each given flow condition) gives a pronounced diameter effect in turbulent-flow correlations.

Typical heat-transfer and pressure-drop data are shown in Figure 7.4. As can be seen, the onset of turbulence for both the pressure-drop and heat-transfer measurements occur at the same Reynolds number. The critical Reynolds number is approximated by the value predicted by the Hedstrom criterion (*Ind. Eng. Chem.*, *44*, 651 (1952)). The heat-transfer transition region extends to Reynolds numbers a factor of four times greater than the critical, as is also the case with Newtonian materials. Heat transfer to ThO_2 slurries in fully developed turbulent flow is the same as that predicted by the usual correlations for Newtonian fluids to within the precision of the experimental data, provided that the Reynolds and Prandtl numbers are calculated using the limiting viscosity at high rates of shear, η, for this viscosity. An approximate form of Martinelli's momentum-heat-transfer analogy correlated the experimental results within +17 percent and −36 percent.

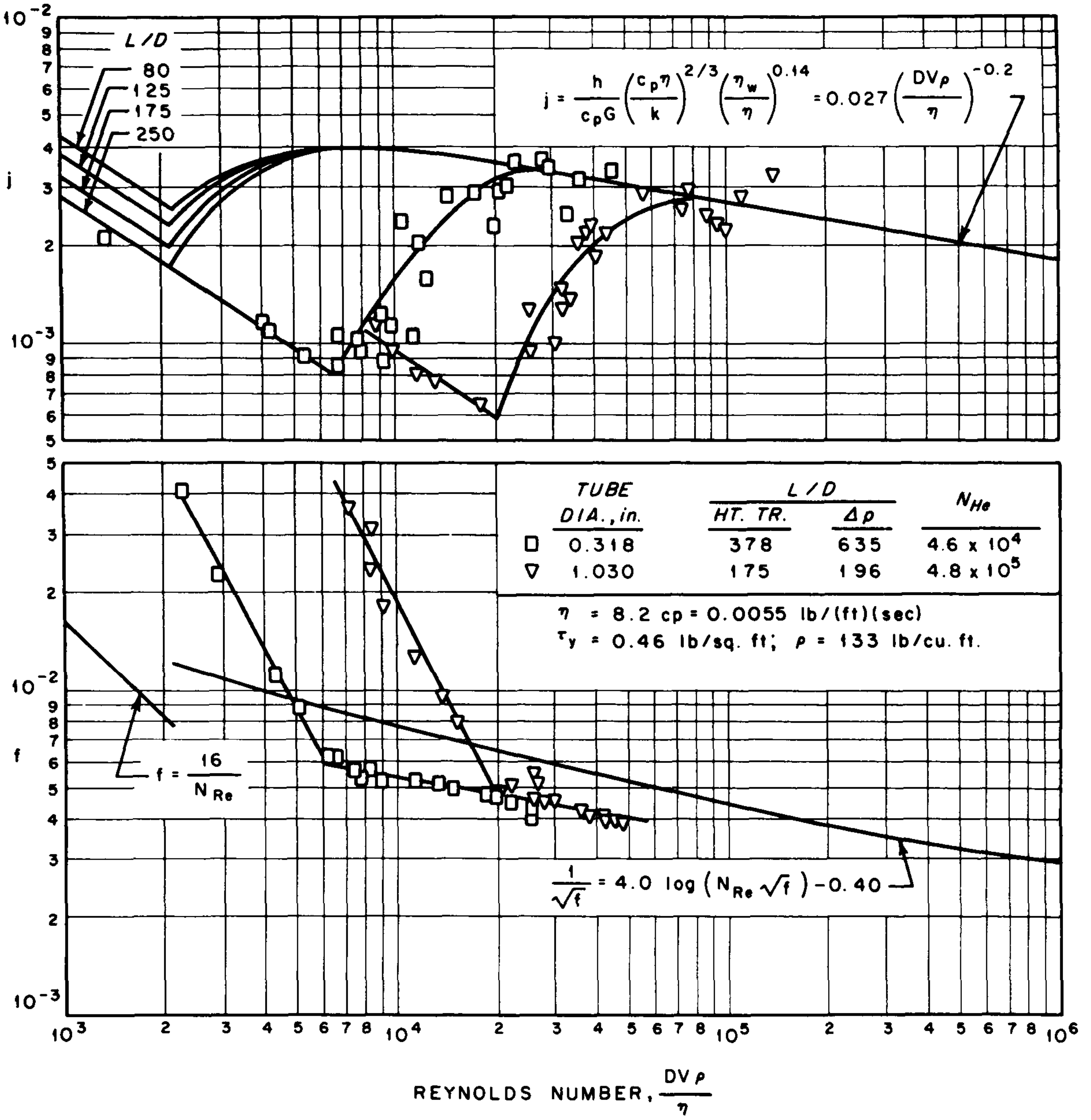

FIGURE 7.4—Heat transfer and fluid flow characteristics of ThO_2 slurries using the limiting viscosity at high rates of shear to calculate the Reynolds and Prandtl numbers.

Suspension Nucleate Boiling.—Nucleate boiling heat-transfer measurements have been made with aqueous ThO_2 suspensions containing up to 0.105 volume fraction solids. Boiling took place from the surface of $\frac{1}{16}$- and $\frac{1}{8}$-inch diameter platinum tubes submerged in slurry. The results showed that the heat flux was proportional to the *n*th power of temperature difference between the tube surface and the bulk fluid. For the slurries studied, the heat flux at a ΔT of 10°F was about 10^4 Btu/(hr)(ft^2) regardless of slurry concentration. However, the value of the exponent, n, decreased as the volume fraction solids was increased. The value of n was 3.3 with no thorium oxide present and approached unity at a volume fraction solids of 0.10. Typical results are shown in Figure 7.5.

The maximum heat flux attainable under nucleate-boiling conditions (often called the critical heat flux or burnout heat flux) at slurry concentrations of 200 g of Th per kg of H_2O was about the same as for water. However, at a concentration of 1,000 g of Th per kg of H_2O, the burnout heat flux was 210,000 Btu/(hr)(ft^2), compared with a value of 490,000 Btu/(hr)(ft^2) for water under corresponding conditions.

At constant heat flux, the temperature difference between the heated tube surface and the

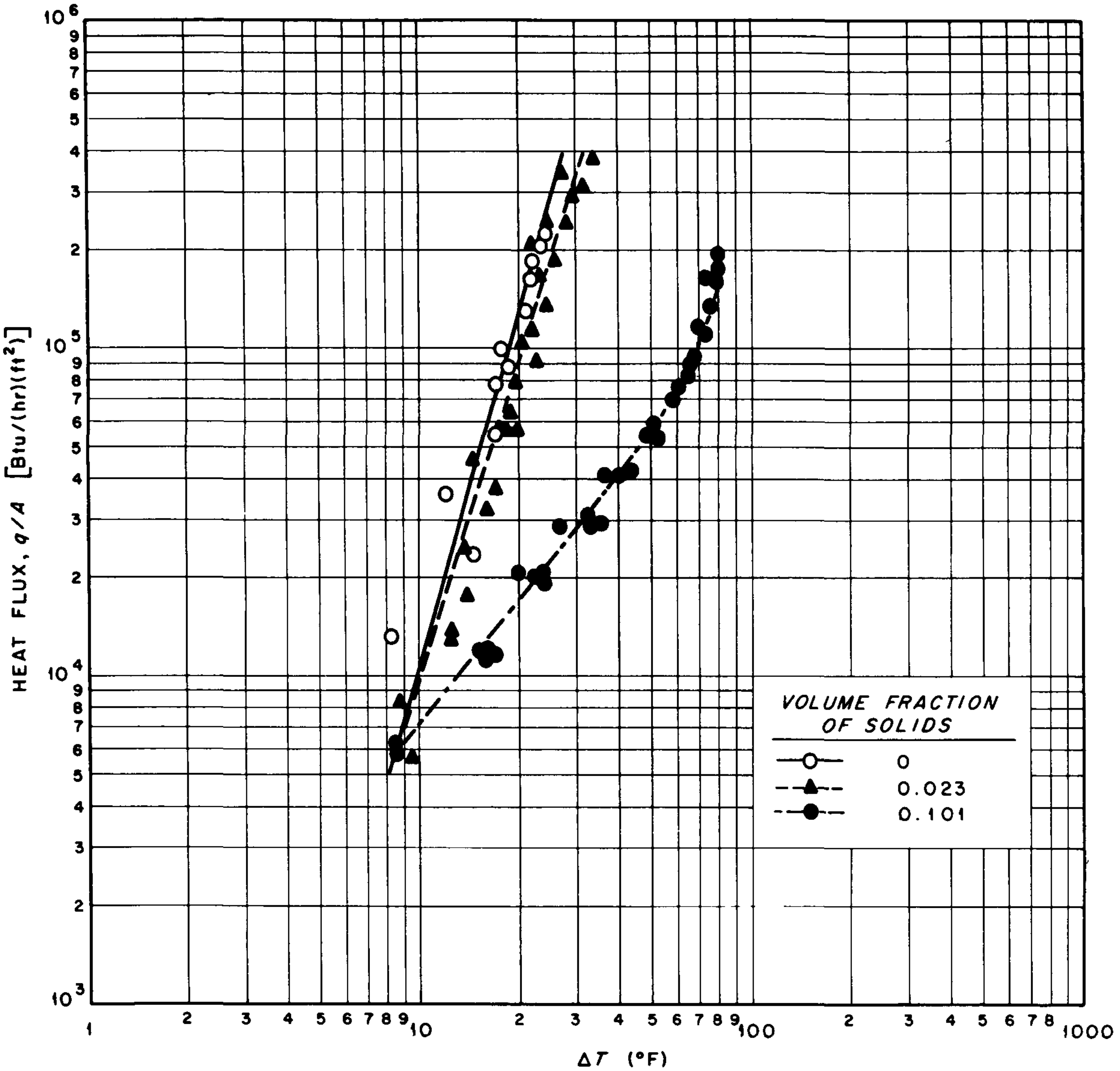

FIGURE 7.5—Effect of ThO_2 suspension concentration on nucleate boiling from platinum tube. (Forced convection flow rate ~1 gpm in tank containing ~3 gal. slurry).

fluid saturation temperature increased 5 to 6°F per hour. This result might be explained by a "soft" film that surrounded the heated metal surface. This film was apparently less than 1/32-inch thick and was never distinguishable as an adhering film after the tube was removed from the slurry system. No hard cakes were observed on the surface from which boiling took place during any of the tests.

The nucleate-boiling tests were made with aqueous thorium oxide slurries which had non-Newtonian laminar-flow characteristics and which were almost Newtonian under turbulent-flow conditions. No phenomena were observed which could be attributed to the effect of the solid particles on the gross physical properties of the slurry, e.g., the non-Newtonian laminar-flow characteristics of the slurry had no discernible effect on the nucleate-boiling heat transfer.

Suspension Transport.—A substantial amount of theoretical and experimental information is available on sediment transport in streams and rivers. However, in most cases, these results can only serve as a guide for studies with ThO_2 suspensions in round pipes. This is because previous studies are primarily concerned with flow in channels and also because many of the studies do not distinguish between fully suspended transport of material and transport by saltation in which the solids bounce and slide along the bottom. The latter case appears most undesirable for nuclear reactor operation.

A variety of tests in the last several years have shown that velocities in the rather narrow range of 2 to 8 ft/sec are required to maintain ThO_2 in suspension over a wide range of operating conditions. These conditions include a range of temperature from 30 to 280° C, particle size from 1 to 20 microns, concentrations from 400 to 1,500 g of Th per kg of H_2O, and pipe diameters of 3/4 to 3 inches.

The problem of "slurry dropout" may be considered under two main headings: (1) the conditions under which vertical concentration gradients will be observed in flowing streams; (2) the maximum concentration of solids that can be transported at any given mean flow rate.

Preliminary studies of possible concentration gradients in ThO_2 suspensions flowing in round horizontal pipes were made at mean stream velocities 10 to 200 percent greater than the dropout velocity. There was less than 5 percent difference in concentration between samples taken at the top of the pipes and at the bottom of the pipes for both mean stream velocities. This result is in accord with theoretical predictions based on the assumption that the rate of transfer of mass in the vertical direction due to turbulent mixing is balanced by a transfer of mass downwards by the action of gravity.

Preliminary results of load-carrying-capacity studies indicate two regions of flow. In the first, the suspension is apparently sufficiently concentrated to be in the compaction zone of the settling curve and hence has an extremely slow settling rate. The second region is observed with more dilute suspensions which are in the hindered-settling region and are thus settling a factor of 10 to 1,000 times faster than the slurries in compaction.

For suspensions in compaction, all the suspension will be transported provided that the Reynolds number, calculated using the effective viscosity, is greater than 2,000 to 3,000. For more dilute suspensions, which have appreciable settling rate, the wall shear velocity (which is roughly proportional to the turbulent velocity fluctuations in a vertical direction) gives the most satisfactory correlation. Dropout-velocity data obtained with suspensions having volume fraction solids up to 0.06 in pipes from 1 to 4 inches in diameter show that a wall shear velocity, $\sqrt{g_c \cdot \tau_w / \rho}$, of 0.15 ft/sec is required to maintain in complete suspension a slurry having a settling rate of 10^{-3} ft/sec. These results have not been generalized sufficiently to allow detailed predictions of transport velocities required at high temperatures.

7.2.6 Radiation Stability of Oxide Slurries

More than 50 irradiation experiments have been carried out in the LITR at 300° C and a thermal-neutron flux of 2.7 x 10^{13} neutrons/cm^2 sec as part of a continuing program to determine the effect of reactor irradiation on aqueous suspensions of thorium and thorium-uranium oxide. The thorium-uranium oxides contained up to 8 percent of natural uranium and up to 0.5 percent of highly enriched uranium, which produced a power density of 5 kw/liter. Most of the irradiations were of 150–300 hours duration, but two long-term irradiations of 2,100 and 3,200 hours duration were carried out with 800° C- and 1,600° C-fired thoria, respectively, as settled slurries. No significant changes were observed in the X-ray crystallite size or particle size of the oxide, slurry viscosity, or settled density as a result of the short-term irradiations. The 800° C-fired thoria recovered from one of the long-term experiments showed no apparent deterioration; the 1,600° C-fired material from the other long-term test had agglomerated to a grainy solid, a possible, but not necessarily a real, irradiation effect.

In all the slurry stability tests where enriched uranium was present, sufficient catalyst was added to prevent any net radiolytic-gas production. Both Pd and MoO_3 were used for this purpose. No detectable radiolytic gas, <25 psi, in excess of steam pressure was observed in these experiments. In the tests with ThO_2 or thorium—natural-uranium oxide no catalyst was necessary.

The experiments were carried out in small cylindrical stainless steel autoclaves (Fig. 7.6). Continuous stirring was accomplished by means of a dash-pot type stirrer of Armco iron clad with stainless steel. The associated instrumentation permitted a continuous monitoring of the stirring operation and the measurement of relative slurry viscosity both in- and out-of-pile. In general, the irradiated slurries were readily poured from the autoclaves, and no tendency toward caking was observed even on samples irradiated in the settled condition.

Total corrosion-product pickup was similar to that obtained in out-of-pile experiments except with the slurries containing sulfate, which showed higher corrosion-product pickup under irradiation. All of the iron and most of the nickel and chromium were associated with the slurry solids. The greater part of the corrosion-product pickup resulted from abrasive attack by the slurry solids under the action of the stirrer.

Chemical and radiochemical analyses of both phases of the irradiated slurries showed the bulk of the fission products, protactinium, and uranium to be associated with the solids. Only cesium appeared in the supernatant in significant amounts. Strontium appeared to adsorb less on the higher-fired materials. The ruthenium analyses were inconsistent, the probable result of the perchloric acid dissolution treatment used. The presence of 5-percent uranium seemed to decrease slightly the amount of iodine adsorbed on the solids, and in one case of the 8 percent uranium bearing material, the supernate could not be clarified and contained appreciable amounts of thoria and fission products in suspension.

During the long-term irradiations of the 800° C- and 1,600° C-fired thorias, 0.14 and 0.22 wt percent, respectively, of mass-233 isotopes were produced. This corresponds to an effective cross section of thorium to LITR neutrons of 10.3 barns. The 1,600° C-fired material, which was recovered as dark grainy particles, was refluxed for 3 minutes in 4 *N* HNO_3 and then 4 *N* HNO_3 containing 1.5 percent H_2O_2. Thirty-six percent of the U^{233}, 40 percent of the Pa, and only 0.2 percent of the thoria were dissolved in the first acid leach. The nitric acid–peroxide leach dissolved an additional 52, 35, and 36 percent of the U^{233}, Pa, and Th, respectively. Sixty-five percent of the gross gamma and beta activities were removed from the solid by the two acid leaches (70 to 80% of the Sr, Zr, Cs, Fe; 58% Cr; 47% Nb; and 25% Ni). Thirty percent of the Cs and

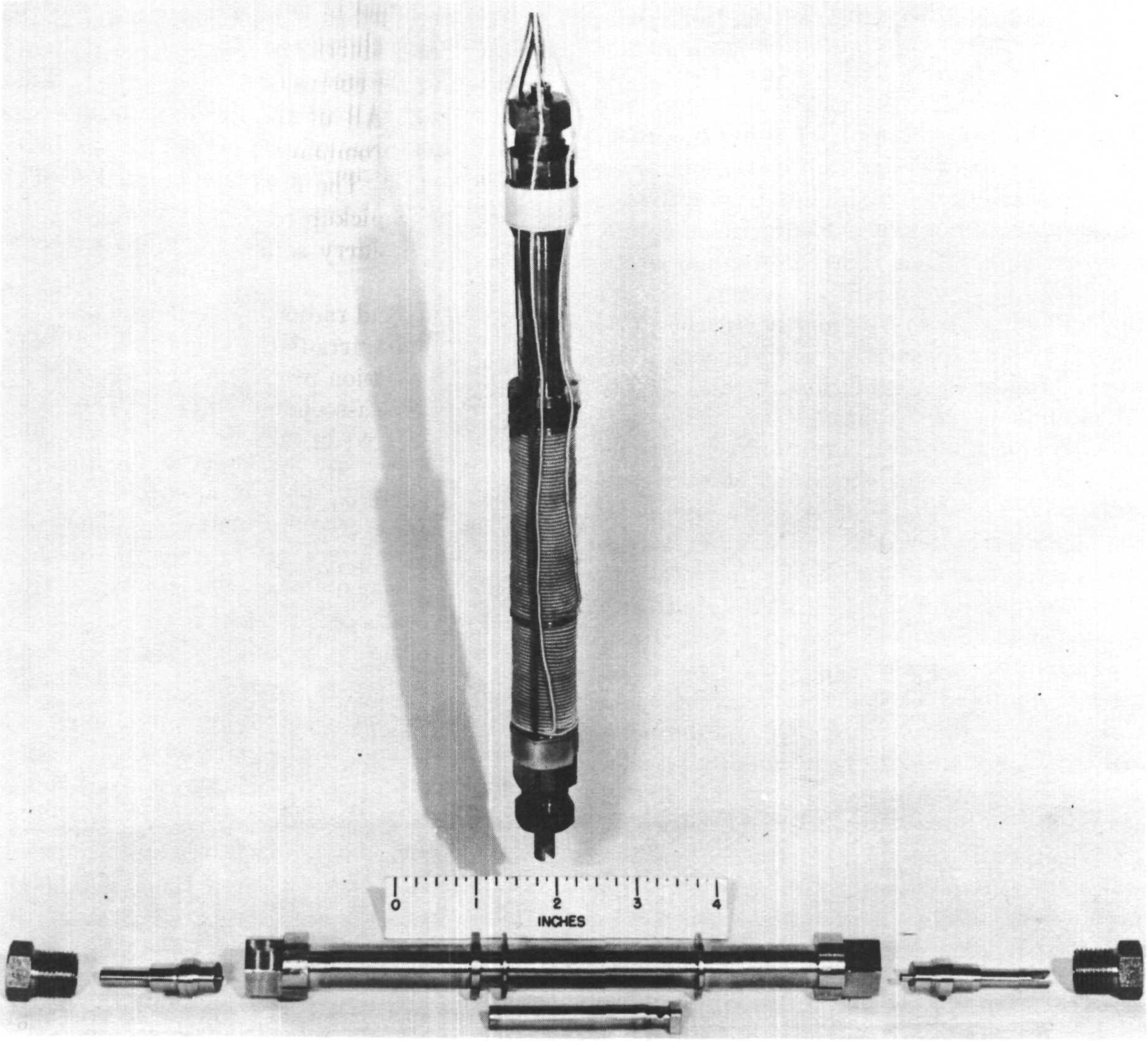

Figure 7.6—Parts and assembly of in-pile autoclave.

97 percent of the Ru appeared on the residual solids.

7.2.7 Catalytic Recombination of Radiolytic Gases in Reactor Slurries

The aqueous phase of a reactor slurry will be decomposed radiolytically into deuterium and oxygen, and the successful use of slurry in a homogeneous-reactor system depends to a great extent on the development of a gas recombination catalyst for use in the slurry. The amount of recombination necessary may be estimated from the fact that from 0.2 to 0.4 mole of D_2 and equivalent O_2 will be produced per kilowatt-hour of radiation energy adsorbed in the slurry, assuming a G value of 0.5 to 1 molecule of D_2O decomposed per 100 ev of energy adsorbed. Studies to develop a gas recombination catalyst for use in slurries have been an important part of the slurry development program of the Homogeneous Reactor Project. The results of both out-of-pile and in-pile experiments indicate that MoO_3 and Pd, either as the metal or hydrous oxide, are suitable for use in slurries for the liquid-phase recombination of radiolytic gas. Recent experience indicates that platinized thoria in a slurry containing molybdenum oxide may also be a useful catlyst system.

Experimental Techniques and Method of Analysis

The out-of-pile tests were carried out in 15-ml stainless steel autoclaves. Stoichiometric quantities of D_2 or H_2 and O_2 were charged to 300–900 psi total pressure in autoclaves containing slurries; the autoclaves were raised to temperature ($\leqq 280°$ C.) and mechanically agitated; and the decrease in total pressure with time was noted.

The experimental data were amenable, in general, to a kinetic treatment involving a first-order dependence of rate on stoichiometric or radiolytic-gas pressure.

$$\log (P-P_r)=\frac{k_r t}{2.3}+C,$$

where P = total gas pressure,
P_r = steam + inerts + excess O_2 or H_2,
k_r = reaction rate constant in reciprocal time.

While the first-order kinetics applied only to the pressure of stoichiometric gas, the data were evaluated in terms of deuterium consumption and catalyst activities indicated in terms of the number of moles of deuterium consumed per hour per liter of slurry at 100 psi deuterium partial pressure. A catalyst performance index, directly applicable to reactors and directly observable in experiment, was used to relate catalyst activity to reactor power density (w/ml) at an equilibrium partial pressure of 100 psi radiolytic D_2. The performance index is

$$\frac{w/ml}{100\text{ psi}}=\frac{\text{moles } D_2/\text{liter}\cdot\text{hr}\cdot 100\text{ psi } D_2}{0.38\, G_{D_2}}$$

where G_{D_2} is the G value for D_2 production.

The results of out-of-pile tests were evaluated on the ability of a catalyst to attain a reaction rate equivalent to the consumption of 2 moles D_2 per hour per liter of slurry at 280° C. and a deuterium partial pressure of 100 psi or a performance index of about 9 w/ml·100 psi D_2, assuming a G value of 0.6.

First-order gas recombination kinetics were found almost invariably in out-of-pile studies with thoria or thoria-urania slurries containing no catalyst or with slurries containing MoO_3. Slurries containing the palladium seemed quite sensitive to pretreatments, and somewhat random reaction orders of 0.5 to 1.5 were observed. The in-pile data, with all slurries with or without Pd or MoO_3, showed reasonable first-order dependence.

Survey of Possible Catalysts

The primary criterion, other than a satisfactory catalytic activity, for a catalyst to be used in an aqueous thorium oxide slurry blanket is that it have a low thermal-neutron absorption cross section. A convenient estimate of the allowable concentration is provided by the rule that the macroscopic cross section of elements other than thorium which are in the blanket slurry should be much less than 10 percent of that of the thorium itself.

On this basis, scouting experiments were carried out with copper sulfate, copper chromite, copper oxide, copper and nickel powders, silver carbonate (reduces to metal at elevated temperature), vanadium oxide, ceric oxide, palladium, and molybdenum oxide. Of these, only the silver, vanadium, palladium, and molybdenum oxide showed sufficient activity at reasonable concentrations. Silver and vanadium were rejected because of their higher thermal-neutron cross section. Recent experience indicates that platinized thoria in a slurry containing molybdenum oxide may also be a useful catalyst system.

Molybdenum Oxide as a Catalyst

While sufficient data have been obtained to indicate that molybdenum oxide or palladium are good catalysts for use in reactor slurry system, specific conditions for the preparation of the most effective catalysts have not been worked out, nor have the limitations of any given catalyst system been completely defined. The molybdenum oxide catalyst used was usually prepared by calcining ammonium paramolybdate at 480° C for 16 hours. It was mixed with the dry slurry solids which were then slurried in water. Prior to its use in a recombination experiment the slurry was heated under O_2 at 280° C. The most active catalyst was obtained, however, by a subsequent heating of the slurry under H_2. The catalytic activity of slurries activated by hydrogen treatment were independent of the method used to prepare the MoO_3.

Molybdenum oxide was inactive with slurries of low-fired thorium oxide, and its activity was decreased by the addition of uranium. There is some evidence that the molybdenum oxide reacts with uranium to form a molybdate. With thoria-urania oxides, the order of addition of slurry solids, the method of incorporating the uranium and particularly the oxide firing temperature and time were important. It was necessary in some cases to fire mixed oxides containing 0.5 mole percent uranium as high as 1,000° C for as long as 16 hours to give an active slurry with molybdenum oxide. Thoria-urania systems containing uranium concentrations higher than 0.5 mole percent in general gave low and nonreproducible activities with MoO_3. Pure oxides fired above 1,000° C gave very active slurries.

A 500 g Th/kg H_2O slurry of 1,600° C-fired thoria-urania oxides (U/Th=0.005) prepared from the coprecipitated oxalates containing 0.012 *m* MoO_3 gave a rate of 6.7 miles H_2/ liter·hr at 250° C and $P_{H_2}=100$ psi after being preheated under O_2. After heating with H_2 the rate was 11.0 moles H_2/liter·hr under the same conditions. The use of a simple mixture of 1,600° C-fired thorium oxide and $UO_3 \cdot H_2O$ required the addition of 0.06 *m* MoO_3 for an acceptable rate of 2 moles H_2/liter·hr under similar conditions, illustrating a deactivation effect of "free" uranium. A 500 g Th/kg D_2O slurry of 1,300° C-fired Th-0.5 percent U oxide containing 0.05 *m* MoO_3 gave a rate of 11.6 moles D_2/liter·hr at 280° C and a 100 psi deuterium partial pressure after deuterium activation. These results would indicate a performance index for MoO_3 in such systems of about 0.15 to 2.4 w/ml per 100 psi D_2 per millimolal concentration of MoO_3, assuming a G value of 0.6.

Palladium as a Catalyst

The palladium catalyst was prepared by suspending a 650° C-fired thorium oxide in an acetone solution of palladium nitrate at room temperature, adding ethyl alcohol to reduce the palladium and deposit it on the theoria surface, and finally refluxing the system for several hours to complete the reduction. In both out-of-pile and in-pile tests with this preparation in 500 g Th/kg H_2O slurries of simple mixtures of 650° C-fired thorium oxide with 3 wt percent U as $UO_3 \cdot H_2O$ and 1,000° C-fired Th-5 percent U mixed oxide containing about 150 ppm Pd, performance indexes of 2 to 6.5 w/ml per 100 psi D_2 per millimolal concentration of Pd were obtained. Preliminary results with other methods of preparation indicate that it may be possible to increase the specific activity of Pd catalyst by as much as 25 times.

In-Pile Studies: Graphite Reactor Experiments

Radiolytic-gas production and recombination rates were determined in the ORNL Graphite Reactor at a flux of 4.2×10^{11} neutrons/$cm^2 \cdot$sec with light- and heavy-water slurries of ThO_2 containing approximately 2.8 percent uranium 93 percent enriched in U^{235}. The mixed oxides were prepared by coprecipitation of thorium and uranous oxalates at 10° C followed by calcination at 650 to 1,000° C. The experiments were carried out in the small, dashpot-stirred stainless steel autoclave used in the slurry irradiation studies (Fig. 7.6).

In the light-water systems with the autoclaves sealed in air and with 650° C-fired oxide at concentrations of 250 to 750 g Th/kg H_2O, the gas production and recombination rates were linear functions of the concentration over the temperature range from 200 to 282° C. The G value for water decomposition was 0.8 molecule H_2 produced per 100 ev energy absorbed. Equilibrium radiolytic-gas pressures showed linear logarithmic dependence on reciprocal absolute temperature and varied from 1,600 psi at 200° C to 190 psi at 282° C. From an Arrhenius plot of the rate constants an apparent activation energy of 16.2 kcal/mole was obtained. Slurries of 900° C-fired oxide in light water at concentrates of 250 and 500 g Th/kg H_2O gave similar results.

Heavy water slurries of the mixed oxide fired at 650 and 1,000° C at 500 g Th/kg H_2O concentration were irradiated in a total of six experiments. The autoclaves were sealed in air, under O_2 at 250 psi at room temperature, and under D_2 at 250 psi at room temperature. Gas production rates for the slurries sealed in air corresponded to a $G_{D_2}=1.2$, about 50 percent greater than for the light-water slurries. An oxygen atmosphere depressed the gas production rate to $G_{D_2}=0.9$ to 1.0. The deuterium atmosphere lowered the gas production rate by a factor of 3 to 5 initially, but the suppression was of temporary duration and was not reproducible. Recombination rates under air and excess oxygen were about the same—first-order rate constants of 0.05 and 0.3 hr^{-1} at 200 and 280° C, respectively. Under excess deuterium the recombination rates were about one-half as fast, assuming a first-order dependence on deuterium partial pressure. No significant differences were noted between the slurries of the 650° C- and 1,000° C-fired oxides.

In-Pile Studies: LITR Experiments

Gas production and recombination experiments were carried out in the LITR in small stainless steel or Zircaloy-2 rocking autoclaves at a flux of 0.5 x 10^{13} neutrons/cm^2·sec with heavy-water slurries of thorium-uranium oxides containing 0.5 percent and 5 percent of highly enriched uranium. Both MoO_3 and Pd were added as recombination catalysts. The recombination data obtained showed reasonable agreement with out-of-pile experiments using similar systems.

In one experiment carried out with a 1000 g Th/kg H_2O slurry of 1,300° C-fired thorium-natural-uranium oxide ($U^{235}/Th=0.005$) under excess O_2, sufficient MoO_3 catalyst was added, 0.02 *m*, to give a small partial pressure of radiolytic gas. An average G_{D_2} value for gas production of 0.6 molecule of D_2 per 100 ev was obtained. From the equilibrium gas pressures at 250 and 280° C, first-order rate constants for gas recombination of 4.98 and 7.14 hr^{-1} were calculated. These values compare well with rate constants of 4.95 and 8.75 hr^{-1} obtained in out-of-pile gas-recombination experiments made with a similar slurry of the same oxide at the indicated temperatures. Catalyst activities of 0.2 to 0.7 mole D_2/liter·hr at 280° C and 100 psi D_2 partial pressures were observed, compared to activities between 0.32 and 0.57 mole D_2/liter·hr obtained in out-of-pile experiments with the same catalyst concentration. This would indicate catalyst performance in both the out-of-pile and in-pile experiments between 0.4 and 1.5 w/ml·100 psi D_2 per millimolal MoO_3 concentration.

A 400 g Th/kg D_2O slurry of 1,000° C-fired Th-5 wt percent uranium oxide, highly enriched, with 0.01 *m* MoO_3 added as a recombination catalyst, was irradiated for 1,000 hours at an average power density of 0.7 w/ml and a maximum power density of 3.2 w/ml. Maximum catalytic activity was 0.26 mole D_2/liter hr and equilibrium catalytic activity near the end of the run about 0.1 mole D_2/liter·hr both at 100 psi D_2 partial pressure and 280° C.

This corresponds to a performance index between 0.04 and 0.1 w/ml·100 psi D_2 per millimolal MoO_3 concentration at $G_{D_2}=0.6$ and indicates a deactivation effect by the high uranium content of the slurry.

A slurry containing 1,090 g Th/kg D_2O of 1,000° C-fired thorium-5 wt percent uranium oxide, highly enriched uranium, 0.0016 *m* Pd, and an oxygen atmosphere was irradiated for 9 weeks at 200 to 320° C. The last 2 weeks of operation were carried out at 280° C at an estimated fission power density of 12 w/ml. Catalyst performance index values of between 2 and 2.7 w/ml·100 psi D_2 per millimolal Pd concentration at $G_{D_2}=0.6$ were observed, in substantial agreement with the out-of-pile results.

7.2.8 Status

General Characteristics of Thorium Oxide Suspensions

Turbulent-flow heat-transfer and fluid-flow characteristics of non-Newtonian ThO_2 suspensions have been shown to be related in a simple way to the laminar-flow characteristics of the suspension. The results of these studies show that principal factors affecting the design of systems is that the more non-Newtonian the suspension, the higher the velocity required to initiate turbulent flow. For instance, the critical velocity of a suspension having a yield stress of 0.001 lb/sq ft is 0.9 ft/sec and for a yield stress of 0.5 lb/sq ft the critical velocity is about 10 ft/sec. Consequently, knowledge of the factors which affect the laminar-flow characteristics of the suspension is of primary importance for satisfactory system design. Other properties such as suspension density, thermal conductivity, and specific heat are reliably known over the complete range of temperature and pressure.

Laminar-Flow Characteristics of Flocculated ThO_2 Suspensions

The results of laminar-flow measurements show that the concentration and particle diameter of the ThO_2 are the major factors affecting the suspension yield stress. In order to meet project specifiications for a suspension yield stress less than 0.1 lb/sq ft at a concentration of 1,000 g Th/liter, the ThO_2 particle diameter must be greater than 2 to 3 microns. Improved manufacturing techniques may produce a spherical particle which would flocculate less readily and thus reduce the limitation on particle size. In addition, more work is required to determine the effect of temperature on the yield stress of ThO_2 suspensions.

Hindered-Settling Characteristics of Flocculated ThO_2 Suspensions

Systematic studies have shown that the agglomerate of loosely bound particles that is responsible for the observed settling rate is about 40 microns in diameter with a density of 1.5 to 4.0 g/cc. Agglomerates or flocs composed of particles larger than 2 microns are essentially unaffected by temperature; hence the hindered-settling rate increases with temperature (i.e., it is inversely proportional to the viscosity of the suspending medium). Adequate equipment is available for measuring the hindered-settling rate over the complete range of temperature.

Caking Phenomena Observed with Flocculated ThO_2 Suspensions

No instance of cake or sphere formation has been observed since the manufacturing procedure for ThO_2 powder was modified by raising the calcination temperature from 850 to 1,600°C. Since this change in manufacturing procedure was based on a particle degradation hypothesis, it is believed that the caking mechanism is understood at least qualitatively. Nevertheless, additional tests are required to determine those conditions that are necessary for the formation of cakes and spheres in order to ensure that these conditions will not occur inadvertently in reactor systems.

Engineering Characteristics of ThO_2 Suspensions

The heat-transfer and fluid-flow characteristics of ThO_2 suspensions are well known and have been shown to be related to the system characteristics, the laminar-flow physical properties, and the intrinsic physical properties of the suspension. However, additional work must be done to provide information on the velocities required to maintain ThO_2 in suspension. It is known that velocities in the range of 2 to 8 ft/sec are required to maintain ThO_2 in suspension, with the lower velocity being associated with the lower concentration. It has also been shown that, once the solids are totally suspended in a round pipe, the concentration is essentially uniform from top to bottom of the pipe.

Radiation Stability of Oxide Slurries

Small-scale slurry irradiation of a few hundred hours duration at power densities of a few kilowatts per liter have resulted in no obvious effect on slurry properties. Much additional work is required to determine whether the slurry properties are changed by long irradiations involving the burnup expected in the cores and blankets of slurry-fueled reactors.

Catalytic Recombination of Radiolytic Gases in Reactor Slurries

The results of both out-of-pile and in-pile experiments indicate that MoO_3 and palladium either as the metal or hydrous oxide, are suitable for use in slurries for the liquid-phase recombination of the radiolytic gas. Recent experience indicates that platinized thoria in a slurry containing molybdenum oxide may also be a useful catalyst system. The MoO_3 appears restricted to use in slurries of thorium oxide and thorium-uranium oxide containing U/Th < 0.005 fired at or above 1,000° C (higher uranium concentrations appear to deactivate the MoO_3). The palladium may be used in slurries of oxide or mixed oxide fired at all temperatures (650 to 1,600°C) and appears suitable for use in slurries of simple oxide mixtures.

Assuming that 100 psi is an acceptable partial pressure of radiolytic deuterium at 280°C, the proposed operating temperature, the natural catalytic activity of a thorium or thorium-uranium oxide slurry appears sufficient to maintain a reactor power level of a few tenths of a kilowatt per liter, depending on slurry concentration. The MoO_3 will maintain about 1 kw/ liter per millimolal concentration in slurries of pure oxide (fired at $> 1{,}000°C$) and an order-of-magnitude lower power density in the thorium-0.5 percent uranium oxide system. The palladium will maintain 2 to 3 kw/liter power density per millimolal concentration in any thoria-urania slurry of current interest. Experience with the platinized thoria-MoO_3 slurry system is too limited to make an estimate of its efficiency.

Gas production studies in-pile with both light- and heavy-water slurries of thorium and thorium-uranium oxides under oxidizing and reducing atmospheres and with and without recombination catalysts gave G values for gas production $\leqq 1.2$ (i.e., molecules of $D_2(H_2)$ produced per 100 ev of energy adsorbed). The presence of a reducing atmosphere (excess D_2) appears to markedly suppress the gas production rate (as much as a factor of 5) under some conditions, but the results to date have been somewhat erratic.

7.3 CORROSION

The objective of the corrosion program is to determine conditions of compatibility for use of structural materials in reactor fuels and other fluids in the reactor environment. It is important that most of the reactor equipment and piping have a corrosion life expectancy of at least 20 years. This ordinarily requires that the corrosion rate be 2 mils per year (mpy) or less, with freedom from severe local attack by pitting or corrosion-induced cracking.

The program has been carried out in the manner of determining the relationships between corrosion behavior and environmental variables such as fluid composition, temperature, flow rate, and radiation level for a variety of materials. Often it is not possible to find a material which meets the special requirements of some piece of equipment, such as low cross section for use in the core tank or satisfactory bearing characteristics for use in a pump, and which also has a 20-year corrosion life under the environment specified for the reactor; or the most corrosion-resistant material may be too expensive, or it may not have satisfactory physical properties. Data obtained in this program are intended to assist the reactor designer in striking a balance between reactor performance and cost of equipment and equipment maintenance.

The program has been unusually extensive because of the problems encountered and the high cost of failures in a reactor. The solution fuels are strongly acidic, the suspension fuels are erosive, and radiation tends to increase the corrosion rate. Maintenance of the highly radioactive equipment is more difficult and expensive than normal maintenance. Escape of appreciable fuel from the reactor equipment would increase the difficulty by contaminating the containment vessel. Thus a substantial effort aimed at maximizing the performance and integrity of all components is justified.

Although corrosion problems of the two-region solution-core breeder have received the most attention, the program has included consideration of other homogeneous-reactor embodiments. Materials have been studied in (1) 1 to 300 g U/liter uranyl sulfate solutions, (2) uranyl fluoride and complex carbonate solutions, (3) 100 to 1,000 g/liter thoria slurries, (4) mixed thoria-urania slurries containing 0.5 to 8 percent urania, (5) water, and (6) nitric acid and other solutions used for cleaning or descaling reactor equipment. Temperatures and pressures have been as high as 325° C and 2,000 psia. The subsequent discussions emphasize data pertinent to the breeder but include significant information obtained on corollary investigations.

Materials of construction for the solution-core system are zirconium alloys for the reactor core tank, austenitic stainless steels (primarily ASA type 347) for equipment external to the reactor core, and zirconium or titanium alloys for special applications in this external equipment. Because of less experience with the slurry systems the material of construction for the bulk of the external equipment is less well established, although stainless steel has been the chief material used in the development program. Again, zirconium and titanium alloys are useful in special applications.

The corrosion work has extended over the past 10 years in a program involving the following:

Five thousand static flask and autoclave tests.—These are relatively simple, exploratory tests carried out primarily with solutions in evaluating new materials or compositions.

One hundred in-pile rocking autoclaves.—The rocking provides mild agitation to maintain liquid-vapor equilibrium rather than to evaluate flow effects. Most of these tests have been concerned with solutions, although the equipment has been adapted to slurry studies in the last year and has been used in exploratory in-pile experiments.

Three hundred out-of-pile toroid tests with slurries.—These are dynamic tests in which flow is obtained in a partially filled circlet of ½-inch pipe by imparting a motion to it similar to that by which liquid is caused to swirl in a flask.

Several hundred thousand hours of experimental investigation of fluid-flow variables have been accumulated in 100-gpm out-of-pile loops designed to study materials problems in both solutions and slurries.

More than 20,000 hours have been accumulated in 17 in-pile loop experiments carried out with a variety of uranyl sulfate solutions.

In addition, field tests have been carried out in engineering equipment primarily designed for the development of components and investigation of other research and development problems. Such tests were also carried out in HRE–1 and are part of the operation of HRE–2.

7.3.1 Materials in Circulating Systems and Auxiliaries

Corrosion problems of homogeneous reactors can be subdivided into the problems of the reactor vessel and problems of the circulating systems and auxiliaries. In the latter there are no restrictions on the nuclear cross sections of materials if the corrosion rates are low enough that the products carried by the fuel do not seriously poison the reactor. Radiations present are: half or more of the beta and gamma radiation emitted by the fission products, low fluxes of delayed neutrons and leakage neutrons from the reactor, and a low fission-fragment flux resulting from capture of some of the neutrons by the fuel. These radiations and chemical changes induced in the fuel by fissioning in the reactor core have not appeared to have an important effect on corrosion in the circulating systems and auxiliaries of in-pile loops or reactor experiments. Results of out-of-pile tests are used as the basis of selection of materials for those systems.

Uranyl Sulfate Solution

Corrosion of materials in uranyl sulfate—copper sulfate—sulfuric acid fuel solutions is a complex process. Some of the variables affecting corrosion are: temperature, concentrations of components of the solution, atmosphere, flow rate, pretreatment, and perhaps others. Many of these variables are interrelated, a fact which complicates a study of the effects of the variables.

While 347 stainless steel has serious limitations in its corrosion resistance, consideration of the additional important factors of cost, availability, and fabrication experience has led to its adoption as the primary material of construction for dilute uranyl sulfate solution reactor systems. Experience in the development programs and with HRE-1 and HRE-2 indicates that with careful design and operating control it is a satisfactory material.

Type 347 Stainless Steel.—The austenitic stainless steels[1] behave essentially alike in uranyl sulfate solutions, and the results obtained with type 347 stainless steel are largely representative of this class of alloys. Three exceptions to this rule have been encountered, however; they are types 316 and 316L, which show a tendency toward intergranular attack, and SRF1132, which does not develop a highly protective coating.

Uranyl sulfate solutions in contact with stainless steel at high temperature must contain between 500 and 1,000 ppm oxygen to prevent reduction and precipitation of uranium and formation of sulfuric acid, which attacks stainless steel at a very high rate. As a consequence, oxygen depletion in crevices can lead to localized attack. Experience has indicated that such occurrences are minimized by maintaining at least 500 ppm oxygen in solution. Other forms of localized attack have been investigated; but, except for stress-corrosion cracking in the presence of chloride ions, no serious problems have arisen. Unstabilized stainless steels that have been sensitized by appropriate heat treatment have shown no severe intergranular attack. Also, the coupling of such noble metals as gold and platinum to type 347 stainless steel has not resulted in any accelerated attack of the stainless steel.

1. Effect of Temperature.—When type 347 stainless steel is placed in uranyl sulfate solution at temperatures up to 100° C, the steel retains its metallic luster, and only after long periods of time does it develop a very thin tarnish film. At higher temperatures the film becomes progressively heavier, and in the temperature range of 175 to 200° C a heavy black scale forms on the surface of the steel in about 100 hours. Up to about 175° C the film that forms is nonprotective, and the corrosion rate is dependent on the composition of the solution and independent of the flow rate past the steel surface. Effects of composition and temperatures to 175° C on corrosion are shown in Table 7.1.

The heavy film that forms in the temperature range of 175 to 225° C offers some protection to the underlying steel, but in most cases the protection is poor. This temperature

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[1] Austenitic stainless steels which have been tested in greater or lesser measure are: 202, 302, 302B, 303, 304, 304L, 309SCb, 310S, 318, 321, 347, Carpenter Alloys 10, 20, 20Cb, Croloy 1515N, Durimet, Incoloy, Multimet, Timken 16-25-6, and Worthite.

range is encountered only in a few places, such as the letdown heat exchanger and circulating-pump thermal barrier. (More resistant materials, such as titanium, can be used to overcome the problem there.) At higher temperatures a heavy scale forms fairly rapidly on the stainless steel, and once it has been established it affords essentially complete protection against further corrosion, provided that the flow rate of the solution is not too great.

The protectiveness of the film appears to be related to its composition. At temperatures up to 175° C the scale, as determined by x-ray diffraction, is composed of mixed, hydrated ferric and chromic oxides. At higher temperatures the amount of hydrated oxide decreases and the amount of anhydrous alpha ferric oxide containing chromic oxide in solid solution increases. At 250° C and higher only the anhydrous oxide is found in the protective scale.

The amount of metal that dissolves during the period of protective-film formation depends primarily on the flow rate, the composition of the solution, the temperature, and the presence of additives. If the other variables remain constant, increasing the temperature decreases the amount of metal that is corroded during the formation of the protective coating and reduces the velocity effect.

2. Effect of Solution Flow Rate.—From room temperature to about 175° C the solution flow rate in the range 1 to 70 fps has essentially no effect on the corrosion rate of the stainless steel. However, at temperatures above 200° C the corrosion rate is profoundly influenced by flow rate. For example, in a solution containing 0.04 m UO_2SO_4, 0.025 m D_2SO_4, and 0.025 m $CuSO_4$ in D_2O at 250° C with flow rates up to 30 fps, type 347 stainless steel corrodes to the extent of about 0.7 mil during the time a protective film forms. At slightly higher flow rates a completely protective film does not form, and in this transition region nonreproducible but high corrosion rates are observed. At flow rates greater than 35 fps, no visible film forms on the steel; and a constant corrosion rate of about 100 mpy is observed. A similar velocity effect is observed at all uranyl sulfate concentrations and at all temperatures above 200° C.

The velocity below which a completely protective scale forms is defined as the critical velocity. The corrosion rate of stainless steel specimens above this velocity is constant. Below the critical velocity the stainless steel corrodes initially at the same rate as at the high velocities, but the rate decreases as the protective coating forms and generally after about 100 hours very little, if any, corrosion occurs. In fact, some specimens have been exposed continuously at flow rates less than the critical velocity for periods as long as 20,000 hours and the amount of metal corroded was no greater than after 100 hours.

TABLE 7.1.—CORROSION RATE OF TYPE 347 STAINLESS STEEL IN URANYL SULFATE SOLUTIONS AT 100 TO 175° C

Solution composition	Temperature (° C.)	Corrosion rate (mpy)
0.02 m UO_2SO_4	100	0.25
0.006 m H_2SO_4	150	0.96
0.04 m UO_2SO_4 0.006 m H_2SO_4 0.005 m $CuSO_4$	150 175	0.87 5.4
1.3 m UO_2SO_4	100 125 150 175	0.40 0.80 2.8 18.0

3. Effect of Uranyl Sulfate and Sulfuric Acid Concentration.—All uranyl and sulfate solutions are acid, and the more concentrated the solution, the lower the pH as measured at room temperature. The acidity of dilute uranyl sulfate solutions must be further increased by adding sulfuric acid to prevent hydrolytic precipitation of copper and uranium at high temperature.

Generally the higher the concentration of uranyl sulfate or free acid in solution, the greater the extent of metal dissolution during film formation below the critical velocity, the lower the critical velocity, and the higher the film-free corrosion rate above the critical velocity. Table 7.2 shows how these three quantities change with uranyl sulfate concentrations at 250° C.

TABLE 7.2.—CORROSION OF TYPE 347 STAINLESS STEEL IN URANYL SULFATE SOLUTIONS AT 250° C

Concentration of UO_2SO_4 (m)	Weight loss at 10 fps (mg/cm^2)[1]	Critical velocity (fps)	Corrosion rate at 60 fps (mpy)
0. 02	1–2	>50	~10
0. 11	2–3	25–30	190
0. 17	12	20–25	190
0. 43	20	10–20	400
0. 84	37	10–20	680
1. 3	50	10–20	1, 400

[1] 1 mil=20 mg/cm^2.

Table 7.3 shows the effect of sulfuric acid added to 0.04 m UO_2SO_4 containing 0.005 m $CuSO_4$ on the amount of metal dissolved during film formation and on the critical velocity of the system. The effect of adding surfuric acid is qualitatively the same at all uranyl sulfate concentrations and at all temperatures above 200° C and produces a result similar to that of increasing the uranyl sulfate concentration. Thus it can be concluded that the acidity of the solution determines, at least in part, how much metal dissolves before a protective coating forms and the critical velocity of the solution. Low concentrations of copper sulfate in uranyl sulfate solutions have no significant effect on the corrosion of type 347 stainless steel.

TABLE 7.3.—EFFECT OF SULFURIC ACID CONCENTRATION ON THE CRITICAL VELOCITY AND ON THE EXTENT OF CORROSION AT LOW FLOW RATES AT 250° C

Solution Composition: 0.04 m UO_2SO_4 and 0.005 m $CuSO_4$

Acid concentration (m)	Weight Loss at 10 fps (mg/cm^2)[1]	Critical velocity (fps)
0.005	1	>50
0.010	1–2	45
0.015	3	40
0.020	6	35
0.025	12	30

[1] 1 mil=20 mg/cm^2.

4. Temperature Dependence of Flow Effects.—It has been stated that increasing the flow rate of the solution generally produces a detrimental effect on the corrosion of type 347 stainless steel. This effect is temperature dependent, as shown in Table 7.4 for a 0.04 m UO_2SO_4 solution containing sulfuric acid and copper sulfate in D_2O and for a 0.17 m UO_2SO_4 in H_2O. Generally no significant difference between D_2O and H_2O as solvent has been noted.

TABLE 7.4.—EFFECT OF TEMPERATURE ON THE CORROSION OF TYPE 347 STAINLESS STEEL IN URANYL SULFATE SOLUTIONS

Solution composition	Temperature (°C)	Weight loss at 10 fps (mg/cm^2)	Critical velocity (fps)	Corrosion rate at 60 fps (mpy)
0.04 m UO_2SO_4	250	4	30–35	100
0.02 m D_2SO_4	275	3	35–40	250
0.005 m $CuSO_4$ in D_2O	300	2. 5	>60	~500
0.17 m UO_2SO_4 in H_2O	250	12	20–25	190
	275	5	25–30	500
	300	2	40–45	1, 100

With a given solution composition, increasing the temperature decreases the amount of the metal that dissolves during film formation, increases the critical velocity, and increases the film-free corrosion rate of stainless steel.

5. Effect of Corrosion Inhibitors and Pretreatment.—A number of possible corrosion inhibitors have been added to uranyl sulfate solutions to determine their ability to reduce the corrosion of stainless steel. The only additive that produced a substantial effect was chromic acid. Even concentrations of 50 to 100 ppm of chromium increased the critical velocity and reduced the amount of metal that corroded during film formation. Unfortunately, chromic acid is not stable in a fissioning uranyl sulfate solution.

The initial exposure or pretreatment of the stainless steel surface is important in determining the subsequent corrosion within certain sulfate solutions at flow rates in excess of the steel in high-temperature oxygenated water forms a film which resists corrosion by uranyl sulfate solutions at flow rates in excess of the normal critical velocity. Although the pretreatment films have remained intact above the critical velocity for thousands of hours in certain cases, they must be considered metastable and subject to failure at any time. They may give temporary protection during brief periods of abnormal operation in a high-temperature system.

6. Stress-Corrosion Cracking.—A major weakness of the austenitic stainless steel alloys is their susceptibility to failure by stress-corrosion cracking [2] in chloride-containing aqueous environments. As a result, considerable attention has been given to study of this problem in the several aqueous environments present in an operating two-region breeder reactor. In general, the results have been similar to those obtained in the much more extensive investigations carried out in connection with the pressurized-water reactor systems. Thus, in the absence of chloride ion, the several aqueous environments present in an operating two-region breeder reactor do not cause stress-corrosion cracking of the austenitic stainless steels; however, in the presence of chloride ions and oxygen, stress-corrosion cracking may occur, depending on specific conditions.

Stress-corrosion cracking of type 347 stainless steel in uranyl sulfate solutions has been studied by exposing several types of stress specimens in many out-of-pile and in-pile loop, flask, and autoclave experiments. Stress-corrosion cracking was encountered only in the presence of appreciable amounts of chloride ion. Also, several hundred thousand hours of operating experience have been accumulated in engineering-scale equipment operating with uranyl sulfate solutions, with only a few failures attributable to this phenomenon, and no such failures have been encountered in over 20,000 hours of in-pile loop experimentation. It has been inferred from the work that under many conditions a threshold chloride concentration of about 10 ppm is required for cracking to occur, and the solutions used have generally contained 5 ppm, or less, of chloride except where higher concentrations occurred as a result of deliberate additions. A perhaps more significant factor has been the demonstration that pretreatment for as little as 50 hours in a chloride-free uranyl sulfate solution at any temperature between 100 and 300° C substantially reduces susceptibility to cracking on subsequent exposure to boiling chloride-containing uranyl sulfate solutions. Thus in laboratory tests with groups of six specimens from two different heats of 347 stainless steel, cracking incidence was reduced from 100 percent and 50 percent to 17 percent and 0 percent, respectively, by pretreatment at 100° C.

Chloride-induced cracking failures which have been encountered in test loops were usually associated with crevices either stemming from equipment design or formed by accumulations of solid corrosion products. Experimental investigations have shown this to be related to the oxygen exhaustion which occurs in such areas.

Recent laboratory studies with cast alloys such as type 347 and CD4MCu [3] stainless steel have shown that these materials have substantially greater resistance to stress-corrosion cracking failure in chloride-containing, oxygenated, aqueous environments than do the wrought alloys. This, and the fact that there is also an economic advantage in fabricating many reactor components by casting techniques, may make these alloys very important in the future technology. However, rigid exclusion of chloride from the several environments of aqueous homogeneous reactors is the only cer-

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[2] Stress-corrosion cracking may be defined as failure by cracking, generally transgranular in nature, due to the simultaneous action of stress and localized corrosion.

[3] SS CD4MCu—Ni 4.75–6.00; Cr 25–27; 0.04 C max.; Mo 1.75–2.25; Cu 2.75–3.25; 1 Si max.; 1 Mn max.
Casting Alloy CF–8C (type 347)—C 0.08 max.; Mn 1.50 max.; Si 2.00 max.; Cr 18.0–21.0; Ni 9.0–12.0; Nb 8 at least x C or 1.00 max.

tain means of controlling stress-corrosion cracking of the austenitic stainless steels.

Titanium and Zirconium.—Commercially pure titanium and Zircaloy-2 are useful supplementary materials in applications such as pump impellers and intermediate-temperature regions, where the stainless steels are not suitable. Both materials have exhibited almost complete corrosion resistance to uranyl sulfate solutions over the entire ranges of composition, temperature, and flow rate. No appreciable changes in corrosion resistance have been observed in tests run in excess of 20,000 hours.

In the case of Zircaloy-2, in-pile loop and HRE-2 data indicate that fissioning in the core does not affect its corrosion behavior in parts of the system external to the core. With titanium, however, the corresponding data are inconsistent. Some results have indicated that titanium external to the core is affected by the fissioning in the core. The corrosion rates encountered, however, are still only a few mils per year and do not obviate the use of titanium in special applications.

No localized corrosion, crevice corrosion, galvanic corrosion, or stress-corrosion cracking have been observed with titanium or Zircaloy-2 in uranyl sulfate solutions. However, an appreciable increase in the overall corrosion rate of zirconium alloys and some localized attack have been observed in the presence of as little as 45 ppm fluoride ion contaminant, and the alloys are rapidly attacked in uranyl fluoride solutions. Titanium, however, has shown good corrosion resistance in the fluoride solutions.

In general, additions of alloying elements to titanium and zirconium results in somewhat increased corrosion in uranyl sulfate solutions. However, the high-strength alloy, titanium A110-AT (5% Al, 2.5% Sn), and some of the experimental zirconium-niobium alloys have good corrosion resistance and are useful in special applications.

Other Materials.—Of the ferritic and martensitic stainless steels, types 410, 416, 420, and 440C in all heat-treated conditions were completely unsatisfactory in uranyl sulfate solutions at 250 C. The corrosion rates of these alloys were nearly constant with time, and the attack was very irregular. Although the precipitation-hardenable steels, 322W, 17-4 PH, and 17-7 showed very low corrosion rates after the formation of the protective film, all displayed a tendency toward stress-corrosion cracking in their fully hardened conditions. Croloy 16-1 demonstrated reasonable corrosion resistance in short-term tests, but long static tests showed the material to be susceptible to intergranular attack in uranyl sulfate solutions. The other ferritic and martensitic stainless steels corroded in the same fashion as did the austenitic stainless steels; that is, after a protective film formed the corrosion rates were in the range of 0.1 mpy. These materials have adequate corrosion resistance for use in high-temperature uranyl sulfate solutions.

Most of the nickel and cobalt base alloys were rapidly attacked by high-temperature uranyl sulfate solutions. The two exceptions were Hastelloy R-235 and Elgiloy. Hastelloy R-235 resembled an austenitic stainless steel in that it developed a film and corroded practically no further. Although Elgiloy corroded only slightly, it was extremely susceptible to stress-corrosion cracking, even in pure water. Thus, of the alloys listed, only Hastelloy R-235 could be considered for use in high-temperature uranyl sulfate solutions. On the other hand, most of the alloys were resistant to uranyl sulfate solutions at 100° C; corrosion rates less than a few tenths of a mil per year were observed. It is particularly significant that many of the very hard alloys, such as the Stellites, are resistant at the lower temperature and are useful in applications such as pump bearings where temperatures no greater than 100° C are encountered.

In dynamic tests platinum and gold were resistant to attack under all conditions, but niobium corroded at a rate of about 7 mpy at 15 fps at the higher temperatures. The corrosion rate of niobium also depended on the flow rate of the solution, and at higher flow rates somewhat higher corrosion rates were observed. Static tests showed that tantalum and chromium are corroded only slightly under most conditions. If the solution contained dissolved hydrogen, tantalum was seriously embrittled. Highly oxygenated uranyl sulfate solutions at temperatures above 250° C oxidized chromium to the soluble hexavalent state, and under these conditions the rate of attack was several mils per year.

Several nonmetallic substances were tested statically in 0.17 *m* UO_2SO_4 at 100° C. They included sintered alumina, graphite, sapphire, silicon carbide, sintered titania and zirconia, and quartz. All corroded at rates of less than 3 mpy, except for one very impure grade of sintered alumina which corroded at 124 mpy. In static tests at 250° C. in 0.17 *m* UO_2SO_4, the corrosion rate of pure, sintered alumina was 3 mpy; sapphire corroded at the rate of 3.6 mpy. In dynamic tests under the same conditions sapphire corroded at 17 mpy, quartz at 58 mpy, and Pyrex glass at 730 mpy.

Present State of Knowledge and Required Future Developments.—As a result of the corrosion investigations it is possible to specify materials suitable for use in the uranyl sulfate fuel systems of aqueous homogeneous reactors. As already indicated, an austenitic stainless steel (type 347) is adequate for the major portion of the system exterior to the core. In the absence of fissioning the corrosion behavior of the austenitic stainless steels is sufficiently well understood to predict with reasonable confidence what will happen under a given set of conditions. Thus the limitations imposed on the use of type 347 stainless steel can be specified. Similarly, a small number of other materials needed in the construction of components of the reactor system have been shown to be adequate within certain limitations.

Unfortunately, few of the materials possess the combination of mechanical properties and corrosion resistance that allows wide latitude in the composition of the fuel solution and in the mode of reactor operation. Thus, while type 347 stainless steel is satisfactory at low flow rates and in the absence of chloride ions, it is wholly unsatisfactory in the presence of reasonably low concentrations of chloride ions or at flow rates above the critical velocity. A container material substantially more resistant to stress-corrosion cracking and flow effects than type 347 stainless steel would materially advance the technology. In the same way, materials for special applications such as valve trim and high-temperature bolts are available, but it would be desirable to have other materials combining improved mechanical properties with increased corrosion resistance.

A continuing program of corrosion testing is necessary to determine the merits of new alloys as they are developed. It is possible that a new alloy, for example, an iron- or titanium-base alloy, may prove superior to some of the materials in use. With regard to large reactors, cast materials offer potential savings and possibly greater resistance to stress-corrosion cracking; hence the behavior of these alloys in uranyl sulfate solutions must be determined.

The corrosion rates of several materials in dilute uranyl fluoride and uranyl carbonate solutions have been measured, but no such tests have been carried out in dilute uranyl nitrate solutions. Recent experiments carried out by others have indicated that there may be advantages (related to solution stability) in the use of uranyl nitrate-copper nitrate-nitric acid solutions as reactor fuels. If such solutions do have real advantages over uranyl sulfate solutions, it will be necessary to determine the corrosion characteristics of many materials in uranyl nitrate solutions.

Slurry

Although chemical conditions in slurry systems resemble those in pressurized-water systems, the addition of large quantities of finely divided abrasive thoria, urania, or thoria-urania particles and the flow necessary to maintain them in uniform suspension result in many more factors which affect the attack on materials of construction. The particles of the slurry are individual in size, shape, surface properties, and durability, and slurries made from batches prepared in different ways or at different times may show different qualities. The individual qualities of the thoria preparation also affect the handling properties, and through these the hydrodynamic factors in the erosive attack.

Additional problems stem from the fact that the thoria originally or ultimately will contain fissionable uranium. The action of fission fragments on water will result in the formation of radiolytic hydrogen and oxygen. An internal catalyst will become necessary in order to permit recombination of these gases, and the presence of both the radiolytic gas and the recombination catalyst may affect the chemistry of the water and the corrosion reactions. These effects combine to make corrosion and erosion in slurries so different from corrosion in pure water that a thorough study of the behavior of materials in slurries is necessary.

Nature of Attack.—The corrosion-erosion of structural materials by aqueous flowing slurries combines water corrosion of the materials and abrasive effects of the suspended slurry particles. Factors affecting corrosion-erosion are impingement of the slurry particles against a protective oxide film on the metal, the breakdown of the film under this attack, and repair of the film by newly formed corrosion products. For all metals of interest, the destruction of a protective oxide film exposes reactive metal to the aqueous media. The rate of reaction of such bare metal is very high, and the rate of film reformation will control this reaction rate and the net amount of metal consumed. Surface damage to oxide film or metal by the impinging particles involves complicated factors. Hardness, elasticity, the strength of the oxide film or metal, and the nature of the metal-to-oxide bond are important. The hardness of thoria minerals has been reported as 6.5 to 7 on the Moh scale. The hardness of many mineral oxides of compositions similar to the protective film on the metals lies between 6 and 6.5. However, sapphire, which has been attacked by high-temperature aqueous thoria slurry, has a hardness of 9, which implies that hardness is not the sole factor involved. The characteristics of the slurry particles are at least equally important.

The most important attributes of the thoria itself appear to be the particle size and particle shape. Large, irregular, sintered aggregates, which are sometimes produced under adverse preparation conditions, appear to give very erosive attack of almost any material. It is necessary, consequently, to work with slurries which do not contain such large particles, and their removal by a size-classification procedure has been made part of the preparation process. Generally, particles above 10μ are regarded as such "clinkers." It has been demonstrated, however, that microspheres of 10μ–15μ diameter can be circulated without undue attack on materials and also without undue degradation of these microspheres.

There are at least three different types of attack by slurry particles: (1) flow abrasion, (2) impingement attack, and (3) eddy erosion. Flow abrasion is a generalized attack, possibly less than 1 mpy at 20 fps, that is found in smooth pipelines and elbows. It is believed to result from a reduction in thickness of the protecting boundary layer as flow velocity increases. Consequently this type of attack should be sensitive to scale-up effects, becoming less severe at equivalent Reynolds numbers, as the flow-channel dimensions are increased.

Impingement attack occurs on upstream surfaces where flow lines have been broken by the moving particles and these particles have abraded the protective oxide film. The upstream surface may be worn away quite severely. Impingement attack is sensitive to the size and shape of the target and the particles. Particles smaller than about 2μ tend to follow the stream lines if the velocity is below about 20 fps and usually do not cause impingement attack.

Eddy attack is noted when the boundary layer near the surface is broken through as a result of severe flow disturbances, such as wakes and eddies, resulting from small cavities or protuberances, cavitation effects, or other conditions. Also, this attack may occur under extreme velocities in simple flow channels where substantial eddies are generated. Eddy corrosion results in smooth, round-bottom, sharp-edged pits which appear to have been gouged in the surface, generally undercut in the direction of flow so that the surface feels rasp-like when stroked upstream. The development of such pits may be self-accelerating for a period.

Operating Variables.—Corrosion-erosion by slurries increases in proportion to concentration, other things being equal. Corrosion increases approximately as the square of linear flow velocity in simple-flow systems. In more complex, turbulent systems the velocity dependence may become more pronounced.

The nature of the atmosphere (hydrogen or oxygen) affects the type of corrosion products which are formed and also their protective character through effects on physical and chemical state. The state and/or presence of the corrosion products in the slurry may also affect the corrosive behavior of the slurry.

Additives.—In general it has been found that additives imparting acidity, such as sulfuric acid or thorium sulfate, tend to increase attack of ferrous-base materials, especially with low-oxygen or reducing atmospheres. Alkaline phosphate in the case of titanium and fluoride in the case of zirconium result in increased attack rates. The concentration of additive required to be effective increases with the surface area of the thoria.

Additions of molybdenum oxide, a potential recombination catalyst, have shown a mild corrosion-inhibiting action. Inclusion of urania in the thoria has not been found to have a definite effect on corrosion rates.

Materials.—Materials demonstrated to be useful in high-temperature water service, such as in pressurized-water nuclear reactors, high-temperature steam boilers, etc., may be considered for service in high-temperature aqueous slurries. Such materials include the stainless steels, particularly the austenitic stainless steels, Zircaloy and zirconium alloys, titanium alloys, and under certain conditions, such materials as Inconel and alloy steels. Although materials found to be unsatisfactory in the purely aqueous system are usually not suitable for slurry systems, the order of excellence and relative importance of different variables for suitable materials have been found to be altered in slurry systems.

The order of excellence usually is unchanged by the particular slurry employed, although one may be more aggressive than another. Ratios of attack rates for specimens of different metals exposed together remain approximately constant for many tests, unless unusual localized attack occurs.

The austenitic stainless steels represent the most useful class of construction material for slurry systems. Of the various types available, ASA type 347 has been tested most. Differences between various types do not appear to be significant. Corrosion rates below 1 mpy with flows up to 20 fps are normally attained. Over 100,000 hours of high-temperature slurry circulation have been achieved in pump loops made for the most part with type 347 stainless steel. No failure or serious penetration of major loop containment has been observed, indicating that the major problems are not associated with ordinary pipeline flow. Erosion of valve fittings, small tubing, and other parts subjected to high localized velocities has occurred. The most severe attack of stainless steel has been localized attack on pump impellers and housings, orifice restrictors, and test specimens in high-velocity regions or regions of unusual flow separation.

The maintenance of adequate oxygen concentrations in pump-loop and toroid tests has appeared to result in less aggressive attack on austenitic stainless steels than similar tests with no added oxygen. In systems using hydrogen atmosphere, stainless steel has been attacked perhaps fourfold more aggressively than in the presence of oxygen.

Stress-corrosion cracking failures have been encountered under thoria accumulations in stagnant regions in equipment in which oxygenated, chloride-containing thorium oxide slurries were circulated. Unfortunately it has not been possible thus far to reproduce the attack under more controlled laboratory conditions.

Ferritic and martensitic stainless steels are attractive for certain operating parts because of their hardness properties. The corrosion resistance of these materials is about the same as that of the austenitic stainless steels. Because certain alloys of this class do not appear to be as susceptible to stress-corrosion cracking as are austenitic stainless steels, they remain potentially a very useful class of materials.

Zirconium alloys, especially Zircaloy-2, have shown extremely good corrosion resistance relative to other materials. Usually the corrosion rates are 10 to 20 percent of the rates for stainless steel exposed under similar conditions. Zirconium alloys appear to be little affected by atmosphere, although they are possibly more easily abraded under H_2. However, there is some evidence of a potentially serious attack on the zirconium under hydrogen atmosphere. In recent toroid tests in which a slug flow of liquid was maintained past pins intruding across the stream, a substantial pickup of hydrogen to form zirconium hydride was observed. This ultimately resulted in a fissuring of the hydride layer. Because observations made on specimens extending across a flowing stream in loops operating under a hydrogen atmosphere have not led to similar findings, it is uncertain whether the phenomenon is associated with the slug flow. Cast Zircaloy has proved to be exceptionally useful for pump impellers, with negligible wear being observed over periods of several thousand hours.

Titanium and its alloys in oxygenated slurry have shown approximately the same corrosion rates as austenitic stainless steels, or perhaps somewhat lower rates. Titanium appears to be equally corrosion resistant in oxygenated and hydrogenated systems, provided that the slurry is not strongly alkaline. In alkaline system with hydrogen atmosphere, a very aggressive attack has been noted.

A number of other materials are of interest in slurry systems because of specialized application, or because of potential low cost. *Low-alloy steels* are of interest because of low cost, and there is a considerable background of experience in boiler service. Results based on corrosion specimens in systems at high oxygen concentrations or with hydrogen added indicate comparatively high initial attack rates which decrease with time, and it is indicated that acceptable rates may be achieved. However, pitting problems and potential embrittlement by hydrogen or alkali have not been explored.

The attack on low-alloy steels varies with the chromium content, the logarithm of the attack rate varying with the square root of the chromium content. The effect is greatest under oxygen and least under hydrogen atmosphere and extends at least between carbon steels containing no chromium and the 18–8 or austenitic stainless steels containing a nominal 18 percent chromium.

Nickel alloys appear to perform somewhat better in hydrogenated systems but generally are not as corrosion resistant as the austenitic stainless steels in oxygenated slurries. Inconel and Inconel X appear to give results approaching austenitic stainless steel under some circumstances. *Stellites* have performed best in hydrogenated systems. Attack by high-temperature oxygenated slurry is appreciable but appears to be due to simple aqueous corrosion.

State of Technology and Required Developments.—Erosion does not appear to be serious under moderate flow conditions with good-quality slurries. However, the relationships between hydrodynamics, slurry properties, and erosion are only qualitatively appreciated, and further work is required to delineate threshold conditions under which localized attack may become appreciable.

In circulation tests of up to several thousand hours the buildup of corrosion products has not produced significantly undesirable effects. However, under oxygen atmosphere in stainless steel systems, appreciable quantities of chromic acid have built up. Questions of the effect of buildup of this material on corrosion, slurry handling properties, and on the solubility of uranium and other materials have not yet been resolved. Other effects associated with long-term circulation, including the durability of slurry particles, the buildup of corrosion, and (simulated) fission products, etc., require extended tests.

Slurry preparations now in use appear to be reasonably satisfactory and could be considered for reactor use. However, the efforts of slurry circulation are so dependent on the properties of the thoria preparation that further search for optimum properties and preparations is strongly indicated.

The use of oxygen atmosphere appears desirable. Generally, lower corrosion occurs under this atmosphere, and it appears likely that the hydriding of zirconium alloys may be relieved. However, reactor atmospheres would contain some radiolytic hydrogen, and the effect of such mixed atmospheres on corrosion, hydriding, and other phenomena must be determined. Hydrogen atmospheres might be attractive in relieving stress-corrosion cracking of austenitic stainless steels, but under reactor conditions some radiolytic oxygen would be anticipated. There is no evidence to indicate that stress-corrosion cracking would be relieved under such a mixed atmosphere.

Austenitic stainless steels, in particular type 347 stainless steel, appear to have satisfactory corrosion rates for use as pressure vessel, piping, and possibly heat-exchanger material. Attack in heat-exchanger-tube inlet regions has not been evaluated yet. Stress-corrosion cracking and corrosion-product problems mentioned above have not been adequately solved. Present loop operating experience is believed sufficient to justify use of type 347 stainless steel in an experimental reactor. However, other materials such as titanium, Inconel, alloy steels, and special stainless steels require further consideration as alternate materials for future reactors.

Pump-impeller erosion has been relieved by the use of cast Zircaloy-2 to an extent which indicates that well-designed impellers of this material should give satisfactory service. However, materials for other special services, such as valve trim, orifices, nozzles, brazing, etc., require much more investigation.

Water

Steam Generators.—Chemical treatment of the feed water to the steam generators of a fluid-fuel reactor is an important problem in the operation of such reactors. The highly radioactive primary-system fluids decompose the secondary water with resultant production of hydrogen and oxygen. A few ppm of oxygen in the secondary-system water will cause aggravated corrosion of the materials of the steam system, and, in the presence of approximately the same amounts of chloride ion, will produce stress-corrosion cracking failures in austenitic stainless steel tubes. Radiation decomposition of the inhibitors conventionally used in this application also introduces novel problems. One of the investigational objectives of HRE-2 has been the use of hydrazine addition to the feed water to inhibit oxygen formation. Several thousand hours of power operation have been accumulated, with indications that in spite of radiation decomposion of the hydrazine, oxygen concentrations in the steam can be reduced two or three orders of magnitude to the few parts per billion level by hydrazine addition. This is adequate for the control of corrosion in the steam system, but whether similar control is obtained in the shell of the generator and the concentrations of hydrazine required at various power levels remain to be established.

Duplex 347-Inconel tubing, with the Inconel in contact with the secondary-water environment, has been proposed for use in this application. The comprehensive investigation of stress-corrosion cracking in chloride-containing boiler-water environments carried out in connection with the Naval Pressurized Water Reactor program has shown that Inconel is not susceptible to cracking failure. Unfortunately, Inconel is not compatible with the uranyl sulfate solutions although it may be usable with some slurries.

Cooling Water, Leak Detector, and Other Auxiliary Systems.—Chloride must also be excluded from other aqueous environments in contact with the austenitic stainless equipment which is not easily replaceable. Failures have been encountered in using chlorinated, potable water as cooling water, and the presence of marking ink containing from 3,000 to 18,000 ppm chloride on the surface of stress U-bend specimens has been shown to induce cracking on exposure to saturated oxygenated steam at 300° C. The importance of the exclusion of chloride from aqueous environments contained in austenitic alloys was clearly demonstrated by the encounter with stress-corrosion cracking in the HRE–2 leak-detector system. The undetected chloride contamination during manufacture of some of the tubing used in fabrication of the system resulted in a rapid succession of failures in parts of the system during shakedown operation. Subsequent penetrant and metallographic examination of the O-ring flanges to which the system was connected revealed stress-corrosion cracks in many of those exposed to high temperatures. As a result, all of the high-temperature flanges were replaced before the reactor operation schedule was continued.

7.3.2 Corrosion of Core Material

Zirconium, or a zirconium alloy of similar low cross section, is the unique material of construction for the core vessel of a two-region thorium breeder. No other material so nearly satisfies all the physical properties, neutron cross section, and aqueous corrosion-resistance criteria for this particular application. However, the rates of corrosion of Zircaloy–2 as well as those of other zirconium alloys in uranyl sulfate solutions and under exposure to reactor radiations are greater than the rates in the absence of radiation. It has been recognized since 1954, the time at which the initial radiation-corrosion tests were made, that this radiation-induced corrosion of the zirconium-alloy core tank in a homogeneous reactor would be a matter of concern, and a program of studies of the effects of radiation on Zircaloy–2 and other zirconium alloys has been in progress since that time. These studies have been concerned, primarily, with characterization of the radiation effects with respect to such variables as time, radiation intensity, types of radiation, temperature, solution composition, solution velocity, specimen surface preparation, and heat treatment. The studies have had the objective of providing information which would enable the prediction and control of Zircaloy–2 corrosion in the core of the homogeneous reactors and which would form a basis for further study of the mechanisms of the radiation-corrosion effects. Zircaloy–2 has received the most consideration in this program, since it is the only commercially available alloy and was the material of construction for the core of the HRE–2. Other experimental alloys have also been tested, but thus far none with unqualified advantages have been found.

Uranyl Sulfate Solutions

Zircaloy–2.—Test temperatures in the range 225° to 330° C have been employed in the experimental program with Zircaloy–2, but the large majority of the tests were at 250° to 300° C. Most of the solutions employed for in-pile tests were of uranyl sulfate concentrations greater than the 0.025 *m* projected for the thorium-breeder reactor. The higher concentrations were necessary in order to achieve, at the thermal-neutron fluxes available, reasonably high fission power densities in solution. However, because of other experimental considerations, the uranium concentrations and thermal-neutron fluxes employed were usually not great enough to yield fission power densities in solution which were near the value of 50 w/ml anticipated near the core wall in a large two-region reactor; the fission power densities employed were usually in the range 1 to 20 w/ml. A few experiments have been made at higher power densities; in one of these, the power density was about 100 w/ml in the 1.3 *m* UO_2SO_4 test solution. Commercially annealed Zircaloy–2 with surfaces in the as-machined and cleaned condition was employed in most tests, and the results summarized below are, in general, those obtained with this material.

When Zircaloy–2 in a U^{235} uranyl sulfate solution is exposed to reactor radiation, the rate of corrosion of the Zircaloy–2 increases above that prevailing prior to the initiation of radiation. The rate of corrosion reaches some maximum value within a short time and then remains approximately constant during subsequent exposure to a constant level of reactor radiation. If the radiation exposure is interrupted by a reactor shutdown, corrosion continues at a decreasing rate until the average additional corrosion penetration is 0.005 to 0.01 mil. Following this, corrosion essentially stops until power operation is resumed. The corrosion which takes place after shutdown appears to delay the onset of attack when irradiation is resumed; the amount of delay about balances off the attack which occurs during shutdown. Zircaloy–2 surfaces in contact with the fissioning solution are attacked fairly uniformly. A pitting type of attack has been detected in only one of the numerous specimens which have been exposed.

The change in the corrosion behavior of Zircaloy–2 under reactor radiation conditions has been shown to be a function of the power density which results from the nuclear reactions in solution. At a given value of solution power density, the rate increases markedly with increasing temperature. No effect has been noted of changing the pressures of hydrogen (or deuterium) and of oxygen within the test limits of 0–350 psi and of 150–1,200 psi, respectively. The presence of nitrogen has little effect on the rate within the test limits of 0–15 psi. No appreciable difference has been noted between corrosion in D_2O and in H_2O solution.

Several experiments have been carried out with the objective of determining the relative importance of the several radiation sources of such power density. Exposure of Zircaloy–2 in uranyl sulfate solutions made up with depleted U^{238} salt gave accelerated corrosion attributed to the power density resulting from fast neutrons and gamma flux. However, exposures to fast electrons from a van de Graaff accelerator gave no accelerated corrosion in spite of estimated power densities of 60 to 90 w/ml in the solution adjacent to the specimens due to adsorption beta-ray energy. These results have led to the conclusion that the major accelerated corrosion effects of exposure of Zircaloy–2 in fissioning uranyl sulfate solution stem from the action of heavy nuclear particles, that is, fission-fragment recoils and fast neutrons. In solutions containing appreciable fissionable uranium, the effect of the fission-fragment-recoil power density is dominant.

It has been observed that specimens removed from in-pile experiments have varying amounts of uranium contained in the scale present on them. The amount of uranium found in the scale has been shown to vary with solution composition, decreasing with increasing concentrations of sulfuric acid and/or sulfate additives, such as lithium sulfate, in solution and also with fluid flow velocity. Because of the short ranges of fission fragments, a few micrograms of uranium per square centimeter immediately proximate to the metal oxide interface can contribute significantly to the power density at the surface. It has been estimated that in the 10 g U/liter solutions, 20 μg of U/cm^2 deposited on the thin scale on the metal surface is equivalent to the uranium in the solution within fission-recoil range of the surface. Geometry considerations further indicate that the fission of the uranium on the surface may result in dissipation of five times as much recoil energy in the surface as fission of the uranium in solution. Thus an effective power density at the surface rather than the apparent solution power density must be used. The relative contribution to the effective power density of a given amount of uranium on the surface is expected to change with the concentration of uranium in solution as shown in Equation 1:

$$P_c=P\left(1+n\frac{U_w}{U_s}\right), \qquad (1)$$

where P_c is the corrected power density at the surface, P is the power density in solution, U_w is the amount of uranium on the surface, U_s is the concentration of uranium in solution, and n is a proportionality constant. The use of an effective power density, calculated on the basis of uranium found on specimens in postirradiation analysis, has permitted rationalization of wide discrepancies in corrosion rates obtained in different solutions at apparently equivalent solution power densities. These discrepancies were related to the effects of solution composition and fluid flow velocity on the amounts of uranium present at the surface and thereby to changes in the effective power density.

The relationship between corrosion rate, R, and solution fission power density, P, for many of the experimental results can be expressed by an equation of the form:

$$1/R=\frac{K_1}{KP\alpha}+1/K. \qquad (2)$$

In this equation α is the factor by which the effective power density at a corroding surface is greater than the power density in solution, and K and K_1 are constants for a given temperature and solution. An equation of the general form of Equation 2 can be derived from a model of the radiation effect on Zircaloy–2 corrosion in which radiation-produced defects in the metal or protective oxide increase the rate of corrosion and in which the defects are removed by thermal and radiation annealing.

A correlation of the available experimental data indicates that the value of K, obtained by extrapolation of the data to infinite power density, does not change appreciably with changes in solution composition. The value of K at 280° C. is 40 mpy and changes with temperature with an apparent activation energy of about 24 kcal/mole. A further correlation of the data, in which it is assumed that the effective power density in a given experimental system does not change appreciably with temperature, shows that the value of K_1/K does not change appreciably with temperature and is approximately 2.2 to 2.5 (w/ml)/mpy. Values of α observed in loop experiments have ranged from 1 to 7. The latter value was found for specimens exposed at low solution velocity in a 0.04 *m* UO_2SO_4 solution. Results obtained in some autoclave experiments indicate still greater values of α.

Zircaloy–2 specimens with surfaces prepared by chemical polishing or by sand-blasting corrode in-pile at rates which differ from those exhibited by as-machined Zircaloy–2 in the same experiments. The rates for polished specimens are somewhat less than those of the as-machined material; those for sand-blasted specimens are somewhat greater. Insufficient data are available to establish whether the differences are due to changes, with changing surface preparation, of one or more of the factors in Equation 2 or to effects of surface preparation on the effective area available for corrosion. No appreciable difference has been noted between the radiation-induced corrosion rates of Zircaloy–2 specimens which have been subjected to different heat treatments.

Status.—The experimental data and correlations summarized above provide a basis for extrapolation and for prediction of the corrosion rates to be expected with a Zircaloy–2 core tank in the thorium-breeder reactor. Estimates of Zircaloy–2 corrosion rates in a 0.025 *m* UO_2SO_4, 0.025 *m* D_2SO_4 solution in D_2O are shown in Table 7.5. The values of α at solution velocities of 5 and 15 fps were estimated from in-pile loop results in 0.04 *m* UO_2SO_4 solutions in light water and from the results of laboratory studies of the adsorption, from UO_2SO_4 solutions in H_2O at 250° C., of uranium on hydrous ZrO_2. The α values are recognized as being approximations because of uncertainties in the effects of velocity and solution composition on uranium sorption. Values for the predicted rates at α values of 1.0 are also listed in Table 7.5.

The corrosion-rate values in Table 7.5, taken at face value, show that the fuel side of a Zircaloy–2 core tank in a large two-region thorium breeder reactor will corrode at appreciable rates

Table 7.5.—ESTIMATED VALUES FOR THE CORROSION RATE OF ZIRCALOY-2 IN A 0.025 *m* UO_2SO_4, 0.025 *m* H_2SO_4 SOLUTION IN D_2O AT DIFFERENT VELOCITIES AND TEMPERATURES

Temperature (°C)	K (mpy)	Solution velocity (fps)	α	Corrosion rate (mpy)	
				At 25 w/cc	At 50 w/cc
250	12	–	1.0	6	8
		5	7.2	11	11
		15	4.0	10	11
260	18	–	1.0	7	10
		5	7.2	15	16
		15	4.0	13	15
280	40	–	1.0	9	14
		5	7.2	27	32
		15	4.0	21	28
300	77	–	1.0	9	16
		5	7.2	37	50
		15	4.0	27	40
330	213	–	1.0	10	18
		5	7.2	53	85
		15	4.0	54	58

if the fuel-solution composition is about the same as that listed in Table 7.5 and if the solution velocities are in the range indicated. For operating temperatures of 260° C and below, the rates are within what is considered a tolerable level of corrosion. For temperatures above 260° C, the predicted rates are undesirably high. The validity of the bases upon which these predicted rates were determined must be regarded as somewhat tentative, especially in the case of the values of α at different velocities and temperatures and in the different solution. Further in-pile experiments are required to determine the influence of these factors on the value of α, as well as to test the validity of the extrapolation of the experimental data to high power density, and the effects of surface preparation and very long exposure times on corrosion. An in-pile experiment to test Zircaloy-2 corrosion under conditions which closely simulate those anticipated for the thorium breeder reactor is also considered necessary.

Considerations of reactor operations and design show that operating temperatures above 260° C are desirable. Studies directed toward finding a better fuel solution, a method of reducing the uranium sorption, and a zirconium alloy for which the radiation-induced corrosion is suitably low at the higher temperatures appear to be important.

Other Zirconium Alloys.—Other zirconium alloys have been tested in some of the in-pile experiments, but none except alloys containing niobium has exhibited appreciably better resistance than Zircaloy-2. In the beta-quenched conditioned Zr—15 percent Nb corroded at rates lower than those observed for Zircaloy-2 by a factor of from 3 to 1.5, respectively, in 250 and 300° C loop experiments. A small reduction in relative corrosion rate has also been observed with crystal-bar zirconium. With both materials the available data indicate that the reduced corrosion rates were related to a lower value for the constant K, the maximum corrosion rate at infinite power density. This suggests the existence of alloys for which the maximum rates under irradiation may be fairly low even at the higher temperatures.

Slurry

The effects of irradiation on corrosion of materials by slurries embody several factors different from effects in water alone and in uranyl sulfate solutions. Fission fragments are produced from uranium in the slurry, and they may attack the protective film on the metal as well as produce radiolytic gas. However, there is essentially no electrolyte dissolved in the water, pH values may be near neutral, and a heterogeneous recombination catalyst is used. Slurry particles may abrade the protective film on the metal, and thus the nature of the radiation or fission-fragment attack may depend on hydrodynamic conditions and particle properties as well as other factors.

The effect of radiation on slurry corrosion has been studied at present only in rocking-autoclave tests in-pile. In these systems the major effect appears to be that of fission-particle bombardment. An increase in fission power density has appeared to result in an increase in corrosion rate of Zircaloy–2. However, this effect appears to diminish as exposure continues but increases again as the power density is increased. The reduction with time implies that the radiation may not be of too much importance in practical systems unless the effect is coupled with that of flow velocity. Studies using in-pile loops are required to clarify this point. In the static systems the rate on Zircaloy averaged less than 1 mpy at average power densities as high as 5 w/ml.

The effect of radiation on the corrosion of materials other than Zircaloy has not been investigated extensively; however, no major effects have appeared for type 347 stainless steel, Inconel, or for a low-allow steel, Croloy 2¼.

Deposition on Heated Metal Surfaces

The evidence of severe attack, very high temperatures, and uranium accumulation in the core of the HRE–2 stimulated interest in the effects of boiling uranyl sulfate solutions on heated surfaces on materials and solution behavior. Investigations have shown that under certain circumstances salts can be caused to deposit on a heated surface in contact with solutions containing dissolved gases. Under favorable geometry conditions, low flow, and sufficient heat flux through the container walls to produce boiling, a stable vapor pocket can be formed in the upper portion of the container. Solution which is then splashed against the heated wall in this pocket evaporates, with deposition of the solutes contained. The process has been shown to be a function of heat flux, system geometry, solution flow rate, total system pressure, gas concentration in solution, and solution temperature.

The process has been caused to take place in a heated ⅜-inch pipe inclined at an angle of ~10 degrees from horizontal with solution flow down the pipe. It has also taken place in the core of an in-pile type loop, operated out-of-pile with electrical heating of the core or in-pile with the utilization of gamma flux as the heat source. In-pile the process appears to be self-accelerating, presumably due to fission heat from the deposited uranium.

The sulfuric acid present in dilute uranyl sulfate solutions is also concentrated on the heated surface by the process. Concentrations achieved in the tests which have been performed severely attacked type 347 stainless steel, Zircaloy–2, and commercially pure titanium.

Similar experiments with slurry have not been carried out thus far; equipment for carrying them out has been fabricated, however.

7.4 METALLURGY

Metallurgical research and development has been concerned primarily with titanium- and zirconium-base alloys, with emphasis on zirconium for use as a core-tank material. Zircaloy–2 (1.5% Sn., 0.1% Fe, 0.1% Cr. 0.05% Ni) developed for naval reactors is now the only commercially available zirconium alloy. It is a single-phase alloy with fair mechanical properties; it cannot be heat treated, is stable at homogeneous-reactor temperature, but difficulties are encountered due to high chemical activity.

Unalloyed A–40 and A–55 titanium and one alpha alloy A–110AT (5% Al, 2.5% Sn) are the titanium metals which have been used most in homogeneous-reactor work. Other titanium alloys have not been available commercially, are structurally unstable under stress at elevated temperature, or cannot be field welded. Unalloyed titanium does not have adequate strength for construction of high-temperature, high-pressure equipment. In such applications it is usually used as a lining or cladding for stronger materials. The A–110AT alloy, which has been the only stable, high-strength, weldable titanium alloy, has not been available in pipe or tube form and is difficult to fabricate. The future of titanium in homogeneous systems depends largely on the success of the new alloys now being developed by the titanium industry.

Stainless steel and carbon steel, the major structural metals for homogeneous reactors, are well developed commercial materials and have required little special attention. Large reactor pressure vessels are constructed of carbon steel clad with stainless steel. Neutron irradiation of carbon steel causes a loss of tensile ductility and an increase in the transition temperature as determined in an impact test. Effect of radiation on steels and on zirconium alloys is being determined for use in reactor design.

7.4.1 Fabrication and Morphology of Zirconium

During the fabrication of the HRE–2 core tank it became evident that very little information was available on the physical metallurgy of Zircaloy–2. The material then available possessed a considerable variation in mechanical properties, in the permissible bend radii, and in the amount of laminations and stringers present, and it was highly anisotropic. Prior to fabrication of that vessel, Zircaloy–2 had been used only in the form of narrow plates in fuel-element fabrication where neither the mechanical properties nor metallurgical requirements were critical; selection was based primarily upon the tests of corrosion resistance. While a fabrication procedure was available for producing strip, the effects of the variables had been determined over a very narrow range and no work had been done on wide plate. A small development program based upon procedures developed by Westinghouse Atomic Power Division did, however, permit the successful fabrication of plate and the forming of the HRE–2 core vessel.

Subsequent to the fabrication of the core vessel a considerable study has been made of the morphology and physical metallurgy of Zircaloy–2. The purpose of study was to answer the questions raised in the vessel fabrication and to develop a basic understanding of the allow. Studies have been made of such changes as may be expected in microstructure, grain size, and orientation under a wide variety of heat treatments; of the formation and properties of the stringers; and of the temperature limits of the alpha-plus-beta field and the effect of composition thereon. This program has been coordinated with the mechanical-property study. A series of standard structures were prepared to assist in the interpretation of failures and to predict performances.

The study showed that the accepted "alpha" rolling temperature of 843° C was in the alpha-plus-beta field such that, for material containing 40–50 ppm H_2, approximately 15 percent beta phase existed in the microstructure at temperature. The beta phase present formed sheets or stringers during rolling. On cooling from the fabrication temperature, the sheets and stringers decomposed to alpha phase plus intermetallic compounds, depositing the alpha phase on the neighboring alpha grains and leaving the intermetallic phase present as the stringer. The alpha/alpha-plus-beta temperature for normal Zircaloy–2 containing 40–50 ppm H_2 was found to be 810° C and the beta/alpha-plus-beta temperature was found to be 970 C. The apparent two-phase temperatures may be varied both by small variations in ingot composition and by the heating or cooling rate. A second type of stringer present in many lots of Zircaloy–2 was shown to have resulted from gas voids present in the ingot and elongated during fabrication. It is now possible to obtain Zircaloy–2 essentially free from stringers by double vacuum melting the ingot to eliminate the gas pockets, and to fabricate at temperature either above 1,000° C or below 800° C to eliminate the intermetallic stringers.

While Zircaloy–2 does undergo a phase transformation, it has not been possible to make use of it and to obtain improved properties by simple heat treatments as is done with steel. Temperature cycling through the transition temperature leads to grain coarsening and increased perfection of the preferred orientation on the first cycle and no changes with additional cycles. However, coupling the physical-metallurgy studies with the mechanical-property information has led to the development of a fabrication schedule yielding improved properties. The improved schedule takes advantage of the fine martensitic structure produced by beta quenching which is reduced even further by cold working a minimum of 20 percent and then recrystallized with an alpha anneal. A fine-grained (ASTM 6 to 8) nearly randomly oriented structure was produced. The superiority of such a material to standard commercial material has been demonstrated by metallography and X-ray diffraction and by the determination of its mechanical properties. Such a schedule has now been used successfully by two different fabricators for the production of wide plate and rod.

The control samples developed in this study were of great value in determining what conditions have existed within the HRE–2 reactor core during operation. Comparing structures of samples which had been inserted in the core with others of known history has revealed unexpected conditions, such as very high local temperatures.

Information on the structure and morphology of Zircaloy-2 has now been fairly well developed. Information is still required, however, on the effects of variations of composition and the true role of the metals used in the alloy. While a fabrication procedure has been developed that provides much better material than was previously available, it has not been shown that such material is the ultimate that may be obtained. Work is required to extend any developed procedure to the fabrication of shapes other than plate.

7.4.2 Forming of Zircaloy–2

The core vessel of a two-region homogeneous reactor separates the core solution from the blanket and preferably serves as an intermediate pressure vessel. Its shape and dimensions are very important both from stress and from hydrodynamic considerations. While the HRE–2 vessel is a sphere with a conical entrance, various shapes and sizes have been envisioned in other homogenous-reactor proposals. Studies of methods of forming various shapes and the dimensional tolerances that might be expected have been started so that meaningful recommendations can be made to the designers.

The HRE–2 core vessel was fabricated by the tedious process of warm-pressing small segments which were then welded together, followed by repressing to achieve the tolerances necessary to ensure a fit with other sections for additional welding and pressing. Such a procedure was made necessary by the absence of wide plate plus a lack of knowledge about forming Zircaloy.

By using wide plate produced by the new fabrication procedure, techniques were developed for warm-spinning of an entire hemisphere from a flat plate. A reverse flare was warm-pressed into the polar region of the hemisphere, thereby incorporating a transition region from the sphere to an inlet pipe without welding. A photograph of a flared 15-inch hemisphere fabricated from a flat plate is shown in Figure 7.7. A matching flare has been warm-pressed into a pipe section. Vessels produced by such techniques would therefore require only three welds, one at the equator and one at each end for joining to the system; all would be high-strength welds of simple configuration.

While a more reliable and cheaper method for forming Zircaloy–2 vessels has been developed, whether a satisfactory vessel can be

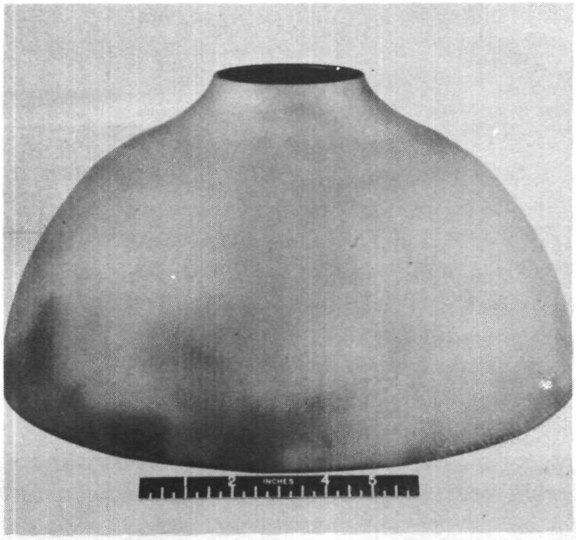


FIGURE 7.7—Flared Zircaloy–2 hemisphere formed from single flat plate.

formed by simple spinning and flaring will depend upon the required tolerances. For very close tolerances on radii or sphericity it may be necessary to use a two-stage flaring and pressing operation or to fabricate a vessel with a thick wall and to machine the surface. Procedure must be developed for fabricating such items as guide vanes, flow channels, shrouds, and transition joints required for reactors of advanced design.

7.4.3 Welding of Titanium and Zirconium

Titanium and zirconium and their alloys used in homogeneous-reactor work have simple structures and are weldable, but will react with oxygen, nitrogen, hydrogen, water vapor, and carbon dioxide at elevated temperatures to form brittle alloys. Successful welding is dependent on protecting the molten metal and adjacent area from all contaminants. Three methods have been developed by which sound uncontaminated welds of reactor quality can be made with titanium or zirconium. Welds on small complex shapes which are difficult to shield are made in an inert-atmosphere box (dry box). A conventional torch with increased gas flow and careful gas backup is used for general-purpose and field welds. Either a hand torch or mechanized equipment with inert-gas trailers surrounding the torch are used for repetitive production-type welds or for critical welds.

Prior to construction of the HRE–2 core tank, the only method used for welding zirconium was single-pass fusion welding inside dry boxes. This method is still used for welding of small complicated shapes. The use of $\frac{5}{16}$- and $\frac{3}{8}$-inch plate for the HRE–2 core vessel required development of multipass welding techniques, while the large size of the vessel made the use of dry boxes difficult. In a joint effort, the Newport News Shipbuilding & Dry Dock Company and Oak Ridge National Laboratory developed a machine for multipass welding of Zircaloy–2. Face protection was achieved by the use of trailers attached to the torch, and root protection either by special back-up devices, or where possible, by purging closed systems. The shape of the trailer and method of support were varied from joint to joint to give as close a coupling with the shape being welded as was possible. In all cases the torch was held fixed in a vertical position and the work was moved past it. Filler metal for the root passes was added in the form of preplaced inserts which had been machined from swaged Zircaloy–2 wire; the wire itself was used for the other passes. Meticulous care in cleaning all components and in removing surface discolorations before making a following pass aided in ensuring against contamination. Many satisfactory multipass welds were made in assembling the HRE–2 core tank. Since that time the procedure has been improved, allowing the root pass to be a simple fusion pass, thereby eliminating the insert and its accompanying very close fitup.

In both this work and that which subsequently developed from it, the determination of quality was a major problem in the welding development. Welds were examined visually, with liquid penetrants, and usually with radiography; however, none of these methods provides information about the degree of contamination. Measurement of the average microhardness of a prepared sample was developed as a sensitive indication of the contamination. Average hardnesses of less than 200 DPH (diamond pyramid hardness) are indications of an uncontaminated weld. The absence of contamination was confirmed by vacuum fusion analyses of weld sections. Average hardnesses of over 350 DPH are found in lightly contaminated welds, with hardness of over 500 in contaminated metal. Although this is a destructive test, it has been adopted as a standard for qualifying weld procedures.

Use of mechanical equipment or trailers is usually impractical for field welding of titanium and zirconium. A method which minimizes contamination by use of very low heat input, small molten pools, careful cleaning before and after each pass, and careful study of each weld to provide adequate backup-gas protection has been developed for making acceptable field welds in unalloyed titanium or in Zircaloy-2 with conventional tungsten-inert-gas arc-welding equipment. The procedures have been used successfully for butt and related types of joints. Some welds are very slightly contaminated, as indicated by small increases in hardness, but they are well within acceptable limits based on mechanical tests. When extreme care is used, welds comparable in hardness to dry-box welds are achieved, and they are in almost all cases superior metallurgically.

In the construction of Zircaloy-2 and titanium parts and test components, many successful butt welds have been made with only conventional equipment. However, parts with very close dimensional tolerances are required, and great reliance is placed on the skill and reliability of the welder; so the practice would not be recommended for the extremely critical welds in a reactor vessel, unless the welds could be tested by a nondestructive method that would reveal contamination. As yet no such test is available. Sizes of the proposed core vessels still preclude the use of dry boxes, and therefore it appears that any proposed reactor core will be fabricated by use of protective-trailer welding methods. Development is still required on procedures for welding configurations other than butt welds, such as those that might be required in flow channels.

7.4.4 Mechanical Properties of Zirconium and Titanium

Both titanium and zirconium have hexagonal structures, rather than the more common cubic type, and such structures may lead to increased preferred orientation and anisotropic mechanical properties in structural plates and shapes. In addition, mechanical properties of metals are determined by standard tests developed for cubic metals. Design standards have not been established for applying those tests to hexagonal metals. The relationship between test results and the failure of vessels and structures has not been demonstrated. Neither zirconium nor titanium has been tested sufficiently to be accepted for construction of pressure vessels by the ASME Boiler Code.

When round tensile samples of commercial Zircaloy-2 or unalloyed titanium plate were broken, it was noted that while comparable and adequate mechanical properties were obtained with both longitudinal and transverse samples for fractures always had an elliptical cross section. The major axis of the ellipse was always in the thickness, or normal, direction of the plate, indicating a greatly reduced ductility in this direction. Reductions in length of the axis of over 45 percent were found in either the longitudinal or transverse direction, but in each case that in the normal direction was less than 5 percent. That such variations in properties were caused by preferred orientation was demonstrated by both polarized-light examination and X-ray diffraction studies on samples cut to expose the various directions. The orientation was such that few slip or twin systems were available for deformation in the normal direction. A considerable study has been made of these ellipses both in the fracture area and also in the entire reduced portion of the broken sample. The study has included both commercial material and material fabricated to 18 special schedules. The shapes and sizes of the ellipses show a wide variation but are reproducible for a given material. Although the relationships have not been completely developed, they do appear to be a sensitive index of the anisotropy of a material and should afford a simple acceptance standard.

Impact-type tests may also show that, unlike for most materials, uniformity in results from transverse and longitudinal tensile samples is not sufficient to assure uniform material in zirconium or titanium. Curves differing in both energy values and location of the transition region were obtained from samples cut from different directions in the plate, and even larger differences occurred when the notches were cut in different faces. The poorest properties occurred with the notch in the plane of the plate.

Under this condition the location of the transition region approached the operating temperature of the reactor. The variations between the curves vary with the fabrication schedule. Attempts are being made to correlate these differences with those found by tensile and X-ray tests.

The effects of notches and cracks in zirconium were studied by use of the drop-weight test developed for steels by Pellini and others at the Naval Research Laboratories. This test determines brittleness by measuring the highest temperature at which a crack will propagate through a specimen undergoing limited deformation. For steels this temperature is distinct and reproducible and has been labeled the NDT (nil ductility transition) temperature. Commercial Zircaloy–2 showed surprisingly good properties based on this test. The NDT temperature was −160° C for the longitudinal direction and between −100° and −150° C for the transverse direction. However, when the fracture faces were examined, shear lips, which are normally a mark of a ductile fracture, were found even at lower temperatures. The NDT temperature was on the lower flat portion of the Charpy V impact curve well below the lower break, where it customarily occurs in steel. The NDT temperature for A–55 titanium was found to be below −200° C. Incomplete fractures were found at this temperature for both longitudinal and transverse specimens.

The field of mechanical properties of hexagonal metals is one that still requires a great deal of work both of a basic and an applied nature. Guided by the limited information now available, the HRE–2 core tank was designed to minimize stress in the direction normal to the surface of the plate and thereby circumvent the anisotropy problem. This may not, however, always be possible in future vessels, and therefore an understanding of the problem must be obtained. An important portion of this work is the development of methods for correlating mechanical-property data with behavior in service. Mechanical-property relationships which have been developed, combined with the results of the fabrication study, have resulted in the production of more nearly isotropic plate, and further improvement is likely.

7.4.5 Combustion of Zirconium and Titanium

After several equipment failures in which evidences of melted titanium were found under operating temperatures not exceeding 250° C, a study of the ignition and combustion of titanium and zirconium was started. It proved to be surprisingly easy to initate combustion of titanium or zirconium in several different type of tests. Ignition and complete consumption occurred when these metals were ruptured or when an oxide-free surface was exposed, even at room temperature, in high-pressure oxygen.

The limiting conditions for the ignition of commercially pure titanium varied with total pressure, the percentage of oxygen, and the gas velocity as shown in Figure 7.8. The dotted curve in Figure 7.8 was obtained from a test in which the gas passes over the fracture surface with a considerable velocity; it is added for

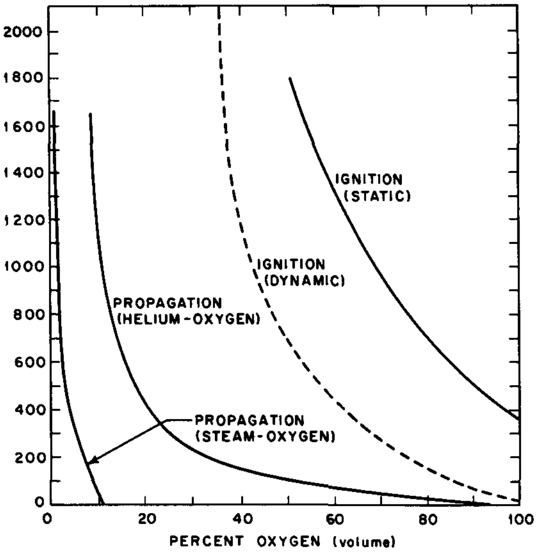


FIGURE 7.8—Approximate room-temperature limits of ignition and propagation of titanium in oxygen diluted with helium or steam static conditions.

comparison and shows the much lower critical pressures found in the dynamic test. The critical pressure for ignition is also temperature sensitive and under comparable conditions drops from 350 psi at room temperature as shown in Figure 7.8 to 50 psi at 1,200° C. Similar values for the ignition pressure were obtained when the oxygen was diluted with steam or with helium. In no case was a reaction noted when samples were fractured under oxygenated water.

As might be expected, lower critical pressures were required for the propagation of the combustion than for the ignition. If a molten spot was formed by an external means, propagation occurred with low oxygen pressures. Under these conditions steam is a more reactive diluent than is helium. When metal was ignited in the vapor space above water, the burning continued below the liquid level but eventually quenched; the distance burned depended on the surface-to-volume ratio of the sample.

Studies of the autoignition of titanium were followed by tests of other metals and alloys, such as stainless steel, aluminum, magnesium, iron, tantalum, columbium, molybdenum, Zircaloy–2, and alloys of titanium in oxygen at pressures up to 2,000 psi. Only the titanium alloys and Zircaloy–2 reacted. Within the limits of accuracy of these studies (±50 psi) no differences were found in the behavior of the various titanium alloys.

While it has been shown that autoignition can occur with zirconium, the techniques are not so well developed as are those for titanium. With zirconium, difficulty has been encountered in obtaining reproducibility in the results. Ignition of tensile-test specimens occurred at room temperature with oxygen pressures ranging from 650 to 1,500 psi. Critical pressures as low as 250 psi oxygen were obtained by first dissolving the oxide surface film in the base metal at high temperature under high vacuums and then exposing the samples to oxygen. The ignition limit under dynamic conditions depended upon the condition and extent of the exposed surface, with the lowest oxygen value obtained being 50 psi.

It has been shown that combustion of titanium or zirconium may readily occur but that it would not be expected under conditions normally present in a homogeneous reactor. Experience in HRE–2 and in loop operations has shown that combustion can occur under unusual operating conditions. Additional work is required with zirconium so that the combustion and propagation limits may be more closely defined and specified. The work for both metals must be extended to learn the effects of variables such as the surface-to-volume ratio and surface condition of the samples.

7.4.6 Development of New Zirconium Alloys

While Zircaloy–2 is satisfactory as a core material in present experimental reactors, a material with greater resistance to corrosion under radiation is desired for large power reactors. Several such alloys have been found in the zirconium-niobium system; however, most of them do not possess satisfactory metallurgical properties. A detailed study is being made of this system in an endeavor to develop such properties. Some of the alloys show promise of being heat-treatable and having much higher strength at reactor temperatures.

In conjunction with the in-pile corrosion group approximately 50 zirconium alloys have been exposed to uranyl sulfate solutions in autoclaves and in in-pile loops; however, only alloys of zirconium with niobium, and under some conditions those with palladium or platinum, showed greater corrosion resistance than Zircaloy–2. Except for two-phase diagrams for the zirconium-niobium system (one American and one Russian) and a few mechanical-property tests on low-niobium alloys, no information on any of these systems was available in the literature. A cursory check of the phase relations by determining the eutectoid temperature and approximate composition, confirmed the American diagram issued by Rogers and Adkins at Ames. A few preliminary transformation specimens, with near-eutectoid compositions, revealed complicated and embrittling transformation structures. Since the zirconium-niobium alloy system showed promise from a corrosion viewpoint, these alloys with niobium contents varying from 2 to 33 wt percent and many ternary alloys with small additions to the Zr–15Nb base were studied with the objective of eliminating the undesirable properties. Information that is being obtained includes the transformation kinetics and products, morphologies, in-pile corrosion resistance, fabrication techniques, metallographic procedures, and mechanical properties.

At least three transformation reactions occur in the zirconium-niobium binary system. The transformation sequence is quite complex, with the only straight-forward transformation being a eutectoidal transformation occurring close to the eutectoid temperature (Fig. 7.9). The most troublesome transformation is the formation of an embrittling omega phase, which is a problem in any heat treatment or fabrication that does not involve deliberate overaging. Time-temperature hardness studies for beta-quenched material showed very high hardnesses (>400 DPH) in short times with low-temperature aging treatments, including temperatures approaching those expected in a reactor. Aging times of 3 weeks did not result in over-aging and softening of such material at temperatures of 400° C and below.

Because of the hardness and slow transformations of the binary zirconium-niobium alloys, ternary additions to the Zr-15Nb base of up to 5 wt percent Mo, Pd, and Pt; up to 2 percent Fe, Ni, Cr, Al, Ag, V, Ta, and Th; and 0.5 percent Cu have been studied. In general, the primary effects of the addition of small amounts of the ternary substitutional alloying elements are the lowering of the maximum temperature at which the hardening reaction can occur, an increase in incubation time for the beginning of the hardening reactions, a lowering of the temperature for the most rapid rate of hardening, and an increase in rate for the higher temperature conventional hypoeutectoid reaction. Of the ternary additions, Fe, Ni, and Cr have the least effect, Pt and Pd an intermediate effect, and Mo the largest. The beneficial effect of molybdenum in delaying the embrittling reactions may be seen by comparing the transformation curves in Figure 7.9. The additions of Cu and Al drastically reduced the maximum temperature at which the hardening transformation can take place at the maximum rate, without increasing the incubation time.

Cursory fabrication studies have been performed during the course of the alloy development program in the preparation of sheet specimens for studies of the transformation kinetics. All of the Zr-Nb-X alloys have been hot-rolled from 800° C quite successfully. A sponge-base Zr-15Nb arc casting has been successfully extruded at 950° C to form rods. While the fabrication techniques developed are adequate for the production of specimen material, they are not necessarily optimum for the commercial production of plate, sheet, bar, rod, and wire in these alloys.

An ultimate tensile strength of Zr-15Nb at room temperature of 200,000 psi, with no elongation, was obtained on specimens beta-quenched and aged at 400° C for 2 hours. Similar specimens aged at 500° C for 2 weeks and measured at room temperature had an ultimate strength of 150,000 psi, a yield strength of 135,000 psi, and an elongation of 10 percent. At 300° C such aged material had an ultimate strength of 105,000 psi, a yield of 90,000 psi, and an elongation of 16 percent in 1 inch.

The physical metallurgy has been fairly well developed for the zirconium-niobium binary alloys and for a few of the more promising ternary alloys. Metallurgical studies are continuing on additional ternary systems and especially on copper additions, which have appeared favorable from a corrosion viewpoint. Additional corrosion information is required for all the alloys. Either a Zr–15Nb–2Mo or

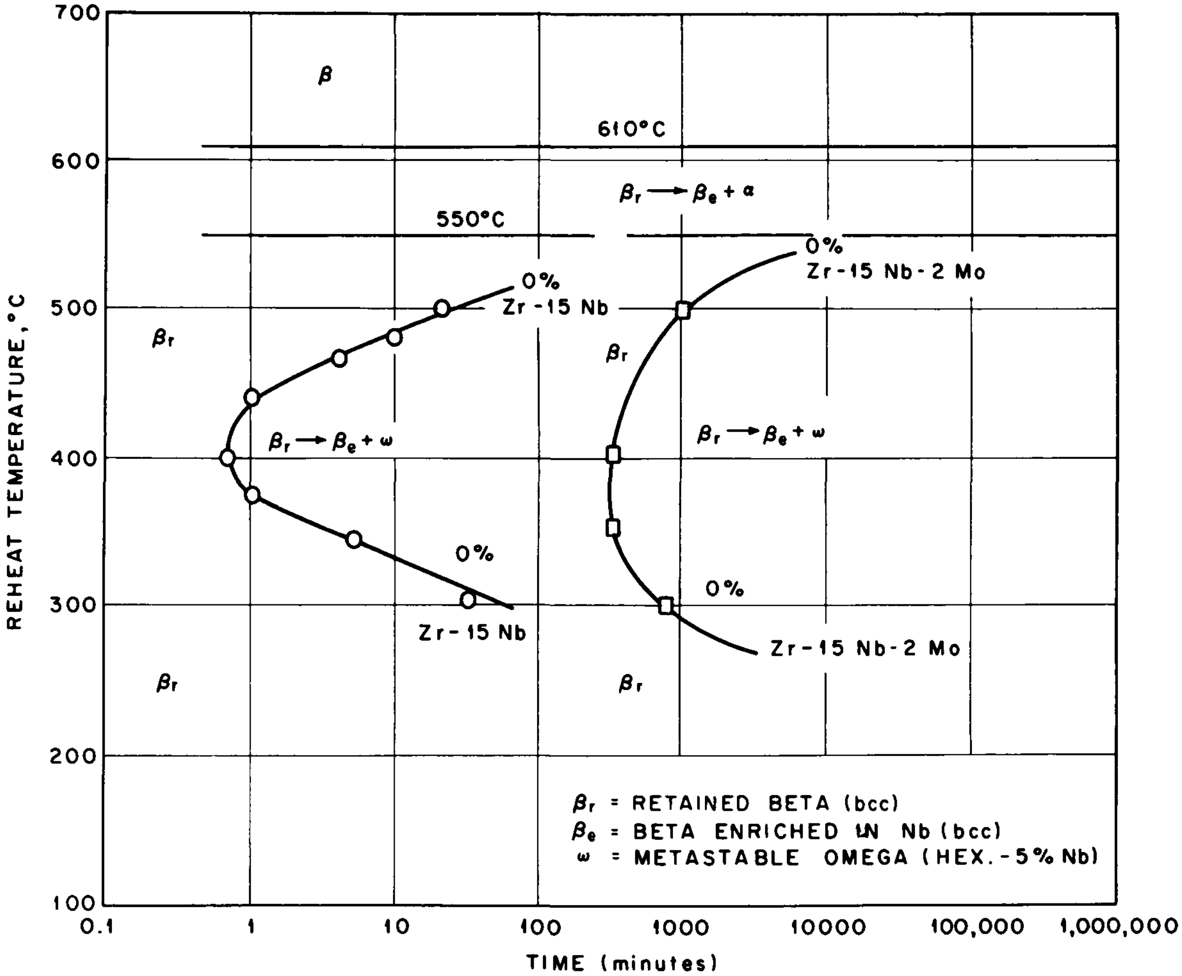


FIGURE 7.9—Tentative time-temperature-transformation diagram for beta-quench and reheat omega phase reaction in zirconium-niobium alloys.

a Zr–15Nb–5Pd alloy appears to be the most promising for fabrication of a more-corrosion-resistant core vessel. These alloys are weldable as formed and may be stabilized by a heat treatment of 1 week at 500° C. These alloys are now being developed into engineering materials.

While the Zr-15Nb base ternary alloys are still of interest primarily for their potential improvement in corrosion resistance, they show promise of wider, general use as structural material. These are the first zirconium alloys that may be heat-treated to high strength and yet are weldable and fabricatable.

7.4.7 Radiation Effects on Zirconium and Titanium

In the majority of reactor applications Zircaloy-2 is used as a fuel element. The mechanical-property requirements are not severe, and the life of an element is relatively short; thus radiation damage to the metal is not an important problem. This is not true for a homogeneous reactor; here the core vessel is a pressure vessel, and it is highly desirable that it last for 10 to 20 years. It would be equally serious if embrittlement or lsss of strength occurred through conventional radiation damage to the metal or from changes in the metal such as hydrogen pickup induced by the reactor environment.

In spite of the many questions that have been raised about the adequacy of mechanical-property tests for hexagonal metals, the difficulties of which are magnified in testing irradiated samples, some mechanical-property tests of irradiated titanium and zirconium samples have been attempted. Subsize tensile and impact specimens of Zircaloy–2, crystal-bar zirconium, and A–40 titanium have been irradiated in fissioning uranyl sulfate solution, in in-pile corrosion loops, at temperatures of 250 to 280° C, to total fast fluxes (>1 Mev) of up to 10^{19} nvt. Zirconium appears to be resistant to radiation damage under these conditions. The only changes noted have been small changes in yield point. Titanium seems to undergo some embrittlement, with the tensile and yield strengths increasing while the reduction in area and ductility decrease. The changes were about 10 percent of the unirradiated values. Very little change was apparent in the impact properties of either metal.

Since it was well known that under certain conditions Zircaloy–2 may become embrittled by picking up hydrogen from a corrosion reaction, it was feared that a similar pickup might take place from the dissociated water present or from the corrosion in a homogeneous reactor. Hydrogen analyses and mechanical testing have produced no evidence of this; presumably it is prevented by the oxygen present in the solution.

It appears that zirconium and titanium undergo no significant changes in mechanical properties during very short irradiation under the proposed homogeneous-reactor conditions. However, much longer tests to higher fast-flux doses must be made in fuel solutions under reactor design conditions to confirm that neither damage by fast-neutron irradiation nor hydrogen pickup will have an important deleterious effect on the metals.

7.4.8 Radiation Effects on Pressure-Vessel Steels

The fast-neutron dose experienced by the pressure vessel of an aqueous homogeneous power reactor during its lifetime will be greater than 5×10^{18} neutrons/cm^2. Fast-neutron doses of this magnitude are capable of causing significant changes in the mechanical properties of pressure-vessel steels, such as a loss of tensile ductility, a rise in the ductile-brittle transition temperature, and a loss in energy absorbed in the notch-impact test in the temperature region where the steel is still ductile.

For several years, investigations of an exploratory nature have been carried out to determine the influence of radiation effects on pressure-vessel steels. Although it is not yet possible to give definitive answers to many questions, it has become apparent that radiation effects in steels depend upon a large number of factors and that the unusual properties of irradiated metals may force a reappraisal of standards used for predicting performance from mechanical-property data.

Changes in tensile properties of steels start to become evident at fast-neutron doses (>1 Mev) of 5×10^{18} neutrons/cm^2 and at doses of 1×10^{20} very large changes in properties are observed. The changes are reflected as decreases in uniform elongation and ductility and increases in yield and tensile strength. In some cases the yield strength even exceeds the fracture strength. Because of the loss of ductility care will have to be observed in using steels after such an exposure.

The effect of increasing the irradiation temperatures is to reduce the yield-strength increase, but the tensile-strength increase may be greater under the same conditions. The uniform elongation is usually greater for elevated temperatures of irradiation. In some cases the reduction of area is drastically reduced by elevated-temperature irradiations, and fracture has occurred without necking. Thus it is not clear whether elevated irradiation temperatures are always beneficial.

Changes in properties of the steel with irradiation dose are even more apparent when measured in impact-type tests. Increases in transition temperature (the temperature at which a change from ductile to brittle fracture occurs) of several hundred degrees have been found at doses approaching 1 x 10^{20}. In addition, decreases in the energy required for fracture, even in the ductile region, of over 50 percent were noted.

Preliminary results indicate that elevated irradiation temperatures invariably reduce the extent of radiation effects on the notch-impact properties, although the amount of reduction varies greatly between different steels of similar composition and heat treatment.

The following suggestions and recommendations for the selection of pressure-vessel steels that will be irradiated in service are based on the data obtained.

1. On the basis of tensile ductility (uniform elongation) steels of carbon content greater than about 0.2 percent are preferable.
2. The steel should be aluminum-killed to secure a fine-grain material, but it is not certain that a small-grain size *per se* is preferable to a large-grain size.
3. The processing and heat treatment should be carried out to attain the lowest possible transition temperature before the steel is put into service.
4. There is some tendency for alloy steels (particularly when heat treated to obtain a structure that is not pearlitic) to show more severe radiation effects than pearlitic steels. This is not to say that alloy steels are unsuitable; but there are insufficient data to choose between the various alloy steels.

Currently ASTM type A–212 grade B steel made to satisfy the low-temperature ductility requirements of ASTM A–300 specification is regarded as a good choice for reactor vessels. It is by no means certain that this is the best grade of steel to use, but there are other types that seem to be much less desirable. Such a steel, with only minor limitations on the operation, should be acceptable for test reactors. However, much more information is required before any steel can be used with assurance at high fast fluxes in a large power reactor.

8. CHEMICAL PROCESSING

The possibility of continuous processing of fuel and blanket materials for removal of fission and corrosion products and for rapid recovery of fissionable material is one of the potential advantages of homogeneous reactors. Major objectives of chemical processing are (1) to maintain a favorable neutron economy, (2) to reduce the biological hazards associated with the reactor, and (3) to contribute to the reliability and operability of solution-fuel reactors by removing precipitates that could interfere with heat transfer and fluid flow in the reactor and soluble contaminants that could contribute to solution instability.

8.1 CORE PROCESSING, SOLIDS REMOVAL

Studies of the neutron-poison contribution of fission-product elements formed in a homogeneous reactor from which krypton and xenon are being constantly removed showed that the buildup of neutron poisons in the system is chiefly due to rare earths. These rare-earth fission products may be divided into three groups on the basis of yield and cross section. One group, typified by Sm^{149} and Sm^{151} are produced in low yield (1.3% and 0.5%, respectively) and due to their high neutron-capture cross section (50,000 and 12,000 barns, respectively) reach a burnout equilibrium after a few days operation and contribute a constant poison effect to the reactor. Another group, characterized by such isotopes as Ce^{141}, may be produced in large yield (6.0% for Ce^{141}) but have a low cross section for neutron absorption. The third group is characterized by high yield and intermediate cross section (Nd^{143}; yield, 6.2%; absorption cross section, 290 barns) and over a period of several weeks of operation will build up a significant poison level. Studies of the behavior of these elements, as well as other fission- and corrosion-product elements, showed that many of them were only slightly soluble in uranyl sulfate–sulfuric acid solutions under conditions proposed for reactor operation, and a processing method based on solids removal was developed.

These elements were studied in detail, and devices for separating solids from liquid at high temperature and pressure were constructed and evaluated. Based on this work, a pilot plant to test the processing method and equipment was installed as an adjunct to the HRE–2.

8.1.1 Chemistry of Insoluble Fission and Corrosion Products

All the rare-earth sulfates, and yttrium sulfate, showed a negative temperature-solubility effect in all the solutions studied and a strong tendency to supersaturate the solutions. With the exception of praseodymium and neodymium, the positions of which are reversed, the solubility of the rare-earth sulfates, at a given condition of temperature and uranyl sulfate concentration, increased with increasing atomic number, with yttrium falling between neodymium and samarium. Typical solubilities are shown in Table 8.1 Increasing the uranyl sulfate concentration of a solution from 0.02 *m* to 0.04 *m* approximately doubled the amount of rare earth in solution. In 0.02 *m* UO_2SO_4 solution increasing the concentration of H_2SO_4 from 0.005 *m* to 0.01 *m* did not appreciably change the amount of rare-earth sulfate in solution at a given temperature. On the basis of only a few observations, substituting D_2O for H_2O in such solutions lowered the amount of rare earth in solution at 25–100° C by a factor of about ½.

TABLE 8.1.—SOLUBILITY OF VARIOUS RARE-EARTH SULFATES IN 0.02 *m* UO_2SO_4 −0.005 *m* H_2SO_4 AT 280° C

Salt	Solubility (mg/kg H_2O)	Salt	Solubility (mg/kg H_2O)
$La_2(SO_4)_3$	10	$Nd_2(SO_4)_3$	110
$Ce_2(SO_4)_3$	50	$Y_2(SO_4)_3$	240
$Pr_2(SO_4)_3$	170	$Sm_2(SO_4)_3$	420

The solubility of an individual rare-earth sulfate is reduced by the presence of other rare-earth sulfates. For example, in a particular simulated fuel solution the solubility of praseodymium sulfate at 280° C is 170 mg/kg when it is the only rare earth present, but is only 12 mg/kg when a mixture of rare earths containing only 6 percent $Pr_2(SO_4)_3$ and 94 percent other rare earths is used. Samples of the precipitating salts isolated from solution at 280° C have usually contained only rare-earth sulfates, but under special experimental conditions a mixed sulfate salt of neodymium and uranium has been observed.

Barium and strontium also show a negative temperature dependence, but not so strongly as do the rare earths; almost no solubility effect can be seen in increasing the temperature of precipitating solutions from 250 to 300° C. At 295° C in 0.02 *m* UO_2SO_4–0.005 *m* H_2SO_4 solution, the amount of barium sulfate in solution is 7 mg/kg H_2O; for strontium sulfate at 295° C the solubility is 21 mg/kg H_2O. Both the alkaline and rare-earth sulfates show a strong tendency to precipitate on and adhere to steel surfaces hotter than the precipitating solutions, and this property can be used to isolate and concentrate such elements from solutions at high temperatures.

Other fission- and corrosion-product elements hydrolyze at 250 to 300° C and precipitate, leaving very small amounts of the elements in solution. Iron (III) at 285° C has a solubility of 0.5 to 2 mg Fe/kg H_2O; and chromium (III), 2 to 5 mg/kg H_2O. At 285° C less than 5 ppm of zirconium or niobium remains in solution.

For some elements of variable valence, such as technetium, the amount of the element in solution will be determined by the stable valence state under reactor conditions. In general, the higher valence states resist hydrolysis better and remain in solution. Thus at 275° C in 0.02 *m* UO_2SO_4, Tc (VII) is reduced to Tc (IV) if hydrogen is present, and only 12 mg Tc/kg H_2O remains in solution. However, a slurry of TcO_2 in the same solution with oxygen present dissolves to give a solution at 275° C with a technetium concentration greater than 9 g/kg H_2O. The same qualitative behavior is observed with ruthenium. Selenium and tellurium in the hexapositive state also are much more soluble than when in the tetrapositive state.

8.1.2 Experimental Study of Solids Removal by Hydroclones

The maximum processing advantage to be realized by solids removal can be gained only if the soldis are separated from the fuel solution at a temperature not lower than the maximum reactor fuel-solution temperature. This is due to the inverse temperature-solubility relationships shown by the rare-earth sulfates. Also, advantage is to be gained if large amounts of solids are discharged from the reactor accompanied by only small amounts of fuel solution. Of the several devices capable of performing this type of operation the most promising appeared to be a solid-liquid cyclone separator called a "hydroclone."

In operation, a solids-bearing stream of liquid is injected tangentially into the wide portion of a small conical vessel. Solids concentrate in a downward-moving layer of liquid along the wall of the vessel and are discharged from the bottom of the clone. Partially clarified liquid leaves from the top of the clone through a vortex finder. Control of the underflow-overflow ratio is necessary for successful operation of the hydroclone, but mechanical control can be avoided by placing an appropriately designed vessel beneath the hydroclone to act as a receiver and accumulator of the solids discharged in the underflow. The driving force for the system is provided by a mechanical pump.

Factors influencing hydroclone design have been studied, and hydroclones designed for use in homogeneous reactors processing have been tested in the laboratory and on circulating loops. All tests have shown conclusively that such hydroclones can separate suspensions of insoluble sulfates or hydrolyzed materials from liquid streams at 250 to 300°C.

Only a fraction of the injected or naturally produced solids were collected in most of the loop tests. Competition from mechanisms such as deposition on pipe walls and gravity settling in semistagnant areas resulted in the disappearance of solids from suspension before they could be collected by the hydroclone. Material balances varied widely, but in most cases only 10–20 percent of the solids were collected in the underflow receiver. In all cases concentrations of solids in circulation were held to a few parts per million.

8.1.3 Experience with Operation of the HRE–2 Chemical Processing Plant

An experimental facility to test the hydroclone solids-removal process on a reactor was constructed as an integral part of HRE–2. A schematic flowsheet for the plant is shown in Figure 8.1. In operation a 1.3-gpm bypass stream from the reactor fuel system at 280°C and 1,700 psi is circulated through the high-pressure system, which consists of a heater to make up heat losses, a screen to protect the hydroclone from plugging, a 0.6-inch diameter hydroclone and underflow receiver, and a canned-motor circulating pump to make up pressure losses across the system. In order to ascertain reliably the amount of solids collected in the chemical plant, equipment is included in which the solids can be dissolved in sulfuric acid and then sampled.

In practice the high-pressure portion of the chemical plant is operated for a specified period of time at reactor temperature and pressure. At the end of the processing period the chemical plant is isolated from the reactor, cooled, and depressurized. The solids and solution contained in the underflow pot are removed and sampled, and the D_2O is recovered by evaporation. Dissolution in sulfuric acid is followed by sampling and transfer to storage after which the plant can be freed of light water and reincorporated into the HRE–2 reactor circuit. Fourteen such cycles have been accomplished without contaminating the reactor with H_2O or losing significant amounts of D_2O.

During operation of the HRT chemical plant the performance of the hydroclone has been practically the same as that observed on loop operations. In the first 2,670 hours of operating time with the HRE–2, 2.2 kg of corrosion-product solids were collected, which is about 10 percent of the solids calculated from corrosion data to have been produced in the core system. The overall average removal rate of 0.8 g/hr (compared with normal corrosion rates of ~ 3 g/hr) was augmented considerably by high removal rates during the first 200 hours of operation following a reactor shutdown. Solids flake off the piping as a result of thermal cycling or drying during the shutdown and are redistributed during the first few days of subsequent operation. In this initial period, rates varied from 0.6 up to 2.6 g/hr, but under all conditions, dropped to and remained consistently at 0.3 g/hr after 250 hours of reactor operation. The only factor which significantly affected removal rates was a reactor shutdown and startup. Two periods of high corrosion produced substantial quantities of solids at rates considerably above normal, but significantly the solids removal rate was not higher in those periods. Other variables, such as reactor power and total accumulated solids inventory, have not had a marked effect on removal rates.

Data from the hydroclone-plant operation were interpreted to indicate that the circulating-solids concentration is controlled more by the competing removal mechanisms than by the hydroclone. From this it follows that solids removal rates are proportional to processing

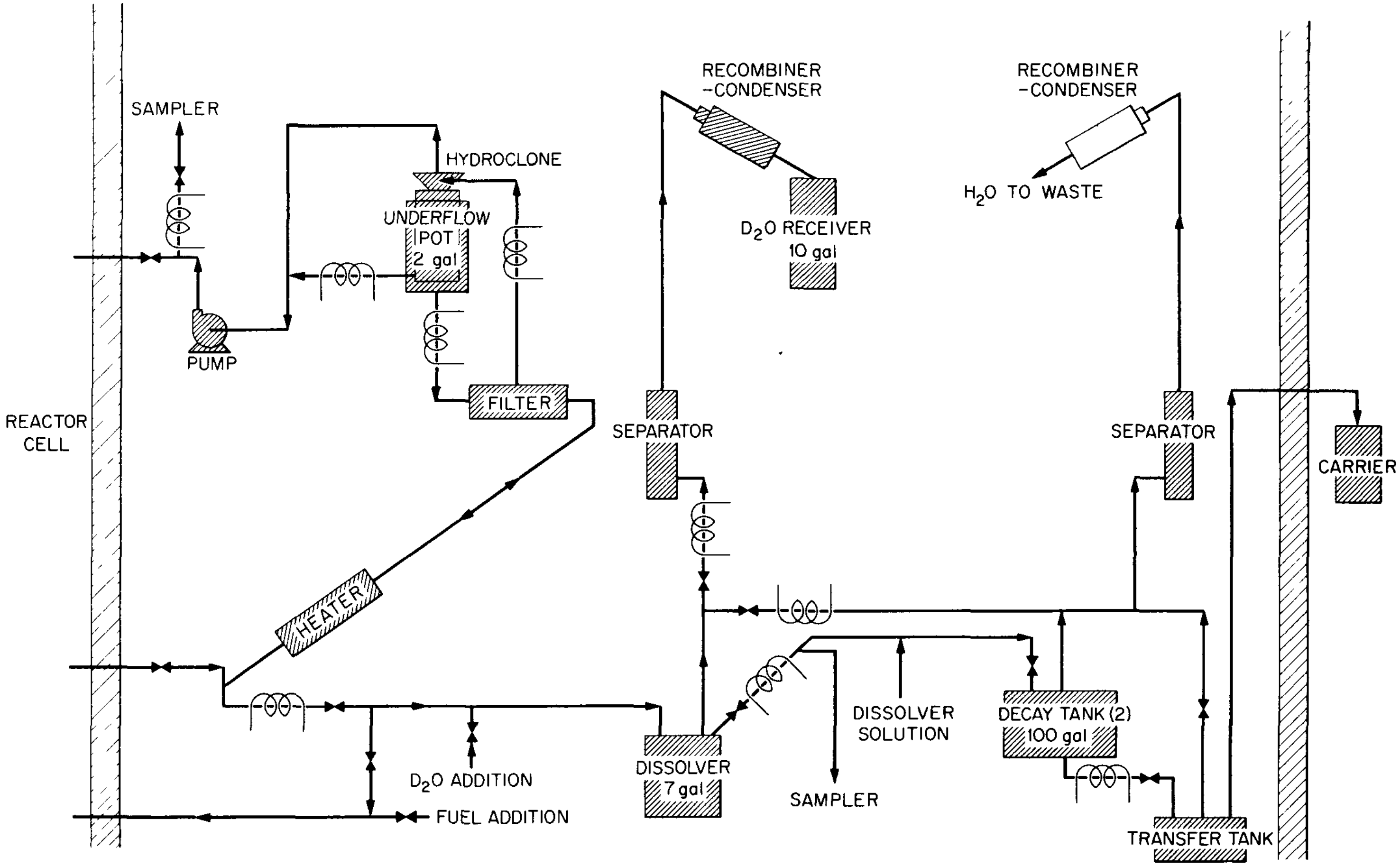


FIGURE 8.1—Schematic flow sheet of HRT chemical plant.

rates, and, within limits, removal rates can be increased by faster processing. A multiple-hydroclone assembly containing thirteen 0.6-inch hydroclones in parallel was designed, fabricated, and installed to test this interpretation. A primary flow of 10 gpm is circulated through the multiple clone, and the concentrated underflow stream (1.3 gpm) is routed to the original hydroclone for collection of solids. Removal rates should increase by a factor of only 3 to 4 since the flow rate through the 13 clones is only 10 gpm compared to 1.3 gpm with the single unit, and additional losses are incurred in the overflow stream from the single clone which is used as a final solids collector.

Data from the first two short runs with the multiclone unit gave indications that the predicted increase in removal was being realized. Approximately 300 g was collected in each of the runs, which were of 50 and 95 hours duration. The removal rates were 4 and 3 g/hr, compared with rates which varied from 0.6 to 2.6 g/hr in comparable runs with the single hydroclone. However, the real worth of the multiple-clone installation can be determined only after prolonged periods of stable reactor operation. In the event that this installation does not separate solids at a rate essentially equal to the rate of production, some alternative method must be found for removing them from the reactor.

8.1.4 Status of Solids Removal

Radiochemical data thus far obtained during operation of the HRE–2 chemical plant show that certain of the fission products do precipitate in the reactor and have been concentrated by the hydroclone in the chemical plant. The reactor has not operated long enough for the concentration of rare earths to build up to a level which will permit accurate spectrographic analysis, but indications are that they are less soluble than was previously estimated. Solids accumulation by the single hydroclone has not been fast enough to compete successfully with other parts of the reactor system, but the multiple-clone installation may prove to be more effective. In the event that it does not, other methods for solids removal, such as dissolution of solids and scale during maintenance periods, may be necessary. The data thus far obtained show clearly the need for careful consideration of chemical processing needs in the design of the reactor. The data also confirm the contention that solids separation, whether by chemical plant or deposition, can control the buildup of certain elements in the reactor.

8.2 CORE PROCESSING, SOLUBLES

While a solids removal scheme will limit the total amount of insoluble materials circulating through the reactor system, soluble elements will continue to accumulate in the fuel solution. Nickel and manganese from the corrosion of stainless steel and fission-produced cesium will not precipitate from fuel solution under reactor conditions until concentrations have been reached which could result in fuel instability or significant loss of neutrons. Several methods for limiting the buildup of soluble poisons in an aqueous homogeneous reactor have been investigated.

8.2.1 Solvent Extraction

Processing of the core solution of a homogeneous reactor by solvent extraction is the method presently available which has been thoroughly proved in practice. However, the amount of uranium to be processed daily is so small that operation of a solvent extraction plant just for core-solution processing would be unduly expensive. Therefore the core solution would normally be combined with blanket material from a thermal breeder reactor and be processed through a Thorex plant (discussed in Section 8.5.1). The uranium product from this process would certainly be satisfactory for return to the reactor; but since solid-fuel-element refabrication is not a problem with uranyl sulfate fuels, decontamination factors of 10 to 100 from various nuclides are adequate and some simplification of present solvent extraction schemes may be possible.

8.2.2 Uranyl Peroxide Precipitation

One process for decontaminating the uranium in D_2O for quick return to a reactor is based on the insolubility of UO_4. In this method, the hydroclone system is periodically isolated from the reactor and allowed to cool to 100° C. The hydrolyzed solids remain as such, but the rare-earth sulfate solids concentrated in the underflow pot redissolve upon cooling. The contents of the underflow pot are discharged to a centrifuge, where solids are separated from the uranium-containing solution and washed with D_2O, the suspension being sent to a waste evaporator for recovery of D_2O.

Uranium in the clarified solution is precipitated by the addition of either D_2O_2 or Na_2O_2. By controlling the pH and other precipitation conditions, a fast-settling precipitate can be obtained while less than 0.1 percent of the uranium remains in solution. The UO_4 precipitate is centrifuged or filtered, washed with D_2O, dissolved in 50 percent excess of D_2SO_4, and heated to 100° C, with a trace of copper and iron present, to destroy the remaining peroxide before returning the uranium to the reactor. Uranium losses consistently less than 0.1 percent and decontamination factors from rare earths, nickel, and cesium, respectively, of 10, 600, and 40 have been obtained in laboratory experiments.

Results of tests in a hot cell on a 5-cc sample of HRE-2 fuel solution were practically the same as obtained in cold laboratory experiments.

8.2.3 Electrolysis

The rate of processing of the uranyl sulfate solution from the core may be governed by the concentration of soluble contaminants permitted by solution-stability considerations and the rate of increase of nickel concentration by corrosion. In this event a reliable, inexpensive process for removing nickel would be useful.

Laboratory studies of the removal of nickel and manganese from uranyl sulfate—sulfuric acid solutions have shown that essentially all the nickel and manganese, along with the copper present in HRE–2 fuel solution, can be removed electrolytically from such solutions if mercury is used as the cathode. With solid-metal cathodes no manganese and only a small amount of nickel can be removed, and for a given cell the removal is more rapid and more complete in D_2O than in H_2O. Regeneration of the mercury for cathode use can be accomplished by treatment with various reagents, the best of which appears to be 1 *M* nitric acid containing 1.5 percent hydrogen peroxide, or by a slurry of mercurous sulfate or nitrate in the corresponding acid of 1 *M* strength. During electrolysis, hexavalent uranium is reduced to tetravalent uranium, and the rate of nickel removal appears to be affected by the valence-state distribution of the uranium. Reoxidation of the uranium to the hexavalent state prior to returning it to the reactor can best be accomplished with an oxygen-ozone mixture at 25° C. The procedures for the electrolysis and for cathode regeneration have been tested but not completely demonstrated with HRE–2 scale equipment.

8.2.4 Status of Solubles Removal

Concentrations of soluble fission and corrosion products in the uranyl sulfate solution fuel in a power-breeder reactor can be controlled by removing fuel in small amounts periodically, combining it with thoria from the blanket, and processing the mixture by solvent extraction methods in a Thorex plant. It is expected that the core fuels will be processed on a 100-day, or longer, cycle and that it will be done in this manner. The processes require very little additional development.

A UO_4 precipitation method and an electrolytic method have been shown to be promising for processing in D_2O on much shorter cycles if this proves to be necessary to control the concentrations of nickel or other soluble corrosion products. The methods have been investigated in the laboratory but require considerable additional development before they can be applied to reactor systems.

8.3 CORE PROCESSING, IODINE REMOVAL

Removal of iodine from the core solution of an aqueous homogeneous reactor is desirable for several reasons. Iodine would be a serious biological hazard in the event of an incident in which fuel solution escaped from the reactor system. Iodine–135 is the precursor of Xe^{135}, the removal of which is important in attaining a high breeding ratio in the reactor. A simple chemical removal of I^{135} could be an improvement in a large power reactor over the gas stripping methods used in HRE–1 and HRE–2. Iodine will poison platinum catalysts used for radiolytic-gas recombination in the reactor low-pressure system and may catalyze the corrosion of metals by the fuel solution; therefore its removal may contribute to successful reactor operations.

8.3.1 The Chemistry of Iodine in Aqueous Solutions

Iodine in aqueous solutions at 25° C can exist in several oxidation states. The stable species are iodide ion, I^-; elemental iodine, I_2; iodate, IO_3^-; and periodate, IO_4^- or H_5IO_6. The last of these exists only under strong oxidizing conditions, and is immediately reduced under the conditions expected for a homogeneous reactor fuel. Iodide ion can be formed from reduction of other states by metals such as stainless steel, but in the presence of the oxygen necessarily present in a reactor system it is readily converted to elemental iodine; this conversion is especially rapid above 200° C. Therefore the valence states of chief concern in reactor fuel solutions are elemental iodine and iodate, and under the conditions found in the high-pressure fuel system iodine is largely, if not all, in the elemental form.

Volatility of Iodine

Since the elemental state of iodine is predominant under reactor conditions, volatilization of iodine from fuel solution is the basis for proposed iodine-removal processes. The vapor-liquid distribution coefficient (ratio of mole fraction of iodine in vapor to that in liquid) for simulated fuel solution and for water at the temperatures expected for both the high-pressure and low-pressure systems of homogeneous reactor is given in Table 8.2.

TABLE 8.2.—VAPOR-LIQUID DISTRIBUTION OF IODINE

Solution	Distribution coefficient vapor/liquid	
	High pressure (260–330° C)	Low pressure (100° C)
Clean fuel solution (0.02 *m* UO_2SO_4—0.005 *m* H_2SO_4—0.005 *m* $CuSO_4$, 1–100 ppm, I_2)	7. 4	0. 34
Fuel solution with mixed fission and corrosion products	----------	2. 4
Water (pH 4 to 8, 1–13 ppm I_2)	0. 29	0. 009

A number of conclusions are evident from these data. Iodine is much more volatile from fuel solution than from water at either temperature. Fission and corrosion products appear to increase the volatility of iodine from fuel solution at 100° C. Other data show that increasing the temperature of fuel solution from 100 to 200° C. increases the volatility of iodine relative to that of water. No systematic variation of iodine volatility has been found by varying iodine concentration from 1 to 100 ppm or temperature from 260 to 330° C.

The volatility of iodine from simulated fuel solution has been verified by experiments in high-pressure loops by injecting potassium iodide solutions into the loop solution and measuring the rate at which iodine was removed from solution by a stream of oxygen. Within the accuracy of flow-rate measurements the vapor-liquid distribution coefficient obtained in the dynamic system agrees with the average value of 7.4 obtained in numerous static tests over the high-temperature range.

Oxidation State of Iodine at High Temperature and Pressures

While iodate ion is quite stable at room temperature, at elevated temperatures it decomposes according to the equilibrium reaction

$$4IO_3^- + 4H^+ \rightleftharpoons 2I_2 + 5O_2 + 2H_2O$$

The extent of this decomposition in uranyl sulfate solutions above 200° C. is not known with certainty since all observations have been made on samples that have been withdrawn from the system, cooled, and reduced in pressure before analysis, but the data indicate that the equilibrium is in favor of elemental iodine. Iodine/iodate ratios ranging from 1 to 70 have been observed in various samples taken from both static and dynamic systems, with the most frequently observed values being in the range of 7 to 10. Although the iodine in such samples is principally elemental, some iodate is always present, possibly because of reversal of the iodate decomposition as the temperature drops in the sample line. Such measurements therefore give an upper limit to the iodate content of the solution. Periodate introduced into uranyl sulfate solution at elevated temperatures is reduced before a sample can be taken to detect its presence. Iodide similarly disappears if an overpressure of oxygen is present, although iodide to the extent of 40 percent of the total iodine has been found in the absence of added oxygen.

In loop experiments the data for decomposition of iodate corresponded to first-order reaction kinetics with a rate constant of 6.2 min^{-1}. Iodate contents averaging about 10 percent of the total iodine have been observed in 0.04 m UO_2SO_4—0.005 m $CuSO_4$—H_2SO_4 solution, rapidly sampled from a static bomb through an ice-cooled titanium sample line. The observed iodate content was not affected by varying (1) the free sulfuric acid concentration between 0.02 and 0.03 m, (2) the temperature between 250 and 300° C., or (3) exposure to cobalt gamma radiation at an intensity of 1.7 watts/kg.

Oxidation State of Iodine at Low Temperature

At 100° C, iodate decomposition and iodine oxidation are both slow to reach equilibrium, and while both states can persist under similar conditions iodate is the more stable valence state. Under the influence of radiation, iodide is oxidized, iodine is oxidized if sufficient oxygen is present, and iodate is reduced temporarily. At the start of irradiation, iodate is reduced, but in the presence of sufficient oxygen, iodine is later reoxidized to iodate, probably by radiation-produced hydrogen peroxide which accumulates in the solution. Finally, a steady state is reached with a proportion of iodate to total iodine which is independent of total iodine concentration in the range of 10^{-6} to 10^{-5} m and temperatures from 100 to 110° C but which is strongly dependent on both uranium and sulfuric acid concentrations and on the hydrogen/oxygen ratio in the gas phase. When the temperature is increased to 120° C, there is a marked decrease in iodate stability under all conditions of gas and solution composition.

8.3.2 Removal of Iodine From Aqueous Homogeneous Reactors

It is clear from the preceding data that under the operating conditions of a homogeneous power reactor, iodine in the fuel solution should be mainly in the volatile, elemental state and could, therefore, be removed from the fuel solution by stripping into a gas stream. Iodine could then be removed from the gas stream by trapping in a solid absorber, or by contacting the gas with a suitable liquid.

As a solid absorber, silver supported on alundum is a very effective reagent for removing iodine from gas or vapor systems, although its efficiency is considerably reduced at temperatures below 150° C. In one in-pile experiment 90 percent of the fission-product iodine was concentrated in a silvered-alundum pellet suspended in the vapor above a uranyl sulfate solution. Silver-plated Yorkmesh packing is effective for removing iodine from vapor streams in the range 100 to 120° C. Contact between these absorbers and fuel solution must be avoided since silver is appreciably soluble in UO_2SO_4–H_2SO_4 solutions at 120° C.

A stripping scheme has been considered which makes use of a circulating oxygen stream. Iodine is scrubbed from the fuel solution by gas in one contactor and then stripped from the gas by heavy water in a second contactor. This water is let down to low pressure and either stored for decay or processed to remove iodine. Although solutions containing sodium hydroxide, sodium sulfite, or silver sulfate are much more effective than pure water, their use would require elaborate provisions for preventing entrainment in the gas and subsequent contamination of the fuel solution. Also, a plant based on the data shown in Table 8.2 would discharge such a small volume of iodine-containing solution that further reduction in volume probably would not be advisable.

Iodine Removal in HRE–2

A silvered-Yorkmesh absorber was installed in the HRE–2 low-pressure system for removing iodine from the vapor stream before it reaches the recombiner catalyst. The purpose of the installation is to prevent poisoning of the catalyst and to obtain information about the removal of iodine from a reactor.

Examination of the iodine data obtained during operation leads to two opposing conclusions. Quantitative measurement of the amount of iodine present in the fuel solution indicates that iodine is being removed from the solution on a 1- to 2-hour processing cycle time. This indicates that essentially all the iodine in the fuel solution transferred to the low-pressure system is being caught in the silver absorber unit. However, measurement of I^{133}/I^{131} activities in the fuel solution indicate that iodine in the reactor is 20 to 24 hours old and is therefore being removed by the silver bed with only a low efficiency.

The difference may be attributed to uncertainties in both the chemical and nuclear behavior of the tellurium precursors of iodine. These uncertainties are the chemical behavior of tellurium after sampling and prior to radiochemical separation and the values of the branching ratios of the tellurium precursors that should be used in calculating the steady-state iodine concentration in the reactor. A few laboratory experiments have shown that iodine is adsorbed by or reacted with corrosion-product solids and that at 270° C exchange of such iodine with iodine in solution occurs rapidly, but no data have been obtained at lower temperatures. Holdup of iodine by corrosion solids or scale in the reactor could also account for the apparently longer residence time of iodine in the reactor.

8.3.3 Status of Iodine Removal Processing

Laboratory experiments, both static and dynamic, with and without radiation, have shown that a processing scheme based on the volatility of iodine from fuel solutions at elevated temperature is possible. This scheme has been verified on the HRE–2 mockup loop by using a silver absorber unit for removing iodine from a gas stream. Iodine is being removed from the reactor in a similar manner. Uncertainties about iodine behavior in HRE–2 should be resolved as more specific information is obtained from reactor samples.

8.4 CORE PROCESSING, GAS REMOVAL

In the operation of HRE–2, fuel solution is let down continuously from the high-pressure system to the low-pressure system. In the process, dissolved oxygen escapes from the fuel solution, carrying with it gaseous fission products such as iodine, krypton, and xenon, thereby providing a means for removing the undesirable Xe^{135} isotope from the reactor. Recirculation of the oxygen to the high-pressure system would be difficult; so the gas stream, chiefly oxygen, is vented to the atmosphere. In order to prevent the release of radioactive krypton and xenon to the atmosphere, the gas stream is passed through a series of charcoal-filled traps. The traps are sized to provide holdup time sufficient that the effluent gas contains only oxygen, Kr^{85}, inert krypton and xenon isotopes, and insignificant amounts of other active isotopes. Similar systems are proposed for large reactors. If necessary, Kr^{85} could be concentrated from the gas stream and bottled for long-term storage, although no specific development for such a process has been undertaken.

8.4.1 Laboratory Studies of Fission-Product Gas Adsorption

Evaluation of adsorber materials based on experimental measurements of the equilibrium adsorption of krypton or xenon under static conditions has been completed. Charcoals generally have the highest adsorptive capacities, but other materials such as molecular sieves and silica gel have sufficient capacity (25% and 10%, respectively, of the capacity of Columbia G charcoal) to be considered as possible adsorbents. The capacity of all three types of adsorbers was decreased by adsorbed water. Charcoal could be freed of water by heating about 100° C. in a dry gas stream, but regeneration of the sieves materials was not possible at 100° C.

A radioactive-tracer technique was developed to study the adsorption efficiency (holdup time) for small, dynamic laboratory-scale adsorber systems. This technique consists of sweeping a brief pulse of Kr^{85} through an experimental adsorber system, with an inert gas such as oxygen or nitrogen, and monitoring the effluent gases for Kr^{85} activity. The activity in the gas stream vs. time after injection of the pulse of Kr^{85} gives an experimental elution curve, from which various properties of an adsorber material and adsorber system may be evaluated.

Among the factors which influence the adsorption of fission-product gases from a dynamic system are (1) adsorptive capacity of adsorber material, (2) temperature of adsorber material, (3) volume flow rate of gas stream, (4) adsorbed moisture content of adsorber material, (5) composition and moisture content of gas stream, (6) geometry of adsorber system, and (7) particle size of adsorber material.

The temperature of the adsorber material is of prime importance. The lower the temperature, the greater will be the adsorption of the fission gases; and therefore longer holdup times per unit mass of adsorber material will result. At a given temperature, the average holdup time is inversely proportional to the volume flow rate of the gas stream. If the volume flow rate is doubled, the holdup time will be decreased by a factor of 2. Adsorption of Kr^{85} is decreased by the presence of CO_2, and in a pure CO_2 atmosphere the holdup time for Kr^{85} is one-half the value observed in pure oxygen.

The particle size of the adsorber material is important for ensuring intimate contact between the active surface of the adsorber material and the fission gases. A system filled with large particles will allow some molecules of fission gases to penetrate deeper into the system before contact is made with an active surface, while the pressure drop across a long trap filled with small particles may be excessive. Material between 8 and 14 mesh in size is satisfactory from both viewpoints. The relationship between trap geometry and the number of theoretical stages in the system is being studied.

8.4.2 HRE–2 Fission-Product-Gas Adsorber System

The HRE–2 uses a fission-product-gas adsorber system containing Columbia G activated charcoal. Oxygen, contaminated with the fission-product gases, is removed from the reactor, dried, and passed into this system, and the effluent gases are dispersed into the atmosphere through a stack.

The adsorbed system contains two units filled with activated charcoal and connected in parallel to the gas line from the reactor. Each unit consists of 40 feet of ½-inch pipe, 40 feet of 1-inch pipe, 40 feet of 2-inch pipe, and 60 feet of 6-inch pipe connected in series. The entire system is contained in a water-filled pit, which is buried underground for gamma shielding purposes. Each unit is filled with approximately 520 pounds of charcoal. The heat due to beta decay of the short-lived krypton and xenon isotopes is minimized by an empty holdup volume composed of 160 feet of 3-inch pipe between the reactor and the charcoal adsorber system.

Before the adsorber system was placed in service, its efficiency was tested under simulated operating conditions. A pulse of Kr^{85} (25 millicuries) was injected into each unit of the adsorber system and swept through with a measured flow of oxygen. In this way the krypton holdup time was determined to be 30 days at an oxygen flow rate of 250 cc/min per unit, in substantial agreement with predictions based on laboratory data from small adsorber systems. The holdup time for xenon is larger than that of krypton by a factor of 12.

Temperature rise in the beds during reactor operation was found to be considerably less than was calculated on the basis of operating conditions, known holdup times, and fission-product decay schemes. A temperature rise of 100° C was expected in the front sections, but a maximum rise of only 10°C has been noted. This difference was at least partly resolved by recent laboratory tests which have shown that the thermal conductivity of a packed bed of the charcoal used is a factor of 4 higher than the handbook value used in design calculations.

While originally designed for flows of only 250 cc/min through each adsorber, it has been possible to operate at flows up to 1.5 liters/min with release of only minute quantities of activity other than Kr^{85}. A minor activity release followed five days after the accidental ignition of one bed by the recombination of D_2 and O_2 vented from the reactor. Studies of the hazards of such an event, made prior to the actual fire, had shown that a fire could easily be stopped by halting flow of gas and the activity release would not be great. Analysis of the gas stream from the bed indicated that about 10 pounds of charcoal had been consumed, and after a 2-week shutdown to allow for radioactive decay of nuclides near the exit the bed was used again, with no deleterious effects.

8.4.3 Status of Fission-Gas Disposal

Laboratory data, coupled with HRE–2 operating experience, indicate that a charcoal gas-absorption system could be designed with confidence for any projected homogeneous reactor. The ultimate disposal of Kr^{85} may be a problem with large power reactors under some conditions, and there needs to be devoloped a satisfactory method for such disposal.

8.5 THORIUM OXIDE BLANKET PROCESSING

At present the only practical method available for processing irradiated thorium oxide is conversion of the oxide to a natural water-thorium nitrate solution and treatment by the Thorex process. Although this method is satisfactory, it will be expensive unless one plant can be built to process thorium oxide from several full-scale power reactors. Therefore, more economical methods for reprocessing ThO_2 have been sought which could be incorporated into the design and operation of a single power station. Such new methods would, ideally, reprocess the ThO_2 without dissolving, thereby avoiding the need for reconstituting solid ThO_2 after processing. Some very brief scouting-type experiments have indicated some possible alternatives.

8.5.1 Thorex Process

The Thorex process has been developed to separate thorium, U^{233}, fission-product activities, and Pa^{233}; to recover the thorium and uranium as aqueous products suitable for further direct handling; and to recover isotopically pure U^{233} after decay-storage of the Pa^{233}. The chemistry of the Thorex process has been exhaustively studied, and the flowsheet, which includes two solvent-extraction cycles for thorium and three solvent-extraction cycles plus ion exchange for the uranium, has been thoroughly demonstrated in pilot-plant operation. The only modification needed for homogenous reactors is in the dissolution and feed preparation step.

In the feed preparation step, the small amount of uranyl sulfate solution which has been withdrawn from the reactor core for complete cleanup and the thorium oxide from the blanket system, freed of D_2O and suspended in ordinary water, would be fed into the dissolver tank. The solvent would be 8 *N* nitric acid containing catalytic amounts (0.04 *N*) of hydrofluoric acid. After dissolution the feed would be adjusted to Thorex specifications.

After the Thorex treatment and prior to return to an aqueous homogeneous reactor, the decontaminated uranium would probably be precipitated as the peroxide, washed free of nitrate, and then dissolved in D_2SO_4 and D_2O. Product thorium would be converted to thorium oxide. Although the activity in both the uranium and thorium product obtained after processing short-cooled material might be higher than would be permitted were the materials to be used in fabrication of solid fuel elements, the chemical operations necessary to convert these materials to a form suitable for use in a homogeneous reactor presumably can be performed remotely, but such operations remain to be demonstrated.

8.5.2 Alternative Processing Methods

Experiments have shown that both the protactinium and uranium produced in ThO_2 particles by neutron irradiation are rather uniformly distributed throughout the mass of the ThO_2 particle, and migration of such ions at temperatures up to 300° C is extremely slow. However, calculations show that the recoil energy of fragments from U^{233} fission is sufficiently large to eject most of them from a particle of ThO_2 not larger than 10 μ in diameter, and this behavior may offer the means of separating fission and corrosion products from a slurry of Tho_2 without destroying the oxide particles. Success of such a separation would depend on being able to remove adsorbed fission- and corrosion-product elements from the surface of ThO_2.

Experiments have shown that trace quantities of Zr^{95}, Nd^{147}, Y^{91}, and Ru^{103} are so strongly adsorbed by ThO_2 in aqueous slurry at 250° C that they cannot be removed by boiling dilute nitric or sulfuric acid at atmospheric pressure. The adsorption of macroscopic amounts of such elements as uranium or neodymium on ThO_2 at 250° C is influenced by the nature and extent of the surface area available. This cation adsorption on ThO_2 can be decreased by coslurrying the ThO_2 with another oxide which will adsorb fission products much more strongly than ThO_2 and which can then be separated easily from ThO_2. In a mixture of PbO_2-ThO_2, more than 99 percent of the cations added to the slurry was adsorbed on the PbO_2. Addition of dilute nitric acid to the ThO_2-PbO_2 slurry completely dissolved the PbO_2 and the cations adsorbed on it without disturbing the ThO_2.

Although cations adsorbed on ThO_2 at 250° C are so tightly held that dilute nitric or sulfuric acid at boiling temperature will not remove the adsorbed material, they can be desorbed by refluxing the ThO_2 in 4 *M* HNO_3 containing 1.5 percent H_2O_2. A sample of irradiated, 1,600° C-fired thoria was refluxed for 30 minutes with 4 *M* HNO_3 and then 4 *M* HNO_3 containing 1.5 percent H_2O_2. Thirty-six percent of the U^{233}, 40 percent of the Pa, and only 0.2 percent of the thoria were dissolved in the first acid leach. The nitric acid-peroxide leach dissolved an additional 52, 35, and 36 percent of the U^{233}, Pa, and Th, respectively. Sixty-five percent of the gross gamma and beta activities were removed from the solid by the two acid leaches (70–80 percent of the Sr, Zr, Cs, Fe; 58 percent of the Cr; 47 percent of the Nb; and 25 percent of the Ni). Thirty percent of the Cs and 97 percent of the Ru appeared on the residual solids. If 1,600° C-fired ThO_2 is used, this treatment will dissolve only a few percent of the slurry particles, but a 650° C-fired oxide would be 90 percent dissolved.

8.5.3 Status of ThO_2 Slurry Processing

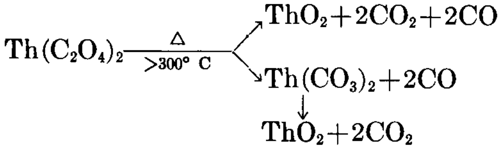
The Thorex process is a proven method for processing the blanket material from a thermal breeder reactor. Results of laboratory experiments indicate that it may be possible to leach U^{233} and Pa^{233} from ThO_2 and to eliminate the dissolution and refabrication of the slurry particles.

8.6 THE PREPARATION OF SLURRY OXIDES

Oxide preparation is an essential part of the overall effort to develop aqueous oxide slurries for homogeneous reactor use. The immediate objective is to prepare thorium oxide in a form which in aqueous suspension has good handling characteristics in engineering systems and is suitable for reactor experiments. The long-range objective is to develop economical methods of preparing both thorium and thorium-uranium oxide for use as aqueous blanket and fuel slurries in homogeneous reactors.

8.6.1 Thorium Oxide from Thorium Oxalate

The principal method of preparing thorium oxide for use in aqueous slurries has been the thermal decomposition of the oxalate. Thorium oxalate, precipitated from thorium nitrate solution, is crystalline, and is easy to wash and filter; the oxide product is readily dispersed as a slurry. In addition, the oxide particle resulting from oxalate thermal decomposition retains the relic structure of the oxalate, and hence the particulate properties are determined by the precipitation conditions. The mechanism by which the thermal decomposition takes place has been quite widely investigated. The following is the mechanism proposed by D'Eye and Sellman for the thermal decomposition:



$$Th(C_2O_4)_2 \xrightarrow[>300^\circ\ C]{\Delta} \begin{cases} ThO_2 + 2CO_2 + 2CO \\ Th(CO_3)_2 + 2CO \\ \quad \downarrow \\ ThO_2 + 2CO_2 \end{cases}$$

Thorium oxide is being produced as cubic crystals in a pilot plant according to the flowsheet in Figure 8.2. Solutions 0.7 to 1 *M* in thorium nitrate and oxalic acid are mixed in an agitated tank with controlled temperature, addition rate, and order of addition. The slurry of precipitated thorium oxalate is digested for 6 hours at 85° C and filtered. The oxalate cake is then washed, air-dried, and tray-calcined at 650° C, and the resulting oxide is calcined a second time at 1,600° C. The thorium oxide product contains about 10 percent of particles larger than 5 μ. These overproduct has an average particle size of 1 to 3 μ and contains only 1 or 2 percent of particles greater than 5 μ and 2 percent or less of the particles under 0.5 μ. This material is then refired at 650° C to decompose the oxalic acid dispersant before being used in engineering studies.

Oxide particles formed by the thermal decomposition of thorium oxalate retain the shape and size characteristics of the starting oxalate materials. Firing temperature up to 1,600° C does not cause a change in the particulate properties but does decrease the surface area (mostly internal) to about 1 m^2/g (650° C-fired materials have 20–35 m^2/g of surface area). The high-fired oxide has handled well in high-temperature engineering loop tests at slurry concentrations as high as 1,500 g Th/kg D_2O. Removal of the oversize particles has decreased the erosive attack on loop components. Engineering experience with slurries of oxide prepared similarly but without a digestion period and with a final firing at 800° C showed them to be unsuitable for blanket use because of the extremely high yield stresses at concentrations greater than 750 g Th/kg D_2O and an occasionally bad caking characteristic. The 6-hour digestion period and firing at 1,600° C appear, in large part, to have removed or substantially diminished these undesirable properties. At concentrations less than 750 g Th/kg D_2O the materials fired at less than 1,600° C appear suitable for use.

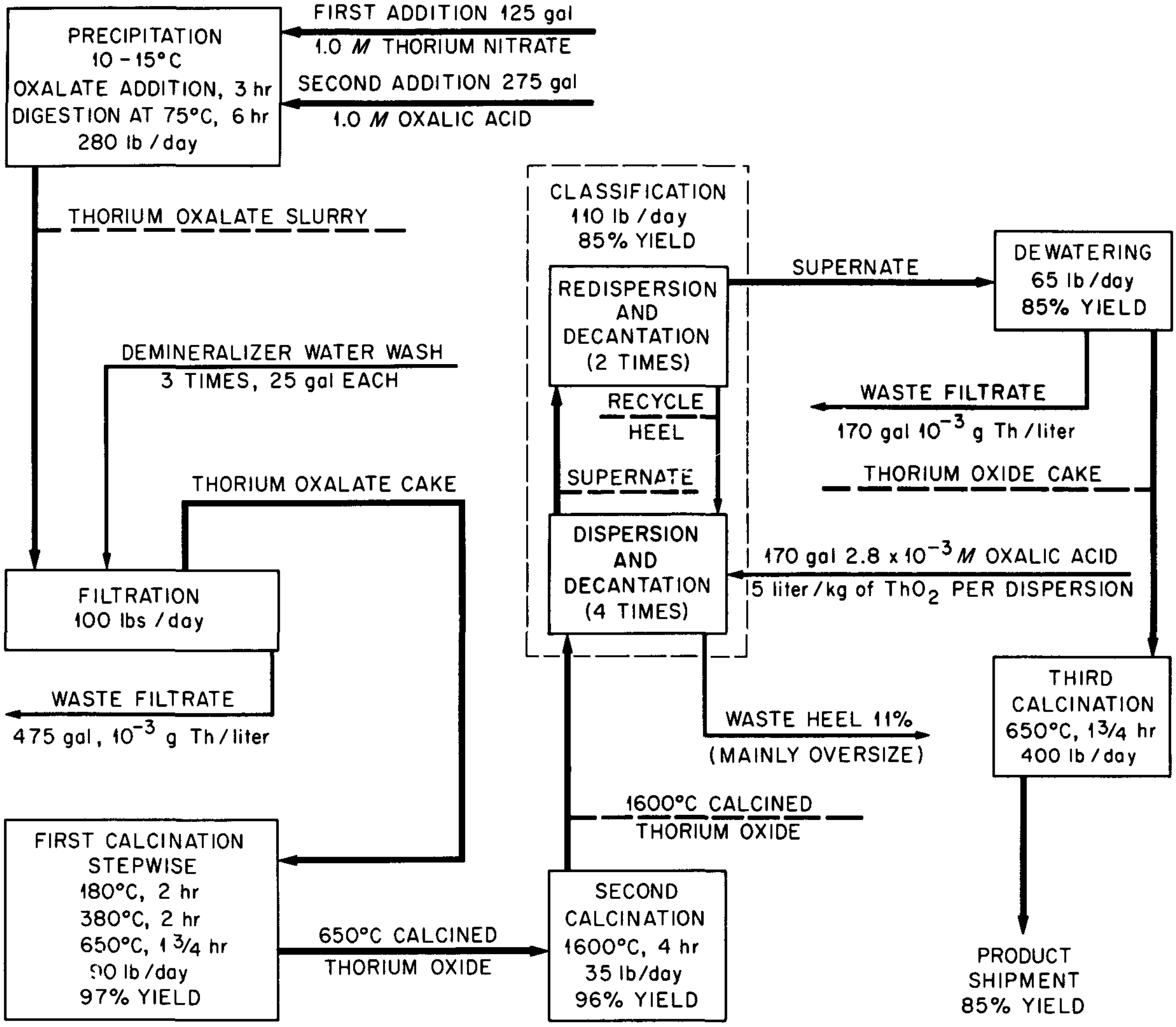


FIGURE 8.2—Thorium oxide pilot plant chemical flowsheet. Percent yields based on initial thorium input.

8.6.2 Thorium-Uranium Oxides

Thorium-uranium oxides of controlled particle size have been prepared by an adaption of the oxalate preparation method and by adsorption of uranium on preformed thoria solids and subsequent firing. In the former method, thorium-uranous oxalate was precipitated from thorium nitrate solution by the addition of an oxalic acid—ammonium oxalate—uranous oxalate solution. The mixed oxide is prepared by thermal decomposition of the oxalate mixture. In the latter method, uranyl carbonate was precipitated on preformed thoria solids from an ammonium uranyl carbonate solution (by heating a slurry of ThO_2 in the solution at 90° C). The uranium was incorporated in the solid by subsequent firing at 1,000° C. Particle size was controlled in the oxalate method by controlling the temperature, precipitation rate, and reagent concentration during precipitation. The product from the latter method retained the particulate properties of the thorium oxide used. The upper firing temperature which could be used in the preparation of mixed oxides by either method was determined by the amount of uranium. Sintering temperatures were as low as 1,300° C for a mixed oxide with a U/Th ratio of 0.005 and 1,000° C for a U/Th ratio $\geqq 0.05$.

For the production of mixed oxide by the coprecipitation method with U/Th ratio of 0.05, total precipitation times of 45–60 minutes, precipitation temperatures of 30–50° C., and the use of 0.5 *M* thorium nitrate and oxalic acid gave mixed oxides of average particle sizes between 1.6 and 4.2 μ. With 0.7 *M* reagents the average particle sizes were 1.1 to 2.0 μ. The production of mixed oxides containing U/Th >0.05 by this method was difficult, and uranium losses resulting from oxidation of the uranium oxalate during precipitation were hard to control. Uranium losses were minimized most effectively by metering in the uranous ammonium oxalate spike through a jet mixer into the oxalic acid precipitating reagent just upstream from the point of addition to the thorium nitrate solution and carrying out the precipitation as quickly as possible.

Thorium-uranium oxides with U/Th ratios from 0.005 to 0.33 were readily prepared by the adsorption method. In a typical preparation, 650° C-fired thorium oxide was slurried in ammonium uranyl carbonate solution (solubility $\sim$0.15 *m*) and the solution was boiled until all the uranium had deposited on the thoria. The solids were filtered, washed, and refired. When a 1,000° C-fired sample was autoclaved at 300° C for 24 hours as an aqueous slurry with an oxygen overpressure, the recovered supernatant contained only 0.2 percent of the total uranium, and refluxing the recovered solids for 1 hour with 8 *M* HNO_3 removed only an additional 0.07 percent. That the uranium was distributed uniformly in the solid was shown by successive refluxing with 8 *N* HNO_3, 4 *N* HNO_3 containing 5 percent H_2O_2, and 4 *N* HNO_3 containing 10 percent H_2O_2. The thorium dissolved in the sucessive leaches were 0, 25, and 40 percent, respectively, and the uranium-to-thorium ratios in the acid leaches and final solids were 0.1, 0.13, 0.12, and 0.09.

8.6.3 Alternative Preparation Methods

Other methods of preparing both pure thorium oxides and mixed oxides for slurry use were also investigated in the search for improved preparation methods. Thorium oxides prepared by the more expensive hydrothermal decomposition of thorium oxalate and the thermal decomposition of thorium formate did not appear to offer any advantages over the oxide prepared from the oxalate. Direct calcination of thorium hydroxide or thorium nitrate did not appear to be suitable. Micron-size thorium and thorium-uranium oxides were also prepared by the hydrothermal decomposition of aqueous nitrate solutions at 300° C.

An interesting method for producing either pure or mixed oxide was by the flame calcination of nitrate solutions in alcohol, developed first by Hansen and Minturn and then at ORNL. Spherical thorium-uranium-aluminum oxides with a U/Th ratio of 0.08 and containing alumina concentrations of 2.5 to 10 wt percent were prepared by this method using reflected-flame temperatures of 800–1,500° C. With 0 or 1 wt percent alumina the products were random-shaped, 1- to 3-μ aggregates.

Cubic particles 1 to 20 μ in average size were prepared by the addition of certain bi- or polydentate organic compounds, principally amines, to the oxlate precipitation system, which caused the precipitated thorium oxlate to grow on digestion into square-faced more-or-less-cubic particles whose characteristics were essentially retained in the fired product. The reagents investigated, in the order of effectiveness, were versene>triethanolamine>propylenediamine>ethylenediamine>citric acid>pentaerythritol>guanidine>urea.

Thoria microspheres with particles from 3 to 40 μ were prepared by gel techniques in which a thoria sol was coagulated with hexamethylene tetramine solution and the beads were formed in oil, washed, dried, and calcined at 1,000° C. A second method of sphere preparation currently under development forms the beads by jetting a sol into isopropyl alcohol. The latter method appears capable of producing smaller, more uniform particles, and is less time consuming.

8.6.4 Status

Thorium oxide of controlled particle size which appears suitable for use in a slurry blanket has been prepared by precipitating thorium oxalate under controlled conditions, firing the oxalate at 1,600° C, and classifying to remove oversized particles. Thorium-uranium oxides of controlled particle size have been prepared by adaptation of the oxalate method and by adsorbing uranium on preformed thoria solids and firing to incorporate the uranium in the solid. Spherical thoria and thoria-urania particles have been made in small quantities by flame calcination of nitrate solutions and by formed-gel techniques. Improvements to obtain more economical preparation methods, such as reduction of the final firing temperature and elimination of some of the process steps, are being sought. Materials have not been produced under conditions of remote operation required for a power-breeder plant.

9. ENGINEERING DEVELOPMENT

Aqueous homogeneous reactors are similar in many respects to pressurized-water, solid-fuel reactors; however, the use of uranyl sulfate solution and thoria slurry fuels and the high radiation levels in all primary systems and in many of the auxiliaries impose special requirements on the engineering of homogeneous reactors. Homogeneous reactor technology borrows heavily from pressurized-water reactor technology, but the two are different enough that extensive development of reactor equipment and systems is necessary. The work has been aimed primarily at satisfying the requirements of reactor experiments. Very little has been done on large-scale reactors.

In the engineering development program individual components are tested in order to obtain information for design use and for verification of adequate performance. Circulating systems (loops) are constructed and operated in order to study the handling of the fluids, especially of slurries which exhibit unusual properties, and the performance of equipment. Knowledge gained from component tests and loop operation is applied to the development of systems which contain many prototype components in flowsheets approaching a reactor flowsheet in complexity. Finally, methods of maintenance are developed for reactor systems. The work includes continuing improvement of existing technology as well as development of new technology.

9.1 DEVELOPMENT OF REACTOR COMPONENTS

The reliability of equipment for handling radioactive fuel solutions and suspensions is especially important in homogeneous reactors, because the residual radioactivity of such equipment after shutdown of the reactor precludes direct maintenance. Moreover, the possibility of failure of individual components is increased by the corrosive or erosive nature of the media being handled and the temperature fluctuations encountered during startup and shutdown operations. The technical feasibility of circulating-fuel reactors is so dependent on the behavior and reliability of mechanical components that there is little likelihood that large-scale plants will be operated before the performance of each piece of equipment has been adequately demonstrated. In this regard, values, feed pump, mechanical joints, and remote-maintenance equipment for large-scale plants present the most difficult development problems.

The component development work has been directed primarily toward equipment for use with the solution fuels. Slurry fuels have not been used in either of the reactor experiments; so the slurry equipment problems have received less attention. Much of the solution-fuel technology can be applied to slurries although additional difficulties such as the settling tendency, the non-Newtonian fluid flow behavior, and the erosiveness of slurries must be taken into consideration.

9.1.1 Core and Blanket Vessel

Core Hydrodynamics

Fluid flow tests with water at room temperature have been conducted on a variety of spherical vessels simulating reactor cores. A spherical vessel has a high strength-to-wall-thickness ratio, important in obtaining maximum strength with a minimum of structural material, and high power-density-to-total-power ratio, important in investigating power density effects at low total power inexperiments. The goal of the development work is to obtain a core in which the following criteria are satisfied:

1. Heat removal from all points must be rapid and orderly to prevent hot spots from being generated.
2. Gases and solids which are formed or circulated into the core must not accumulate there.
3. The pressure drop should be low.
4. The core tank should be maintained at a comparatively low temperature to prevent excessive corrosion.

The investigations included (1) the use of flow models in the determination of residence time and flow distribution by dye injection, solution conductivity, and solids and gas addition techniques; (2) measurement of pressure distribution and in some instances velocity distribution; (3) measurement of local heat transfer coefficients in some vessels, and (4) theoretical studies of some types of flow in spherical vessels.

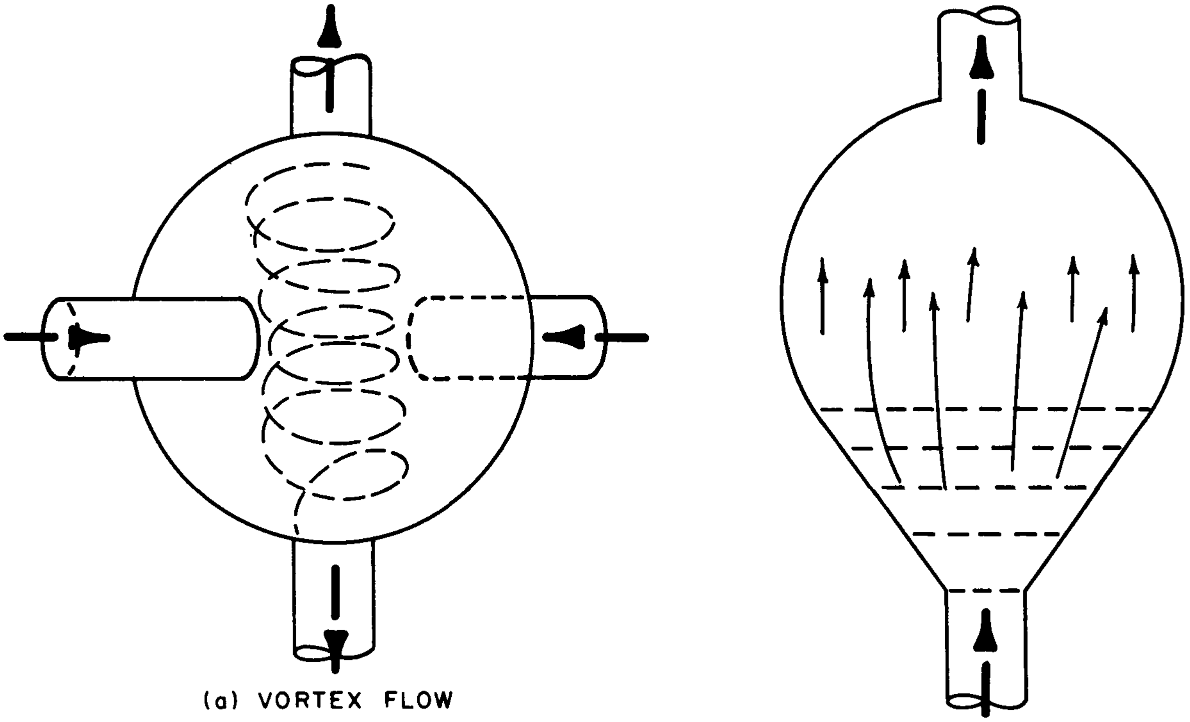
An 18-inch-diameter rotational-flow core was developed for HRE-1. It operated satisfactorily at average power densities as high as 32 kw/liter. This type of core design in the form shown in Figure 9.1a was then investigated for use in large reactors. Fluid is introduced into the vessel tangentially at the equator and removed through the center of a vortex at the poles. The temperature increases gradually in the direction of the central axis, which is at outlet temperature. If gas is present the bubbles are centrifuged into and removed through a void which forms along the central axis. Models in sizes from 6 inches to 8 feet in diameter were tested with flows as high as 50,000 gpm in the large model.

The tests indicated that the pressure drop through a large reactor would be undesirably high. Installation of a large core tank appeared to present enough difficult problems that this type of core design was abandoned. However, with this core, cooled fluid flows along the core tank at high velocity. Experience has shown that these features are important for solution-fuel reactors; so the design may be considered again.

A straight-through-flow core (Fig. 9.1b) was used in HRE-2. Fluid enters through a conical diffuser containing perforated plates and flows upward through the vessel in smooth slug flow. The metal wall is cooled by convection or by boiling. This design appeared to be satisfactory in tests of 32-inch-diameter, 400-gpm models and in 48-inch-diameter 4,000-gpm models prior to its use in HRE-2. Subsequent reactor operation and loop experiments suggested that corrosion-product solids and heavy liquids introduced or produced in the core were not removed readily and could lead to local overheating and that boiling could not be depended on for cooling the wall. The fluid velocities were not high enough to guarantee satisfactory heat removal.

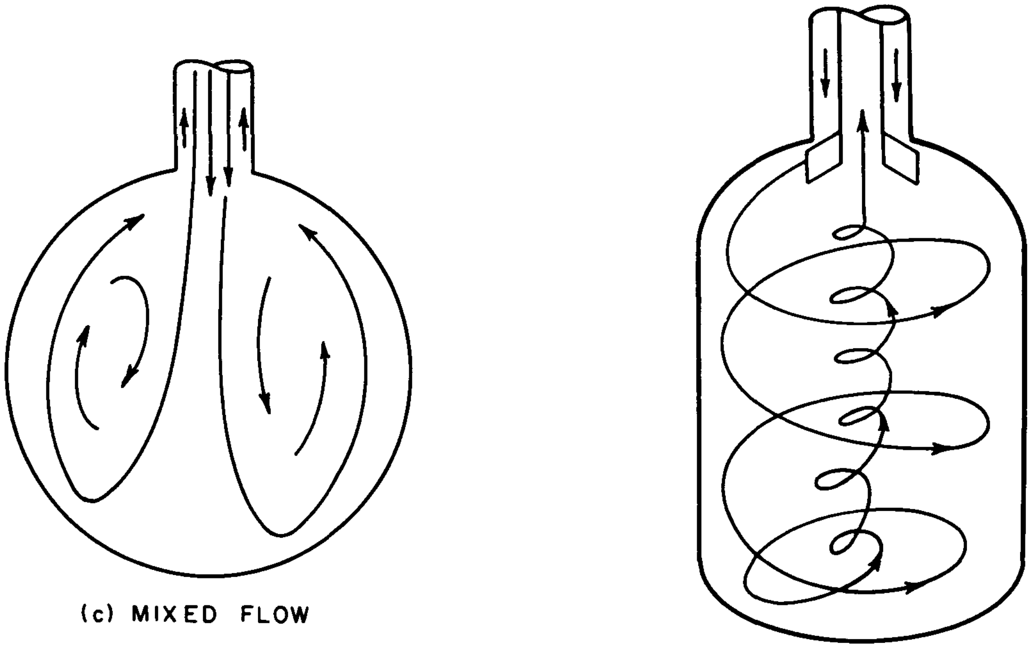
A mixed-flow core (Fig. 9.1c) in which the inlet and outlet are concentric at the top of the sphere has been studied in 6-inch to 48-inch-diameter models and at flows to 6,000 gpm in the latter. The inlet jet coincides with the vertical axis of the sphere and is dispersed when it hits the vessel wall. A strong recirculation is induced and, except for the jet, the core is highly turbulent at the outlet temperature. The velocity of eddies is high enough so that the gas bubbles, heavy liquids, and solids travel with the liquid and are removed from the core. Heat transfer measurements indicate that the core-tank surface would be maintained at a temperature close to that of the core fluid.

The mixed-flow core has a simple mechanical design and appears to satisfy all of the performance criteria, except that it would be desirable for the core tank to be in contact with cooler fluid. Some work has been done on similar vessels in which the flow is introduced through the annulus and removed through the central pipe (Fig. 9.1d). Rotation is induced by vanes in the inlet to stabilize the flow. The testing has not progressed far enough to determine whether a satisfactory flow distribution can be obtained.



(a) VORTEX FLOW

(b) STRAIGHT-THROUGH FLOW



(c) MIXED FLOW

(d) MODIFIED VORTEX FLOW

FIGURE 9.1—Flow systems for reactor cores.

Although the HRE–2 core design has proved unsatisfactory, there are at least two other types of flow that should be satisfactory for experimental reactors that are operated at average power densities of 20 kw/liter and higher. Much additional work is necessary to demonstrate a practical hydrodynamic design for a large reactor operated at 50 to 100 kw/liter.

Slurry-Blanket Hydrodynamics

The suspension contained in the blanket vessel must be sufficiently well dispersed to assure that the core leakage neutrons are absorbed within the blanket, the neutron reflection from the blanket to the core remains steady, and the transport of fluids through regions of high heat generation are sufficient for heat removal. Two types of blanket flow systems have been studied to date. Inlet nozzles were installed in the bottom of the HRE–2 pressure vessel to direct the fluid in such a manner as to create a mild swirl in the annulus between the spherical core and pressure vessels. Tests at low temperature in an 18-inch-diameter model indicated that the flow would keep the solids suspended and swept off horizontal and slightly inclined surfaces. Subsequent tests at 100 to 200° C in a 5-foot-diameter model of the reactor vessel showed that the flow is unsatisfactory because the slurry cannot be kept in suspension at the low circulation rates provided in the reactor.

In the second design, slurry is pumped at high velocity through a narrow annulus between the core tank and a concentric shroud to provide adequate flow in the high-flux region and then it is circulated at lower velocity through the remainder of the blanket. High circulation rates are maintained to ensure good mixing. Promising results have been obtained in tests with water in a 30-inch-diameter model at 25° C. Tests have not been made with slurry yet.

Mechanical Problems

The reactor pressure vessel may be designed from consideration of stresses resulting from the confined pressure, and from thermal stresses resulting from internal heat production. Material can be chosen on the basis of corrosion resistance and structural and thermal properties, with little regard for nuclear properties.

The HRE–2 reactor-vessel assembly presented several special design and fabrication problems. Zircaloy–2 was used for the core tank, which is 32 inches in diameter and 5/16 inch thick. The main pressure vessel, 60 inches in inside diameter and 4.4 inches thick, was constructed of carbon steel with a cladding of type 347 stainless steel. Because of uncertainties in the long-term irradiation damage of carbon steel, the pressure vessel was surrounded by a stainless steel, water-cooled blast shield to stop missiles in the event that the reactor vessel fails. The pressure vessel is cooled to near an optimum temperature distribution from the thermal-stress standpoint by radiating heat to the blast shield.

A special mechanical joint was developed to joint the Zircaloy core tank to the stainless steel piping system. A bellows expansion joint was used to permit differential thermal expansion between core and pressure vessel. Welding procedures were developed for joining Zircaloy and for making the final girth weld in the clad pressure vessel entirely from the outside. Duplicates of the joints were thermal- and pressure-cycled in special tests to demonstrate their adequacy.

Because of uncertainties in the strength of the HRE–2 Zircaloy core tank when subjected to internal or external pressure, full-scale aluminum models of the HRE–2 core vessel were pressure-tested to failure. The data obtained can be applied to the design of larger core tanks.

Nothing has been done toward solving the mechanical problems of a vessel assembly for a large two-region reactor. However, experience gained in the fabrication of vessels for large boiling and pressurized-water reactors is applicable; so the major problems will be concerned with the core tank and making it replaceable.

9.1.2 Circulating Pumps

Solution Pumps

Pumps are required in aqueous homogeneous reactors to circulate solutions and slurries at 250–300° C and 2,000 psi pressure, at heads of up to 100 psi. The two main considerations for these pumps are that they must be absolutely leak-free and must have a long maintenance-free life. Hermetically sealed canned-motor centrifugal pumps are considered capable of meeting the requirements.

Westinghouse type 150° C pumps with modified hydraulic design were purchased for HRE–2. They were tested extensively in fuel solutions at 250 to 300° C, and the following weak points were found and corrected:

1. excessive heat transfer through the thermal barrier,
2. poor cooling of the lower radial bearing and the thrust bearing,
3. excessive leakage of hot fluid around the thermal-barrier seal,
4. excessive corrosion on the upper impeller hub and at the thermal-barrier gasket,
5. excessive mixing of radioactive solution through the shaft labyrinth into the motor.

The initial tests of the pumps resulted in bearing failure after an average life of approximately 150 hours. The cooling flow around the lower radial and thrust bearing was modified, and the thermal barrier was redesigned. This increased the life to approximately 1,000–2,000 hours, at which time excessive flow around the thermal barrier, accompanied with corrosion of the gasket surfaces, caused shutdown. Attempts to find a suitable gasket design failed, and the thermal barriers were welded in place. Titanium hydraulic parts were substituted for type 347 stainless steel, because a safe velocity from the standpoint of corrosion was being exceeded in the impeller. An endurance run incorporating the above modifications was voluntarily terminated after 13,000 hours of maintenance-free operation. Except for the thrust bearing, no damage or wear was observed. Stellite-overlaid thrust shoes have been chemically attacked, causing wear of approximately 0.001 inch per 1,000 hours of operation. This has been reduced by using solid Stellite thrust shoes, which are resistant to chemical attack.

Calculations indicated that the pump life might be shortened by radiation damage to the electrical insulation in the motor. Therefore the HRE–2 pump motors were shielded with lead, and the shaft labyrinth sleeve was modified to reduce the mixing of fuel solution into the motor. A stator-irradiation test was conducted which indicated that the present pump stators should last more than 10 years in the HRE–2.

The original HRE–2 pumps, both fuel and blanket, failed due to burning of the titanium hydraulic parts after approximately 4,700 hours of maintenance-free life. Replacement pumps were installed with stainless steel hydraulic parts until means are developed to circumvent this problem.

Two designs have been completed for a 6,000-gpm top-maintenance pump (i.e., the main flange closure is located at the top of the pump where more direct maintenance is practical). The main area of uncertainty is this type of pump is the thermal-barrier seal, which is important from the standpoints of motor temperature, corrosion, and high radiation level as mentioned above. Tests were completed which indicated that a heavy Belleville spring with gold sealing surfaces could be made to work satisfactorily. Uranyl sulfate solution has been circulated at 250° C by a 4,000-gpm Byron-Jackson pump designed for water service in an investigation of problems.

Slurry Pumps

Slurry circulating pumps are similar in construction to solution pumps but must cope with the additional problems of high bearing wear and severe corrosion and erosion of the hydraulic parts. Runs of up to 3,800 hours at 280° C have been completed on a 200-gpm pump using Stellite-graphitar bearings and stainless steel hydraulic parts. The bearings, however, usually showed considerable wear and the hydraulic parts were rather severely eroded. Superior resistance to slurry erosion was demonstrated through use of titanium and Zircaloy hydraulic parts.

A 2,800-hour run was completed recently by a pump using aluminum oxide bearings and titanium hydraulic parts; there was no measurable bearing wear and essentially no erosion on the hydraulic parts. For pumps up to 400 gpm, it is believed that a life of 1 to 2 years can be obtained by the use of titanium or Zircaloy hydraulic parts and aluminum oxide bearings. For larger pumps, however, the hydraulic erosion problem may be more difficult, because higher fluid velocities are used.

Satisfactory circulating pumps for both solution and slurries are available for use in experimental reactors, although some minor refinements are desired. Major refinements and performance demonstrations are required for large pumps.

9.1.3 Steam Generators

The leaktightness during long-term operation that is required of steam generators for homogeneous reactors considerably exceeds the requirements for similar units in other reactor plants. Leakage of fuel through holes in tubes or tube joints will pass directly into the steam system and will contaminate the turbogenerator and piping. Methods to detect and repair leaks in place are in a preliminary stage of development; replacement of units is time consuming and expensive.

Most of the effort to ensure leaktightness has been expended in the development of fabrication techniques and the inspection of raw materials, fabricated parts, and finished units to obtain steam generators of superior construction. One steam generator which contained about one hundred $\frac{1}{4}$-inch-diameter tubes was used in HRE–1. A spare tube bundle was purchased and used in subsequent development programs. Two steam generators, each of which contains two-hundred and fifty $\frac{3}{8}$-inch-diameter tubes, are in use in HRE–2. A spare steam generator containing eighty-eight $\frac{5}{8}$-inch-diameter tubes was also obtained for HRE–2. All of the steam generators were shell-and-tube units. Although repairs were required in some instances during testing, all were made completely tight against leakage of high-pressure helium detectable by mass spectrograph techniques. No failures were detected in service during the 2 years of intermittent operation of HRE–1 and the first 3 years of intermittent operation of HRE–2.

In fabricating these steam generators, all-welded construction was used of components that were to be exposed to the process solution. For the HRE–2 units, considerable attention was given to obtaining the highest quality tubing, which was inspected by ultrasonic and magnetic flaw detectors capable of detecting imperfections as small as 0.002 inch. Subsequent to the bending and annealing operations, each tube was inspected for surface defects with a liquid penetrant and was subjected to a 4,000-psi hydrostatic test. After completion of these tests, the tubes were rolled into the tube sheet, welded by an inert-gas-shielded tungsten-arc process, and inspected by dye-penetrant methods. Quality-control welds were made periodically during the tube-joint welding and were subsequently examined by radiographic and metallographic methods.

After fabrication, the original HRE–2 units were subjected to 50 primary-side thermal cycles, covering temperature changes more severe than those likely to be encountered in subsequent operation; diphenyl was used as a heating medium. The units were then helium-leak-tested at atmospheric pressure with mass-spectrometer equipment capable of detecting leakage lower than 0.1 cc of helium at STP per day. Leaks were repaired, and the thermal-cycle test and leak tests were repeated until no leakage was detectable.

The replacement unit was designed to eliminate the crevice corrosion and stress-corrosion problems which are present in the normal tube-to-tubesheet joint. This was done by bringing each tube through the shell with a "thermal sleeve" and welding the tubes into a header outside the actual vessel. The fabrication and inspection procedures were similar to those used for the original units with the exception of the thermal cycle test, which was less severe. Helium leak testing was completed as above; no leakage was found.

Operating experience with slurry tubular heat exchangers has been limited to small models. Several tubes have been operated successfully as bypasses on high-temperature slurry loops. However, plugging is reported with some slurries if the velocity is permitted to fall below the "dropout" velocity. On the other hand, plastic seven-tube heat exchanger models, operated at room temperature with various ThO_2 slurries, could not be plugged intentionally.

Preliminary designs have been prepared for 50- and 300-Mw heat exchangers. Both single-drum integral units and units with separate steam drums were considered in the 50-Mw size; only two-drum units were considered in the 300-Mw size. The major problems introduced by increasing the size are higher tubesheet thermal stress and increased difficulty in the manufacture of large forgings. The Westinghouse PAR Project designed 140-Mw slurry heat exchangers; their emphasis was on remote maintainability. It appears that these large units could be built with present technology.

9.1.4 Pressurizers

Solution Pressurizers

A pressurizer is required in an aqueous fuel system to provide a surge chamber for relief of volume changes. It has an important function from the standpoint of reactor safety in limiting the pressure rise accompanying a sudden increase in reactivity. In some reactor concepts, the pressurizer is also used to manufacture purge water for the circulating pump. The pressurizer is normally operated at a sufficiently high pressure to reduce bubble formation and cavitation in the circulating stream.

Two general methods of pressurization applicable to reactor systems have been used in test loops and experimental reactors. These are:

1. steam pressurization, such as is used in the HRE–2, where liquid in the pressurizer is maintained at a higher temperature, hence a higher vapor pressure, than that of the circulating system;
2. gas pressurization, where liquid in the pressurizer is at the same temperature as the circulating system but excess gas is added to the vapor above it; if the pressurizing gas is free to diffuse into the circulating liquid, it reduces the amount of radiolytic gas that can be dissolved before reaching the bubble point.

The HRE–2 pressurizer, developed in an experimental program, consists of a high-pressure electric water boiler and steam drum. Test loops have been operated successfully with fuel solution using both gas pressurization and boiling of the solution in titanium piping. Boiling of uranyl sulfate solution at elevated pressures in contact with stainless steel has been found to lead to excessive corrosion of stainless steel and precipitation of uranium. The gas-pressurized systems are generally operated with the pressurizer slightly above loop temperature and are usually restricted to systems requiring no purge-water production.

Slurry Pressurizers

The physical problems of slurry pressurizers are similar to those of solution pressurizers.

The chemical problems are fortunately not present. It is necessary, however, that the pressurizer be designed to prevent accumulation of cakes or sludges. This is usually accomplished by flowing all or part of the circulating stream through the bottom of the pressurizer. It must be done carefully in steam pressurizers to prevent mixing of cool circulating fluid with the heated pressurizer fluid above.

Several test loops are operating on slurry using steam pressurization with thermal-convection loops in the vapor phase for condensing purge water for the circulating pumps. Gas entrainment from the pressurizer into the main circulating loop has restricted the use of gas pressurizers in a slurry system. A gas pressurizer with a jet pump to circulate the steam-gas mixture through the purge condenser was designed and built, but the gas-entrainment problem prevented its successful operation.

Numerous pressurizer designs have been operated in solution and slurry applications. No design for universal application is available, but each system in use has operated reasonably well.

9.1.5 Flange Closures

Piping Flanges

All-welded piping systems are preferable for homogeneous reactors, but no practical machine has been developed for remotely rewelding pipe. Equipment which must be removable from the system for replacement or maintenance must be connected to the system with mechanical joints. Several types of mechanical joints applicable to pressure systems have been described in the literature, but most have been eliminated from consideration for homogeneous reactor service because their reliability, with respect to leaktightness, following thermal cycling has not been adequately demonstrated.

The ring-joint flange incorporating ASA welding-neck flanges and ring-joint gaskets was used in HRE–1 and HRE–2 and is considered to be the most reliable closure for reactor piping systems. This type of flange was tested thoroughly in a steam system capable of thermal cycling between room temperature and 330° C. Typical leakage experienced with a 4-inch 2,500-pound flange was equivalent to 6×10^{-5} gram of water per day at reactor temperature and pressure.

The bolting of flanged joints presents a serious problem, because the bolts loosen after only a very few thermal cycles, thus threatening the integrity of the joint. Whereas the flange bolts of a conventional pressure piping system may be retightened after a few cycles, this becomes impractical in a homogeneous reactor system after the reactor has gone critical. In the test system, it was found desirable to stress the low-alloy-steel flange bolts initially to a stress of 45,000 psi. After about three thermal cycles this bolt loading fell to an asymptotic value of approximately 30,000 psi, which was found to be adequate to prevent leakage through the joint during further operations; no retightening of the bolts was found to be necessary. With the use of flanges and rings machined to close tolerances, there was no leakage even after test joints had been opened and reassembled ten to a hundred times.

Although torque-wrench measurements usually do not give an accurate indication of load, special techniques were developed which permitted bolts to be tightened reproducibly to within ±10 percent of the desired load. Bolts were lubricated with molybdenum sulfide, and nuts were tightened several times against test blocks which approximated the flange spacing. Nut-and-bolt combinations were accepted for use after reproducible compressive stresses were produced in the test blocks for given torques.

Bolts have been loaded more precisely with the use of pin extensometers. In this technique, a pin is spot-welded into one end of a hole drilled axially through the bolt. A depth gage measures quite precisely the relative strain between the loaded bolt and the unloaded pin. Since both pin and bolt are at the same temperature, thermal effects are compensated automatically. Extensometers are inconvenient for use in remote maintenance, however.

Because mechanical joints can be expected to lead eventually, provision is made to supply pressure greater than reactor system pressure to the ring-joint grooves. By this means, leaks can be detected by observations of a drop in pressure in the auxiliary system. At the same time inleakage of a nonradioactive fluid to the reactor system in the event of a leak prevents radioactive spills. In the case of the HRE–2, D_2O is supplied to the sealed annuli formed in the gasket grooves at a pressure approximately 500 p.s.i. greater than that in the reactor system.

Ring-joint flanges up to 24 inches (HRE–1 blanket closure) have been used successfully in HRE–1 and HRE–2.

Bimetallic Joints

A two-region reactor has the problem of obtaining a leaktight low-differential-pressure mechanical joint between the two regions. In the HRE–2, a zirconium vessel had to be joined to stainless steel piping. Conventional flanges were not satisfactory because of the large difference in thermal coefficients of expansion for the two materials. A solution to the problem for the HRE–2 was obtained by using a titanium cylindrical-sleeve gasket with gold inserts for sealing. The joint is loaded with titanium-alloy bolts. It was subjected to experimental stress analysis and thermal-cycling tests before being used in the reactor.

A ring joint for connecting stainless steel and titanium piping in ½-inch to 1-inch sizes at temperatures up to 650° F. has also been developed for possible use in the HRE–2. The different thermal coefficients of expansion of the two materials are bridged by use of a stainless-steel-clad carbon steel flange in the stainless half of the joint. An HRE type of leak detector is placed in the clad flange. A prototype joint passed thermal-cycle tests under design conditions; several joints are being used currently in loops.

9.1.6 Gas Separators

The problem of removing relatively small amounts of radiolytic and fission-product gases from a reactor system has been solved in the HRE–2 by using a pipeline or axial gas separator. The pipeline gas separator consists of a set of stationary rotation vanes, followed by a section of pipe in which gas is centrifuged into a void which forms at the pipe axis. Gas is removed from the axial void through a take-off nozzle. The energy of rotation is partially recovered with straightening vanes at the discharge end of the separator. The separator development was based on low-temperature low-pressure flow studies. Models of several sizes were tested; the largest would handle a liquid flow of 5,000 g.p.m. Performance of the HRE–2 type separator, 4-inch diameter and 400-g.p.m. liquid flow, was checked in tests at reactor temperature and pressure.

Although gas has been removed from slurries in an axial separator, the design criteria have not been established.

9.1.7 Gas-Handling System

The radiolytic and fission-product gases released from aqueous homogeneous reactors must be processed to recover deuterium and prevent release of activity to the atmosphere. Most of the D_2 is recovered as a result of solution-phase recombination at high pressure. In HRE–1 and HRE–2 some liquid is let down continuously, sending D_2, O_2, D_2O, Kr, Xe, and I_2 and usually carrier O_2 gas to the low-pressure system.

First, a highly efficient entrainment separator is required to prevent spread of uranium into the gas-handling system. The entrainment separator must be designed to function well during normal operation and also during the emergency dumping operation of the reactor. The HRE–2 entrainment separator design was based on literature data and experimental tests. Three modes of entrainment removal were used in series: centrifugal separation, corrugated plates, and wire-mesh demister elements. Full-scale parts of the assembly were tested by using potassium salt tracers, and the final assembly was demonstrated to keep the concentration of entrained solids below 1 ppm.

The next step is the recombination of D_2 and O_2, which is desired for reasons of economy as well as safety. The two most promising methods of vapor-phase recombination are the use of flame and catalytic recombiners. In a flame recombiner, the D_2 and O_2 are actually ignited and burned to form water. The HRE–1 recombiner was of this type. It consisted of a combustion chamber of 10-inch pipe 3½ feet long, jacketed by a 12-inch pipe through which cooling water was circulated. At low flow rates the flame burned too close to the nozzle, resulting in over-heating and flashbacks. To prevent flashbacks at low flows, a steamer pot ahead of the flame recombiner added steam to the gas stream.

In developing flame recombiners to obtain an explosion-proof automatic-load-adjusting unit, the multiple-spark-plug model was tested. As the steam-gas mixture traveled up past alternate condenser-coils and spark plugs, the mixture eventually lost enough steam to become combustible. The location at which the moisture burned depended on the input concentration of gas. The test model operated satisfactorily but has not been used in a reactor.

For catalytic combination of D_2 and O_2, platinum black has proved to be the most satisfactory catalyst. It has been supported on alumina pellets and on stainless steel wire mesh. The platinum adheres better to the alumina pellets, but the wire mesh is less liable to mechanical damage. Because of its greater simplicity and safety when compared to flame recombination, catalytic recombination is used in the HRE–2. The design of the catalyst bed, from the mass-transfer standpoint, was based on tests performed in several systems at pressures of atmospheric pressure to 1,000 psi. It was found necessary to include a steam-heating coil to dry the catalyst during startup. Furthermore, tests showed that poisoning of the catalyst by fission-product iodine could be prevented by first passing the vapor mixture through silvered alundum or wire mesh.

The heat of recombination and most of the heavy-water vapor are removed in stainless steel shell-and-tube condensers of conventional design. The heavy water is returned to the reactor system directly, or is diverted to a distilled-water storage tank. The condenser off-gas consists of carrier O_2, D_2O vapor, Kr, and Xe.

Cold traps are provided in the off-gas lines to recover D_2O and to dry the gases before they are discharged to the charcoal adsorbers. Exit gas temperature is maintained between -10 and $-30°$ F. Cooling by evaporation of Freon in the cold-trap jackets has been used, but a circulating liquid refrigerant system was provided for HRE–2 and is preferred for use in high radiation fields. Freon is evaporated at -50 to $-100°$ F in the primary system to cool a secondary refrigerant, which is circulated through the cold traps. After testing many liquids, Amsco (kerosene) was selected as the best secondary refrigerant because the liquid and the radiation-damage products are relatively noncorrosive to the metals in the reactor and refrigeration systems.

The HRE–2 cold traps are double-pipe stainless steel heat exchangers. Flow of refrigerant is countercurrent, with the traps pitched to drain the D_2O when defrosting. The insulation is in the form of sealed cans of Santo-Cel (SiO_2) fitted around the traps, this material having markedly better resistance to radiation damage than the more commonly used low-temperature insulating materials. Cold traps are used in pairs so that icing and defrosting can be conducted simultaneously.

Research and development has been supported in a number of areas to increase the reliability and lower the cost of gas-handling in future homogeneous reactor systems. Gas solubilities and reaction limits in saturated steam in the range 100 to 300° C, high-pressure physical properties of gas-vapor mixtures, and basic information on high-pressure detonations have been obtained.

The use of high-pressure recombination in homogeneous reactors would eliminate the need for continuous letdown of the radiolytic gases and continuous feed-pump operation. High-pressure recombination has been investigated in gas circulating-loop tests. Recombination rates were satisfactory. However, stress-corrosion cracking was encountered in the stainless steel loop. The cracking problem was solved by substituting Inconel for austenitic steel; this material would be suitable in a slurry reactor system but not in a uranyl sulfate system. One of the ferritic stainless steels might be suitable for the latter application.

A natural-circulation high-pressure recombiner, which eliminates the need for mechanical circulation of diluent steam, was tested successfully at 1,500 psi for 2,500 hours. A 20-cfm high-pressure canned blower was developed and tested as a means of mechanical gas circulation if needed.

9.1.8 Storage Tanks

Solution Tank-Evaporator

In the HRE-2 the storage-tank system has a threefold purpose: (1) It acts as a storage tank for fuel solution during shutdowns and after emergency dumping and for solution removed from the high-pressure system during the letdown of gaseous decomposition and fission products; (2) it acts as a generator of diluent steam to lower the radiolytic D_2 and O_2 concentration to a nonexplosive mixture prior to recombination; and (3) it serves as a purge-water generator.

The storage tank-evaporator is designed to furnish the required amount of steam diluent and purge water and also to agitate and mix the solution stored in the tank. A full-scale tank was tested and modified until its performance met specifications.

Slurry Storage Tanks

Several approaches were pursued in the development of slurry drain and storage tanks for reactor use.

The development of a mechanically agitated tank accepts the problems involved in obtaining the necessary reactor-grade mechanical components of motor, seals, drive shaft, bearings, and agitators. A 36-inch-diameter mechanically agitated storage tank has been built and operated. It was concluded that the test was adequate to demonstrate that the rotary, multiple-impeller type of agitation is an effective means of assuring slurry suspension in drain tanks. The feasibility problem remaining with this type of mixer was believed to be that of obtaining a reliable mechanical shaft seal or a hermetically sealed drive.

In other tests it was demonstrated that a reasonably uniform concentration could be obtained by steam sparging after settling periods of up to 70 hours. Tests showed also that adequate agitation could be obtained by boiling of the slurry, both by the addition of heat from outside the storage vessel and by heating coils submerged in the slurry.

Limited, and as yet incomplete, tests indicated that certain storage-tank-feed-pump configurations will permit the pumping of slurries from storage tanks without agitation.

9.1.9 Feed Pumps

High-pressure low-capacity pumps are required to feed solutions, slurries, and water into aqueous homogeneous reactor systems. In HRE-2, 0.5 to 1.5 gpm of fuel solution must be returned to the reactor, 0.25 gpm of purge water to the pressurizer, and 0.1 gpm of purge water to the circulating pump against 2,000 psi pressure. The hydraulically driven diaphragm pump with the following advantages was developed for the HRE-2.

1. The pump head and check valves are of all-welded construction and are leakproof and maintenance-free for long periods of time.
2. The only moving parts inside the shield are the diaphragm and the check valves.
3. The drive mechanism is outside the shield, where conventional lubricants and maintenance techniques may be used.
4. The pump output is adjustable by changing the output of the drive unit.
5. In the event of a diaphragm rupture, radioactive fluid is still retained within the piping system.

Development work has demonstrated that diaphragm pumps will operate satisfactorily for 1 year or more in this service.

Diaphragm Development

The first heads used were purchased commercially; they had a cavity 0.125 inch deep, a 0.019-inch thick annealed stainless type 347 diaphragm, and no screening. The diaphragms suffered early failure due to irregular contour machining and dents caused by the trapping of dirt particles between the contour face and the diaphragm. In order to reduce the overall diaphragm stress level and to reduce or eliminate the localized stress risers, the contour depth was reduced to 0.010 inch, the machining procedure was changed to produce a smooth, continuous contour, and 40-mesh screens were installed in the head. These changes increased the average diaphragm life to about 4½ months. However, some failures occurred in as little as 2 months. An intensive program was initiated to develop a head that would function consistently for 1 year or more.

The first objective of the program was to reduce or eliminate stress risers caused by dirt particles. Substitution of 100-mesh screen tubes for the 40-mesh screens reduced the denting of test diaphragms by an order of magnitude. A sintered stainless steel porous tube with 20-μ openings is being evaluated at the present time in an experimental pump to reduce the problem further.

A second objective was to investigate possible improvements in contour in order to minimize diaphragm stress for the desired volumetric displacement. Theoretical and experimental stress analyses showed that the original contour was nearly optimum, and it was retained.

A third objective was to determine the nature of the diaphragm motion and improve it if necessary. A special spring-loaded magnetic instrument was built to indicate diaphragm position while operating. Three such indicators were installed in a standard head and recorded simultaneously on a fast multichannel instrument. It was observed that the diaphragm was displaced in a wave motion starting at the top of the head and producing a sharp bend at the bottom where most failures occurred. It was observed also that there was considerable flutter in the diaphragm, so that it was being flexed more frequently than anticipated. By increasing the thickness of the diaphragm from 0.019 to 0.031 inch, symmetrical deflections with less flutter were obtained. Changes in the drive system were effective in creating more smooth diaphragm deflection. These changes were incorporated into later pumps.

The fourth point of the program involved determining the endurance limit of annealed 347 stainless steel and other possible diaphragm materials in fuel solution. A literature review indicated that in a corrosive environment there may be no endurance limit as such, but that the curve of stress vs. number of cycles would continue its downward trend indefinitely. The literature also suggested that significant gains in endurance limit may be achieved by cold-working stainless steel, or by using a precipitation hardening steel such as Allegheny-Ludlum AM-350. Standard reverse-bending sheet specimens of each material were operated at 2,000 cycles per minute in environments of air, distilled water, and fuel solution. It was found that hardened materials suffered a drastic reduction in endurance limit in fuel solution but not in water, whereas the annealed 347 stainless steel endurance at 107 cycles was 39,000, 36,000, and 34,000 psi, respectively, in air, water, and fuel. None of these media produces appreciable corrosive attack on any of the materials tested.

Check-Valve Materials

Stellite balls and seats have been operated in fuel solutions for more than 10,000 hours with no sign of damage. During preoperational testing of the HRE-2, four sets of valves failed in oxygenated distilled water in about

500 hours. Further testing showed that preconditioning by operation in uranyl sulfate made Stellite suitable for oxygenated-water use. Armco 17–4 PH stainless steel was also demonstrated to be an excellent seat material in both water and uranyl sulfate.

HRE–2 fuel pumps now contain Stellite Star J balls and Stellite No. 3 seats. Check valves are pre-run in fuel solution before being welded to the pump heads. HRE–2 pumps contain Stellite Star J balls and 17–4 PH seats.

Slurry Diaphragm Pumps

Two methods of pumping slurry with the diaphragm pump are being tested. In the first, the check valves are located several feet below the head and connected to it by a vertical pipe. By sizing the vertical leg so as to maintain low oscillatory velocities, a stable slurry-water interface forms, permitting the diaphragm head to operate in relatively pure water while slurry pumps through the check valves. A venting system is necessary.

The second method uses a diaphragm head having a contour in the driving flange, a recessed cavity in the pumping flange, and an arrangement that permits the diaphragm to operate only from the driving contour to center. This arrangement precludes the possibility of slurry being trapped between the diaphragm and contour, leading to undesirable diaphragm deflection patterns. Both this pump and the one described above have been operated at conditions approximating those of a reactor for 5,000 hours without diaphragm failure.

The abrasive nature of the ThO_2 slurry creates a difficult pump-check-valve material problem. Metals and cermets have a life of a few hours to a few days when pumping slurry to 2,000 psi. Very hard ceramics such as aluminum oxide and boron carbide have operated for several months. This problem appears to be the only one requiring serious attention for experimental-reactor feed pumps.

9.1.10 Sampler

Operation of an aqueous homogeneous reactor requires that numerous samples be taken from both the high- and low-pressure systems in maintaining control of the chemical composition of the solutions. A sampler for use in HRE–2 was designed, built, and modified during a nonradioactive test program. The sampler has operated exceptionally well under difficult cirsumstances, but is must be improved considerably to be satisfactory for routine operation.

A technique for removing an accurate sample from a slurry reactor system has not been developed. Slurry samples are removed from high-pressure, high-temperature test loops by throttling and cooling the slurry through a long capillary tube, but it is known that these samples are not always representative of the slurry flowing in the pipe.

9.2 SYSTEMS DEVELOPMENT

9.2.1 Circulation of Aqueous Slurries in High-Temperature Pumps Loops

High-temperature circulation tests have been carried out which demonstrate that suspensions of thorium oxide can be pumped at the temperatures of 250 to 300° C required for reactor operation, and that the slurries can be contained within conventional materials of construction in the absence of radiation. These tests have been performed with a range of slurry concentrations and compositions which cover the properties expected for core fuels for large reactors (200 to 300 g Th/liter with approximately 0.04 g U/g Th), for the blanket fuels (1,000 g Th/liter with approximately 0.005 g U/g Th) and for core fuels for experimental reactors (200 to 300 g Th/liter with 0.08 g U/g Th). Appropriate additives to the slurry simulated the effects of fission products which would be formed in reactor operation and of materials added to the slurry for recombination of radiolytic gas. In some instances other materials were added to the slurry for the purpose of improving the circulation characteristics. During the tests, slurries have undergone various operations characteristic of reactor systems such as heating, cooling, concentration change, and re-startup after pump stoppage. The slurry must perform excellently in these tests to be certified for use in a reactor.

The tests have been performed in flow systems (200- and 100-gym loops) involving primarily a canned-motor pump for circulation, piping to form a closed-flow loop, and heating equipment to maintain the high temperature and pressure. Slurry flowmeters, slurry sampling facilities, and instrumentation to give a continuous record of the test conditions were necessary auxiliary equipment. The usual pipe velocities are 10 to 20 ft/sec. Pressurization is achieved by boiling water in a vertical pipe. Slurry enters the vertical pressurizer at a side inlet connection and then flows out at the bottom of the vertical section to the main pipe loop. The volume above the side inlet connection on the vertical pipe serves as a slurry settling chamber, with a layer of supernate maintained above a slurry-water interface.

Chemical and physical analyses of samples withdrawn from the high-temperature slurry loops indicated the extent of particle size and shape changes, the accumulation of corrosion products on the slurry, and, in the case of thoria-urania mixed-oxide slurry, the chemical stability of the oxide particles. In some loops corrosion-sample holders were inserted in the main flow stream. In all loops corrosion-erosion attack rates on the pump impeller and other pump parts were determined. Rheologic data were measured by means of capillary-tube viscometers. High-temperature measurements were made with a capillary-tube viscometer-sampler through which loop slurries were withdrawn.

Slurry Circulation Experience at ORNL

Thorium oxide prepared by calcination of the oxalate at temperatures from 650° to 1,600° C has been used in high-temperature slurry systems. Thoria prepared in this manner has a crystallite size near 200A, and in water suspensions stable agglomerates of these crystals were found which range from 1 to 10 microns in diameter. There is some tendency for further agglomeration of the thoria particles at high temperatures to effective floc sizes of 50 to 300 microns, and in some instances hard deposits or cakes are formed on pipe walls and in pumps. The flocculated slurries behave as Bingham plastic or pseudo-plastic materials. The coefficient of rigidity and the yield stress increase with increasing volume fraction solids and decreasing particle size.

Thoria deposits have formed in high-temperature circulation tests with oxides calcined to 650° C and to 800° C. Such deposits were formed in approximately 40 runs in 100-gpm loops and in at least two 200-gpm loop runs. Hard cakes were found only in runs with 800° C-calcined oxide. A plausible explanation for the caking tendency of thoria slurries has been advanced; recent loop runs show that caking does not occur with properly prepared oxides.

Various additives, such as UO_3, MoO_3, sulfate, and silicate, have a pronounced effect on the thoria circulation characteristics. Of these materials, only UO_3 has consistently improved qualitative loop performance.

Good slurry particle integrity seems to be the key to preparation of thoria slurries which have stable circulation characteristics. The 650° C- and 800° C-calcined thoria particles degrade rapidly in loop tests from 1 to 2 microns mean diameter to less than 0.5 micron, with undesirable erosion and caking frequently observed. Slurry particles of greater integrity have been produced by calcination of thorium oxalate at 1,600° C, thus fusing thoria crystals to form larger crystallites, and by controlled digestion of the thorium oxalate.

Two runs, each of approximately 4,000 hours duration, have been made with the 1,600° C-calcined thoria slurry in 200-gpm loops. The slurries were circulated at 300° C, 2,000 psig, at 10 ft/sec in the main pipe loop; and the mean particle size decreased from 2.5 microns to about 1.5 microns, with little change over the latter 2,000 hours of the run. There was no evidence of caking or excessive corrosion. Circulation could be stopped and the slurry could be readily resuspended upon initiation of flow. There was no evidence of plugging in the system even with slurry concentrations up to 1,500 g Th/kg H_2O. Addition of 0.5 percent uranium as UO_3 and molybdenum oxide to the circulating slurry gave no undesirable effects.

Similar slurries have been circulated for much shorter periods in 100-gpm loops with similar experience. On the other hand, excessive erosion was found in several 100-gpm runs when the slurry contained a significant fraction of particles greater than 5 microns in diameter. There was also evidence of sludge formation in 100-gpm loops with slurry with a mean particle diameter of 0.9 micron, re-emphasizing the importance of particle-size control.

Two 1,000-hour 200-gpm-loop runs demonstrated that ThO_2–UO_3 (calcined at 1,050° C) particles are stable under high-temperature circulating conditions. The attack rate on stainless steel piping was less than 0.1 mpy, and pump parts were free of visible damage by slurry abrasion. The slurry could be resuspended readily following periods of slurry settling, and no cakes were found in the loops following the circulation tests. Mixed-oxide slurries which had settled in a vertical section pipe in one of the 200-gpm loops for periods of 2 and 11 days were caused to flow by application of pressure differences of approximately 20 psi across a 14-foot column of settled slurry 1 inch in diameter.

It has been demonstrated that ThO_2 and mixed Tho_2–UO_3 slurries can be circulated successfully in high temperature loops for long periods of time. However, the detailed specifications for a preferred slurry have not been developed, particularly for a 1,000 g ThO_2/liter blanket. Many of the high-temperature dynamic properties of slurries need further study.

Slurry Circulation Experience on PAR Project

More than 30,000 hours of high-temperature slurry circulation tests were carried out at Westinghouse CAPA Laboratories as part of the PAR development program. For the most part the tests were made at 300° C, 1,700 psig, with thoria prepared by calcination of the oxalate at 650° C containing approximately 0.04 g U/g Th. In the last year of the project, runs were made with an ORNL 800° C-calcined oxide, an oxide prepared by the controlled oxalate digestion procedure developed at ORNL, and a 950° C-calcined oxide.

The slurry circulation tests were made in four 200-gpm loops similar in construction to the ORNL loops. Extensive corrosion data were obtained on a variety of materials of construction. Characterization tests to determine settling rates, rheologic properties, settled-bed behavior, radiolytic-gas recombination rates, and other physical properties were made on slurries removed from the high-temperature circulation tests. Similar slurry characterization tests were made with slurry, following circulation tests in a large 4,000-gpm loop used for evaluation of prototype reactor components and system testing.

The tests with 650° C-calcined thoria containing 0.04 g U/g Th demonstrated that this slurry can be circulated successfully in high-temperature reactor systems at concentrations near 200 to 300 g Th/liter. The chief circulation difficulty was due to the formation of sludges or muds in the loop pressurizer at loop concentrations greater than 500 g Th/liter. The addition of simulated fission products and various materials proposed as radiolytic-gas recombination catalysts produced no deleterious effects with respect to tendency to form deposits in the system, slurry erosion rates, or other physical properties.

One test with ORNL 800° C-calcined oxide indicated that the rheologic properties of this oxide are highly influenced by the state of oxidation of the corrosion products in the circulating slurry. The yield stress of material pumped approximately 1,000 hours under reducing conditions increased by a factor of 100, compared to that of the material charged. Upon the addition of H_2O_2 and the subsequent change to oxidizing conditions there was a fivefold reduction in yield stress.

One 2,500-hour run was made with a 950° C-calcined thoria slurry. The run was regarded as highly successful by PAR project personnel with respect to handling behavior. Little change in physical properties was noted as alterations were made in the oxidation state of the fuel system. Acceptable (<10 mpy) erosion rates at a 65-ft/sec slurry velocity were found for Zircaloy-2 and titanium. Low attack rates (<0.2 mpy) at an 11-ft/sec slurry velocity were found for materials of construction of interest for reactor plant components and piping (i.e., 300 series stainless steels, Croloy 16–1, Carpenter 7 Mo).

9.2.2 HRE–2 Mockup

During the design and construction of HRE–2 some of its major pieces of equipment were assembled and operated at design conditions on unenriched uranyl sulfate solution. The purposes of this engineering mockup were (1) to study the behavior and removal of gases in the high-pressure system, (2) to study fuel-solution stability in a circulating system similar to the HRE–2, (3) to establish a reference corrosion rate for the reactor circulating system, (4) to study the behavior and removal of corrosion- and fission-product solids in the system, and (5) to establish the reliability of components, pointing out weaknesses and possible improvements.

The major components of the mockup are prototype reactor components. They include the circulating pump, the electrically heated steam pressurizer, the centrifugal gas separator, a ⅛-scale heat exchanger, the letdown heat exchanger, the bellows-sealed letdown valve which throttles the fluid removed from the high-pressure system, the liquid-level controller which positions the letdown valve, the dump-tank-condensate system, the feed pumps, and the oxygen-feed system to maintain oxidizing conditions in the circulating fuel. A hydroclone system for removal of corrosion- and fission-product solids was installed after the mockup had been in operation for 15 months.

Operation of the mockup for a total of more than 20,000 hours in the 4-year period from February 1955 to June 1959 provided valuable information pertinent to the construction and operation of HRE–2. Items of major importance included (1) a satisfactory demonstration of the operation of the equipment for removing gases from the high-pressure system, (2) demonstration of the out-of-pile chemical stability of the uranyl sulfate solution at operating temperatures and pressures over a long period of time, (3) determination of the oxygen injection and excess sulfuric acid requirements to prevent uranium precipitation in the high-pressure loop, (4) detection of an unsatisfactory pressurizer design in which excessive corrosion and precipitation of uranium occurred and tests of a revised model which proved suitable, (5) a demonstration of the successful removal of injected fission-product solids and insoluble corrosion products by means of hydroclone, (6) demonstration of long-term operability of the circulating pump and other pieces of equipment, (7) successful operation of a titanium letdown heat exchanger and a pressurizer in which UO_2SO_4 solution was boiled, and (8) demonstration of the practicability of reversing the direction of flow in the HRE–2 core system.

9.2.3 Operating Experience With the HRE–2 Slurry Blanket Test Facility

The HRE–2 slurry blanket test facility was constructed to determine whether the blanket system installed in the HRE–2 could be used with slurry. The facility was a full-scale replica of the HRT blanket circulating system with respect to the reactor-vessel dimensions, piping size, circulating pump, and heat exchanger tubing size. The heat exchanger contained only three tubes, as opposed to 250 in the HRE–2 heat exchanger, and only a small fraction of the total flow through.

The circulating system was divided into high- and low-pressure sections, since the pressure vessel available was a steel prototype, good for service below 300 psi and could not be used during circulation and heat transfer tests at reactor design conditions. One test was carried out at reactor design conditions with the heat exchanger in the circuit. However, the bypass loop containing the heat exchanger plugged before the loop could be heated to design temperature. It was unplugged on two occasions, but plugged again in 1 or 2 hours each time. The plug was due to a combination of flow rate below the dropout velocity and insufficient pressure drop to overcome the yield strength of the slurry.

After this run, attention was turned to testing of the blanket proper. The heat exchanger and its connecting piping were removed from the system, and the reactor prototype was connected. The slurry stream entered the 60-inch-diameter mockup pressure vessel (which contained a stainless steel replica of the HRE–2 core) through two nozzles in the bottom which were arranged to direct the flow in opposite directions on either side of the core inlet. It was expected that the sweeping action of the jets across the bottom of the vessel would prevent solids from accumulating there. The slurry was removed at the top of the vessel by putting a shroud around the core outlet pipe, allowing the slurry to enter the top and bottom of this shroud, and carrying it to the exit nozzle at the vessel wall by a pipe connected to the center of the shroud. It was also expected that the inlet nozzles would produce swirling flow which would help sweep the slurry off the top of the core tank. The inlet and outlet design was based on successful tests with an 18-inch-diameter vessel.

Initial experiments at 230 gpm in the 60-inch-diameter vessel at 170 to 200° C showed that homogeneity was not achieved. Above 180° C most of the charge remained essentially stagnant in the blanket, with quite dilute slurry circulating through the piping loop.

In the following tests, a 300-gpm pump impeller was used, and the blanket nozzle diameters were decreased. These relatively minor changes resulted in a significant improvement in blanket operation, although some dropout was still suspected. To confirm whether part of the slurry charge was stagnant, uranium trioxide tracer was added to the circulating slurry. This test showed that at least 25 kg of the charge of 850 kg of thorium present in the system at that time was not mixing.

Subsequently, the original inlet nozzles were reinstalled to determine whether increased flow rate or increased inlet velocity had been more effective in improving the distribution. The annulus at the top of the exit shroud was closed so that nearly all the slurry passed across the top of the core in leaving the vessel. Tests at flow rates of 170, 225, and 316 gpm and temperatures of 150, 170, and 200°C in all possible combinations indicated that the increased flow was probably more important, and the change in exit shroud represented a considerable improvement.

During the series of tests, circulation was interrupted over 100 times for periods ranging from 1 minute to 4 hours and once during the last run for an entire week. After all of the relatively brief shutdowns, the initial slurry distribution became re-established in approximately the time required for the slurry to make one complete circuit of the loop. After the slurry had been allowed to settle for a week, 16 hours were required to complete resuspension of the slurry. Whenever circulation was interrupted, the slurry settled to a concentration of 800–850 g Th/liter in 1 or 2 min and then compacted gradually to over 1,000 g Th/liter.

All four runs were terminated by dumping the loop. In the first two dumps, made no supplementary agitation, only about 50 percent of the solids were drained. In both cases the solids were drained. In both cases the solids settled to a dense bed in the blanket vessel, and the supernate formed channels in this bed to the inlet nozzles. During the third dump, steam agitation was used but was shut off before the dump was complete due to a leak in the steam piping. Approximately 75 percent of the solids ultimately recovered by dumping and rinsing were drained during the dump proper. Steam agitation was used during the entire final dump, and over 90 percent of the solids were drained during the dump.

The mockup studies indicated that provisions for circulating slurries in the HRE–2 blanket made on the basis of studies in a small model at low temperature were inadequate. This factor, plus the hole in the reactor core tank, led to the abandonment of all plans to use slurry in the blanket of HRE–2.

300-SM Test System

When the HRE–2 investigations were completed, the mockup was revised as a general-purpose facility for testing models of slurry reactor vessels at high temperature and pressure and for testing new components for both high-pressure and low-pressure systems in simulated reactor systems.

A new reactor vessel was obtained which is a 29½-inch-inside diameter sphere with a 60° included-angle conical bottom. It is designed for operation at 2,000 psi and 600° F, so that experiments may be conducted at reactor design temperature and pressure. A new low-pressure slurry storage and handling system was provided . A 30-inch-diameter cylindrical dump tank with a 90° included-angle conical bottom is the principal component of this system. The cooling necessary when the high-pressure system is dumped is provided by condensing the steam which flashes from the slurry as it enters the dump tank. The low-pressure system also includes a diaphragm injection pump and standby acid-egg system for charging the high-pressure system when it is operating.

The revised system was first assembled to conduct tests of a proposed small single-region slurry reactor. Based on room-temperature studies in a 6-inch plastic model and a 30-inch flow model, a re-entrant core flow design was adopted with flow entering at the bottom. The first run was made at concentration levels of 530, 375, and 240 g of Th(U)/kg H_2O, temperatures of 150 and 200° C, and flow rates of 126 to 380 gpm. These tests indicated that the rebuilt system suspends slurry much more effectively than the original HRE–2 prototype system.

9.2.4 PAR Project Test Loop D

The PAR Project assembled a large component test system (called Test Loop D) which contained a 4,000-gpm vertical centrifugal pump, a 24-inch vertical pressurizer, and 10-inch IPS piping. The total circulating-system volume was approximately 450 gallons. Auxiliaries included a letdown system to low-pressure storage tanks, a high-pressure drain tank capable of receiving a rapid dump under adiabatic conditions, and an Aldrich feed pump. Additional components, including a core vessel and a steam generator, were to have been added as developed.

Two slurry tests were carried out at 250–300 g Th/liter. A 650° C-calcined, controlled-oxalate-digestion thoria was used. Severe pump-impeller erosion was experienced in both, but this may have been caused by the initial high fraction of large particles in the slurry ($66\% > 8.4\ \mu$). In the second run, dropout of the slurry in the piping occurred to some extent.

In the first run slurry was loaded in the loop prior to starting the pump and was removed at the end by letting-down slurry and adding water. The second run was started up with water in the system, and slurry was loaded by means of an Aldrich positive displacement pump after operating pressure and temperature had been attained. By the time the loop was loaded, the check-valve seats in the pump, which had operated for 60,000 cycles in loading the loop, required replacement. At the end of this run the loop was dumped to the high-pressure drain tank at a rate of 50 gpm. Approximately one-third of the thoria remained in the loop after the dump. This is not surprising, since much of the loop volume is in horizontal lines and the slurry had shown a tendency to drop out during the run.

9.3 DEVELOPMENT OF MAINTENANCE OPERATIONS FOR HOMOGENEOUS REACTORS

Maintenance of the equipment in the circulating systems of an aqueous homogeneous reactor is difficult because of the intense radioactivity emanating from the surfaces following prolonged operation at high power levels. This problem, more acute than in the case of heterogeneous reactors because fission-product activities are not confined to the reactor core, must be successfully resolved in a practical manner if the homogeneous reactor is to be an economical power producer. Practical systems for maintenance and repair must provide adequate shielding for personnel to reduce radiations to tolerable biological levels while simultaneously providing access to the equipment. The concepts which have been proposed for the maintenance of equipment in a circulating-fuel homogeneous reactor system have been based on the philosophy of either dry maintenance or underwater maintenance or combinations of the two. In general, it has been assumed that the item requiring repair will be replaced with a new item and that the faulty component will be removed to a shielded hot-cell area for maintenance. It may be possible, also, to so arrange some of the larger items, such as heat exchangers and pressurizers, to permit repair in place by the strategic use of remotely operated tools and judicious placement of shielding.

The HRE–2 underwater-maintenance concept was designed on the basis of HRE–1 experience, with refinement as a result of reactor application both before and after power operation. The HRE–2 was designed with flanged joints, adjacent to the equipment, which may be disconnected underwater and remade with suitably designed tooling. These tools are generally simple units mounted on long handles; they include manual, air-operated, and water-operated socket wrenches for turning nuts, a hydraulic torque wrench, a flange-spreader tool, hooks, clamps, magnets, etc. Jigs are generally used to prepare standard replacement assemblies of valves and pumps.

The HRE–2 has proved the concept of underwater repairs to be completely practical. Soon after the reactor attained significant power it was found necessary to replace all the electrical power wiring—nearly 4,000 feet of wire. This was accomplished in a period of 3 weeks, with the cell completely flooded. Other important underwater replacements have been circulating pumps, feed pumps and valves.

Heavy-water freeze plugs are used on open HRE–2 process lines to prevent shield H_2O inleakage during underwater operations. The plugs are frozen by circulating refrigerant through permanent or clamp-on jackets which are placed around the pipe. Freezing time of a few minutes for ½-inch and smaller lines and up to several hours for 3- and 4-inch sizes were observed in component tests.

In addition to underwater-maintenance facilities, dry-maintenance facilities were designed and used successfully for replacing small items such as corrosion specimens and rupture discs. Dry maintenance is accomplished through an eccentric-plug portable lead shield. A light and television camera are lowered to view the operation. Because of the relative convenience of direct dry maintenance, it is used in preference to wet maintenance when practicable in the HRE–2.

Following the appearance of a hole in the HRE–2 core tank, a short-range program was conducted to develop equipment to observe the hole in the core. It was found necessary to construct a full-scale mockup of the reactor vessel and a portion of the shield in order to perfect a successful viewing device. Tools developed for use in the HRE–2 core and blanket vessel in this manner included optical periscopes, remotely operated mirrors and lights, a 2-inch television camera and manipulator, remotely operated grappling tools for recovery of loose objects, and cutters for obtaining specimens of the Zircaloy diffuser screens. Although none of these operations had been anticipated in the design of the reactor, these tools were tested successfully in the mockup, and all but the television camera were used in the reactor.

The miniature television camera was developed for resistance to radiation and was tested in a high gamma field. The only electronic components in the camera are the Vidicon tube, the deflection coils, one ceramic capacitor, and a carbon resistor. The remaining electric components associated with the camera are in a preamplifier chassis which is connected to the camera by a 10-foot cable. By using this remote preamplifier, most of the electric components can be kept out of the high radiation zone either by the use of intermediate shielding from strong sources or physical removal from weaker sources.

There was no observable initial effect on the camera operation when it was lowered into a 1.5×10^6 r/hr field. However, the picture then faded rapidly and required maximum target voltage after 20 minutes. After 1 hour of additional exposure in a reduced field of approximately 5×10^5 r/hr, the picture was not readable. After further exposure for a total dosage of 5×10^6 r, the camera head was removed and the camera lens was found to be practically opaque. After replacement of the lens, the camera operated satisfactorily with some loss of sensitivity, probably due to browning of the Vidicon-tube faceplate. A lens made from nonbrowning glass will be used in additional tests.

Since further operation of the HRE–2 and associated development work indicated the desirability of changing the flow pattern in the HRE–2 core and of patching the hole, tools for making these changes have been designed, tested on the mockup, and prepared for use in the reactor. The tools all are operated through the eccentric-plug shield 20 feet above the reactor vessel. Access to the core is through a 2-inch opening; the blanket opening is 3 inches in diameter. Two types of cutters are available for detaching the diffuser screens from the core tank; tools have been devised for electrolytically decomposing the loose screens or cutting them into small strips with an underwater Heliarc torch; a device to make a casting of the hole for use in machining a plug was developed; and the device for inserting a mechanically sealed plug was perfected. These tools contrast with those used in component replacement in that they are designed for specific rather than general operations, and are usually discarded after limited use rather than decontaminated for further use.

Investigation of maintenance problems was a very important part of the work of the PAR Project. The maintenance methods developed for the industrial-scale Pennsylvania Advanced Reactor consisted of remote dry operations exclusively. All-welded construction was proposed for those portions of the system in contact with contaminated fluids, and equipment replacement therefore required remote pipe-cutting and welding.

A program was formulated to demonstrate the technical feasibility of remotely maintaining the homogeneous reactor power plant and to provide sufficient cost information to permit an evaluation of equipment and plant costs. This program, based on the use of remote handling equipment, included the following.

1. A complete survey was made of many existing reactor maintenance facilities, equipment, and techniques. As a result of the survey, it was concluded that a limited amount of the existing technology could be directly applied to PAR without extensive research and development.

2. Using preliminary maintenance concepts, work was started on the problems of plant layout on a continuing basis. As new maintenance techniques and component designs were con-

ceived, the layout was changed to reflect the new concepts. The use of three-dimensional models played a significant role here. There was a striking difference between successive reference designs as a direct result of the development of more realistic techniques.

3. A program was initiated to design, build and test working models of many of the specialized maintenance devices so that their feasibility could be demonstrated. This program resulted in the design of a special manipulator for repairing the steam generator and various devices, such as positioners and welders, for repairing plant piping. Numerous tools and fixtures were fabricated for use with an electromechanical manipulator to dismantle and reassemble typical components or equipment mockups.

A considerable amount of development was carried to various stages of completion by the PAR staff on equipment to accomplish remotely the positioning, cutting, beveling, and welding of 1-, 4-, 10-, and 16-inch pipe, and inspecting the soundness of the weld by ultrasonic methods. An experimental 10-inch pipe welder was built and used for a large number of welds. Random samples were tested and found to be completely satisfactory based on section IX of the ASME Boiler Construction Code. A Heliarc process for cutting and beveling pipe was successfully demonstrated. A report by Sperry Products, Inc., concluded that ultrasonic methods, with further development, can be used to inspect stainless steel welds. Special equipment and techniques will be required, however, to carry out these procedures remotely.

Special attention was given by the PAR project maintenance of main circulating pumps and heat exchangers. It was proposed that the working portion of a "top-maintenance" pump would be transferred from the reactor to a hot-cell facility for repair; a spare would be available for immediate installation into the reactor. A mockup hot cell, with associated manipulating equipment, was constructed to aid in the development of a maintainable pump. Dismantling of a standard centrifugal pump was practiced, and a special plant-size pump mockup was built for evaluation of assembly and disassembly.

Because of its extreme size, routine removal of a steam generator from the plant for repair was believed to be economically prohibitive. It was therefore felt necessary to repair tube leaks with the generator in place, and detail design of the generator layout and of repair procedures was well under way when the PAR project was suspended.

A faulty tube is repaired by (1) cutting a large access port to the tube header with adapted standard pipe-cutting equipment, (2) locating the leaking tube with a scanning helium leak detector, (3) preparing the tube joint, (4) welding a tube plug, (5) television inspection of the welded plug, and (6) cleanup and rewelding the head. Preliminary testing of tools for locating the leak was started. After trying several types of cutters for joint preparation, a hydraulically-fed, air-driven end mill cutter was found to perform best. A commercially available tube welder was adapted for welding the plug, and the machine performed successfully. Detail design of a manipulator to operate these machines was in progress.

Considering the progress made in demonstrating maintenance techniques at the HRE–2, and by PAR, the feasibility of these operations is believed to be established. However, many additional tools and methods need to be developed before firm maintenance practices and costs can be specified.

9.4 INSTRUMENTATION AND CONTROL

9.4.1 Introduction

The instrumentation and controls system and components for an aqueous homogeneous reactor are similar in many respects to those used in modern steam power and chemical plants and in other types of reactor plants. However, problems attendant to radiation damage to electrical insulations, the difficulty of performing maintenance or replacement operations, the uniqueness of some of the applications, the necessity for absolute leaktightness, and the very high reliability required of components has necessitated the testing and improvement of standard components and development of some special components.

Objectives of the instrumentation work are:

1. To develop complete control systems for aqueous homogeneous reactors; aimed recently at utilizing electrical transmission and solid state elements, transistors and magnetic amplifiers, for increased reliability.
2. To develop and evaluate primary sensing elements.
3. To develop control valves for aqueous homogeneous reactors.

Unusual requirements of the instrumentation include:

1. The reactor fuel solution and blanket slurry are very radioactive. Radiation damage to electrical insulations and elastomer seals necessitates the development of components not incorporating organic materials.
2. The relatively high system pressure and temperature and the radioactive nature of the fluids necessitates the use of double-sealed or individually safety-housed instruments. The primary seal is required to be a weld or ASA ring-joint to ensure a reliable high-pressure seal.
3. All valves and instruments should be self-draining so that radioactive fluids will not be retained during reactor shutdown periods to complicate maintenance operations.
4. The values and instruments should be amenable to remote adjustment or replacement by extension tools while flooded with water which may be used as a radiation shield.
5. Because of the expense and difficulty of maintenance operations, maximum reliability is required of all components. Accuracy may be sacrificed in instruments to gain a simple design.
6. Damping of spring-mass instrument mechanisms is necessary to minimize the noise signals caused by positive displacement feed pumps connected to the system.
7. The instruments and valves must be corrosion resistant to acidic solutions used in the process and for decontamination and pretreatment.

In the course of instrumenting HRE–1, HRE–2, and the component and system test loops, much experience has been gained in the application of instruments and valves to aqueous homogeneous reactors. Some new instruments and valves have been developed and commercial instruments have been modified to meet the special requirements.

9.4.2 Signal Transmission Systems

A complete instrumentation and control loop contains a sensing element, a transmitting means, transmission lines, transducing elements, and a final control element. This loop must provide a record or indication of the controlled variable, must control the variable, and may require means for providing an alarm or safety control action if the variable exceeds preset limits.

In a homogeneous reactor plant the primary sensing and transmitting elements, and usually the controlled element, are inside a containment vessel and biological shield. The remainder of the loop components are in a control room or located with auxiliary process equipment. To provide a means of communicating information between these areas, a signal transmission system must be employed.

A system that allows the use of the best features of electric and pneumatic systems was designed and developed for HRE–2 and illustrated in Figure 9.2. It utilizes electric transmission from primary variable sensing elements auxiliary control-room transduction to pneumatic signals, miniature pneumatic-instrument control-room display and control, and pneumatic valve actuation. The escape of radioactivity through pneumatic transmission lines is prevented by the automatic closure of "block" valves upon a signal indicating release of radiation within the vapor-contained area. Radiation damage to primary elements is

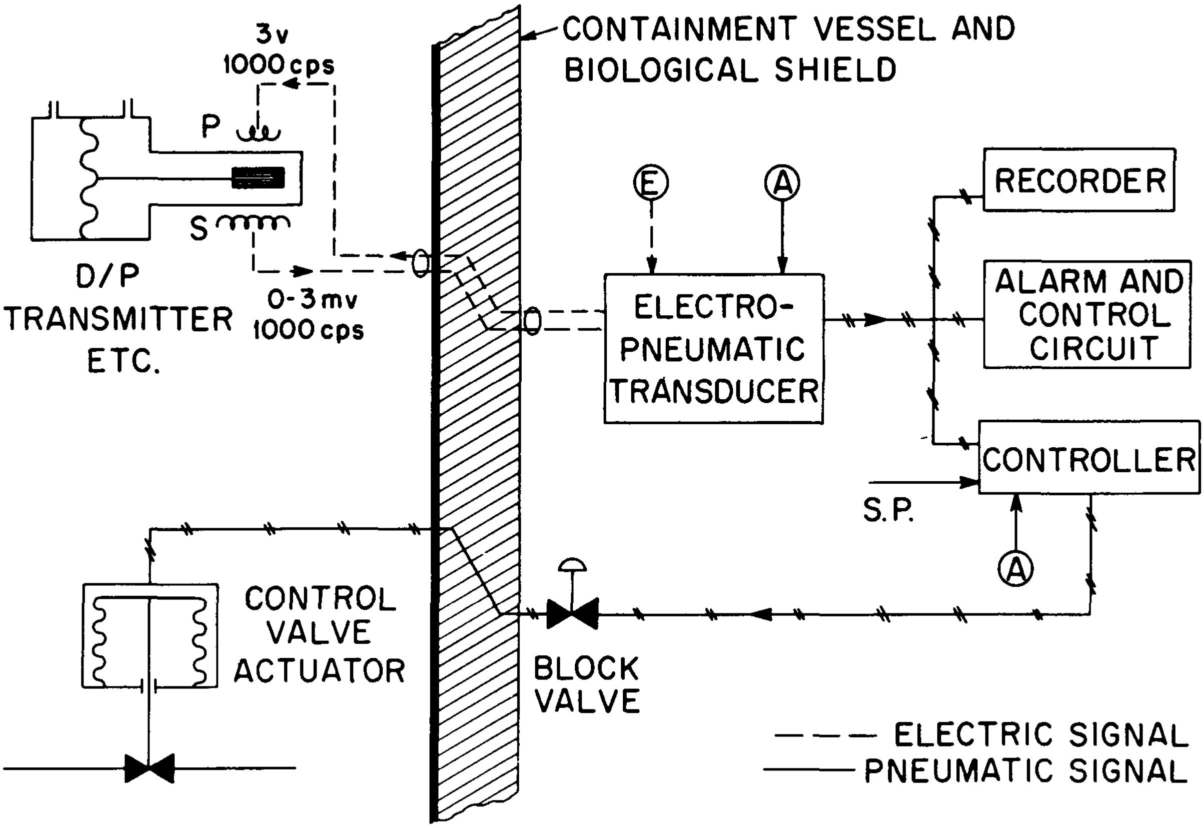


FIGURE 9.2—Typical nuclear plant instrumentation and control loop.

avoided by the use of inorganic electrical insulations such as ceramics, mica, metal oxides, and magnesium silicate. Electric control actions are derived from the pneumatic signals by precision pressure switches. Electric interlock control of the pneumatic signals to final control elements is achieved by the use of solenoid-actuated pilot valves.

Advantages of electric transmission from primary elements include the ease of readjusting sensor zeroes and spans from the control room by the use of bucking potentials and bridge adjustment, and the ability to sense motion from sealed transmitters by magnetic induction to a differential transformer. The speed of information transmission, the ease of switching signals, and the ability of the electrical sensing elements to operate over a wide temperature range is also important.

Advantages of the pneumatic part of the system include the utilization of simple pneumatic-powered metal-bellows linear actuators for the control valves, the high state of the commercial development of the miniature pneumatic recorder-controllers, the relatively low cost, and the ease of paralleling receiving elements.

9.4.3 Liquid-Level Transmitters

The measurement of liquid level in homogeneous reactors is necessary to indicate or control the vapor-liquid interface in process vessels. The liquid phase may be uranyl sulfate, thorium oxide slurry, or water.

Both displacement and differential-pressure instruments have been developed for continuous measurement of liquid level in vessels at high pressure. The displacement transmitters have been used with ranges as low as 0 to 5 inches of water. The minimum range of the differential-pressure transmitters used to date is 25 inches of water.

The HRE-2 pressurizer liquid-level transmitter consists of a 5-inch long displacer suspended by two helical springs. An extension rod above the springs positions a magnetic piston in the center of a differential transformer. Vibration of the float is damped by the action of the field from permanent magnets on a one-turn copper ring. The only nonwelded closure is the ASA 2,500-psi ring-joint flange, which makes the unit amenable to remote replacement.

The displacer suspension and motion-transmitter design does not involve torque tubes, bellows, or diaphragm motion-transmitting pressure seals, which are subject to fatigue from float vibration. An electro-mechanical transducer for converting linear motion to a proportional a-c electric signal is used to sense the displacer motion through the nonmagnetic austenitic stainless steel pressure housing. This device is a differential transformer whose construction is such that the position of the stainless steel shielded ferromagnetic core determines the voltage coupled from the center primary coil to the two symmetrical secondary windings. This instrument is illustrated in Figure 9.3.

A second displacement-type liquid-level transmitter was also developed for systems with maximum operating pressures of 500 psi. This transmitter, which has been used with displacers as long as 47 inches, is damped by the interaction of two moving vanes attached to the float and a baffle attached to the housing. The transmitter also uses a differential-transformer motion-sensing pickoff.

The measurement of liquid level by the differential-pressure technique is done by comparing the variable level in the vessel with a fixed reference level. This method has proved satisfactory only when the constant reference level can be maintained by condensation or by periodic addition of fluid.

9.4.4 Inventory Measurement

A weigh system utilizing pneumatic weight cells was developed as the only feasible method of measuring the quantity of liquid in the long, horizontal storage tanks of HRE-2. A pneumatic system was selected primarily because taring can be done remotely with balancing air pressures and the components are less susceptible to radiation damage. The pneumatic load cells have an accuracy of $\frac{1}{10}$ percent; however, when used in a system with solid pipe connections to the weighed vessels, an accuracy of 1 percent of full load results.

9.4.5 Pressure Transmitters

All-welded pressure transmitters utilizing type 347 stainless steel C-spring and twisted Bourdon elements as well as spring reinforced bellows have been developed for homogeneous reactor applications. All common pressure ranges are easily derived by the use of a properly sized tube or spring. Tests have shown that twisted elements are superior in their resistance to calibration shifts caused by the application of higher than design pressure as is necessary during hydrostatic safety tests. Secondary pressure housings are provided for fluid containment in case the relatively thin sensing elements should fail. The motion of a ferrite core in proportion to applied pressure is sensed through the backup containment housing in two commonly used instruments. In a third type the electrical leads are brought through the containment housing by glass-to-metal sealed feed-through bushings.

Pressure transmitters are usually connected into the steam or water portions of aqueous homogeneous systems to reduce the probability of corrosion or other damage. However, a transmitter using a spring reinforced bellows sensing element has given good service when connected directly to a process line containing fluid at 300° C. This transmitter, which also has a secondary seal bellows is illustrated in Figure 9.4.

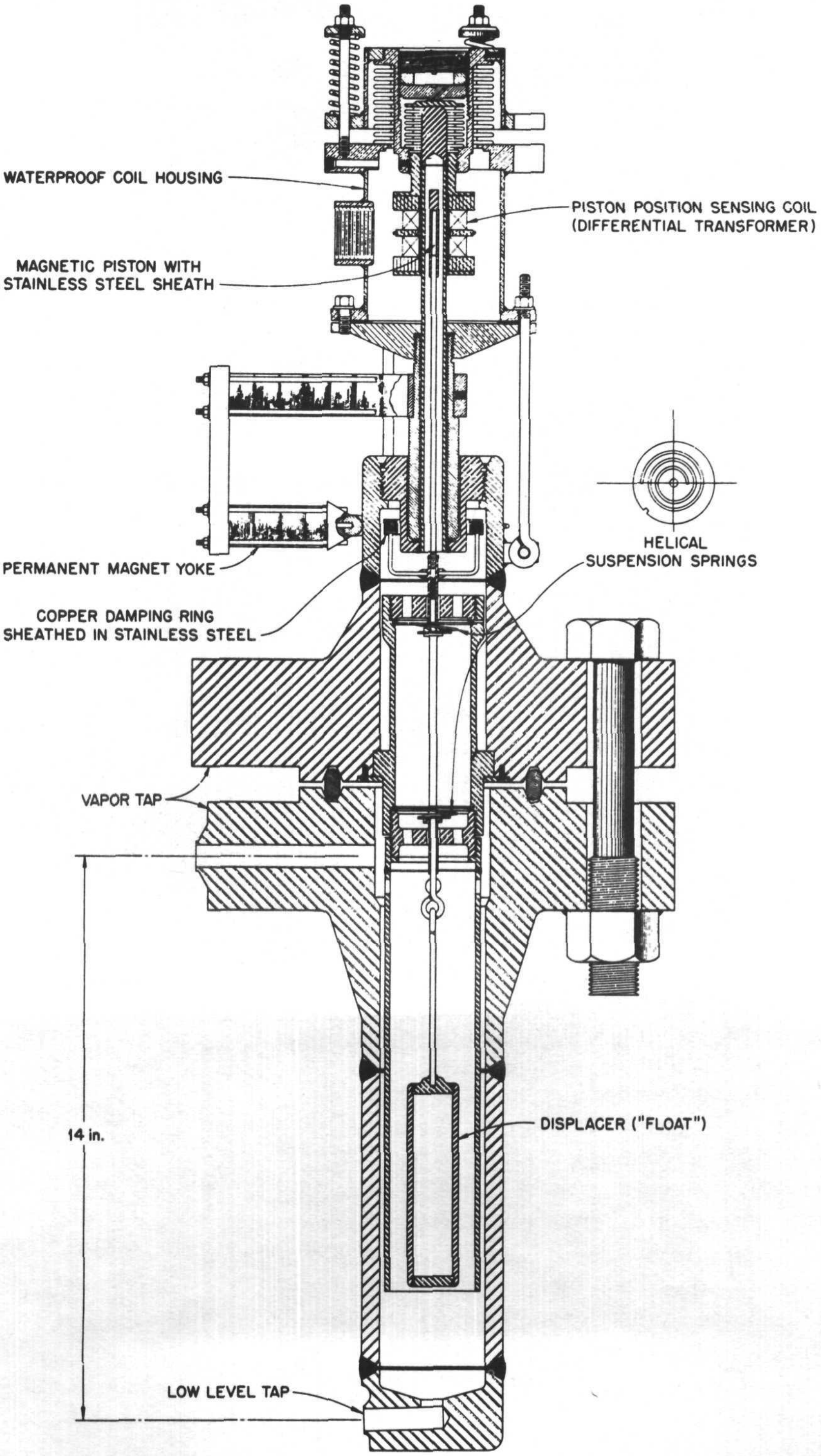


FIGURE 9.3—HRE–2 level transmitter covers a 5-in. range at 2,000-psi operating pressure.

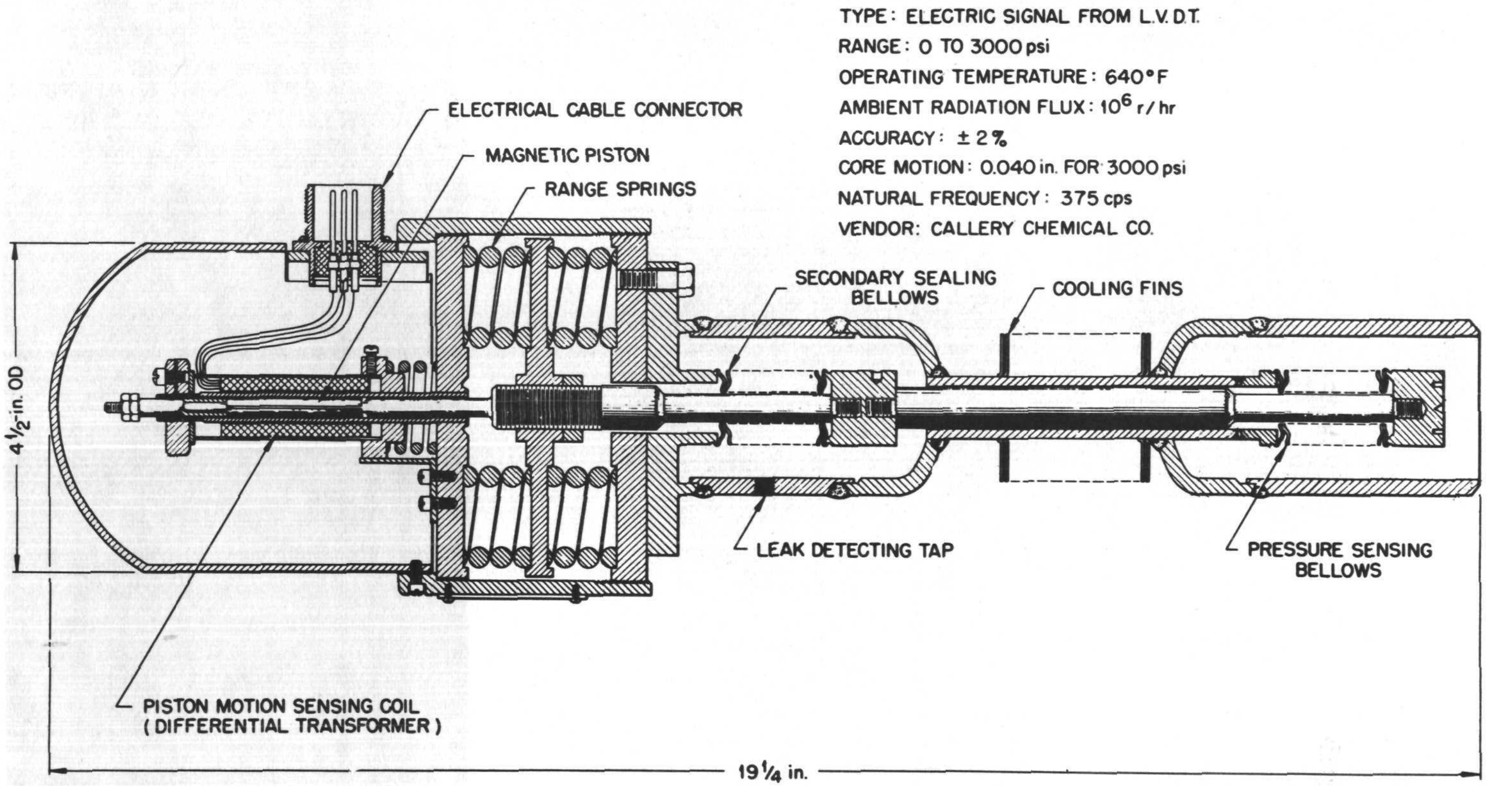


FIGURE 9.4—Pressure transmitter with secondary seal.

9.4.6 Differential-Pressure Transmitters

Differential-pressure transmitters with diaphragm or bellows sensing elements have been used with measurement ranges from 25 inches of water to 125 psi. The sensing element is mechanically-coupled by a rod to the ferrite core of a differential transformer. An all-weld-sealed design has been developed in which motion of the stainless steel clad core is sensed through a pressure housing.

A transmitter is now under development for slurry applications which has a diaphragm which will mount flush with the pipe or vessel wall to avoid plugging by slurry. The back side of the diaphragm will be pressure-reference connected to a system vapor space or other constant gas pressure. This transmitter is illustrated in Figure 9.5 (LR–DWG. 34722R).

Transmitters without this flush diaphragm feature have been used on slurry systems with the pipe connections being purged with 10 to 30 cc/min of water to prevent plugging. Unpurged relatively large vertical piping connections with the transmitter mounted above the primary piping have also been satisfactorily used at moderate slurry concentrations. A water-slurry interface is established in the vertical dead ended connection to the instrument and the instrument is filled with water.

9.4.7 Flow Transmitters

Relatively large flow measurements are made in high-pressure lines by sensing the pressure drop across a calibrated orifice or venturi with differential-pressure transmitters connected as described previously.

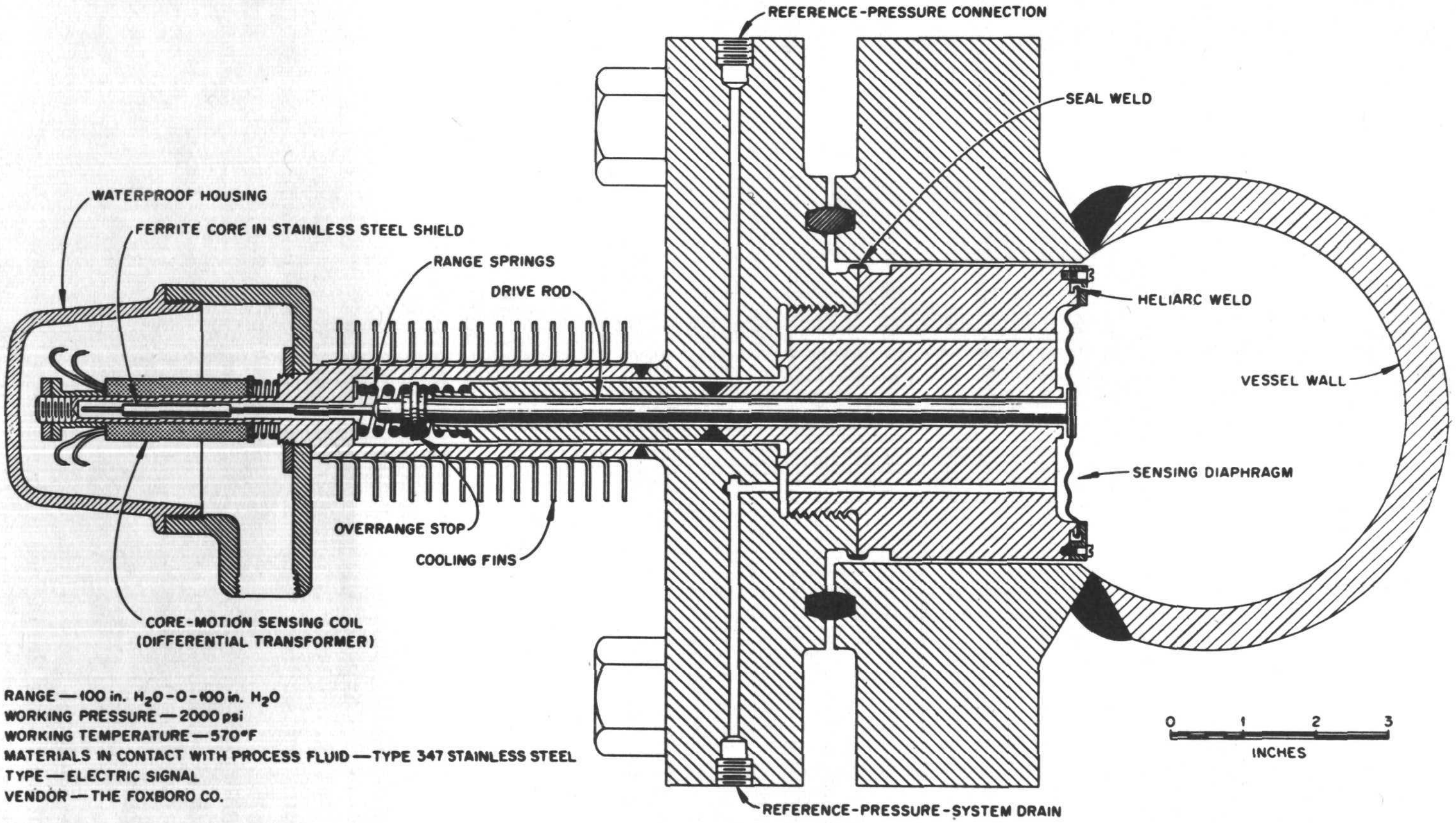
Transmitting flowmeters of the variable-area type are being used for measurement of the very low purge-water flows to the pressurizers and circulating pumps in test loops. These flowmeters have worked very well because the in-line connection avoids stagnant areas which might fill with sediment and plug the meter. Other features of this meter include the linear output signal necessary to produce a true average of the pulsing flow when damped by a suitable electric filter, and a low head loss which allows the transmitter to be installed in the low-pressure suction line of the pumps. These transmitters were not developed when the HRE–2 was constructed and "heat balance" meters are used to indicate small flows in this plant. Flow is deduced by noting the temperature change when a known amount of heat is added or extracted from the process stream. Satisfactory accuracy has yet to be achieved by this technique and frequent calibration checks are necessary.

9.4.8 Control-Valve-Stem Position Transmitter

A valve-stem position transmitter which uses a simple 60-cps transducer system was made to withstand HRE–2 reactor-cell environmental conditions of 140° F. ambient temperature, flooding by water, and high levels of radiation. The differential transformer has a linear range of 0 to ½ inch, a linearity of 2 percent and an output of 0.1 volt for ½-inch core travel. Fiberglas-insulated lead wires leave the waterproof transformer housing in a ¼-inch copper tube conduit.

9.4.9 High-Temperature Radiation-Resistant Differential Transformers

A key element in most of the process measurement systems described above is the linear variable differential transformer for sensing the primary element motions of sealed instruments. A differential transformer capable of operating at 300° C and in high radiation fields has been developed. There was no change in characteristics when the transformer was cycled from 25 to 350° C with a span setting of 0.025 inch, and the shift in zero and span was less than 2 percent in a 3-month test at 300° C. The transformer has a sensitivity of 0.1 mv/volt per 0.001 inch at 1,000 cps when used with appropriate exciting and impedance matching circuitry.



RANGE—100 in. H_2O-0-100 in. H_2O
WORKING PRESSURE—2000 psi
WORKING TEMPERATURE—570°F
MATERIALS IN CONTACT WITH PROCESS FLUID—TYPE 347 STAINLESS STEEL
TYPE—ELECTRIC SIGNAL
VENDOR—THE FOXBORO CO.

FIGURE 9.5—Flush diaphragm differential-pressure transmitter.

The transformer is wound with No. 24 AWG ceramic-insulated nickel-plated copper wire on an Inconel form. The two secondary windings are wound on the Inconel form and are separated by a Lava spacer. The primary is wound over both secondaries and the windings are impregnated with Allen PBX ceramic cement. The transformer is also sealed in an Inconel housing and has a ⅝-inch-diameter bore for the instrument pressure housing extension. The lead wires are brought out through the housing in a ¼-inch-OD tube. In HRE–2 the pressure housing is stainless steel. The 1⅛-inch-long movable transformer core is Armco iron clad with stainless steel.

The resistivity of the coil form was found to be a significant factor because the coil form acts as a shorted secondary turn on the transformer and results in a phase shift and a reduction in amplitude of the output signal. For this reason, materials of low resistivity and high temperature coefficient of resistivity, such as aluminum, were found not to be desirable. Inconel, which has a high resistivity and a very low coefficient of resistivity, now appears to be the best choice for a metal coil-form material. Inconel is much better than the 300-series stainless steels in this respect since its temperature coefficient is about one-tenth that of stainless steel.

For the windings used on the motion-sensing coils of instruments, 30-gage anodized aluminum wire has successfully withstood temperatures to 300° C and exposure to 6×10^{17} nvt of neutrons and 1×10^{8} r of gamma irradiation without failure.

Impregnation of the windings with a high-temperature ceramic cement is necessary to avoid zero and null shifts with temperature due to mechanical displacement of the windings. Pressure-crimped joints are necessary for reliable connection to the transformers.

9.4.10 Signal Transducers

The electropneumatic converter with its six vacuum tubes and its power supply of 115-volt ac, 60 cps, is the least reliable component in the control loops now in service in HRE–2.

To improve this situation, a transistorized electropneumatic converter which can be powered from the battery supply available in most power plants is under development. This instrument converts a low-level millivolt a-c output from such devices as differential transformers, inductance bridges, and strain gages to proportional 3- to 15-psi pneumatic signals and operates from 48-volt dc.

As the transistorized converter can be powered from a 48-volt battery and an emergency air supply can be furnished by high-pressure storage tanks, the instrumentation system is capable of uninterrupted operation in the event of a failure of the normal utilities. A prototype instrument has been built for testing.

Transducing equipment designed around magnetic amplifiers is now available and would certainly be more reliable than vacuum tube equipment. However, 60-cycle carrier systems are used in the presently available equipment which necessitates the use of differential transformers with many more turns of smaller wire than required with the 1,000 cps vacuum tube and transistorized equipment described above. An emergency a-c power supply for the mag-amp equipment also requires rotating machinery in comparison to the battery supply for the transistorized equipment.

9.4.11 Control Valves

Valves are key components in homogeneous reactor systems as they are the means by which process gas and liquid streams are controlled. In the HRE–2 system, which has no control rods, temperature and reactivity are controlled by valves which control the concentration of the fuel solution, and the power is controlled by valves which control the rate of steam removal from the heat exchangers. "Dump" valves perform an emergency scram and normal drain function by controlling the flow of fuel solution to low-pressure storage tanks. Other valves perform pressure-control functions, allow noncondensable gases to be bled from the system, or are used to isolate equipment. A complete line of bellows-sealed valves and actuators was developed for HRE–2 in cooperation with manufacturers and the development has been continued to obtain improved equipment for slurry reactors and other systems.

HRE–2 Type Valves

HRE–2 valves are made of stainless steel in sizes from ¼ to 1 inch and equipped with bellows seals. The valves are rated at 500 psia and 2,500 psia for low-pressure and high-pressure applications respectively. Normally the seat is type 347 stainless steel and integral with the body and the plugs are Stellite–6 or type 17–4 PH stainless steel. Developmental valves have been made with replaceable trim of stainless steel, Stellite, Zircaloy, titanium, tungsten carbide, and other materials. A gold-gasketed valve has been developed for tight shutoff of gases. The gasket is placed into a groove machined in the valve plug, which mates with a tongue machine into the seat.

The primary bellows seal is mechanically formed of three plies of 0.0085-inch-thick type 347 stainless steel and is 3¾ inches long. Four of these bellows assemblies have been cycled at 285° C and 2,300 psi for an average of 132,000 ⁹⁄₃₂-inch strokes before failure. Two such bellows assemblies are joined to provide the ½-inch-stroke length required of larger valves. An average life of 50,000 ⅝-inch strokes at 500 psi has been obtained in testing the tandem assembly. Three-ply bellows also have been made of A55 titanium and tested satisfactorily at shorter strokes.

In all valve designs, the bellows seal is backed by a graphited-asbestos packed seal. A tube connected to an opening between the bellows and the secondary seal affords a means of detecting a bellows leak while the asbestos seal prevents gross leakage of process fluid in the event of a bellows failure.

Low-pressure valves are fitted with integral ring-joint grooves. Long bolts at the corners of the valve body hold the companion flanges; the valve is replaceable with the disassembly of only one set of bolts.

The main problems encountered with the valves have been misalignment of the stem and corrosion of the plugs.

Typical construction of HRE–2 valves is illustrated by the high-pressure throttling valve shown in Figure 9.6.

Slurry Service Valves

A 1-inch-diameter-port Y-body valve has been designed and fabricated for 500-psi slurry applications. The prototype valve has a tandem bellows assembly stem-seal which can be butt-welded to the valve body to provide a reliable leaktight seal. A secondary stem seal of graphited asbestos backs up the bellows, and a pressure tap between the two seals is provided for leak detection. Provision is made to flush the bellows compartment with a flow of condensate introduced through the bonnet and discharged through the lower stem guide.

A valve especially designed for high-pressure service is now being tested in a slurry system development loop. The valve shown in Figure 9.7 incorporates a long-radius-bend body configuration to minimize erosion by the slurry. The bellows compartment can be purged to prevent slurry from entering through the annulus between the Stellite No. 6 stem guide pads and the Colmonoy hard-faced stem. As the two-ply type 347 stainless steel bellows used in this valve is rated at only 450 psi, provision is made to back-pressurize the bellows when the valve is used in applications above this pressure. The valve body is designed for a working pressure of 2,000 psi at 300° C. The plug and seat are fabricated of tungsten carbide for wear resistance, although tests subsequent to the installation of this valve indicate that Zircaloy-2 is a superior trim material for high-temperature slurry valve applications.

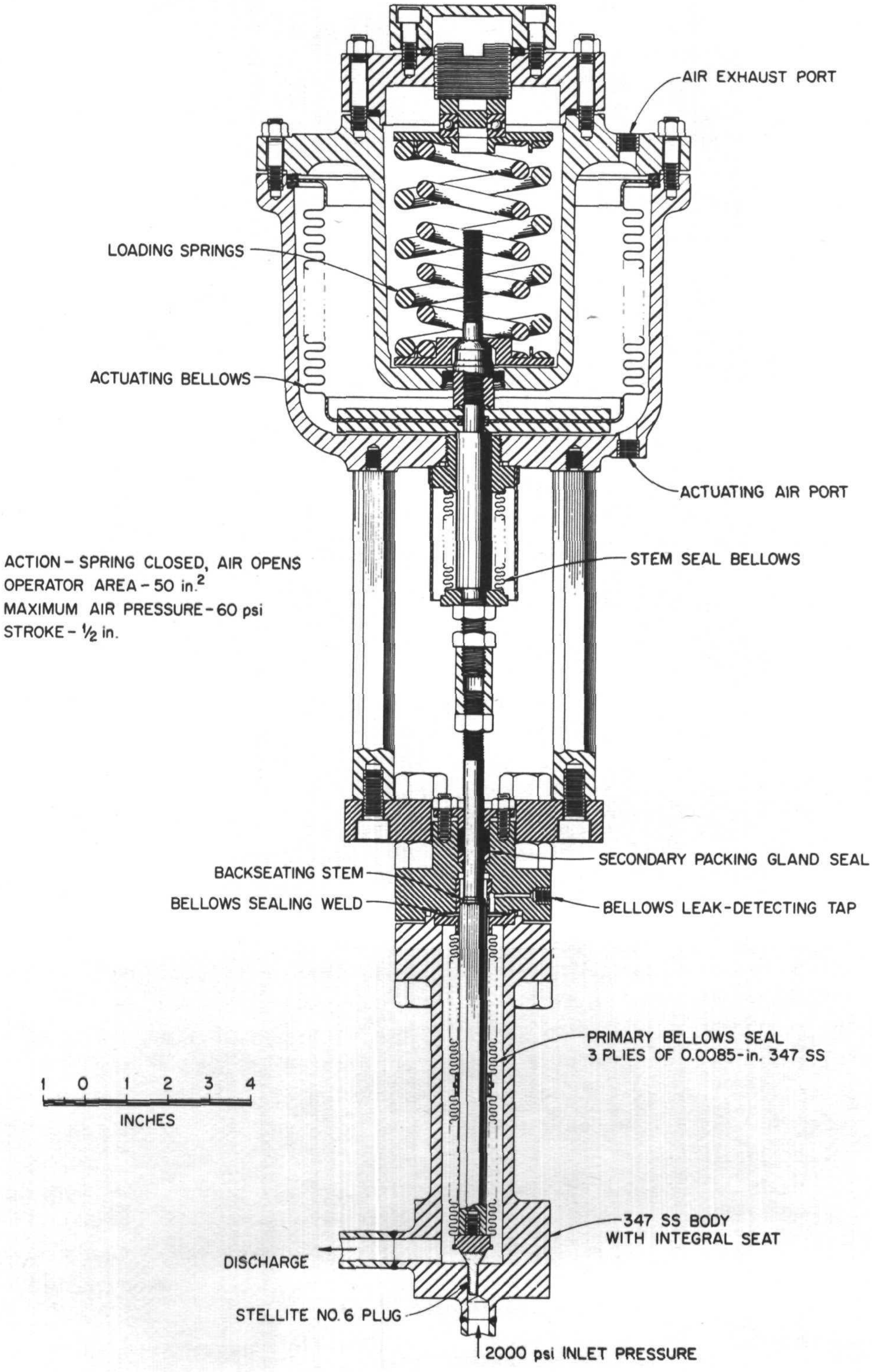
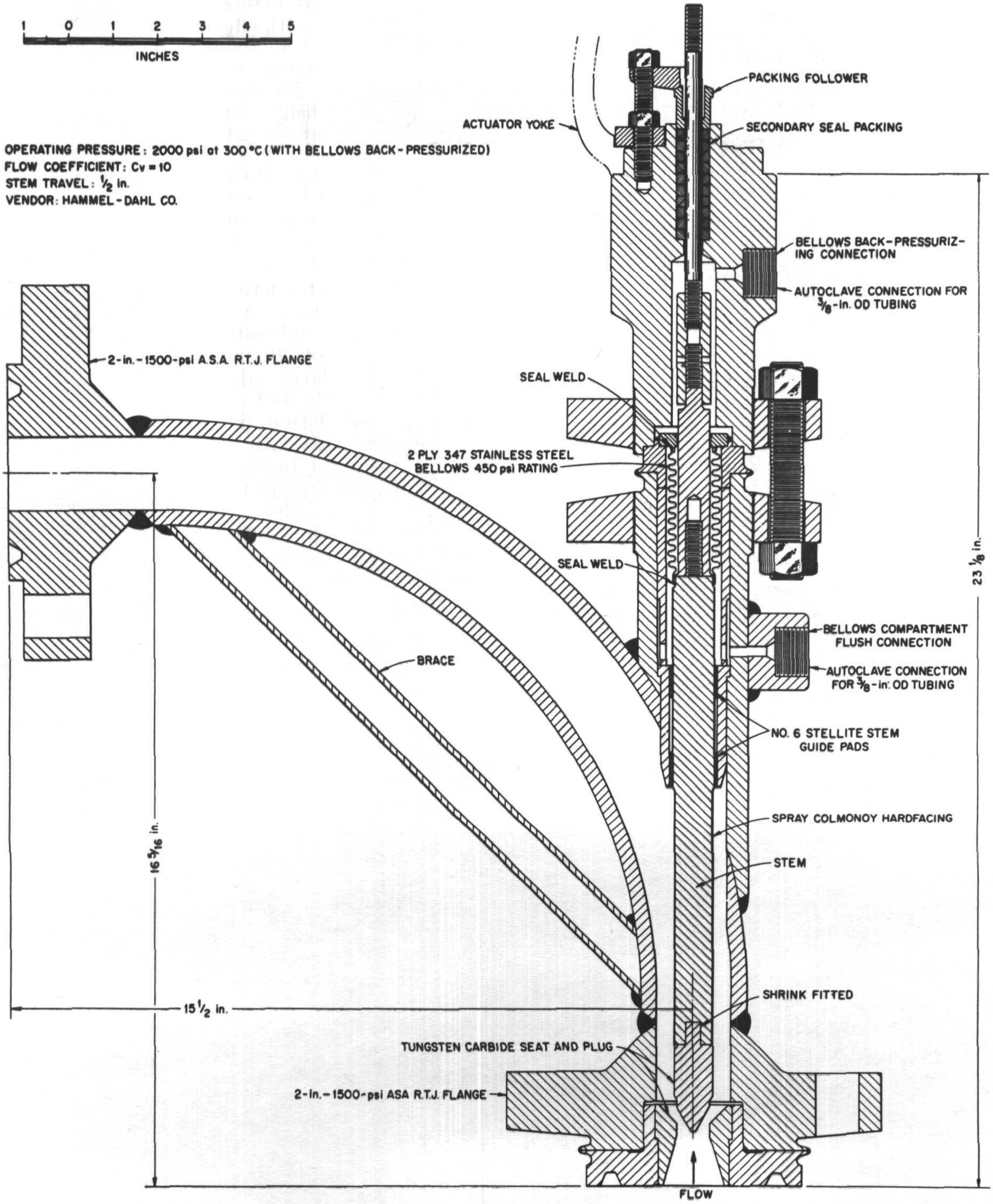


FIGURE 9.6—High-pressure throttling valve.



OPERATING PRESSURE: 2000 psi at 300 °C (WITH BELLOWS BACK-PRESSURIZED)
FLOW COEFFICIENT: Cv = 10
STEM TRAVEL: 1/2 in.
VENDOR: HAMMEL-DAHL CO.

FIGURE 9.7—High-pressure slurry valve.

Special Gas-Metering Valve

A differential-thermal-expansion metering valve has been developed to regulate the flow of oxygen gas to the HRE–2 high-pressure system. The required flow is very small and is difficult to control by conventional mechanical positioning methods. The valve is operated by heating the assembly electrically and utilizes the difference in thermal coefficient of expansion of tantalum and stainless steel to effect flow control. A tantalum plug is used to avoid any possibility of an ignition reaction between the oxygen gas and the metal, which for a flow of 2,000 standard cc/min with a 400 psi differential is heated to about 330° C. The design incorporates all-welded construction and is covered with a waterproof protective housing. The resistance heating element and thermocouple are duplicated to ensure continuity of service.

Actuators

Pneumatically-powered metallic bellows actuators have been developed for remote operation of the valves to avoid problems of radiation damage to hydraulic fluids, elastomers, or electrical insulations. The actuator is a simple linear device which can be controlled with standard pneumatic controllers or regulators. The bellows may also be stacked to multiply the forces available. Pneumatic actuators in HRE–2 develop up to 5,440-pound force. Upon loss of air pressure these actuators are made to either open or close the valve by the proper placement of loading springs.

HRE–2 metal bellows actuators have now been developed with effective areas of 23, 40, 50, 68, and 123-in.^{2} to meet a variety of needs. Maximum actuating air pressure rating is about 75 psig except for the 23-in.^{2} actuator which is rated for 30 psig. Nominal rated strokes are ½ inch. All of the actuators have been tested to more than 100,000 cycles. An actuator capable of developing a thrust of about 6,000 pounds has been cycled four times per minute at a stroke of ½ inch and a pressure of 80 psig for 265,000 cycles before developing a small leak in the stem sealing bellows.

A control-valve actuating system using water at 500 psi as the working fluid has been tested also. Possible advantages of the water-operated system over air-operated and oil-operated actuators for large valves are the size reduction of the cylinders and the relative immunity of water to radiation damage. Some difficulty was experienced with the packing in the pump during the first 15,000 cycles, but operation of the cylinder remained satisfactory to approximately 35,000 cycles. At this time an appreciable leak developed due to worn piston rings. The leak did not appreciably increase on further operation to a total of 55,000 cycles.

10. REACTOR PHYSICS AND SAFETY

Nuclear characteristics of homogeneous reactors refer to the conditions and material concentrations under which reactor systems will remain critical, the relative changes in concentration of materials within the system as a function of reactor operation, and the time behavior of variables in the reactor system which occur when deviations from criticality take place. The nuclear characteristics thus determine the relations between critical concentration, heat generation rate, reactor safety, and design conditions, and help determine the reactor design that will satisfy the diverse requirements associated with successful operation of a thorium breeder reactor system.

To date, information concerning reactor control and safety has been obtained from operation of aqueous-homogeneous reactors and from calculational studies. In studies of criticality, experimental results have been compared with calculated results, and survey-type calculations have been made of fuel concentrations required for criticality, power densities in vicinity of wall regions, breeding ratios, and doubling times. Measurements have been made pertaining to the number of fission neutrons emitted per neutron absorbed in $U^{233}(\eta^{23})$. This value directly affects the breeding ratio and doubling time attainable in thorium-breeder reactors. At present there is still need for comparison and correlation of calculated and experimental results, even though significant progress has been made in that direction. Increasing sophistication in reactor physics calculations has increased understanding of the problems to be considered in reactor design, and led to improved reactor evaluation.

10.1 REACTOR CONTROL AND SAFETY

Aqueous-homogeneous systems have a relatively large negative temperature coefficient of reactivity, which leads to inherent reactor control and safety. A number of homogeneous reactors have been built and operated, such as HRE–1, HRE–2, various water-boiler-type reactors, LAPRE–1, and LAPRE–2. All of these systems have operated satisfactorily from the viewpoint of reactor control and safety. Some have had control and safety rods; in the case of HRE–1, rods were placed into the system as safety measures but later proved to be unnecessary. Water-boiler-type reactors normally have control rods for the sake of convenience; however, as illustrated in kinetic experiments on water boilers (KEWB program), such reactors have a high degree of inherent safety. The HRE–1 and –2, and the LAPRE–1 and –2 have operated satisfactorily without the use of any control rods.

The nuclear safety of homogeneous reactors is a function of the maximum permissible reactivity addition and the possible reactivity additions. Despite the inherent safety associated with a large negative temperature coefficient of reactivity, it cannot be stated a priori the homogeneous reactors are safe under all operating conditions. The limiting feature with respect to reactivity addition is the permissible pressure rise within the reactor system. This is usually either the maximum permissible core pressure rise or the maximum permissible pressure rise within the pressure vessel, as determined by the mechanical strength of the vessels.

With a given limit on the maximum permissible pressure rise, it is possible to specify the maximum permissible reactivity addition. Reactor operations can then be restricted by design, so that reactivity additions associated with physical events will not exceed the maximum permissible reactivity addition.

The potential reactivity available in homogeneous systems is inherently large, because a high operating temperature is coupled with a high negative temperature coefficient of reactivity. However, all reactivity additions involve a time element. Since it appears desirable to allow continuity of physical operations, the safety design criteria should be applicable to continuous, linear rates of reactivity addition. Specifically, the maximum permissible linear rate of reactivity addition should specify what restrictions are necessary on the physical system so that this rate is not exceeded.

A feature related to control and safety is reactor stability. The purpose of stability studies is to determine whether the reactor power will return to a stable equilibrium condition following a system disturbance. Although inherently connected with safety, stability studies usually treat small reactivity additions and concern time intervals long in comparison with those involved in safety studies. The general stability problem can be broken into simpler problems by eliminating those parts of the physical system which have only a small influence upon the time behavior of the variable of interest.

10.1.1 Homogeneous Reactor Experiment (HRE–1)

The HRE–1 was primarily built for the purpose of demonstrating the inherent safety and self-control characteristics of aqueous homogeneous reactors. The reactor consisted essentially of an 18-inch-diameter spherical core inside a 39-inch-diameter reflector vessel, a circulating pump, and a heat exchanger where steam was produced for the operation of the turbine generator. The design conditions were 250° C temperature, 1,000 psig pressure, and 1,000 kw reactor power. The material of construction was type 347 stainless steel. A low-pressure system contained dump tanks for the storage of fuel solution, an evaporator and condensate tanks for changing concentration, and recombiners for the decomposition gases released in the core. The fuel was a light-water solution of UO_2SO_4 with a U^{235} enrichment of 93 percent, and the reflector was heavy water.

Extensive calculations were made for the purpose of predicting the nuclear behavior of the reactor, and these served as a guide in the building and experimental testing of the reactor. The total available reactivity increases (Δk_e) were potentially large—reflector, 7 percent; fuel concentration, 25 percent; temperature, 20 percent—but were normally limited to rates under 0.05 percent per sec. Under unusual circumstances in which the circulating pump was turned off, the fuel fluid in the heat exchanger was cooled to about 100° C, followed by pump startup, reactivity rate additions up to about 0.7 perecent Δk_e per sec could be reached. Under these circumstances the maximum net reactivity addition was that which could be introduced into the reactor before the power reached a level at which the heating rate was sufficient to compensate the rate of external reactivity addition. Consequently, the situations of greatest interest were those involving low initial power and high rates of reactivity increase.

During the reactivity-addition experiments, the power level rose to some peak value (in some cases several times higher than the rated power of 1 Mw) followed by a rapid decrease to the equilibrium value determined by the rate of reactivity addition. For the most violent experiment, in which cold fuel from the heat exchanger was injected into the core, a minimum period of 35 milliseconds was attained, and a peak power of 11 Mw was observed. The peak powers were in reasonable agreement with calculations in which a solution of the kinetic equations with the temperature coefficient of reactivity neglected (valid at low power) was joined to a solution in which the delayed neutrons were neglected (valid when prompt critical is exceeded).

Under design conditions the HRE–1 operated in a satisfactory manner; no nuclear instabilities were observed, which agreed with prior calculational results. It was found that the fraction of fission neutrons which are delayed exerts a powerful damping influence on power oscillations, and affects the stability. In a circulating-fuel system some of these delayed neutrons are emitted outside the reactor; however, the decrease in the effective delayed-neutron fraction does not appear to have a significant effect on stability.

Studies were made concerning the effect that fuel circulation has upon the stability of the system; the results indicate that circulation of the fuel causes power oscillations to be damped.

Studies were also made of the HRE–1 power and temperature after stopping the pump. If the circulating pump of a homogenous reactor fails, the decay heat generated by the reactor raises the fuel temperature; it is conceivable that the temperature rise due to the power generated after pump failure may result in excessive system pressures. For the HRE–1 when operating with a core outlet temperature of 250° C, calculations indicated that the temperature would not exceed 282° C after stopping the circulating pump.

The demonstration of control, safety, and stability in HRE–1 led to the elimination of control rods in the HRE–2 design.

10.1.2 Homogeneous Reactor Test (HRE–2)

The HRE–2 was initially a two-region reactor, with a $U^{235}O_2SO_4$–D_2O solution in the core region and D_2O in the blanket region. The core tank is 32 inches in diameter and is centered in a 60-inch-ID pressure vessel. Reactivity control is by adjustment of the fuel concentration in the core region and by means of the negative temperature coefficient of reactivity. Nominal design conditions were 280° C, 2,000 psi, and 5 Mw.

Safety calculations were done for the HRE–2 to determine the permissible rates of reactivity addition for core and pressure-vessel integrity; the safety of the reactor is dependent upon the core temperature coefficient of reactivity, which has a value of about -2×10^{-3} $\Delta k_e/°$ C when a D_2O blanket is present. Under design conditions and source power level, the maximum permissible rate of reactivity addition is 0.8 percent Δk_e/sec, and the maximum permissible instantaneous reactivity addition is 1.9 percent Δk_e, if the limiting pressure rise within the system is 400 psi. Increasing the initial power level increases the permissible rate of reactivity addition significantly.

A number of physical events can occur during HRE–2 operation which will introduce reactivity into the reactor. These were investigated to determine whether the pressure rise associated with the reactivity addition exceeded the permissible pressure rise. The particular events studied were: addition of cold fuel solution into the hot critical core by misoperation of the heat exchangers and/or pump; addition of concentrated fuel solution into the reactor by means of the Pulsafeeder pump; the possibility of achieving criticality before the reactor core is filled; and loss of pressure in the blanket which would result in core-tank rupture and net addition of fuel into the reactor region. Where necessary, operational and design changes were incorporated such that the estimated reactivity addition would not cause core-tank rupture. In no case did it appear that rupture of the pressure vessel would take place.

Stability of the reactor system was studied to determine whether the reactor power would return to a stable equilibrium condition following a system disturbance. The problem was broken into three separate parts, termed nuclear, load demand, and physical stability. The nuclear stability studies considered the high-pressure system alone, and assumed that the power demand was constant. The load-demand stability studies assumed the fuel fluid to be incompressible and neglected the low-pressure system, but allowed the power demand to vary. The physical stability studies assumed an incompressible fuel fluid and that the power demand varied linearly with the fuel fluid temperature. These latter studies established whether physical operations associated with fluid flow between the high- and low-pressure systems would lead to a change in operating power level. In all of these studies, the lineralized equations of motion were used. For all cases, the HRE–2 was found to be stable under design conditions.

Although initial operation of the HRE–2 was as a two-region reactor, a hole developed in the core tank in April 1958, and subsequent operation was with the core and blanket regions connected through this hole. By blanking off the blanket pressurizer and pumping D_2O into the blanket region, a blanket-to-core purge was established, which maintained the blanket-fuel concentration about 0.3 that of the core-fuel concentration. The safety of the reactor operating under these circumstances was evaluated; calculations indicate that with the core hole present, the fuel concentration in the blanket may be as great as that in the core without endangering the safety of the reactor. Even with no hole present and the blanket pressurizer filled, there does not appear to be a safety problem if the blanket-to-core fuel concentration ratio is less than about 0.4.

During operation, a number of power variations have occurred which are attributed to fuel movement within the reactor core; analysis of these power variations showed that under no circumstances was the reactor near prompt-critical, and that pressure rises which took place could be attributed to the compression of the pressurizing vapor associated with thermal expansion of the fuel fluid.

10.1.3 Control and Safety Experiments in Water-Boiler Reactors

The first homogeneous reactor was the Los Alamos Water Boiler built in 1944; since that time the reactor has undergone several improvements and modifications, and numerous other water-boiler-type reactors have been built and operated. These reactors are normally used as research reactors, and control rods are employed rather than fuel-concentration control. However, they do have a large degree of reactor safety as illustrated in Los Alamos experiments and in KEWB experiments (Kinetic Experiments for Water Boilers). In the Los Alamos experiments about 0.5 percent Δk_e was injected into the reactor, with the fuel fluid at temperatures from about 30° C to boiling temperature (about 94° C). No rods were used to control reactor behavior; the reactor exhibited inherent control characteristics through its density coefficient of reactivity. It was found that at boiling temperatures the power transient was less than at lower temperatures; the results indicated that radiolytic-gas formation played an important factor in limiting the peak power during an excursion.

The KEWB program has provided extensive experimental evidence of the inherent safety of water-boiler-type reactors. About 4 percent Δk_e has been injected into the KEWB reactor without damage to the system. Data obtained through this program indicate that formation of radiolytic gases increases reactor safety to a marked degree. Although the effect of radiolytic-gas formation on the peak power decreased with increasing operating pressure (for a given reactivity addition), it appears that the effect could be significant even at high pressures. To date, safety calculations concerning aqueous homogeneous power reactors have assumed that inherent control was available through the temperature coefficient alone. During a power surge associated with a large reactivity addition, radiolytic-gas formation may occur due to inability of any recombination catalyst to recombine all the gases formed during the surge: under these circumstances, the results obtained from KEWB indicate that the power surge would not be as great as that which would occur if gases did not form. This control due to gas formation would normally be associated only with a large reactivity addition, but this is the circumstance under which it is most desired.

10.1.4 Slurry Reactors

Because of possible changes in fuel concentration and/or distribution associated with use of slurry-type fuels, the question naturally rises concerning reactivity changes which might take place in slurry reactors; as used here, "slurry" implies either uranium oxide in water, thorium oxide in water, or uranium oxide and thorium oxide in water. A number of calculations pertaining to this question have been carried out for specific reactors and events, and two series of experiments have been performed.

In one series of experiments, a UO_3–H_2O slurry containing uranium highly enriched in U^{235} was placed in a 12-inch diameter cylindrical vessel, surrounded by a partial reflector of H_2O. Critical masses were measured at concentrations ranging from 40 to 300 g U/liter at several stirrer speeds (the stirrer maintained the UO_3 in suspension). Under near-critical conditions, the stirrer was shut off, and the relative reactivity was measured as the UO_3 particles settled in the reactor core. The results indicated that large reactivity changes (5–10% Δk_e) can take place concurrent with fuel settling in small reactors which are reflected with light water, but that the rate at which this reactivity is added is relatively slow; i.e., 0.1–0.2 percent Δk_e/sec. Startup of the stirrer after particle settling can lead to much higher rates of reactivity addition.

In a reactor experiment at the KEMA Laboratories in the Netherlands, a UO_2–H_2O slurry was circulated in a system having a 12-inch diameter cylindrical core, surrounded by a BeO reflector. The maximum slurry concentration was about 200 g U/liter ($\sim$10% enrichment in U^{235}). The reactor was brought near critical (a strong neutron source was provided, and the multiplication of this source was used as a measure of reactivity; the largest value of k_e obtained was about 0.95). The reactivity fluctuations associated with normal fluid flow were estimated to be about 0.2 percent Δk_e, and these changes took place over periods corresponding to the core residence time (7 to 18 sec.). Stopping the pump caused a drop in reactivity, but restarting it resulted in a peak value of k_e greater than that under normal fluid-flow conditions. During several hours of circulation k_e was constant within 0.01 percent Δk_e, which indicated essentially zero change in circulating-slurry concentration. By means of a hydroclone, approximately 50 percent of the UO_2 was removed from the reactor in about a minute. Results obtained from this experiment have indicated that slurry fuels can be handled without encountering large reactivity changes.

The reactivity addition associated with fuel settling is a function of reactor fuel, geometry, and size. Based on results from two-group calculations for D_2O–ThO_2–$U^{233}O_3$ cylindrical reactors 10 and 12 feet in diameter and containing 200 and 300 g Th/liter, settling of fuel and fertile material in large one-region reactors leads to a decrease in reactivity. However, if slurry (containing 1,000 g Th/liter) settles in the blanket of a two-region reactor, reactivity additions of about 10 percent Δk_e may take place. Such additions, however, would not occur instantaneously; rather, they would be a function of time, the rate of reactivity addition being controlled by the rate at which the slurry settled. Settling rates for slurries containing 1,000 or 500 g Th/liter correspond to rates of reactivity addition of less than 0.02 percent Δk_e/sec. These rates are well within permissible rates of reactivity addition; however, the total reactivity added may be large enough to necessitate dilution or dumping of the fuel system to prevent the critical temperature and the reactor pressure from exceeding permissible values.

Calculated reactivity changes associated with slurry settling in the core region of a small slurry-core reactor indicate that such reactivity changes can be restricted to manageable proportions by proper nuclear design. It appears that by proper choice of core diameter and fertile-material concentration, settling of fuel material will lead to a decrease in reactivity. This appears to be true for slurry-core reactors which are either reflected or bare.

Calculations of the nuclear characteristics of spherical double-blanket reactors show that changes in blanket slurry concentration near the core wall cause larger changes in reactivity than corresponding changes in regions away from the core. The reactor considered had a 4-foot diameter, solution-fuel, spherical core, surrounded by a 0.5-foot-thick blanket region, which in turn was surrounded by a 1.5-foot blanket region. Slurry was assumed to be in both blanket regions. It was found that settling of slurry (initially containing 1,000 g Th/liter) in the outer region had a negligible effect on reactivity if the inner-blanket slurry contained 4,000 g Th/liter and did not settle. However, total reactivity additions of about 10 percent Δk_e were associated with settling of slurry in the inner-blanket region.

In a recent calculational study, the reactivity effect associated with slurry settling in the blanket of a fluidized-blanket reactor was investigated. The cylindrical reactor core was 4 feet in diameter and 12 feet long and was assumed to operate at about 280° C. If the blanket region contains slurry having 3,000 g Th/liter and is originally only as high as the core (12 ft), slurry settling to a maximum bed density of 5,300 g Th/liter (compaction) leads to a reactivity addition of about 11 percent Δk_e. To compensate for this amount of reactivity addition, the core temperature would need to rise over 50° C. However, by increasing the fluidized-blanket height, the reactivity addition associated with settling of blanket slurry is decreased (if in the example cited the initial blanket height were taken as 22 feet, slurry settling would add a bout 1 percent Δk_e). Another means of decreasing the reactivity addition accompanying slurry settling would be to add an additive, such as Al_2O_3, to the thoria; this would decrease the compaction density of the slurry, and lead to smaller changes in bed height (and thus smaller reactivity additions) than obtainable with thoria alone. In the calculations cited, a two-dimensional, two-group model (with fissions in the fast and slow groups) was employed.

10.1.5 Boiling Reactors

Boiling homogeneous reactors have been considered for many years, but relatively little effort has been devoted to them. The studies to date have concerned the control and safety of these reactors, determination of the rate of formation and growth of vapor bubbles, and the power removal capability as a function of average fraction vapor. There are several known instances of operation of the Los Alamos Water Boiler as a boiling homogeneous reactor; one series of experiments occurred in August 1953, at which time the reactor was operated under boiling conditions at a total power of about 5.5 kw. Although the "normal power oscillations were greater under boiling than under nonboiling conditions, the reactor compensated reactivity additions more rapidly when boiling was taking place. The density coefficient of reactivity was the means of control during the boiling runs; no difficulties were encountered.

In boiling systems the most important parameters are those associated with vapor formation and growth, vapor removal from the system, and the control system. With regard to control, boiling reactors have the disadvantage of producing more power when less power is demanded unless a control system is used in which an increase in reactor pressure leads to ejection of fuel from the core region. Alternatively, power-demand control can be obtained by permitting the boiling process to generate only a fraction of the total reactor power, the remainder being removed by fuel fluid which is circulated through a heat exchanger.

10.2 CRITICALITY CALCULATIONS

A large number of criticality calculations have peen performed for many homogeneous-type reactors; these have aided in specifying the design of planned reactors, and in optimizing a system with respect to minimum fuel costs. Some specific results which have been obtained pertain to: the critical concentrations and conversion ratios in large, one- or two-region reactors utilizing either the U^{238}–Pu^{239} or the Th–U^{233} fuel cycle; the effect associated with a decrease in the resonance value of η^{23} on the breeding ratio in large, single-region Th–U^{233} reactors; the critical concentrations, breeding ratios, doubling times, and core-wall power densities in two-region reactors containing thoria in the blanket region and either $U^{233}O_2SO_4$ or UO_3–ThO_2 in the core region; the nuclear characteristics of two-region thorium-breeder reactors under startup conditions and also equilibrium conditions; the effects that fission-product poisons, core-tank absorptions, H_2O contamination, and corrosion products have on the breeding ratio in two-region thorium breeder reactors; and the effects that geometry, size, and parameter values have on the nuclear characteristics of reactors.

In the majority of cases, results have been based on two-group diffusion theory. Some multigroup calculations have been performed; the results obtained did not differ significantly from two-group results. For some small reactors, "harmonics" calculations were employed.

10.2.1 Experimental Reactor Calculations

For the HRE–1, criticality conditions and the various reactivity coefficients were obtained under a variety of circumstances using two-group diffusion theory; generally, the calculated information was in fair agreement with the experimental data. The decrease in the effective delayed-neutron fraction due to fuel circulation was also calculated, and agreed with results based on experimental evidence. Values for the various nuclear constants obtained experimentally were as follows: the fuel critical concentration increased from 24.8 g U^{235}/kg H_2O at 20° C to 38.9 at 235° C; the core temperature coefficient of reactivity decreased from -0.37×10^{-3} $\Delta k_e/°$ C at 20° C to -1.15×10^{-3} at 220° C; the reactivity worth of the reflector was 6.5 percent Δk_e at room temperature and 7.5 percent at 225° C; at room temperature the reactivity worth of the control rod was 0.4 percent Δk_e while that of the shim and safety rods was 0.5 percent Δk_e each; at 200° C the worth of these rods increased by about 20 percent; the effective delayed-neutron concentration in the core decreased by about 25 percent when circulation of the core fuel was initiated.

The initial statics calculations for the HRE–2 utilized a "harmonics" method to obtain critical concentrations, and two-group diffusion theory to calculate nuclear constants. Where checked, agreement between theory and experiment was excellent. The fuel critical concentration at 20° C was 2.5 g U^{235}/kg D_2O and at 280° C was 9.7 g U^{235}/kg D_2O. Calculations were also performed for reactors of various core diameters, blanket thicknesses, and blanket compositions. In addition to obtaining critical concentrations, calculations were performed to obtain neutron flux distributions, adjoint functions, mean lifetimes of prompt neutrons, temperature coefficient of reactivity, and blanket heat-generation rates. At design conditions, the core temperature coefficient was -1.85×10^{-3} $\Delta k_e/°$ C, and the blanket temperature coefficient was -1.07×10^{-3}; the mean prompt neutron lifetime was 5.7×10^{-4} sec.

After a hole developed in the HRE–2 core tank, additional calculations were performed. In these, the flux distributions, critical concentration, power-density distribution, various reactivity coefficients, and the distribution of nuclear importance were obtained with the blanket-to-core fuel-concentration ratio as a parameter. With the core hole, the blanket-to-core fuel concentration ratio was about 0.3. Under these circumstances about 40 percent of the power is generated in the blanket. Addition of the corrosion-sample holder to the core region increased the core critical concentration by about 7 percent. Movement of 1 g of U^{235} from a region outside the reactor to a region of average importance would add about 0.023 percent reactivity. Deposition of small amounts of U^{235} on the core wall was calculated to be equivalent in reactivity to 3 or 4 grams distributed throughout the circulating system, but deposition of large amounts of U^{235} over a small area had a reactivity worth less than if this uranium had been uniformly distributed. The critical concentration and flux distribution were also calculated as a function of core and blanket temperatures; the power density at the core wall was only slightly affected by changing the blanket-fluid temperature from 280 to 200° C, with the core fluid remaining at 280° C. Additional studies were made concerning the effect of moderator composition on core fuel concentration. For a moderator-reflected core, the smallest core diameter which would permit a U^{235} concentration less 10 g/liter at 280° C was about 29 inches, corresponding to a water moderator containing 85 percent D_20.

10.2.2 Two-Region Thorium-Breeder Calculations

Two-region, solution-core reactors appear to be capable of attaining, under practical conditions, average breeding ratios of about 1.10, and doubling times of 10 to 15 years. Such reactors would have cylindrical geometry (approximately), with an overall diameter of about 9 feet and an overall height of about 16 feet. The blanket would contain about 1,000 g Th/liter and 3 g U^{233}/kg Th, while the core-fuel concentration would be about 5 g U/liter. Factors which have been studied include the relations between breeding ratio, doubling time and fuel cost, and the effect of various chemical processing rates on the nuclear characteristics. Neutron balances were also obtained; these help determine what design changes will improve the overall neutron economy of the reactor. In addition to core-wall fission-power densities, total heat generation rates in the core wall were obtained; such rates help define any heat transfer problems which may exist.

Based on survey-type calculations in which various thoria concentrations in the core and blanket were considered, the breeding ratio increases when the core diameter decreases, when the blanket U^{233} concentration decreases, and when the thorium concentration is increased in either the core or blanket region. The core-wall power density decreases when the thorium concentration is increased in the blanket region and when the core size increases, but is relatively insensitive to changes in the blanket fuel concentration for thorium concentrations greater than 100 and 500 g/liter in the core and blanket, respectively. The critical concentration of U^{233} in the core decreases with decreasing core thorium concentration and with increasing core diameter, and varies only slightly with changes in blanket thickness, blanket U^{233} concentration, and blanket thorium concentration. The fraction of total power generated in the blanket increases nearly linearly with increasing blanket U^{233} concentration, increases with decreasing core diameter, and also increases with decreasing core- and blanket-thorium concentrations. Finally, the U^{233}-to-thorium ratio required in the core for criticality passes through a minimum when the core thorium concentration is permitted to vary. In the above, changes in condition normally refer to deviations from 1,000 g Th/liter in the blanket, 3 g U^{233}/liter in blanket, and a blanket thickness of 2 feet.

A large number of two-region reactor systems were analyzed to determine breeding ratios and doubling times under a number of design conditions. Cylindrical reactors investigated had core diameters and lengths of 4 and 12 feet, 6 and 25 feet, and 7 and 18 feet, respectively; the blanket thickness varied from 1 to 2 feet, the core thorium concentration varied from 0–300 g Th/liter, the blanket thorium concentration varied from 500 to 1,000 g Th/liter, the thermal power was 200 Mw for those reactors having a 4-foot diameter, and was 1,000 Mw for the other reactors. Both nuclear and economic computations were performed with equilibrium concentrations of isotopes, neutron poisons, and corrosion products. Addition of thorium to the core, while improving the breeding ratio, did not always decrease the doubling time. When the neutron economy was already good, the improvement in breeding ratio associated with addition of thorium to the core region was not sufficient to overcome the increased inventory required for criticality. This was markedly true for the smaller reactor, in which the critical concentration for the solution core was sufficiently high to give good neutron economy without the thorium. Within the range of 500 to 1,000 g Th/liter, increasing the blanket thorium concentration always resulted in a decrease in the doubling time.

10.3 RECENT MEASUREMENTS OF η^{23}

The importance of high breeding ratios and short doubling times in future power reactors has been emphasized in recent studies. Since the value of η^{23} (neutrons produced per neutron absorbed) in U^{233} directly affects the breeding ratio and also the doubling time, its value, to a large extent, determines the future potential of Th–U^{233} systems. Although various measurements related to the value of η^{23} have taken place over the past 15 years, there is still some questions as to the thermal value as well as to the variation with energy.

The initial values obtained for η^{23} in the thermal region were relatively high, being greater than 2.30. However, measurements by Knolls Atomic Power Laboratory in 1955 indicated that the thermal value was about 2.25. Measurements in Britain indicated that η^{23} in the thermal region might be 2.18 or even lower.

At Oak Ridge National Laboratory a number of experiments have been carried out to determine the thermal value of η^{23}. In the fall of 1953, critical experiments were performed to determine η^{23} relative to η^{25}. Using water-moderated and -reflected reactors, critical concentrations of U^{233} and U^{235} were determined in small-diameter (26.4- and 3.20-cm-diameter) core tanks. A value of 2.31±0.03 was obtained, based on $\eta^{25}=2.08$. In 1958, the thermal value of η^{23} relative to η^{25} was obtained through measurements of reactivity effects in a flux-trap critical assembly. The reactor consisted of an annular, aqueous-fuel region, having cylindrical geometry (O.D.∼12 in.), with a 6-inch diameter water column inside the annular fuel region. Samples of aqueous solutions of fissionable and absorbing materials were inserted axially into the water column, and the resulting reactor periods were utilized to calculate reactivity changes. Experimental determinations were made of the reactivity importance of the fast neutrons which were generated at the sample point, and also of the importance of the thermal neutrons which were absorbed at the sample point, by use of U^{235} and boron samples. In combination with reactivity measurements made with U^{233} samples, the value of η^{23} in the thermal-energy region was found to be 2.31±0.06.

Also during 1958, critical experiments were initiated in which relatively large bare spheres were used. Aqueous solutions of U^{233} and U^{235} were employed. The value of η^{23} was calculated on the basis that the neutron leakage spectrum was the same for a critical system containing U^{233} as for one containing U^{235}. Results based on measurements using 27- and 48-inch-diameter spheres have given thermal values for η^{23} between 2.27 and 2.30 with an uncertainty of ±0.04; what are believed to be the best experimental results have given a value of 2.295±0.036.

Recently, an experiment was undertaken to measure the absolute value of η^{23} in the thermal region. The experiment consists of permitting a measured number of thermal neutrons to be absorbed in a U^{233} foil, and essentially counting the number of fission neutrons which are generated. The U^{233} sample is placed inside a region containing a $MnSO_4$–H_2O solution, and a beam of thermal neutrons is impinged upon the sample. The uranium sample absorbs essentially all incident neutrons, while the manganese sulfate solution absorbs all the fission neutrons released by the U^{233}. By measuring the activation of the manganese following exposure of a U^{233} sample, and also the activation when no sample is present, an absolute value of η^{23} is obtained. There are a number of corrections to be made to the experimental data, but it is believed that an accuracy of ±1 percent is achievable. To date, four measurements of the absolute value of η^{23} have given a weighted average of 2.29±0.02.

Since a significant number of fissions may take place at energies greater than thermal, the variation of η^{23} with energy is also of importance. Several measurements have been made at energies above thermal; the most detailed information has been obtained with fast-chopper time-of-flight spectrometers. These measurements give relative values of η^{23} as a function of energy. Up to about 1 ev there does not appear to be much variation of η^{23} with energy; in the range from 1 to 10 ev, there is considerable variation, with the average value about 90 percent that of the thermal value. Measurements from 10 to 30 ev also indicate a variation with energy, but not so severe as in the 1- to 10-ev range, with the average η^{23} value being about 95 percent of the thermal value. Measurements above 30 ev have been broad spectrum measurements, and these indicate that η^{23} is on the average about the same as at thermal energies.

11. REACTOR EXPERIMENTS

11.1 HOMOGENEOUS REACTOR EXPERIMENT (HRE–1)

11.1.1 Introduction

In 1950, Oak Ridge National Laboratory undertook to design, build and operate a fluid-fuel reactor experiment, the Homogeneous Reactor Experiment (HRE–1). It was designed to deliver 1,000 kw of heat with a maximum fuel-solution temperature of 482° F, yielding, after heat exchange, a saturated-steam pressure of about 200 psi.

The objectives of HRE–1 were:

(1) to demonstrate the nuclear stability and operational feasibility of a circulating-fuel reactor at high specific power;

(2) to obtain information concerning the radiation stability of the fuel and corrosion behavior of materials in a homogeneous reactor at flux densities of the same order as those which might be encountered in a large-scale plutonium producer or central-station power reactor;

(3) to demonstrate electrical power production from a homogeneous circulating system.

The reactor system operated for 24 months, during which time liquid was circulated for about 4,500 hours. The reactor was critical a total of 1,950 hours and operated above 100 kw for 720 hours. The maximum power level attained was 1,600 kw. HRE–1 was shut down in the spring of 1954 and dismantled to make room for HRE–2.

11.1.2 Description

Reactor-Vessel Assembly (*Cross-Section View, Fig. 11.1*)

The core was an 18-inch-diameter stainless steel sphere with a 3/16-inch thick wall. Fuel entered near the equator through a 1½-inch-diameter pipe which was installed on a tangent to the sphere and directed downward at an angle of 45°. It left through a polar outlet at the top and there was a ¼-inch dump line at the bottom. The core was suspended inside a 39-inch-ID pressure vessel by attachment of the inlet and outlet pipes to the pressure-vessel head. The vessel walls were 3-inch thick, A–105 carbon steel; the head was flat and bolted to the vessel. Three control-element drive mechanisms and a steam-heated pressurizer were also attached to the head. Control elements consisted of plates made from a boron-containing compact and clad with stainless steel.

High-Pressure Fuel System (*Flowsheet, Fig. 11.2*)

The high-pressure fuel system consisted of the reactor core and pressurizer, a shell-and-tube heat exchanger, a canned-motor circulating pump, and piping assembled in a loop. An H_2O solution of uranyl sulfate containing 40 g U/liter (0.17 *m*) 93 percent enriched in U^{235} was circulated in the loop at a rate of 100 to 150 gpm. It was heated to 482° F by the nuclear reaction in the core and was cooled to 410° F in the heat exchanger. The total volume of solution in the high-pressure system was 90 liters, 50 liters of which were in the core. A pressure of 1,000 psi was maintained in the system by heating a small volume of fuel in the pressurizer. Radiolytic gas was withdrawn from a void formed along the axis of the core by the vortex flow and together with some liquid was discharged to the fuel low-pressure system through a heat exchanger and throttling valve.

Fuel Low-Pressure System

The fuel low-pressure system consisted of a pair of weighed horizontal dump tanks that were "operationally ever-safe" (i.e., they could

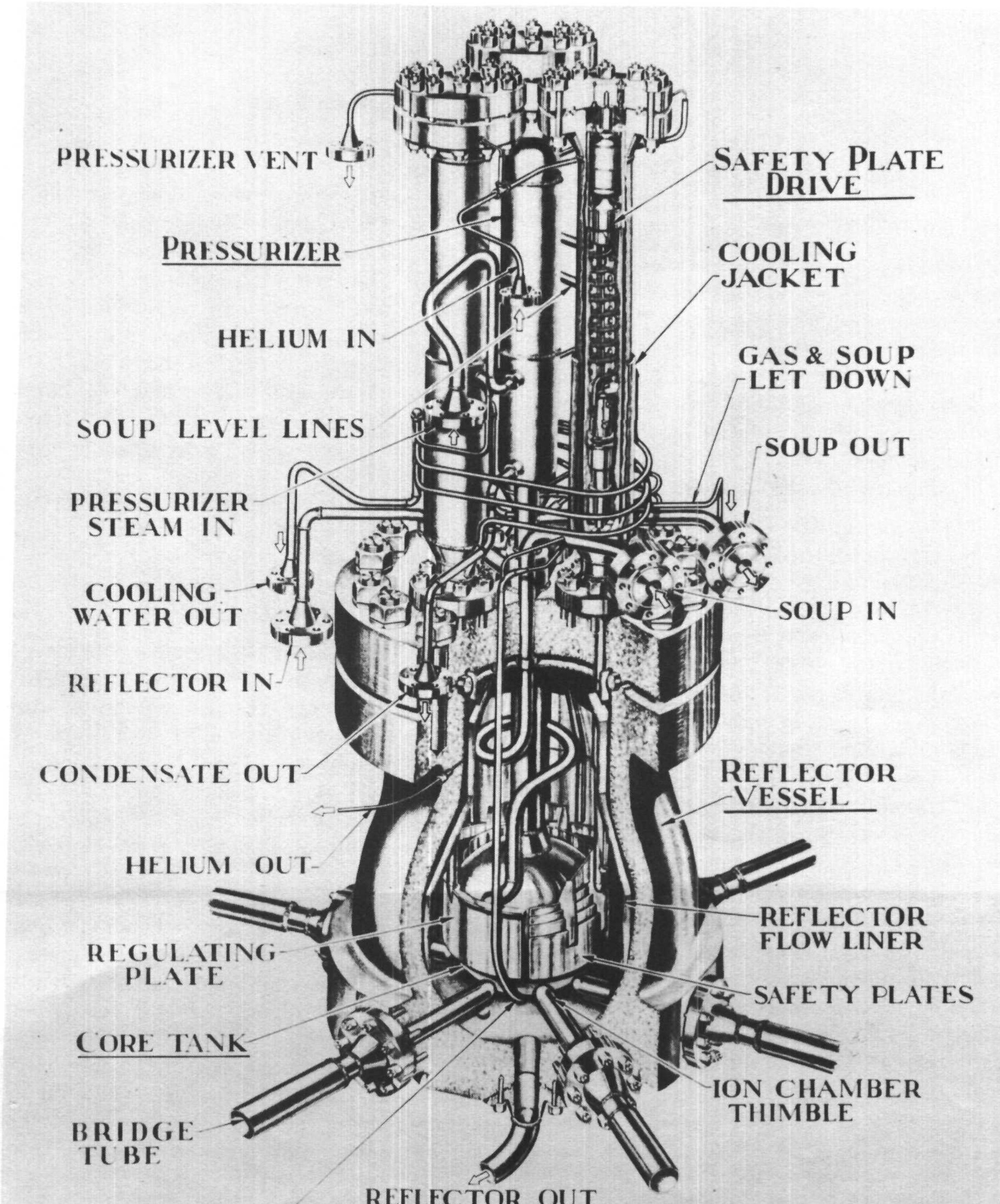


FIGURE 11.1—HRE–1 reactor tank assembly.

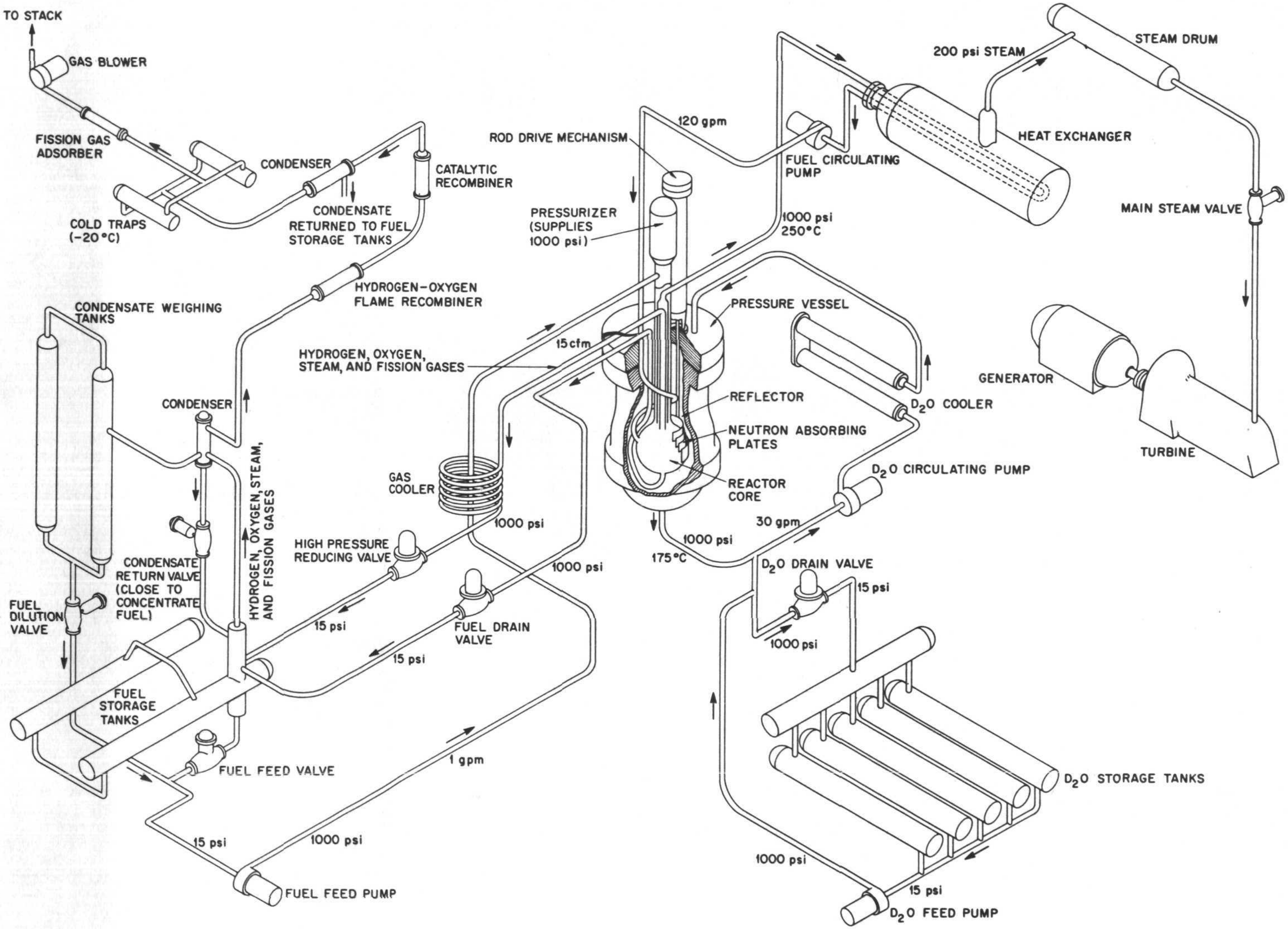


FIGURE 11.2—HRE-1 schematic flow diagram.

not be made critical with the maximum amount of U^{235} charged into the system for reactor use); a fuel evaporator; condenser; flame recombiner; catalytic recombiner; gas cooler; and cold traps.

Radiolytic gas and fuel from the high-pressure system entered the dump tanks, where the gas was mixed with steam produced in the evaporator and sent to the condenser. Vapor was removed there and left a combustible mixture at the burner nozzle of the flame recombiner. The flame recombiner was merely an oversized Bunsen burner, with a spark plug for ignition, enclosed in a water-jacketed cylinder.

The exit gases from the flame recombiner passed through a catalytic recombiner containing a catalyst of platinized alumina pellets, which functioned at low reactor power levels when insufficient radiolytic gas was let down to support a flame at the burner nozzle.

From the catalytic recombiner the off-gas stream (mostly oxygen with a very small fraction of fission gases) was cooled in a condenser and dried in a cold trap before being sent through charcoal adsorption units to the 100-foot-high stack for final discharge to the atmosphere.

The condensate from the condenser was returned either to the fuel dump tanks or to a weighed condensate holdup tank, which provided the means of adjusting the concentration of fuel in the dump tanks. Since fuel was pumped continuously at approximately 0.8 gpm from the dump tank to the core by means of a diaphragm pump, it was possible to vary the concentration of fuel in the core system.

Reflector System

The outer pressure vessel was filled with D_2O, pressurized with helium to within ±100 psi of the fuel pressure, and maintained at about 350° F. About 50 kw of heat conducted through the core wall to the reflector liquid was removed by circulating the D_2O with a 30-gpm canned-rotor pump through a cooler which acted as a boiler feedwater preheater. A jet was located in this high-pressure circulating loop, the suction of which drew a continuous stream of gas from the vapor space above the liquid to a catalytic recombiner to keep the concentration of deuterium and oxygen gases in this space below explosive limits.

A low-pressure system was provided for the reflector also. It consisted of dump tanks, feed pumps, a condenser, catalytic recombiner, and cold traps.

Reactor Control

The critical temperature of the reactor was controlled by controlling the uranium concentration of the fuel solution. Power level was controlled by regulating the rate of release of steam from the heat exchangers to the turbogenerator. Rapid reduction of about 7° C in critical temperature at 250° C could be effected by dropping the safety plates. Both the core and the reflector could be dumped rapidly in an emergency. Regulation and safety of the reactor against very rapid fluctuations was dependent on the large negative temperature coefficient of reactivity.

Containment and Shielding (Fig. 11.3)

Reactor equipment and piping were the primary containment. The piping was assembled with ring-joint flanges, and the flange grooves were kept at a higher pressure than the core with water from the leak-detector system, which would indicate flange leakage by loss in pressure.

There was no secondary containment vessel; however, the reactor shield compartments were kept at a pressure slightly below atmospheric by the operation of a blower which drew air through the reactor shield for cooling and ventilation and discharged it up the stack. This subatmospheric pressure was intended to prevent the escape of activity into the building in the event of a small leak in the piping.

The shield was constructed of heavy aggregate concrete blocks, loosely stacked, with only the outer 16 inches of blocks being mortared.

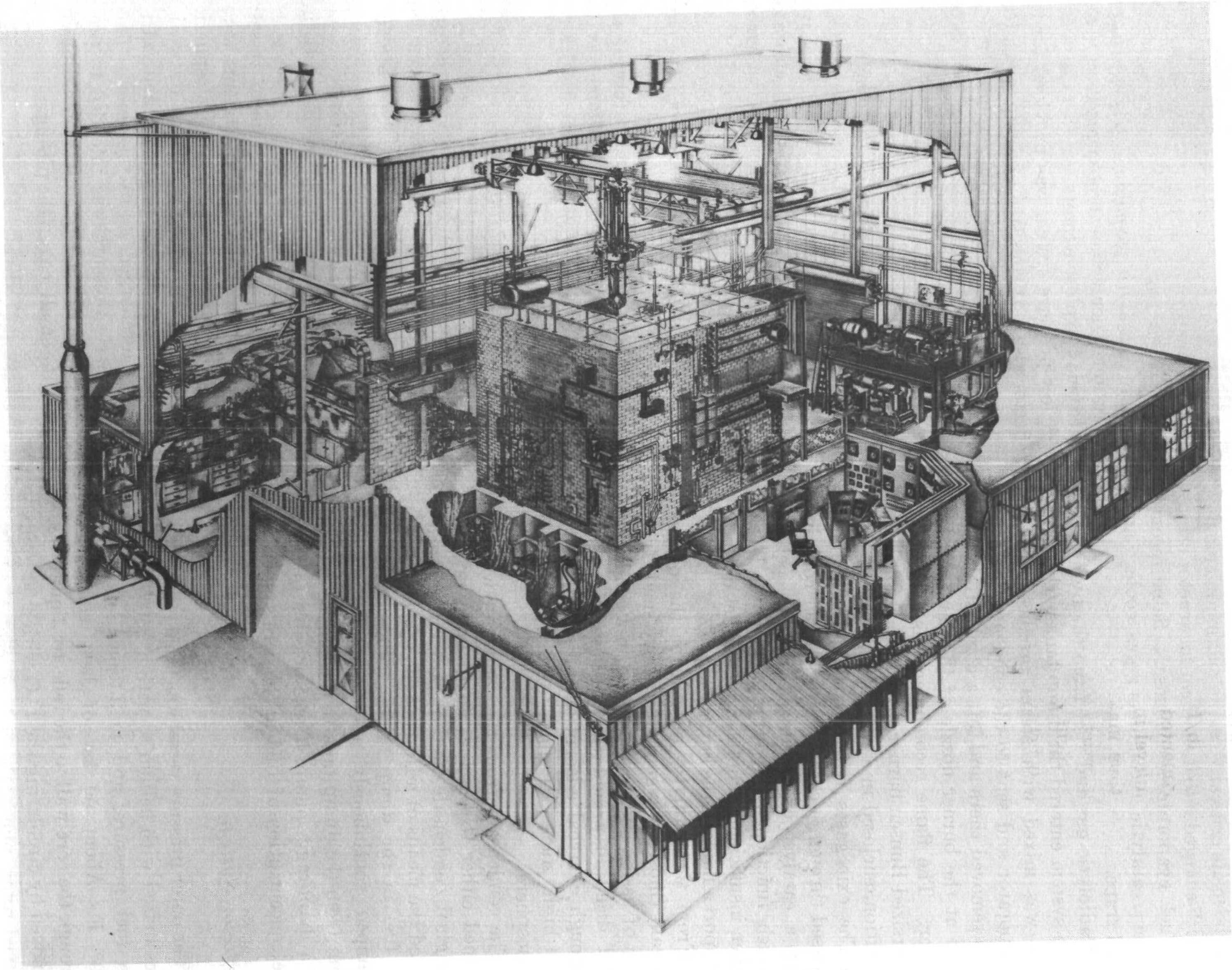


FIGURE 11.3—Homogeneous Reactor Experiment No. 1.

The density was 225 lb/ft^3. Space inside the shield was compartmented to reduce to a minimum the radiation level in the vicinity of various components, thus making it easier to do maintenance. The reactor vessel was located in the center compartment surrounded by a minimum of 7 feet of concrete, at least 2 feet of which separated it from the nearest auxiliary compartment. The entire shield structure was 22 feet wide, 26 feet long, and 18 feet high.

Power Removal

The steam generated in the fuel heat exchanger was fed to a conventional multistage condensing turbogenerator rated at 312 kva. With the reactor operating at 1,000 kw and 250° C, steam produced at 200 psi generated about 140 kw of electricity.

Upon increase in generator load, the turbine governor opened the turbine throttle valve, increasing the steam demand, lowering steam pressure and temperature, and reflecting itself into increased cooling of the uranium solution, which automatically increased the reactivity in the core and completely compensated for the increased load.

11.1.3 Chronology

Date	*Event or Test*
August 1949	Preliminary design of major components.
September 1950 to November 1951.	Construction.
November 1951 to April 1952.	Pre-operational testing.
April 14, 1952	Reactor critical.
April to July 1952	Operation at low power levels to obtain nuclear data; temperature coefficient, pressure coefficient, delayed-neutron fraction, control-rod calibration, reflector level calibration.
July to October 1952.	Repairs and clean-up following leak of fuel solution through crack in oxygen addition line. Fuel inventory measured. Hydrostatic and leak tests.
October 1952	Operation at low power. Closed cooling circuit installed on recombiner condenser to permit operation of reactor with leak in rolled joints of condenser tubes.
November 1952 to February 1953.	Maintenance and clean-up following leak of fuel solution through d/p cell in O_2 system. Fuel solution treated to remove chloride contamination.
February to April 1953.	First operation of reactor at design power of 1,000 kw. Operation at powers to 1,400 kw in corrosion tests. Demonstration of coupling of reactor and turbogenerator.
April to July 1953.	Reactor maintenance and intermittent subcritical operation. Circulating pump replaced twice. Feed-pump head replaced. Fuel removed and reactor equipment cleaned.
July to August 15, 1953.	Corrosion rates for system in absence of radiation determined by operation with natural-uranium solution.
August 15 to October 8, 1953.	Enriched fuel added and reactor operated in investigation of effects of radiation on corrosion. Kinetics experiments to demonstrate safety of reactor and control by negative temperature coefficient.
October 8 to November 15, 1953.	Intermittent operation. Repairs to pressurizer-level instrument and electrical leads to fuel circulating pump. Cleaning of steam side of heat exchanger to restore heat transfer performance.
November 15, 1953 to February 1954.	Operation at powers to 1,600 kw accumulating 473 Mw-hr. Demonstration of recombination of gas in solution by copper catalyst.
February to March 1954.	Intermittent operation at 200–400 kw for production of Xe^{135} for cross-section experiments. Critical experiments without reflector.
March to June 1954.	Decontamination and dismantling of reactor and shield to begin construction for HRE–2.

11.1.4 Significant Design Parameters

(1) Coolant	UO_2SO_4–H_2O solution
(2) Moderator	H_2O

(3)	Thermal power rating	1,000 kwt
(4)	Electrical power rating	140 kwe
(5)	Thermal efficiency	14%
(6)	Temperature and Pressure	250°C, 1,000 psi
(7)	Core size	18-inch-dia sphere
(8)	Power density	20 kw/l
(9)	Fuel enrichment	93%
(10)	Specific power	250 kw/kg 25
(11)	Central fuel temperature	250° C
(12)	Total inventory	~4 kg 25
(13)	ΔT across core	72° F

11.1.5 Operating Experience

(1) Thermal power generated—0.578 x 10^6 kwt-hr
(2) Electrical power generated—0.081 x 10^6 kwe-hr
(3) Activity levels, r/hr—

	Dump-tank cell	*Reactor cell*	*Heat exchanger cell*
a. At full power	47,000	34,000	27,000
b. At shutdown	17,000	3,200	2,800
c. 24 hr after shutdown— 3 curies/cc	2,000	700	600
d. During maintenance	------	200–400	------
e. After decontamination for dismantling	55	200–404	22

Equipment Problems

The fuel circulating pump was replaced five times: four of the failures were electrical, which were mostly attributable to overloading of the motor, and one failure was caused by a cracked bearing. Pumps of different design were specified for HRE–2.

The diaphragm-type fuel feed pump was removed and replaced four times; there were only three failures. Perforation of the diaphragms by trash in the piping and stress-fatigue failures were the principal causes of failure. In the development effort for HRE–2, these faults were eliminated or minimized by providing more reliable strainers and redesigning the diaphragms and heads to minimize bending stress.

The liquid-level instrument was sometimes unreliable because of binding of the float. This instrument was redesigned for HRE–2, and made completely reliable.

A leak developed in the fuel gas condenser, presumably in one of the rolled tube-tubesheet joints as a result of a pressure surge from one of the recombiner flash-backs. All-welded tube joints were specified for similar heat exchangers in HRE–2.

Much difficulty was had with operation of the control-rod mechanisms. These were found to be unnecessary; HRE–2 was constructed without control rods.

Operation was finally terminated, after the decision to build HRE–2 in the same building, because of a leaky letdown valve that would have been very difficult to replace. As a result of this experience, valves in HRE–2 were designed to be easily removed and replaced.

Systems Problems

The only important transient problem encountered was caused by the concentrating effect of removing more water from the core at high power and gas letdown rates (as water vapor mixed with the gas) than was being returned to the core in the fuel feed stream from the dump tank. This phenomenon was know as "walk-away" since the rate of concentration change was slow, causing a slow, but accelerating, increase in the critical temperature. This effect was eliminated by adding copper to recombine nearly all of the radiolytic gas in solution; it was also reduced by increasing the fuel feed rate.

General Maintenance

Maintenance of reactor components was accomplished by working from above using long-handled tools and temporary shadow shielding. Some major repairs were accomplished in radiation fields as high at 2,000 r/hr without exposing personnel beyond accepted tolerances. However, provision was made for maintaining only a few of the components, and the high radiation levels made the work very difficult. Maintenance was made an important consideration in the design of HRE–2.

After final shutdown of the HRE–1 the reactor was decontaminated in preparation for disassembly. Over a period of 30 days, starting with activity levels of the order of 1,000 r/hr, the activity was reduced sufficiently by decontamination and decay to permit dismantling of the system with long-handled tools.

The decontamination treatment consisted of repeated washing alternately with 35 percent HNO_3 and aqueous solutions of 10 percent sodium hydroxide, 1.5 percent sodium tartrate, and 1.5 percent hydrogen peroxide. The overall decontamination factors were 22 to 25, including 30 days decay, but the factor for decontamination with a single reagent was only between 1 and 2.25. Large amounts (of the order of 10^3 curies) of cerium, zirconium, barium, lanthanum, strontium, niobium, and ruthenium were removed. The significant contaminants remaining were zirconium and niobium, which were bound in the oxide film. Although these could have been removed from the system by descaling the oxide corrosion film, which would have given a further decontamination factor of approximately 100, such a treatment would have made it impossible to determine whether significant corrosion had taken place during nuclear operation.

11.2 HOMOGENEOUS REACTOR TEST (HRE–2)

11.2.1 Introduction

During the operation of HRE–1 in late 1953 it became evident that a second reactor experiment should be operated before attempting to construct a full-scale homogeneous power reactor. In order that the objective of a significant test of the engineering feasibility be satisfied, it was necessary that the physical size of the reactor and its auxiliaries be increased appreciably beyond that of HRE–1; yet in order to hold the cost within reasonable bounds for an experiment, it was necessary to limit the power output. The size of the reactor core represented a compromise between two objectives, attainment of high specific power required for economy in a large plant and use of dilute uranyl sulfate solution in heavy water as the fuel. The power output was, therefore, set at 5,000 kw (thermal), and the core diameter at 32 inches. Although these together result in a low specific power of 17 kw/liter in the core, this was considered acceptable, since operability at a relatively high specific power of 30 kw/liter had been demonstrated in HRE–1. Other changes were made in design and equipment to take advantage of experience with HRE–1 or to test ideas that were being proposed for power reactor systems.

The objectives of HRE–2 were:

(1) to demonstrate that a homogeneous reactor of moderate size can be operated with the continuity required of a power plant;
(2) to establish the reliability of fuels, engineering materials, and components of designs which can be adapted to full-scale power plants;
(3) to evaluate equipment modifications which will lead to simplifications and economy;
(4) to test simplified maintenance procedures and, in particular, maintenance underwater;
(5) to develop and test methods for the continuous removal of fission and corrosion contaminants.

11.2.2 Description

Reactor-Vessel Assembly

The HRE–2 reactor vessel is constructed so that there are two regions—an inner core (Fig. 11.4) of Zircaloy-2 (32-inch inside diameter, 5/16-inch wall thickness), surrounded by a 60-inch diameter, 4.4-inch thick carbon steel pressure vessel, clad with stainless steel on its inside surface. Surrounding the pressure vessel is a 1½-inch thick, 74-inch ID 304 stainless steel blast shield, which was provided to stop fragments in the event of a brittle-fracture type of failure of the carbon steel pressure vessel.

Thermal stresses caused by gamma heating in the pressure vessel are reduced by removing

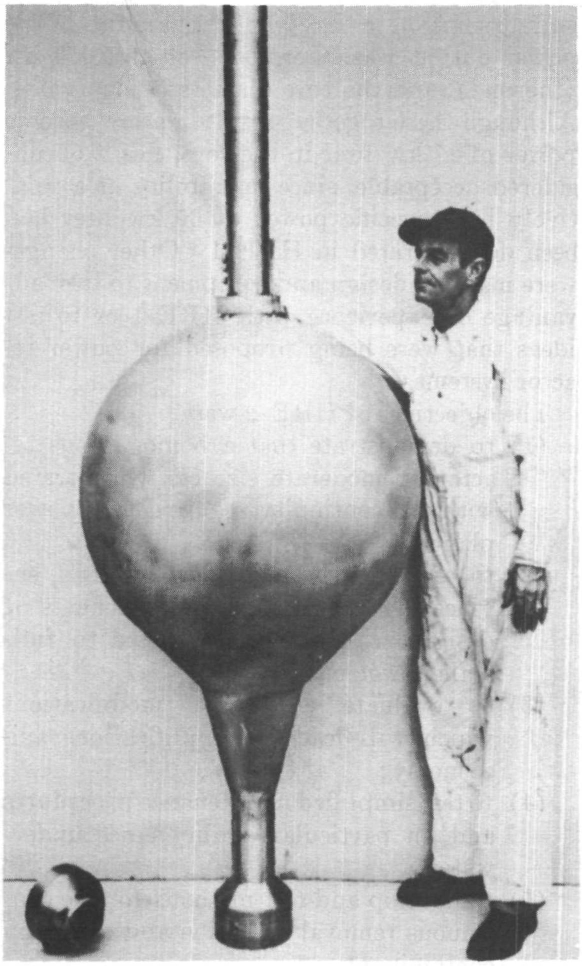


FIGURE 11.4—Zircaloy core vessel.

heat from its outside surface at approximately the same rate that heat is transferred to the blanket solution inside the vessel. This heat removal on the outside surface is accomplished by radiative heat transfer to the blast shield, which is provided with cooling coils on its outer surface. Figure 11.5 is a drawing showing the arrangement of core, pressure vessel, blast shield, and nozzles for connection to the piping of the fuel and blanket flow circuits.

Flow through the core is upward, and nine perforated plates are installed in the bottom conical diffuser section to provide a velocity distribution through the core that corresponds approximately to the flux distribution.

No control rods or other mechanical means of reactivity control are provided since fuel-concentration control and the effectiveness of a large negative temperature coefficient had been demonstrated in HRE–1.

Fuel and Blanket High-Pressure Systems

Figure 11.6 is a schematic flow diagram of the reactor.

Fuel for HRE–2 is a D_2O solution 0.04 *m* in UO_2SO_4 (10 g U/liter, 93 percent enriched in U^{235}), 0.02 *m* in $CuSO_4$, 0.02 *m* in excess H_2SO_4, and containing 500 ppm of excess O^2. Copper sulfate is present to recombine radiolytic gas, sulfuric acid to increase the stability of the fuel against hydrolysis, and oxygen to stabilize the uranyl ion.

The fuel solution is pumped into the bottom of the reactor core at 256° C and at the design flow rate of 400 gpm and power of 5 Mw, is heated to 300° C as it proceeds upward to the outlet pipe. At the top of the outlet pipe is attached the electrically heated pressurizer, which generates steam at 1,700–2,000 psi by boiling heavy-water condensate fed to it from the low-pressure system by a diaphragm-type pressurizer purge pump. The fuel solution flows past the pressurizer connection to the gas separator, where directional vanes induce vortex flow in the fluid. If undissolved gasses (oxygen and unrecombined radiolytic D_2 and O_2) are present, they are bled from the center of the vortex and sent to the low-pressure system with about 1 gpm of fuel solution.

Most of the fuel solution then flows to the fuel heat exchanger (steam generator, Fig. 11.7) where it is cooled from 300° C to 256° C by transferring its heat to the boiler feed water surrounding the tube bundle. From the heat exchanger, the fuel solution then flows to the suction side of the canned-motor circulating pump which discharges to the inlet of the core.

The blanket circuit is nearly identical with the fuel high-pressure system except that with the use of pure heavy water in the blanket system, only about 200 kw of heat is produced

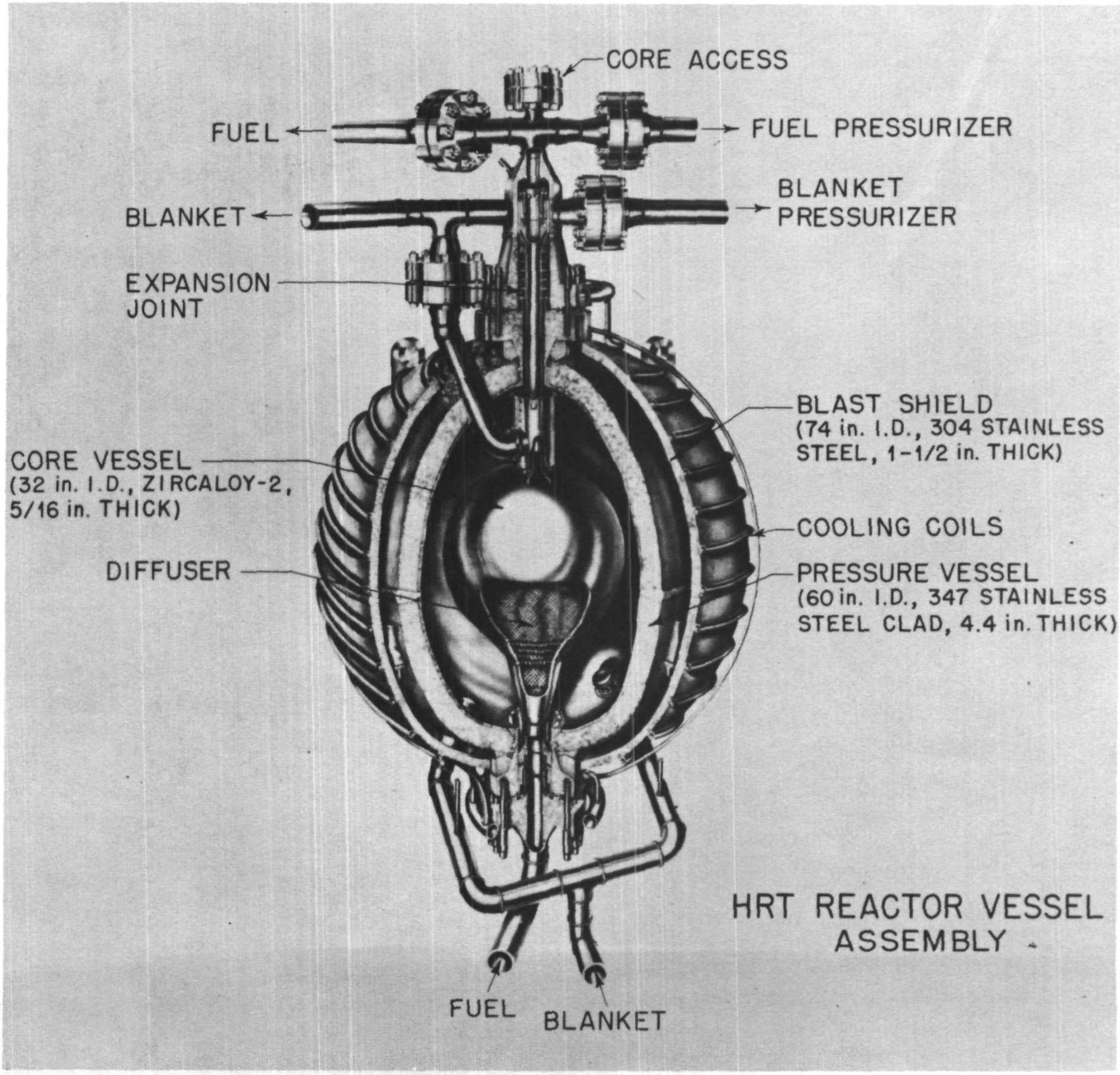


FIGURE 11.5—HRE–2 reactor vessel assembly.

with the reactor operating at 5 Mw, and the blanket flow rate is 230 gpm. After a hole developed in the core tank, the reactor was operated with fuel in both core and blanket and about 40 percent of the heat was generated in the blanket.

Power Generation and Heat-Removal System

Steam produced in the fuel and blanket heat exchangers can be sent either to the 350–kva turbogenerator originally used for HRE–1, or to an air-cooled steam condenser, or both.

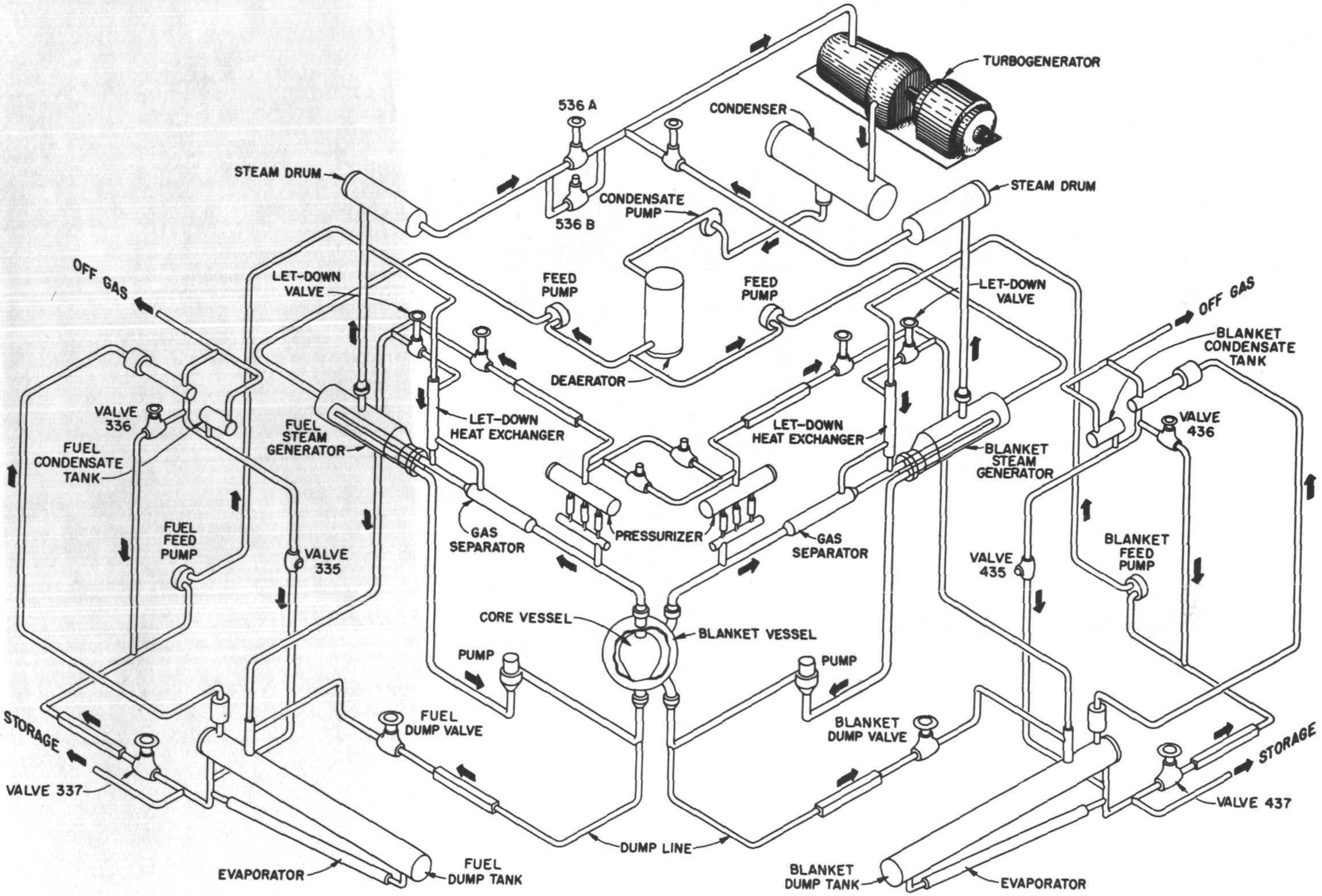
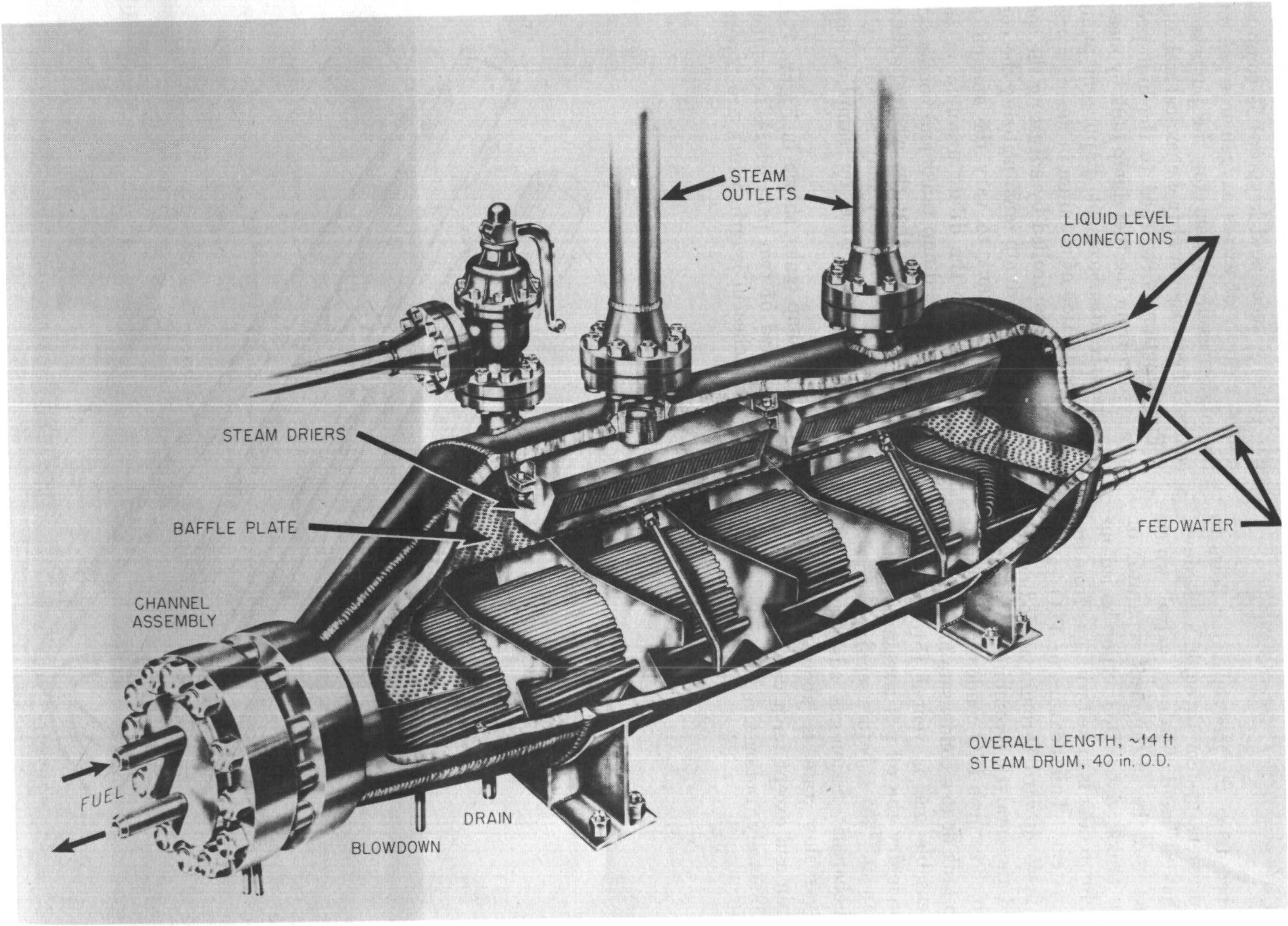


FIGURE 11.6—HRE–2 flowsheet.



OVERALL LENGTH, ~14 ft
STEAM DRUM, 40 in. O.D.

FIGURE 11.7—HRE–2 5–Mw steam generator.

Fuel and Blanket Low-Pressure Systems

Fluid bed from the gas separator flows to the low-pressure system through a "letdown heat exchanger" and "letdown valve" which discharges into the entrainment separator of the dump tanks where D_2O vapor boiled up from the dump tank is mixed with gas from the letdown system. This mixture of D_2O vapor and gas flows upward through an iodine removal bed and catalytic recombiner into a condenser which returns D_2O condensate either to the dump tank or to a condensate holdup tank. Noncondensable gas is vented through cold traps which dry the off-gas stream to a dew point of about −25° C before sending it to the activated-charcoal fission-gas adsorber units. The off-gas flow rate is about 2½ liters (STP)/min and except for a very small fraction of intensely radioactive fission-product gas (chiefly xenon and krypton) is composed almost entirely of excess oxygen injected into the high-pressure system for the purpose of control of corrosion and fuel chemical stability.

Fuel solution is returned to the high-pressure system from the fuel dump tank by means of a positive-displacement diaphragm pump. The concentration of uranium in the high-pressure system is controlled by adjusting the concentration in the dump tank, utilizing the condensate holdup tank to vary the amount of D_2O available to the dilute uranium in the dump tank. The dump tanks and condensate tanks are weighed so that the whereabouts of the reactor fuel inventory may be physically determined at any time by sampling and weighing.

The fuel dump tanks, shown in Figure 11.8, are constructed of two parallel 14-inch pipes, 15 feet 9 inches in length, which are "opera-

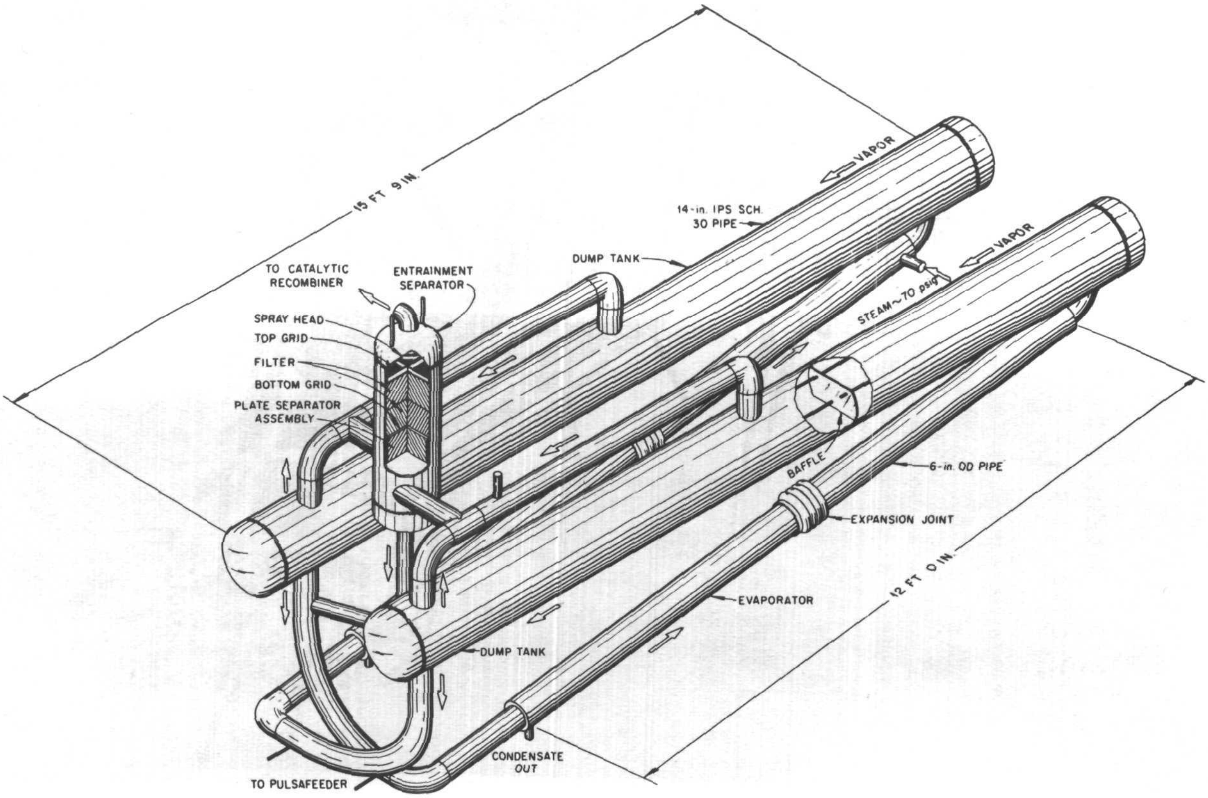


FIGURE 11.8—Fuel dump tanks.

tionally ever-safe"; i.e., they cannot be made critical using the entire inventory of fuel charged into the reactor. Heavy-water vapor is produced in the inclined steam-jacketed 4-inch pipes attached beneath the dump tanks. The entire reactor fuel charge may also be contained in fuel storage tanks of identical volume and geometry, which are provided for storing the fuel during periods of reactor shutdown during maintenance.

The blanket low-pressure system is identical to the fuel low-pressure system except for the size of the dump and storage tanks.

Containment and Shielding

The reactor equipment and piping are the primary containment. The piping is assembled with ring-joint flanges, and the flange grooves are maintained at a pressure 300–500 psi higher than the reactor system pressure with heavy water from the leak-detector system in the control area (Fig. 11.9). If a flange leak occurs, it is indicated by loss in level or pressure in the leak-detector system, and any leakage would be from the leak-detector system into the reactor system, or into the reactor cell. There has not been the slightest indication of leakage of radioactivity from the reactor equipment. The normal leakage from the leak-detector system has been 24 cc/day during periods of steady operation; higher rates are experienced during periods when the system is being cooled.

All the reactor equipment described thus far, except for the steam system, is contained in an underground rectangular steel tank (Fig. 11.10) 54 feet long, 30½ feet wide, and 25 feet deep, which has been built of ¾-inch welded steel plate, supported so as to withstand an internal pressure of 30 psig. The roof is of high-density concrete, 5 feet in total thickness; it consists of two layers of removable slabs with a completely welded steel sheet sandwiched between the layers and extending across the top

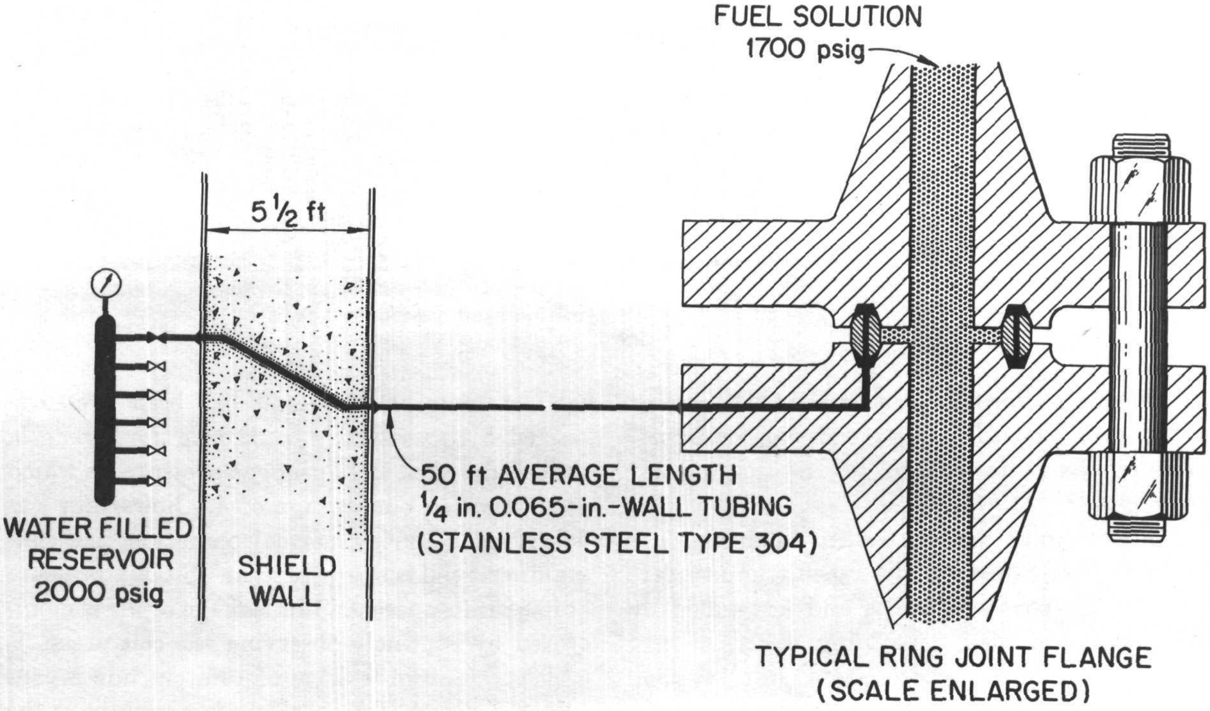


FIGURE 11.9—Leak detector system.

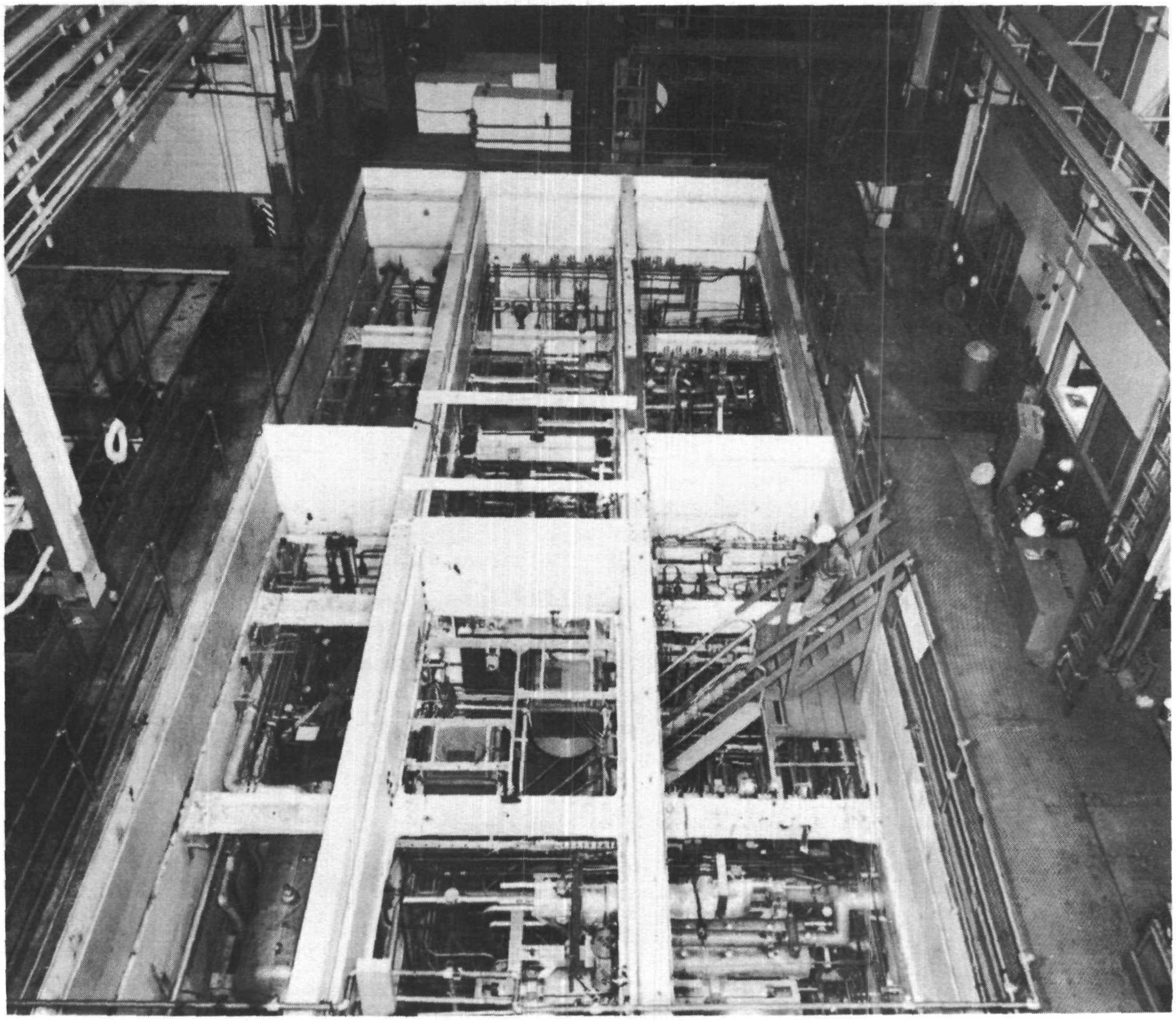


FIGURE 11.10—HRE–2 containment vessel.

of the pit to form a gas-tight lid. The roof slabs are anchored to the girders and supporting columns by means of a slot-and-key arrangement.

Service piping and instrument conduits penetrate the wall between the reactor and underground control-room areas, and are sealed by welding. Conduits containing electrical and thermocouple leads are connected into junction boxes filled with transformer sealing compound to form a gas-tight seal.

The containment vessel has been pressure-tested hydrostatically to 32 psig for strength, and leak tested at 15 psig gas pressure, at which condition an out-leakage of 4.3 liters/min was observed. During normal operation, the containment cell is operated at an absolute pressure of ½ atmosphere, and in-leakage of air is monitored by routinely observing the cell pressure. Although an in-leakage of 10 liters/min is considered permissible, the rate is normally in the range 1 to 3 liters/min.

The shield design is such that nowhere outside the shield will the radiation dosage exceed 10 mrep/hr when the reactor is at 10 Mw. For the purpose of decreasing neutron activation of equipment inside the containment tank, the reactor vessel is surrounded by a cylindrical flat-topped thermal shield with a 2-foot-thick wall containing barytes aggregate, colemanite, and water.

Fission-Gas Disposal System

Off-gas from the reactor containing gaseous fission products passes through two of three parallel adsorption units, each containing 520 pounds of Columbia grade G activated charcoal in successive 40-foot lengths of ½-inch, 1-inch, and 2-inch pipe followed by 60 feet of 6-inch pipe. The entire charcoal system is contained in a shallow water-filled concrete tank (for cooling) covered with 9 to 10 feet of earth for shielding. All species of radioactive xenon and krypton, except 10-year Kr^{85}, are adsorbed and retained on the charcoal long enough to decay to harmless levels. The gas discharged from the charcoal goes to a 100-foot tall stack where it is mixed with about 1,400 cfm of air and then discharged to the atmosphere.

Solids-Removal Plant

An experimental facility to test the solids-removal fuel processing concept is constructed in a 12-foot x 24-foot x 21-foot underground cell of similar construction and adjacent to the reactor cell. A more complete description of this facility is included in Section 8.1.3.

A 1.3-gpm bypass stream is taken from the reactor fuel system at reactor operating temperature and pressure and is circulated through a system consisting of a heater to make up heat losses, a filter to protect the hydroclone from plugging, the hydroclone with underflow receiver, and a canned-motor circulating pump to make up pressure losses across the system. The underflow receiver is drained approximately weekly during operation to remove accumulated solids as a slurry, which is then sampled, evaporated to recover D_2O, and the solids are dissolved in sulfuric acid for sampling and recovery of uranium.

Normal Operational Techniques and Special Procedures

1. Reactor Startup.—The reactor startup consists of filling the fuel and blanket high-pressure systems with heavy-water condensate from the dump tanks, pressurizing to normal operating pressure (usually 1,700 psi), heating to about 200° C by circulating the heavy water through the heat exchangers which are fed steam from an oil-fired package boiler, and then pumping concentrated fuel from the fuel dump tank until the solution in the core becomes concentrated enough to achieve criticality. The fuel high-pressure system is then heated to the desired operating temperature (in the range 240 to 280° C) by increasing the fuel concentration in the core with continued addition of fuel to the high-pressure system from the dump tank. After reaching the desired operating temperature, power withdrawal is begun. A constant circulation is maintained between the fuel high-pressure system and fuel dump tanks.

2. Interlocks.—Interlocks in the control circuit are provided so that reactor startup and operation cannot commence until all of the required safety features such as having the containment vessel at ½ atmosphere absolute pressure, stack fan on, etc., are satisfied. These interlocks also prevent too rapid a pump-up of concentrated fuel, stop the circulating pump if heat exchanger steam pressure drops too rapidly, or stop the fuel addition if the core temperature exceeds a set limit.

3. Sampling.—Sampling stations are provided which permit the taking of 5 cc samples from the core, blanket, fuel dump tank, fuel storage tank, blanket dump tank, blanket storage tank, while the system is being operated at full temperature and pressure.

4. Shutdown.—The normal shutdown is accomplished by merely closing the steam throttling valve, which reduces the power to that

required to equal the heat losses with the reactor critical at 280° C. The reactor temperature is then reduced by diluting the fuel. The cool-down rate is limited to 30° C per hour to prevent excessive thermal stresses. Dilution is continued until the reactor is subcritical at a low temperature.

5. Scram.—A more rapid shutdown, equivalent to an emergency scram in a solid-fuel system, is the "dump". In this situation the reactor is kept circulating for 2 minutes to permit recombination of the radiolytic gas in solution during which time the steam valves are closed to reduce power output. Then the pressure in excess of the vapor pressure of the core and blanket is vented to make pressure balancing between core and blanket easier, and the dump valves are opened, permitting the rapid emptying of the core and blanket vessels so that the reactor is shut down within minutes. This type of shutdown is used only in case of emergencies such as excessive pressures or evidence of a leak of radioactive solution from the reactor.

Operation with Fuel in the Blanket

During the initial power operation a hole developed in the core tank which permits transfer of fluids between the core and blanket. It was determined from hydraulic tests that a constant ratio of core to blanket concentration of about 3 to 1 could be maintained which would result in the generation of about 60 percent of the total reactor power in the core and 40 percent in the blanket. The system modifications which permitted this mode of operation involved installing a blank in place of the rupture disc in the interconnecting line between the pressurizers so that the blanket pressurizer could be operated completely full of D_2O condensate. Using the blanket feed and purge pumps, the blanket high-pressure system was then fed a constant stream of D_2O from the blanket dump tank, which resulted in a net flow from the blanket into the core, minimizing the mixing of core and blanket solutions through the hole. There was no letdown from the blanket high-pressure system to the blanket dump tanks, so D_2O had to be continuously transferred from the fuel dump tanks to the blanket dump tanks through a system of lines that had been provided to drain either set of dump tanks to an external shipping container.

11.2.3 Chronology

January 1954 to May 1956.	Design and construction.
May to July 1956	Performance-testing of components and systems. Chemical cleaning of reactor systems; hydrostatic tests. Remote-maintenance practice of underwater replacement of equipment.
August to October 1956.	Chloride contamination found in leak-detector system. Lines flushed with water, flange grooves cleaned, and gaskets replaced. Hydroclone plant cleaned and hydrostatically tested.
October to November 1956.	First prenuclear operation of reactor at 280°C for 147 hours. Flanged joints thermalcycled. Stress-corrosion cracking found in leak-detector lines. Hydroclone plant operated at 280°C in tests with simulated solids.
December 1956 to January 15, 1957.	Typical flanges and sections of leak-detector tubing removed for metallographic examination. Decision made to replace flanges and tubing, and procurement begun. Further testing of remote-maintenance tools.
January 15 to March 15, 1957.	First extended prenuclear operation at 280°C. Water and depleted uranium circulated for 866 hours to determine corrosion rates in absence of radiation. Hydroclone plant operated with reactor.
March 15 to August 1957.	Reactor operations suspended to permit cleaning and inspection of all flanges; replacement of 132 flanges and 6,000 feet of leak-detector tubing. Dissolver and storage system added to hydroclone plant for disposal of solids. Waste system completed.

August to September 1957.	Chemical cleaning and hydrostatic test of reactor plant.
September to October 15, 1957.	Reactor and hydroclone plant operated with water for 450 hours at 280° C.
October 15 to December 1957.	Final leak testing of reactor system with helium and with Kr^{85} at high pressure. No leaks. Top shield of reactor cell assembled, and cell pressure tested. New refrigeration system installed for cold traps and freeze valves.
December 1957 to January 1958.	Reactor filled with heavy water and operated for 100 hours at 280° C. U^{235} loaded. Reactor critical at 30° C on Dec. 27.
January to February 1958.	Temperature coefficient of reactivity measured from 65° C to 280° C. Final testing of remote-maintenance tools and techniques. Reactor cells sealed and leak tested.
February to February 15, 1958.	Reactor operated for 180 hours at powers to 1,200 kw and temperatures to 280° C. Experienced high initial corrosion of stainless steel and accumulation of nickel in fuel. Test terminated by difficulties with power wiring in cell.
February 15 to March 23, 1958.	All power wiring in reactor cell replaced by copper-sheathed mineral-insulated cable with cell flooded. New charge of fuel added to reactor.
March 23 to April 4, 1958.	Reactor operated at power levels to 6.3 Mw. Total of 275 hours and 327 Mw-hr. Run was terminated when hole developed in core tank after 30 minutes at 6.3 Mw.
April to May 15, 1958.	Approximate location of hole determined by hydraulic tests to be in inlet diffuser sections to core. Core tank and pressure vessel inspected by use of improvised periscopes inserted through core and blanket access ports. Hole was out of field of vision. Minor modifications made to permit operation with fuel in core and blanket. Fuel letdown valve replaced.
May 15 to July 4, 1958.	Nuclear operation resumed. Power raised gradually from 300 kw to 5.3 Mwt during 820 hours of continuous operation; 1,600 Mw-hr accumulated. Operation terminated for inspection of reactor vessel.
July 1958	Interior of pressure vessel and interior and exterior of parts of core tank inspected and photographed with improved periscopes. Lights failed on special periscope and mirror assembly designed for viewing region of hole. One fuel feed-pump head replaced; fuel sampler assembly replaced. Corrosion specimens installed in core and blanket regions.
July 30 to September 12, 1958.	Reactor operated continuously for 1,074 hours accumulating 2,526 Mw-hr. Maximum steady power level was 5 Mwt. Power excursions were experienced, and relationships between temperature, fuel composition, fuel inventory, and excursion behavior were investigated. The maximum excursion raised the power level from 3.5 to 25 Mw in 10 seconds and the system pressure from 1,750 to 2,000 psia without other effect. Run was terminated for inspection of reactor vessel and corrosion specimens.
September 12 to November 26, 1958.	Removed corrosion-specimen holder; inspected core and interior of pressure vessel; cut hole through diffuser screens; and photographed hole from interior and exterior of core. Core specimen holder showed damage from overheating, and specimens had been released into core. Some specimens were recovered; sections cut from screens were removed from the core. Several diffuser screens were found to be detached from the wall. A tube was installed in the core and connected to a new line to the hydroclone plant.

November 26, 1958 to February 2, 1959.	Subcritical operation in investigation of inventory problems and operation at power levels to 1.8 Mw in study of effects of the relationship between power level and uranium inventory under several operating conditions. The reactor equipment was operated continuously during a 68-day period although subcritical much of the time and at low temperature and pressure during an 8-day period while the pump in the hydroclone plant was replaced. Total power 340 Mw-hr. Operation was terminated by the first reactor scram. Fresh fission gas was forced into a closed instrument line near activity monitors in the instrument cubicles and initiated an automatic dump of the reactor. No hazard was involved, and the shutdown was unnecessary.
February to June 1959.	Reactor was operated mostly subcritical to investigate flow in core and blanket high-pressure circulating systems. Titanium impellers on core and blanket circulating pumps were ignited during separate startup incidents in which they were operated for short periods in oxygen gas. Both pumps, corrosion specimens in the circulating systems, one feed-pump head, and one dump valve were replaced. Multiclone was installed in reactor system to increase feed of solids to hydroclone plant. Blanket sampler was removed and repaired.
June to August 1959.	Reactor is being operated in tests to determine the effects of operating temperature and pressure and fuel composition on the power level at which instabilities are encountered. Catalytic recombiners in core low-pressure system required heating above 300° C before they functioned properly at beginning of run. Stable operating power was observed to increase with decreasing temperature at 260° C in first phase of tests. Total hours of continuous operation during run was 1,100 on July 30; 870 Mw-hr of heat had been generated.

During the period Dec. 1957 through July 1959 the reactor was operated for 5,750 hours, 3,420 hours critical, in generating 5,720 Mw-hr of heat. The hydroclone plant was operated in conjunction with the reactor during all runs after May 1958.

11.2.4 Significant Design Parameters

(1) Coolant: UO_2SO_4–H_2SO_4–$CuSO_4$–D_2O
(2) Moderator: D_2O
(3) Thermal power rating: 5,000 kw
(4) Electrical power rating: negligible
(5) Temperature and pressure: 300°C, 2,000 psi
(6) Core size: 32-inch-diameter sphere
(7) Power density: 17 Kw/liter
(8) Fuel enrichment: 93 percent
(9) Specific power: 1,000 kw/kg 25
(10) Central fuel temperature: 300° C
(11) Total inventory: 6.8 kg 25
(12) ΔT across core: 45° C

11.2.5 Operating Experience

(1) Thermal power generated—5.6 x 10^6 kw-hr (as of 7–28–59)

(2) Electrical power generated—not logged; most of heat generated is dumped.

(3) Activity levels—
  a. At full power:
    Above reactor thermal shield: 68,000 r/hr
    Near fuel circulating pump: 42,820 r/hr
    Near fuel feed pump: 74,000 r/hr
    Near blanket feed pump (D_2O blanket): 5.6 r/hr
  b. At shutdown:
    Above reactor thermal shield: 12,000 r/hr
    Near fuel circulating pump: 7,000 r/hr

Near fuel feed pump: 53,000 r/hr
Near blanket feed pump (D_2O blanket): 2 r/hr

c. 24 hours after shutdown:
Above reactor thermal shield: 2,200 r/hr
Near fuel circulating pump: 1,200 r/hr
Near fuel feed pump: 10,000 r/hr
Near blanket feed pump (D_2O blanket): 1 r/hr

d. During maintenance:
In the working environment above lead-covered platform, with reactor shield flooded, activity levels are 5 to 400 mr/hr. Equipment is removed unshielded from the reactor cell and moved to a storage pool during maintenance operations by a remotely operated crane. Radiation levels are several hundred r/hr near some equipment when it is being moved.

(4) Equipment problems:

a. Chloride contamination of the leak detector system and flanges during preoperational testing induced cracking, requiring replacement of all the leak detector tubing and 132 flanges. The contaminant was traced to die-drawing compound which had not been removed from the inside of the stainless steel tubes prior to annealing during manufacture.

b. Failure of the originally installed electrical power wiring necessitated its replacement using mineral-filled copper-jacketed electrical conduit.

c. Failure of titanium impellers (by combustion) in two circulating pumps made it necessary to install two new pumps using stainless steel impellers. The pumps had each operated approximately 5,000 hours.

d. Of 63 valves in the cell two dump valves and one valve to the hydroclone plant have been replaced, and the fuel letdown valve has been replaced twice because of excessive leakage across the seat. Conditions which caused the short life of the letdown valves and at least one of the dump valves have been corrected.

e. Some thermocouples have failed because of rough handling when they were near or associated with equipment being maintained, and some for unknown reasons.

f. Core developed a one- to two-inch-diameter hole through it and also had excessive general corrosion because of unforeseen problems with flow behavior, uranium deposition and heat removal at the Zircaloy surfaces.

g. Four diaphragm-type feed pumps have failed after 2,280, 2,300, 4,900, and 4,900 hours of service. Useful life of diaphragm pumps is expected to be 4,000 to 8,000 hours.

h. Three sampling mechanisms have been replaced because of leaking valves. Two of the samplers were repaired and returned to survice. One sample spill released approximately 20 curies into the fuel sampler cubicle.

i. The two recombiners in the fuel off-gas system have become temporarily unreactive on two occasions—once causing the initiation of combustion of the charcoal in one of the fission gas adsorption units, when a combustible mixture that had passed through the recombiner became ignited—once requiring regeneration of the units by heating to 320° C.

j. Two power leads, connecting the fuel circulating pump to the terminal at the cell-end of the mineral-filled electrical conduit, failed. The mineral-filled conduit was then extended all the way to the pump.

k. The 1-gpm canned-rotor pump in the hydroclone plant failed and was replaced.

l. A steam-system flange in a feed-water line located inside the containment vessel leaked. The cell sumps had to be pumped out frequently until the leak was repaired during a shutdown.

(5) System problems:

In the operation of HRE–2, two types of nuclear power fluctuations have been observed, which have been called "power oscillations" and "power excursions."

The "power oscillations" are small, the peaks being generally less than 3 percent above or below the average power, at frequencies that vary approximately linearly from about 8 per minute at near zero power to about 12 per minute at 3 Mw. The reactivity additions that correspond with these oscillations have been less than 0.02 percent Δk_e.

The "power excursions" are instances when the nuclear power increased or decreased by more than 5 percent from the average power, but in the treatment of data, only those larger than 7 percent are counted. About 800 positive excursions and 70 negative excursions in which the power changed by more than 7 percent were observed in about 2,500 hours of operation above 1 Mw.

The frequency of occurrence of positive power excursions increased from zero at about 2 Mw core power to about 1.6 per hr at 4.5 Mw core power when the reactor operated with fuel in the core only. The frequency increased from zero at 1 Mw core power to about three per hour at 3 Mw core power with fuel in both core and blanket. In the largest positive excursion the power increased from 3.5 Mw to 25 Mw in about 10 sec and the system pressure increased from 1,750 psi to 2,000 psi. In three other excursions the power increased by more than 100 percent. Identification of the mechanism, or mechanisms by which the fuel concentration changes are related to these reactivity changes has been one of the main objectives in the recent power runs.

(6) Fuel failures:

There have been no complete fuel failures, although in the first power run an intial very high stainless steel corrosion rate existed for about 12 hours. This increased the nickel concentration to a level that would severely restrict the latitude of variation permitted in reactor operation and in the investigation of fuel chemistry; so the original fuel charge was removed and replaced by a fresh charge. In subsequent operation there has been very little corrosion of stainless steel and no need for changing the fuel.

There have been several indications of fuel instability as a result of operation at power. These are:

a. gradual reduction in critical temperature

b. a decrease in the mass of uranium in circulation

c. changes in ionic ratios; e.g., U/free acid

d. power fluctuations

The fuel instability is reversible, and uranium lost from circulation can be regained by reducing power level. There are three known mechanisms for depositing uranium—boiling hydrolytic precipitation, and formation of heavy liquid phase—and all of them result from high temperatures.

A postulated sequence of fuel instability is that inadequate cooling of metal surfaces or deposits of uranium-bearing scale results in high local temperatures. Additional uranium is deposited on the hot spots by boiling, precipitation, or formation of heavy liquid phase. Extremely high temperatures are produced, causing severe corrosion or melting of the Zircaloy. Ample evidence of high metal temperatures in the core region has been obtained from thermocouples, the appearance and metallographic examination of a titanium sample holder that was exposed in the core, the photograph of the hole in the core wall, and metallographic examinations of corrosion specimens and samples of the flow diffuser screens all indicate temperatures greater than 1,000° C.

The difficulty is attributed to inadequacies in the hydrodynamic design of the core. No fuel instabilities were experienced in HRE–1 or in in-pile loops where the flow velocities along the metal surfaces were high.

(7) General Maintenance:

The methods which are used for the maintenance of equipment in HRE–2 are based on dry maintenance or underwater maintenance, or a combination of the two. The reactor system was arranged in essentially a horizontal geometry within the containment vessel so that access to any component can be had by removing the shield roof plug above that item. Working through water using long-handled tools, the item requiring repair is replaced with a new item and the faulty component is removed to a shielded area for maintenance. Entry of shielding water into the reactor piping system through flanges opened during maintenance is prevented by freezing a plug of heavy-water ice in the pipe before breaking the flange. Freeze-jackets are placed around piping at flanged-joints for this purpose.

In the operation of HRE–2 both underwater and dry maintenance have been used. Underwater jobs include replacement of nearly 4,000 feet of electrical power wiring, three valves, two circulating pumps, and four feed pumps; removal of the fuel circulating pump to recover corrosion specimens; installation and later removal of a new chemical-plant intake line.

Two valves have been removed and replaced, samples were cut from the core screens, extensive viewing of inside and outside surfaces of the core was accomplished, and the corrosion specimens in both core and blanket were removed using dry maintenance techniques.

Television cameras, mirrors, periscopes, and binoculars have all been used for viewing. A special folding-arm viewing device was made to permit passage through the 3-inch-diameter flanged opening in the pressure vessel and viewing of the hole in the core, which is situated on the back side of the core relative to the position of the blanket access flange. Holes were cut in the diffuser screens and the core tank hole was viewed by manipulation through a 2-inch-diameter access to the core. The hole was subsequently photographed on both the fuel side and blanket side of the core.

Tools and methods are being developed by which the hole in the core may be patched with a gold-gasketed patch, and the screens disintegrated by one of three alternate methods—electrolytic dissolution, Heliarc melting, or by cutting, all through a 2-inch-diameter opening.

Part IV

CURRENT PROGRAM

12. FUELS AND MATERIALS

12.1 CHEMISTRY OF AQUEOUS POWER-BREEDER FUEL AND BREEDER BLANKET SOLUTIONS

Research on solution fuels is concerned with investigation of the details of the physical chemistry of uranyl sulfate fuels, the properties of uranyl nitrate and mixed nitrate-sulfate fuels, decomposition of peroxide in simulated fuel solution, and the mechanism of homogeneous catalysis.

Studies of the five-component system UO_3–CuO–NiO–SO_3–$D_2O(H_2O)$ are being continued to establish the details of the phase diagrams in the region 0 to 0.04 *m* in UO_3, CuO, and NiO and 0.01 to 0.2 *m* SO_3 at temperatures to 350° C. The two-liquid phase region of the five-component system and of the systems UO_3–SO_3–D_2O H_2O) and UO_3–CuO–SO_3–$D_2O(H_2O)$ are being investigated as to boundary limits and compositional equilibria.

Some studies have indicated that dilute uranyl nitrate solutions are free of the liquid-liquid immiscibility problem and that addition of small amounts of nitric acid may substantially improve the stability of uranyl sulfate fuel solutions. Additional work is being done to determine the solubility relationships in those systems.

Since the production of peroxide is a consequence of fissioning in uranyl sulfate solutions and a part of the behavior of the fuel in HRE–2 could be explained by precipitation of uranyl peroxide in the reactor, studies are being undertaken both on the rate of decomposition of peroxide and the solubility of uranyl peroxide at temperatures above 100° C.

Although the rate constants of cupric ion for catalysis of the hydrogen-oxygen recombination in the uranyl sulfate systems have been determined, the reaction mechanisms have not been established. The rate constants are being determined in other systems of reactor interest (primarily the nitrate system) in order to have available constants for design purposes and to provide additional information on the mechanism of the catalysis.

12.2 AQUEOUS THORIUM OXIDE SUSPENSIONS

The present program for studying the characteristics of aqueous thorium oxide suspensions may be divided into two categories: (1) the determination of those factors affecting the laminar-flow properties of the suspensions, (2) the determination of those factors affecting the transport and drop-out behavior of suspensions flowing in horizontal, circular conduits.

12.2.1 Laminar-Flow Characteristics of Flocculated ThO_2 Suspensions

Although it is recognized that particle size and suspension concentration are the principal factors affecting the value of the yield stress, the details of the particle fluid interaction are poorly understood and additional tests are being made to study several other variables:

1. the temperature at which the ThO_2 was calcined,
2. the particle size distribution,
3. the shape of the particle (i.e., spherical, cubical, or platelike),
4. the effect of insoluble metal oxide additives.

Further analytic-experimental studies are also being made of the critical velocity required for turbulent flow.

Another major uncertainty is the effect of temperature on ThO_2 shear diagrams. Preliminary tests suggest that operation at elevated temperatures does not produce adverse effect on ThO_2 flow properties, but this has not been proved conclusively. Two high-temperature viscometers are being employed in current studies. One, attached directly to the high-temperature loops, can be used to determine properties of the suspension as they exist in the circulating loop. The other viscometer is being used to determine suspension properties at different temperatures and concentrations. The data will be used to obtain activation energies for flow as well as the temperature coefficient for the coefficient of rigidity.

12.2.2 Suspension Transport

The mean flow velocities required to prevent drop-out from suspensions are 2 to 8 ft/sec, so high that they present some design problems. Although the general nature of the problem is reasonably well understood, particular aspects require more detailed study. Problems currently being studied include:

1. the determination of the factors affecting the onset of compaction in flowing streams of flocculated materials,
2. the determination of the role of the settling rate on drop-out correlations,
3. the determination of the factors affecting the resuspension of sediment on the walls of a pipe and the transport of the sediment through the laminar sublayer to the turbulent regions of the pipe where turbulent diffusion processes ensure a well-mixed suspension.

12.2.3 Surface Chemistry and Caking Studies

Many of the physical and engineering properties of thoria slurries depend on the surface chemistry of the thoria particles in relation to the environment. Studies are being made of the capacity of thorium oxide to absorb ions from solutions, the nature of adsorption, and the effect of the adsorbed materials on the colloidal properties of the slurries.

Caking is believed to be related to the colloidal properties of the slurries and the hydrodynamic conditions in flowing systems. Laboratory studies and loop tests are being continued to determine the factors which effect caking and to provide methods for preventing caking and for removing and dispersing cakes in loop systems.

12.2.4 Radiation Stability of Oxide Slurries

Studies have shown that irradiation of slurries for a few hundred hours at power densities of a few kilowatts per liter has no observable effect on slurry properties. This work is being continued to determine whether the slurry properties are changed by long irradiations involving the burnup expected in the cores and blankets of slurry-fueled reactors. Where possible, irradiated materials will be used in scouting tests of possible slurry processing methods.

12.2.5 Catalytic Recombination of Radiolytic Gases in Reactor Slurries

The results of both out-of-pile and in-pile experiments indicate that MoO_3 and Pd, either as the metal or hydrous oxide, are suitable for use in slurries for the liquid-phase recombination of the radiolytic gas. Recent experience indicates that platinized thoria in a slurry containing molybdenum oxide may also be a useful catalyst system.

Immediate work in the catalyst program is on development of preparation methods which will give the most active catalysts and assure reproducible results. One objective is to eliminate the necessity of any pretreatment of the slurry containing the catalyst to assure satisfactory recombination. A second objective is to assure uniform distribution of the catalyst in the slurry or catalyst stock preparation. Careful control in the palladium and platinum catalyst preparation is necessary in order to assure that the catalyst will not segregate when it is added to a reactor slurry.

It is necessary that the out-of-pile methods for testing catalysts simulate as closely as possible the actual conditions under which the catalyst is to be used in a reactor. A method for injecting gases into an autoclave at temperature has been developed. A second apparatus which includes an electrolytic cell to generate stoichiometric gas for use at temperature under steady-state conditions of operation is also under development.

Fundamental studies in support of the catalyst development will continue. These include a study of the mechanism of recombination and the kinetics of the reaction. Particular attention is being given to the kinetics of the recombination process where large excesses of oxygen and hydrogen are present. The effect of low-surface-area solids on catalyst efficiency, solubility of oxygen and hydrogen in slurry systems, and the effect of corrosion products, fission products, and uranium concentration on catalyst efficiency are being investigated.

Small-scale in-pile studies with selected slurries with and without catalyst are being continued to define better the effect of gas atmosphere on gas production, determine slurry concentration and oxide particle-size effects, and determine the effects of long-term irradiations on catalyst efficiency.

12.3 CORROSION

12.3.1 Materials in Circulating Systems and Auxiliaries

Uranyl Sulfate Solution

Since solution stability has been shown to be of importance to the corrosion of materials in a variety of ways, such studies are being continued. The effects of solution composition, flow, and heat flux or temperature on boiling deposition and attack on materials are being investigated. Similar studies of second liquid-phase formation and composition and hydrolytic precipitation are being made in an all-titanium loop designed to operate at temperatures as high as 370° C. Many of these studies are cooperative with solution chemistry studies.

Behavior of the casting alloys such as cast 347 and CD_4MCu stainless steel in view of their greater resistance to stress-corrosion cracking failure and possible economic advantages is being studied in the general corrosion program. Experimental zirconium alloys of interest in core and other specialized applications are also being investigated.

Slurry

The out-of-pile tests in toroids and loops continue the delineation of the effects of slurry properties and operating variables on alloy corrosion. Among the alloys those showing resistance to stress-corrosion cracking failure, e.g. cast 347, CD_4MCu stainless steel and Inconel, are of particular interest as major materials of construction. Materials for special applications involving particularly aggressive conditions are being investigated from the standpoint of both materials and slurry properties. Oxide and slurry physical and chemical properties, flow configurations, and material oxide and alloy characteristics are of interest.

The appreciable differences in materials behavior with changes in atmosphere, hydrogen vs oxygen, has stimulated considerable interest in studies made in the presence of both gases, particularly in loops, and thus better approximating reactor conditions. Concomitant studies of catalyst activity and longevity under dynamic conditions are contemplated. Such studies are a very important aspect of the development necessary to the adaptation of the 5-gpm in-pile solution loop to slurry service.

The factors important to hydriding of zirconium are being investigated. Slurry physical and chemical characteristics, hydrogen and/or oxygen effects, and alloy composition and corrosion are significant variables. Boiling at a heated surface is also being investigated in connection with hydriding and other materials and slurry effects. Heat flux and temperature, flow, and slurry composition are variables of interest.

Water

The use of hydrazine in feed-water treatment is being studied in conjunction with operation of HRE–2. Relationships between operating variables such as temperature and power levels and the rate of addition necessary for adequate control of the oxygen content of the steam are being determined.

12.3.2 Corrosion of Core Materials

Uranyl Sulfate Solution

The data which have been obtained on the corrosion of zirconium alloys in fissioning uranyl sulfate solution and the interpretation of those data suggest two avenues of investigation for reducing the observed attack. One of these involves the lowering or elimination of uranium sorption on zirconium-alloy surfaces during exposure; the other stems from indications that the maximum rate of attack at infinite power density appears dependent on alloy composition.

A research program is in progress to obtain systematic information about sorption of uranium from aqueous solutions at elevated temperatures by metal oxides. The effects on sorption of temperature, of solution composition, and of oxide properties such as particle size, surface area, and composition are being investigated. Oxides of zirconium, iron, and titanium are being studied with particular emphasis on zirconium oxide. Solution variables include uranyl sulfate concentration and effects of other solutes such as H_2SO_4, $CuSO_4$, and Li_2SO_4.

In connection with the search for better alloy compositions, considerations of possible mechanisms of the radiation effects have led to an indication that the corrosion characteristics in- and out-of-radiation are related. Thus a better knowledge of the out-of-radiation corrosion characteristics should be useful in determining the radiation-corrosion mechanism and perhaps in reducing the amount of in-pile testing required. The electrochemical polarization method of measuring corrosion rates and processes shows promise of providing a technique for such detailed study of the high-temperature aqueous corrosion of zirconium alloys, and its application to systems of interest is being pursued.

In-pile loop and autoclave experiments are directed at further understanding the mechanism of radiation corrosion. The effects of power density, heat treatment, alloy composition, and temperature are being investigated. Particular attention is being given to demonstrating the relationship between in- and out-of-pile corrosion and the maximum predicted rates suggested by the present model.

Slurry

Slurry in-pile autoclave tests are concerned with extending exposures to higher fission power density levels and examination of the effects of power density. Such studies are expected to provide some understanding of the nature of the transitory increased corrosion of Zircaloy–2 during initial radiation exposure. Concomitant studies of radiolytic-gas formation, recombination-catalyst behavior, and fission-product distribution and effects are projected. Data on other alloys, as suggested by other programs, will also be pursued.

Extension of the in-pile studies to dynamic systems is being attempted through adaptation of the 5-gpm in-pile solution loop to slurry service. Interactions betweeen radiation and flow as regards corrosion, slurry properties, and/or catalyst performance are to be investigated.

12.4 METALLURGY

The metallurgical development program is concerned almost entirely with zirconium alloys. Emphasis is placed on developing new alloys, improving the knowledge of Zircaloy–2, and improving methods of fabricating zirconium metals.

12.4.1 New Zirconium Alloys

Zirconium-niobium base alloys with molybdenum and copper as ternary additions appear to have improved corrosion resistance and are the ones most likely to have acceptable metallurgical properties. Morphology, phase diagrams, transformation kinetics and products, stabilities, and mechanical properties of the alloys are being studied. Some corrosion and metallurgical testing of other zirconium-niobium base ternary alloys and binary zirconium systems is being done in a search for additional promising alloys.

A study of the thin oxides present on zirconium alloys is being undertaken to obtain basic information concerning the formation, rate of growth, composition, and structure of the films. Initially the investigation is limited to films on crystal-bar zirconium and Zircaloy–2, making use of monochromatic bent crystal x-ray diffraction, metallographic, and topographic electron microscopy. New techniques for studying thin films will be developed as the work progresses.

12.4.2 Fabrication

An extensive study of fabrication variables and their effects on anisotropy and preferred orientation is continuing. Fabrication variables being investigated include rolling temperature, forging temperature, reduction per anneal, annealing temperature, number of anneals, number of beta heat treatments, water quenching and air cooling after the beta treatment, and the degree and location of cross rolling. While being made principally on plate, it is expected that the information obtained can be applied to other products with very little additional development.

12.4.3 Forming

Some forming studies on Zircaloy–2 plate are continuing in an attempt to develop a technique that will yield, in one operation, a vessel with dimensional tolerances adequate for a reactor system. Emphasis is placed upon warm pressing and spinning. As plates with more uniform properties are developed in the fabrication program, they are used in the forming studies.

12.4.4 Mechanical Properties

A basic mechanical-property study is being conducted in support of the fabrication work. Examination of the mechanical-property specimens from the wide variety of orientations found in the plates should help in the understanding of effects of anisotropy. It is hoped that theories and rules developed for isotropic materials can be modified to cover the anisotropic case. Theoretical and experimental studies of the anisotropy of plastic strain produced in the tensile specimens have led to the development of an analysis of the cross-sections of fractured tensile specimens which determines, simply and quantitatively, the strain tensor of the material produced by each schedule and thus to a quantitative separation of the effects of the fabrication variables. The determination of the strain tensor enables the calculation of the strain behavior for any tensile direction in the plate material. It is quite probable, but not yet determined, that the strain behavior for biaxial and triaxial tension can be calculated from the results. The studies are continuing in an effort to determine, first theoretically, the relationships of the entire stress-strain tensile curves to the strain tensors, particularly the elastic portions of the curves. The experimental studies show that such relationships probably exist but do not, as yet, indicate their form.

13. CHEMICAL PROCESSING

13.1 CORE PROCESSING

The multiclone installation in HRE-2 is being operated to determine whether hydroclones can complete effectively with other mechanisms in removing insoluble fission and corrosion products from a homogeneous reactor. Additional work is being done on the testing of solutions for descaling complete reactor systems and for decontaminating equipment for maintenance.

Behavior of fission products in HRE-2 is being studied by analysis of radiochemical data obtained from samples of fuel solution. Solubilities of rare earths and the residence time of iodine in the reactor are receiving the most attention. The effects of retention of tellurium in the corrosion scale are being investigated. Examination is also underway of the effects of the adsorption of iodine on corrosion scale or on silver present in the reactor fuel or in the corrosion scale.

13.2 THE PREPARATION OF SLURRY OXIDE

There are two obvious improvements that can be made in thorium oxide production to reduce the cost or improve the performance of slurries. The first is to reduce the final firing temperature to 1,000° C or less. Preliminary results indicate this may be made possible by digesting the freshly precipitated thorium oxalate for several hours at 95° C before filtering and firing. This digestion period imparts improved particle integrity to the final oxide, which may permit lowering the final firing temperature. The second improvement is to produce spherical thoria particles, which have been shown to be nonerosive at particle sizes as great as 15μ. Spherical thoria in the desired particle-size range has been prepared on a laboratory scale by two methods: flame calcination of an atomized solution of thorium-uranium-aluminum nitrate, and by forming beads of thoria gel which can be fired to dense thoria spheres. Oxide preparations produced by both methods are currently under test, and development of the preparation methods to permit scale-up is in progress.

Characterization of thorium-uranium oxide products will continue in an effort to determine the effects of preparation conditions, the furnace atmosphere during firing, and other variables on the oxidation state and distribution of uranium in the thoria. It will also be necessary to relate the preparation conditions of the mixed oxide to the various slurry performance indices in order to ensure the development of a satisfactory thoria-urania slurry.

14. ENGINEERING DEVELOPMENT

14.1 DEVELOPMENT OF REACTOR COMPONENTS

The most important component problem at the present time is believed to be the development of a high-power-density solution-core ThO_2-slurry-blanket assembly. Methods for utilizing hydrodynamics for reducing the problems of core-wall corrosion and solution fuel stability are being investigated in spherical and cylindrical vessels. An important part of this program is the development and testing of experimental tools for making precise measurements of velocity distribution, heat transfer rates, and eddy diffusion rates, as well as the development of analytical methods of predicting reactor performance from experimental models.

Although the feasibility of most other HRE–2 size reactor components is believed to have been demonstrated, numerous minor improvements in equipment appear to be desirable, particularly for handling slurries. The main objective of the present pump development program is a reactor-grade slurry pump capable of circulating thoria at a concentration of 1,000 g Th/liter H_2O for at least 1 year without maintenance. This requires the optimization of design and material selection for hydraulic parts, bearings, and shaft seals. Material selection for the impellers is complicated because of recent HRE–2 titanium impeller fires; a special test system has been set up to investigate how corrosion-resistant titanium and Zircaloy may best be used as impeller materials.

Current steam-generator development is emphasizing the elimination of the chloride stress-corrosion cracking problem by the use of composite stainless-steel–carbon-steel or stainless-steel–Inconel tubing. Small test models containing composite tubing are being constructed by a contractor, and they will be tested in an existing facility. The circulation of slurries through steam-generator models is being investigated. It is planned also to investigate methods of repairing HRE–2 scale steam generators in place in the event of tube failures.

Several slurry pressurizer designs are being tested in the loop program, in efforts to minimize thoria holdup and to improve purge-water production. Since the gas-handling system of the HRE–2 appears to be reasonably satisfactory, no major improvement in its components is anticipated as applied to experimental homogeneous reactors. A contaminated-oxygen compressor is being developed. Designs of reactor systems utilizing new recombiner, adsorber, and recycle concepts are being evaluated. Slurry storage tanks utilizing various methods of agitation are being fully evaluated. Slurry feed-pump check-valve materials are being tested and improved. Techniques for sampling slurry from loops are being developed.

14.2 SLURRY-SYSTEM DEVELOPMENT

Additional slurry-circulation tests are required to fix a specification for the acceptable limits on particle size, particle shape, and thoria calcination temperature in order to meet the slurry-blanket-fuel goals with respect to rheologic and erosive properties. Evaluation of slurries prepared from high-fired thoria microspheres is of particular interest because it appears that they will be less erosive and have lower yield stress than slurries in current use.

The behavior of selected slurries is being tested during long periods of circulation to determine their suitability from the following standpoints:

1. resistance to erosive degradation,
2. resistance to caking,
3. dropout behavior,

4. ability to sustain a catalyst for recombination of radiolytic gas,
5. ability to maintain acceptable properties over the entire temperature range of interest and during thermal cycling,
6. ability to maintain acceptable properties at varying redox conditions,
7. resuspendability after long shutdown,
8. ability to undergo local or bulk boiling in turbulent flow without deposition of solids,
9. separability of purge water from the slurry.

It is necessary at the present time to devise definitive methods of evaluation for some of those characteristics. Improvements in technique are being investigated for high-temperature viscometry and densitometry, and for measurement of inventory. Improved methods of cleaning loops are being developed.

The 300–SM slurry mockup system is being operated to extend present data on flow behavior in a reactor-vessel model to temperatures of 300° C and to concentrations of 1,000 g Th/liter; to test the combined performance of high-pressure and low-pressure systems which approximate those required for a small reactor; and to improve sampling and other techniques of evaluating system performance.

14.3 SOLUTION SYSTEM DEVELOPMENT

The HRE–2 mockup is being operated to investigate reactor operating problems as they arise. The statistical behavior of solution inventory in a complex system and the descaling of a complicated system are being studied.

14.4 DEVELOPMENT OF MAINTENANCE OPERATION FOR HOMOGENEOUS REACTORS

Development of tools for HRE–2 maintenance operations is being continued. This includes removing the screens from the reactor core and closing the hole in the core tank. Methods are being studied for removing slurry from reactor systems prior to maintenance. Study of maintenance requirements for subsequent experimental and power reactors is being undertaken with the objective of establishing a program for the development of remote-maintenance equipment and methods for large power reactors.

14.5 INSTRUMENTATION AND CONTROL

The instrumentation work is concerned with the improvement of instruments and valves for HRE–2 and the development of instrumentation to meet the special requirements of slurry systems. Particular attention is being devoted to the development of density-measuring devices, level indicators, pressure and differential-pressure transmitters, and flow-measuring instruments for slurry systems. Control-valve development involves testing of trim and design or modification of valves to handle slurry satisfactorily.

15. REACTOR DESIGN AND ANALYSIS

Reactor design and analysis work is concerned primarily with the analysis of HRE–2 operation, improvement of the operation of the reactor, and establishment of criteria for new reactor experiments and the large power reactors. Detailed effects of fluid circulation on reactivity behavior are being analyzed so as to better interpret experimental data from HRE–2. Relations between reactivity addition, nuclear parameters, initial power, time during which power rises, and energy generated during power rise are being determined for homogeneous reactors for reactivity additions less than one dollar to obtain a better understanding of the behavior of a circulating-fuel reactor when operating in the region between critical and prompt-critical.

Calculations of the nuclear characteristics of small two-region reactors with solution cores and slurry blankets are being made to establish criteria for the design of an experiment to replace HRE–2. The studies involve determination of the smallest reactor that will operate at 280° C with 10 g U/liter in the core, 1,000 g Th/liter as thoria in the blanket, a ratio of U^{235}/Th less than 0.04 in the blanket, and with D_2O or mixtures of H_2O and D_2O for the moderator. Nuclear safety of particular designs will be studied.

Conceptual designs of a two-region reactor experiment and a large power-breeder station are to be included in the program, and alternatives to the solution-core slurry-blanket circulating-fuel reactors are being analyzed.

Determination of η for U^{233} is continuing to obtain firm values in the thermal-energy region and to evaluate the change with energy in the epithermal regions.

A small low-temperature slurry reactor experiment is operating at the KEMA Laboratory in the Netherlands. Kinetics experiments are being made that should provide data pertinent to the design of a slurry-core reactor.

16. HOMOGENEOUS REACTOR EXPERIMENT NO. 2

Operation of HRE-2 has revealed one problem of major significance to the development of solution-fuel reactors. When the reactor power is greater than about 2Mw, uranium separates from the fuel solution and accumulates in the reactor core, causing power disturbances, excessive temperatures, and high corrosion rates within the core. The phenomenon may result from unknown effects of radiation on the fuel, from the hydrodynamic design of the core, or from a combination of hydrodynamic and solution-stability effects. Operation of HRE-2 is concerned primarily with determining the cause and mechanism of separation and at least partially demonstrating chemical or engineering solutions to the problem.

The reactor is being operated in experiments to establish the relationship between bulk fuel temperature and system pressure on the power level at which uranium begins to separate from the fuel in an attempt to determine whether the separation is initiated by boiling or by hydrolysis and separation of solids or heavy-liquid phase. Data from previous experiments have indicated that a steady state characterized either by the amount of uranium separated or by the acidity of the fuel solution is reached at each power level above 2 Mw. As a part of the experiment, changes will be made in the composition of the fuel to determine the effects of those changes on the separation of uranium.

Following the present fuel separation and chemistry studies, it is proposed to change the flow conditions in the reactor. The screens will be removed from the core, an attempt will be made to close the hole in the core tank, and piping will be changed so that fuel enters as a jet through the top and leaves through the bottom of the core tank. Recirculation induced by the jet will result in a flow pattern which approximates that in a mixed-flow core.

Operation of the reactor will be resumed to determine the effect of the changed hydrodynamics on the separation of the fuel during power operation.

In addition to investigation of the fuel stability problem, the reactor is being used in the study of the behavior of fission products, corrosion products, and materials in the fuel; in the development of improved operating and maintenance procedures; in the testing and improvement of reactor equipment and maintenance tools; and in the establishment of improved design criteria for succeeding fluid-fuel reactors.

Part V

DESIGN STUDIES

17. DESIGN STUDIES

There are three conceptual designs of aqueous homogeneous reactor plants that have carried out in sufficient detail to reveal the major unsolved problems and to indicate the probable direction that the plant designs would take if the problems can be solved in ways that were assumed to be reasonable. Three variations are also available for the purpose of facilitating comparisons and of bringing the earliest design more in line with the present thinking.

These six designs are as follows:

A. *The TBR*—a conceptual design study of a 300-Mwe Thorium Breeder Reactor station by the Homogeneous Reactor Project at ORNL. The station contains three reactors, each reactor being a two-region, uranyl sulfate solution-fueled, thoria slurry blanket breeder. Each reactor produces 440 Mw of heat which is used to generate 370-psig dry saturated steam. There are three 125-Mw turbogenerators, for a total gross plant capacity of 375 Mwe and a net capacity of 300 Mwe. A single Thorex chemical processing plant capable of processing 327 kg per day services all three reactors. Each reactor system is contained in a vertical, cylindrical envelope approximately 66 feet in diameter by 116 feet high, capable of withstanding an internal pressure of 50 psig.

The three reactor containment cells are arranged linearly in a space approximately 80 feet wide, 300 feet long, and 45 feet above ground level. An access hatch is provided in the top of each cell, and items such as circulating pumps, pressurizer-heater elements, evaporators, and valves, for which the probability of maintenance is high, are grouped near this hatch for servicing. A pool is located at one end of the reactor plant for storage of items freshly removed from the containment cells. A gantry crane services the reactors, and its runway extends a distance beyond the reactor structure for access to the pool and to provide lay-down space. Although specific procedures for repairing and replacing equipment were not developed, consideration in the layout was given to the use of both wet and dry maintenance methods. Maintenance facilities were included in the plant investment. Equipment replacement and maintenance labor were not considered in detail.

The TBR design study was completed in 1955 (not published) and is based on the ideas and broad survey presented in ORNL–1642 (1954).

B. *The NPG*—A conceptual design by the Nuclear Power Group and Babcock and Wilcox Company of a 150-Mwe, two-region, uranyl sulfate fueled, thoria pellet blanket reactor that supplies steam to a single turbogenerator. The reactor produces 520 Mw of heat, which is used to generate 620-psia steam in once-through-type boiler heat exchangers. The blanket region of the reactor is composed of 14 cylindrical assemblies arranged around the periphery of the core region. These assemblies contain thorium oxide pellet beds which are cooled by the fuel solution flowing from a ring header below the reactor vessel. The fuel solution (uranyl sulfate in heavy water) leaves the assemblies through top outlets, flows downward through the core region and out of the bottom of the vessel to four groups of six heat exchangers at a rate of 24.9 x 10^6 lb/hr.

In order to facilitate maintenance, the plant layout was designed with the components of the primary system extensively compartmentalized. The plant is laid out horizontally with a minimum of vertical stacking of components in order that each component will be accessible from directly above and that maintenance equipment can be operated as directly as possible through adequate water shields.

The reactor system is contained in a building 196 feet long, 131 feet wide, and 50 feet high.

The equipment is located in a group of gas-tight cells measuring 196 feet by 131 feet overall. Each cell is equipped with pressure-tight concrete lids to facilitate overhead maintenance of the various system components and minimize the radiation shielding required above the floor and outside the building. All components of the plant are designed in accordance with this overhead-maintenance philosophy. All components in contact with reactor fuel at high pressure are themselves enclosed in close-fitting, high-pressure containment envelopes capable of withstanding the full system pressure.

The estimated annual maintenance costs are as follows:

Nuclear Plant

Maintenance labor (117 people)	$1,001,000
Reactor material (replacement parts)	1,806,900
Spares inventory	164,000
Fixed charges on tools	226,000
Total	$3,197,900
Conventional plant	77,500
Total annual maintenance cost	$3,275,400

C. *The PAR-150*—A conceptual design of the Pennsylvania Advanced Reactor, by the Westinghouse-Pennsylvania Power and Light group, a 150–Mwe, single-region, thoria-urania slurry converter reactor. This reactor produces 550 Mw of heat which is converted 400-psia steam in four parallel heat exchange loops and to electricity in a single turbogenerator.

To determine the most practical structure for this plant, an extensive study was made of the various possible container shapes.

One of the reactor-plant layouts studied, which typifies the maintenance and layout philosophy, consists essentially of a rectilinear layout arranged within a 190-foot steel sphere, with biological shielding completely separate from the vapor container. All four of the primary coolant loops are designed with polar symmetry to permit any component to be used as a replacement part in any of the four loops, and any special equipment required to be equally adaptable to all four loops. Like pieces of equipment are grouped to permit the use of relatively permanent maintenance facilities designed into that particular area. Personnel access corridors are provided to permit limited access to certain areas inside of the vapor container during full-power operation of the reactor.

Dry maintenance operations are accomplished primarily through the use of a 100-ton, shielded-cab crane which traverses the length of the reactor container. Since the cab can be occupied during operation, the crane serves as a remote tool for handling heavy shield blocks and removing and replacing equipment. The design is based on an all-welded piping system, and removal of any item requires a remote cutting and welding machine. Because of the vulnerability of the circulating pumps and steam generators, special modifications are provided to permit these items to be repaired in place.

The estimated annual maintenance costs are as follows:

Capital equipment spares	$352,000
Maintenance tools and equipment	332,000
Operating expense	140,000
Maintenance expense:	
Labor (39 people)	260,000
Other	128,000
Total maintenance cost, per year	1,212,000

This design was developed by the Westinghouse–Pennsylvania Power and Light group in 1959, and it embodies the most complete and detailed study, to date, of the critical maintenance problems associated with fluid-fueled reactors.

D. *The AHR*—a 316–Mwe variant of the TBR, differing mainly in the layout and design of containment envelope (a single, large sphere or equivalent for the three reactors), and in utilization of a single turbine-generator instead of pairing one turbine-generator with each reactor. This reactor is included in the AEC Task Force study of fluid-fueled reactors.

E. *The PAR-315*—a 315-Mwe scaled-up version (by Westinghouse) of the PAR-150, employing a single reactor enclosed in a 200-foot sphere and supplying steam to a single turbine-generator.

F. *The PAR-AHR*—a capital-cost study of a three-reactor breeder station of the AHR process design (same power) but scaled on the basis of the PAR layout and maintenance philosophy.

The cost estimates for the six designs (see Section 18) were placed on a common basis by utilizing the direct construction and materials costs from each study, adjusted to the June 1959 *Engineering News Record* cost index, and applying uniform percentages for indirect costs, contingencies, and annual charges (supplied by the AEC for use in the Ten-Year Plan studies) and including certain common items. The same unit costs for D_2O, uranium and thorium, and fuel-use charges were also applied.

Part VI

PROBLEMS AND LIMITATIONS

20. PROBLEMS AND LIMITATIONS

The problems and limitations of aqueous homogeneous power breeder reactors as presently conceived result from the use of a highly radioactive moderator and coolant, from the chemical and physical characteristics of the fuels and container materials (including the mobility of the fuel), and from the combination of requirements which must be fulfilled to achieve an efficient breeder.

Use of an aqueous coolant imposes limitations which are characteristic of all pressurized-water systems. The reactors must be operated at the highest pressures consistent with economic considerations and the capabilities of modern technology to produce steam at temperatures which are low in comparison with modern steam plant practice. It appears likely that the maximum coolant temperature will be 300° to 335° C (570° to 635° F) and the pressure will be 1,500 to 2,500 psia. Indirect power cycles are required whether the ultimate reactor is a circulating-fuel or a boiling reactor. Steam generated in the reactor would be so highly contaminated with gaseous fission products that it could not be used reasonably in a large turbogenerator plant. Steam produced in the steam generators probably will not exceed 550° F and 1,000 psia. Gross thermal efficiencies approaching 35 percent may be achieved by use of this steam in moisture-removal and reheat cycles, but a superheat cycle with steam at higher temperature is preferable. If high thermal efficiency or lower plant cost produced by superheating steam really become important, means for obtaining some superheat in homogeneous reactor systems have been conceived; but other means, chemical or nuclear, presently appear to be more practical.

The high and permanent radioactivity of the fluid fuel and coolant creates the most serious problems in the reactor plant. Exceptional quality of construction and careful inspection are required to ensure complete initial leaktightness of the primary system. Greater dependence must be placed on the integrity of the containment vessels and some of the auxiliaries. If a leak occurs in the primary system, fission products are discharged immediately into the reactor cells, the steam system, or an auxiliary cooling system. All the equipment in contact with fuel becomes highly radioactive and must be maintained by remote methods. Complete containment and remote maintenance have been demonstrated in one and one-half years of operation of HRE–2. However, provisions that must be made throughout a reactor plant for handling and containing the fluid fuels and for doing remote maintenance tend to make the unit costs for homogeneous reactors higher than the costs for similar systems which employ only slightly radioactive coolants.

The most promising solution fuels are acidic and are contained in stainless steel, titanium, zirconium, or similar materials. They become less stable with increasing temperature and more stable with increasing acidity. The acidity required for stability must be balanced against the corrosiveness of the fuel in using stainless steel, and considerable care must be taken in selecting the operating conditions and in design of the reactor to prevent the fuel from becoming heated into the range of instability. Overheating of a solution fuel in a reactor core can result in concentration of the uranium on vessel surfaces and severe overheating and melting of the metal, as in HRE–2. However, experience with HRE–2 also indicates that the nuclear behavior can provide warning of instability before there is serious damage to the reactor.

At the present time uranyl sulfate fuels that can be contained in stainless steels are unstable at temperatures above about 330° C. Care must be exercised to keep the oxygen concentration high and the chloride low to prevent stress-corrosion cracking and excessive corrosion of the steel. Solutions which are sufficiently acid to be stable above 350° C can be contained in titanium. Titanium is not subject to stress-corrosion cracking and not as sensitive to the oxygen requirement, but under special conditions it can ignite in oxygen. Development of steel equipment lined or clad with titanium appears to be required to take advantage of the improved stability of the fuel and corrosion resistance of the metal.

The problems are less obvious for slurry fuels because they have been used less. It is unlikely that a dilute slurry of fissionable material would be sufficiently stable for use in a reactor; so the fissionable material is diluted with fertile material. In order to maintain a uniform suspension, the slurries must be kept in turbulent flow. Although the circulation rates for a slurry fuel in a reactor core would be dictated by heat-removal considerations, the flow rate in a blanket would ordinarily be that required to maintain the suspension. Fluctuations of 20 percent in concentration should not have serious effects on the nuclear characteristics of a reactor, but they would create inventory-control problems. Care must be taken to prevent the accumulation of slurry on surfaces and the overheating of metals in a slurry reactor also. However, the conditions are less severe in the case of the slurry because the uranium in a deposit is diluted by thorium.

Slurry fuel systems are presently constructed of stainless steel (as are solution fuel systems), with titanium and zirconium reinforcement in places where erosion is severe. Stress corrosion cracking has been more of a problem with slurries than with solutions. Inconel and low-alloy ferritic steels, which are less susceptible to cracking, may be satisfactory materials for slurries. Titanium equipment would be highly resistant to erosion and cracking.

The mobility of the fuels presents problems that are unique to fluid-fuel reactors. Continuous indications of fuel concentrations and inventories are desirable and may be necessary to the satisfactory operation of a large reactor. This requires development of complete in-line instrumentation for monitoring both solution and slurry fuels.

Radiolytic gases that are produced in homogeneous reactors present a potential hazard. Catalysts have been developed for both liquid- and gas-phase recombination of the gases, and the gases have been handled without difficulty in HRE–1 and HRE–2. Special consideration must be given in design and operation of the reactors to ensure safe handling of the gases.

The requirements for high conversion ratio in the reactor limit the selection of moderator to D_2O and the selection of core-tank materials. Zirconium alloys are the materials which appear to combine corrosion resistance, mechanical strength at high temperature, and low neutron-absorption cross section to the extent necessary for core-tank applications. A significant improvement in any of the three properties would result in a corresponding significant improvement in the performance, operability, or economics of a large reactor. High breeding ratio and low inventory of fissionable material in the reactor are achieved by processing on short cycles to remove fission-product poisons from the core and bred U^{233} from the blanket. Typical blanket processing cycles are equivalent to burnups of 3,000 to 5,000 Mwd/ton. Shorter cycles are advantageous as more economical processes are developed.

Homogeneous reactor stations require auxiliaries, such as analytical laboratories, radioactive maintenance facilities, and waste disposal facilities, that are more extensive than are required for present designs of solid-fuel reactors. On-site processing, while not required, appears to be desirable. The total of facilities that would be provided for one reactor could be used by several reactors without much increase in size or cost of operation. This favors the use of homogeneous reactors in power stations which contain several reactors and have electrical generating capabilities in excess of 1,000 Mw.

The total power that can be generated in one reactor is limited by nuclear, heat transfer, corrosion, or mechanical considerations. About 50 kw per liter in fuel adjacent to the core-tank wall may be the limiting power density in a solution-core reactor. Zirconium alloys corrode in fissioning solutions at rates that increase with temperature and power density; adequate cooling may not be possible at higher densities. This limit, coupled with the small core size which is desirable in order to obtain high conversion ratio, may result in limiting to 500 Mw the total heat that can be produced in one solution-core reactor. Two or more reactors would be required to provide steam for one of the largest turbogenerators.

In the case of slurry-core reactors, cooling of the core tank or ability to manufacture large reactor vessels and core tanks will probably impose limits on total power, although these cannot be evaluated at the present time. It appears likely that they will be above 1,000 Mw of heat and large enough so that one reactor can produce the steam required for the largest turbogenerator that can be manufactured for use with low-pressure saturated steam. At the present time the limit on turbogenerator size is about 300 Mwe. Limits on sizes of pumps, heat exchangers, pressure vessels, and other equipment are essentially those that apply to all high-pressure water reactors.

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