Contract No. W-7405-eng-26

REACTOR CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

For Period Ending January 31, 1961

Director

W. R. Grimes

Associate Directors

E. G. Bohlmann

H. F. McDuffie

G. M. Watson

Senior Scientific Advisors

F. F. Blankenship

C. H. Secoy

DATE ISSUED

MAY 12 1961

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

DISCLAIMER

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

DISCLAIMER

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

REACTOR CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

SUMMARY

PART I. MOLTEN-SALT REACTOR PROGRAM

1. High-Temperature Phase Equilibrium Studies

Extensive phase equilibrium studies were made of fluoride systems suitable for use as nuclear reactor fuels. Particular attention was focused on the quaternary system $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$ over the concentration ranges of reactor interest. Phase diagrams of all the contained binary and ternary systems were completed and published. The characteristics of specific salt mixtures having special utility in the reactor development program were established and described in detail.

Intensive phase studies were made of the quinary system $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4-\text{UF}_4$ in connection with the possible incorporation of about 5 mole % ZrF_4 , which appears to confer no unsuitable effects upon the fuel system.

The system $\text{CrF}_2-\text{CrF}_3$ has been investigated because of the importance of chromium in connection with the corrosion of structural material, such as INOR-8. The characteristics of the new compound, $3\text{CrF}_2 \cdot 2\text{CrF}_3$, the only intermediate compound in the system, were established through analytical, crystallographic, and x-ray diffraction techniques.

Improvements in the technique of petrographic microscopy, important in the study of fluoride phase equilibria, were achieved by the compounding of immersion oils that had indices of refraction from 1.292 to 1.411 and were free from many difficulties associated with previously available oils.

Crystal properties and crystal structure were determined for the following compounds, of interest to programs concerned with radiolysis of solids, chemical processing of reactor fuel elements, and fluoride phase equilibria: $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{ThF}_4$, $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{UF}_4$, LiSbF_6 , and LiBrO_3 .

2. Precipitation of Oxides from Molten Fluorides

Precipitation of oxides from the system $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4-\text{UF}_4$ by the addition of oxide ions (as BeO) was studied to determine whether inadvertent precipitation of UO_2 could be avoided by the prior addition of ZrF_4 . It was established that a Zr:U ratio in excess of 3.0 prevented precipitation of UO_2 ; the precipitate was ZrO_2 uncontaminated by UO_2 . Other studies established that uranium and zirconium coprecipitated when the Zr:U ratio fell to about 1.5. At a ratio of 1.0, UO_2 was precipitated. Addition of BeO in an amount calculated to precipitate all the UO_2 and ZrO_2 did not cause the precipitation of ThO_2 from a mixture containing ThF_4 .

Small-scale experiments at both tracer and macro levels demonstrated that it was possible to precipitate both protactinium and uranium from fluoride melts by the addition of small amounts of solid beryllium or thorium oxides. The protactinium could be precipitated from solution either by the addition of UO_2 or in the presence of 1000 to 2000 ppm uranium. This suggests that the protactinium oxide is much less soluble than the uranium dioxide and provides a basis for the development of a process for selectively removing protactinium from the blanket of a molten-salt thorium-breeder reactor.

3. Solubility of Gases in Molten Salts

An attractive possibility for reactivity control in molten fluoride systems is presented by the consideration of the properties of BF_3 . It is a volatile gas whose cross section could easily be increased by the use of B^{10} , and its concentration in a molten-salt reactor fluid could be controlled by adjusting the partial pressure of the gas over a free surface of the molten fluoride system. The solubility of BF_3 was determined at 500 to 700°C in a typical reactor fuel composition of $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4-\text{UF}_4$; Henry's law was followed up to 1.9 atm pressure, and the measured solubilities at 500 and 700°C were 0.267 and 0.035 mole of BF_3 per liter of salt per atm pressure respectively. The enthalpy of solution was calculated to be -15.1 kcal/mole. Since adsorption of the BF_3 on graphite would complicate the use of this gas as a soluble poison in unclad graphite systems, the extent of irreversible sorption of BF_3 by graphite was examined experimentally. After exposure to BF_3 at 10 to 15 psig and 800°C for 2 hr, the BF_3 was removed in a helium sweep stream for 2 hr at 1 atm pressure. A mean residual content of only 10 ppm boron was found in the graphite; this amount was independent of exposure temperature and BF_3 pressure, suggesting that it was deposited by reaction with traces of water not removed in the preliminary degassing treatment.

The solubility of HF in a molten fluoride mixture ($\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4-\text{UF}_4$) was determined. Henry's law was obeyed over the pressure range 1.4 to 2.4 atm. Henry's law constants were 17.0×10^{-6} and 8.0×10^{-6} mole of HF per cc of solution per atm at 500 and 700°C respectively. The enthalpy of solution was calculated to be -5.65 kcal/mole over the temperature range studied.

4. Xenon Poisoning in Molten-Salt Reactors Containing Graphite

The parameters likely to affect the seriousness of xenon poisoning in the Molten-Salt Reactor Experiment were reviewed. If xenon were not otherwise removed, appreciable poisoning could occur as a consequence of the diffusion of the xenon into the pores of the unclad graphite moderator which is in contact with the circulating fuel. The effects of various combinations of xenon generation, burnout, decay, removal via helium stripping, and diffusion into graphite were calculated and related to the graphite porosity, permeability, and xenon diffusion coefficient. Incorporation of a facility to permit stripping of a large fraction of the total flow, coupled with the use of graphite of low permeability, would effectively remove the xenon poisoning problem; this problem cannot, however, be solved by the use of improved graphite alone.

5. Thermodynamic Studies in Molten Salts

In further development of the quasi-lattice model theory of molten salts, generalized theoretical calculations were made for stepwise association constants. A method was developed for the evaluation of these constants at infinite dilution for the association of Ag^+ and Cl^- in KNO_3 . Experimental measurements of the activity coefficients of AgNO_3 in dilute solutions of AgNO_3 and NaCl in an equimolar mixture of NaNO_3 - KNO_3 were made at five temperatures between 233 and 528°C. The temperature dependence of the first association constant was that predicted by the theory.

Significant effects on the freezing-point depression of sodium fluoride by added solutes were attributed to cation charge (by comparing CaF_2 , YF_3 , and ThF_4 , which have cations of similar sizes), to polarization (by comparing MgF_2 and ZnF_2 , which have cations of the same charge and size), and to cation size (by comparing BeF_2 , MgF_2 , CaF_2 , SrF_2 , and BaF_2 , which have identical charges). The importance of cation size in relation to the achievement of eightfold coordination was shown by studies of the isostructural tetrafluorides as solutes.

Many intermediate, congruently melting compounds have been found in phase equilibrium studies of fused-salt binary systems, but very little is known about the thermodynamic properties of these compounds. To obtain such information as would be of ultimate assistance in the calculation of ideal phase diagrams for comparison with experimental results, the heats of fusion of certain intermediate compounds in fluoride systems are being measured with the use of a Bunsen ice calorimeter. A value of $13,940 \pm 50$ cal/mole has been established for the compound $3\text{LiF} \cdot \text{ThF}_4$, which melts in the range 568 to 569°C.

The previously determined values of density vs composition in the systems $\text{LiF}-\text{BeF}_2$, $\text{NaF}-\text{BeF}_2$, $\text{LiF}-\text{BeF}_2-\text{UF}_4$, and $\text{NaF}-\text{BeF}_2-\text{UF}_4$ were examined. A linear relationship between molar volume and composition was revealed for these simple systems, which suggested that the volume contribution of BeF_2 might be associated only with its fluoride ions. Extension of this point of view led to equations from which molar volumes could be calculated for other and more complex systems over wide ranges of temperature, with average deviations from observed results being less than 3%.

6. Radiotracer Techniques in the Study of INOR-8 Corrosion by Molten Fluorides

The self-diffusion coefficients for chromium in Inconel and INOR-8 alloys and the applicability of these values to alloys in contact with molten fluoride salts under corrosive conditions have been evaluated. Large-scale tests in polythermal circulating-fluid loops under corrosive and noncorrosive conditions gave results which were in good agreement with those predicted from previously measured diffusion coefficients, suggesting that corrosion rates for large systems can be successfully predicted even for cases in which the affected portions of the alloy have been drastically altered.

7. Behavior of Fission Products in a Graphite-Molten Salt System

A specimen of S-4 graphite exposed at 700°C for 1600 hr in the Materials Testing Reactor to $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$ (67-18.5-1.5-13 mole %) showed penetration by the salt to the extent predicted from out-of-pile studies. Gross fission product activity appeared on the salt only where the intrusion of fuel was observed in regions of high porosity. Except for these regions where fuel had intruded, the graphite was free of fission product activity except for Cs^{134} and Cs^{137} .

8. Purification and Handling of Molten Salts

A facility for the large-scale production of purified molten fluoride mixtures has been maintained and operated as a service to the over-all program. A total of approximately 6000 lb of fluoride mixtures was produced during the year. Additional services rendered to various engineering and research groups included filling, sampling, and emptying test loops, preparing in-pile irradiation-test capsules, consulting on the handling of molten salts, and similar services connected with the handling and production of liquid metals.

PART II. AQUEOUS REACTOR PROGRAM

9. Aqueous Systems at Elevated Temperature

The determination of simultaneous solubilities at 325 and 350°C of $\text{CuO} \cdot 3\text{UO}_3$ and $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$ in solutions of H_2O and H_2SO_4 , 0.02 to 0.03 *m* in total sulfate, gave results quite similar to analogous values at 300°C.

Solubilities of $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{D}_2\text{O}$ at 300, 325, and 350°C were determined in solutions of D_2O and D_2SO_4 . The results showed an almost undetectable change with temperature in the saturation molal ratio, Cu^{2+} :total sulfate, at constant total sulfate. Comparison with saturation molal ratios at 300°C showed higher values in the D_2O than in the analogous H_2O system.

The system $\text{NiO} \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ was investigated at temperatures above 300°C in an attempt to find liquid-liquid immiscibility and to define this subsystem of the multicomponent system $\text{UO}_3 \cdot \text{CuO} \cdot \text{NiO} \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$. Apparently, liquid-liquid immiscibility does not exist in this system at saturation vapor pressure. The solubility of NiO above 400°C in the supercritical fluid may exceed 0.6 *m* in 6 *m* H_2SO_4 . Solid-liquid equilibria as well as critical temperatures were determined for this system.

Temperature-composition boundaries for liquid-liquid immiscibility and critical phenomena (i.e., disappearance of the meniscus between liquid and vapor) were determined for the systems $\text{UO}_3 \cdot \text{CuO} \cdot \text{SO}_3 \cdot \text{D}_2\text{O}$, $m_{\text{UO}_3 \cdot 2+} / m_{\text{Cu}^{2+}} = 1$, $\text{UO}_3 \cdot \text{SO}_3 \cdot \text{D}_2\text{O}$, and $\text{CuO} \cdot \text{SO}_3 \cdot \text{D}_2\text{O}$. These data showed a rising temperature for the appearance of liquid-liquid immiscibility as the molal ratios, metal ions:total sulfate, were decreased and the total sulfate was kept constant. At ratios between 0.2 and 0.4, both UO_2SO_4 and CuSO_4 became soluble in the supercritical fluid.

The temperatures for the appearance of liquid-liquid immiscibility were determined for several aqueous homogeneous reactor fuel solutions and their concentrates. From these and previous data a method was developed, for estimation of the minimum two-liquid-phase temperatures, which makes use only of the acidity molal ratio, D_2SO_4 :total sulfate.

The precise measurement of the pH of intensely radioactive solutions by use of a glass electrode is difficult because of radiation effects on glass. If the radioactive solutions are diluted considerably and then the pH of the diluted solution determined, the effect of radiation on the electrode would be reduced. The pH of dilutions of compositions approximating aqueous homogeneous reactor fuel solutions

was measured. These data showed, to a close approximation, that a single measurement of pH of a diluted, synthetic fuel solution could be related to the free-acid concentration of the undiluted solution. The method may be of potential use for determination of free D_2SO_4 in homogeneous reactor compositions.

Three-dimensional models representing solubility relationships in the system UO_3 -CuO-NiO- SO_3 - D_2O at $300^\circ C$ were constructed for solutions having total sulfate concentrations of 0.06, 0.10, 0.20, 0.30, and 0.50 *m*. The results of previously reported solubility studies were used to establish the location of the surfaces of saturation for the several solid and liquid phases which appear at the boundary limits of the region of unsaturated solutions.

Solubility information for the system UO_3 - N_2O_5 - H_2O was revised to incorporate the results of additional studies at temperatures of 325 and $350^\circ C$.

Previous studies of thorium nitrate solutions were extended by an investigation of the solution-solid equilibrium boundaries of the system ThO_2 - N_2O_5 - H_2O at 200 and $300^\circ C$. Saturation molal ratios, Th^{4+} :total sulfate, in solutions containing 9.0 *M* nitrate were 0.20 and 0.18 at 200 and $300^\circ C$ respectively. In 2.0 *M* total nitrate the ratios were 0.18 and 0.03, illustrating the pronounced tendency toward hydrolysis of thorium at higher temperatures. The rapid rates at which solubility equilibria were established at these temperatures, in marked contrast to the very slow dissolution of refractory thorium at temperatures below $100^\circ C$, suggest applications to the chemical processing of solid fuel elements incorporating refractory oxides.

The construction of cells for the measurement of electrolytic conductance at high pressure and high temperature, as well as an assembly for the generation of high pressures, was completed. Preliminary measurements on a 0.01 *m* KCl solution were made at $800^\circ C$ and at pressures up to 4000 atm. This work represents a new record for reproducible measurements at extremes of pressure and temperature.

10. Reactions in Aqueous Solutions

The rates of peroxide decomposition in uranyl nitrate solution were measured to determine the effects of temperature, acidity, and known catalysts on the decomposition. The results were quite similar to those previously obtained with sulfate and perchlorate systems. Extrapolation of the results to higher temperatures suggested that the rate of peroxide decomposition would prove adequate under hypothetical reactor conditions.

Measurements were made of the relative dissolution rates of various solids at $250^\circ C$ in oxygenated, well-stirred, synthetic HRE-2 fuel solution. The solids tested were UO_2 , U_3O_8 , UO_3 , $CuO \cdot 3UO_3$, and reactor-fuel solids prepared by evaporating fuel solution to dryness and calcining at $500^\circ C$. The solids, representing those which could conceivably have existed in the HRE-2 under conditions of off-design operation, dissolved rapidly, with half-lives of from less than 0.5 to 2.5 min. These results indicate that such solids, if formed, should redissolve promptly under the conditions of good agitation and removal from regions of neutron flux, which are provided by the present modifications in the reactor flow pattern.

Tracer-level experiments showed that protactinium was coprecipitated with thorium from aqueous acidic thorium nitrate solutions when hydrogen peroxide was added in an amount sufficient to precipitate no more than 2% of the thorium. The experiments covered ranges of thorium concentration from 1.0 to 3.0 M and $\text{NO}_3:\text{Th}$ ratios from 4:1 to 5:1. Unconfirmed experiments indicate that uranium was not coprecipitated with thorium under similar conditions when the uranium was in the range 70 to 80 ppm; protactinium, however, was coprecipitated in the presence of this concentration of uranium.

The solubilities of H_2 in water and D_2 in deuterium oxide were determined from room temperature to 250°C.

It was found that protactinium could be recovered from the salt system $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UO}_2$ by a two-step process. This process includes exposure of the melt to the oxides of beryllium or thorium, which adsorb the protactinium, production of a partially water soluble system by addition of KF and hydrofluorination, and, finally, extracting the aqueous material with diisobutyl carbinol. The protactinium was removed from the organic phase by stripping with 18 N H_2SO_4 .

In preliminary studies of the characterization of thorium peroxide, the peroxy salts precipitated from solutions of thorium salts by H_2O_2 , with and without added acid, always contained the original anion. A ratio of two thorium atoms to three peroxide molecules was consistently found.

The temperature dependence of peroxide decomposition catalyzed by iron showed an interesting anomaly over the range 190 to 210°C. This is presently interpreted as the inactivation of iron by hydrolytic processes.

11. An Investigation of Uranium(VI) Hydrolysis at Elevated Temperatures, Using the Glass Electrode

A study of uranium(VI) hydrolysis at 94 and 25°C has been completed. The principal hydrolysis steps appear to be

Equilibrium quotients were calculated for 25 and 94°C. Estimates were made of the enthalpy, free energy, and entropy of each reaction. The importance of the reaction

at higher hydrolysis numbers was established. The importance of the monomeric hydrolysis product, UO_2OH^+ , at higher temperatures was suggested.

12. Isopiestic Studies at Elevated Temperatures

A modified high-temperature isopiestic apparatus was used to measure the osmotic coefficients of seven representative electrolytes (vs NaCl as a working standard) at temperatures from 100 to 142°C.

The osmotic coefficients for 1-1 electrolytes at 121.1°C showed a concentration dependence quite similar to that found earlier at 25°C. The isopiestic ratios of the 1-1 electrolytes were essentially independent of temperature over the range 100 to 142°C; those of the 2-2 and 2-1 electrolytes showed a linear decrease with increasing temperature.

13. Surface Chemistry of Thoria in Dilute Aqueous Electrolytic Solutions

Theoretical estimates of the electrical surface potential required to give an arbitrarily defined degree of stability to a slurry at selected values of temperature, ionic concentration, ionic valence, particle size, and slurry concentration have been made. Experimental determination of ionic adsorption equilibria on ThO_2 surfaces in various aqueous systems is in progress. Surface potentials will be calculated from these data, thus providing a basis for the prediction of slurry stability in terms of the directly determinable parameters listed above.

Engineering design of a precision adiabatic calorimeter has been completed and construction is in progress. The instrument will be capable of precise determination of thermal quantities on aqueous systems at temperatures up to about 250°C. The intended initial use will be the measurement of heats of wetting and heats of adsorption (ionic) on thoria surfaces.

14. Corrosion by Solutions

The corrosion of types 347 and cast CD4MCu stainless steel was investigated in a simulated fuel solution containing 0.04 *m* UO_2SO_4 and 0.025 *m* H_2SO_4 at 250 and 300°C. At 250°C, critical velocities were about 10 fps for type 347 stainless steel and less than 10 fps for cast type CD4MCu; at 300°C, respective critical velocities were 45 to 50 fps and about 30 fps. Pretreatment of the type 347 stainless steel specimens in water at 280°C for two days before exposure to the 250°C solution resulted in a critical velocity of 15 to 20 fps. When the specimens were pretreated in water at 280°C and then exposed to the fuel solution at 300°C for about 300 hr, a relatively thick, adherent oxide film developed on the specimens at velocities up to about 50 fps. Subsequent exposure of these specimens to the fuel solution for 560 hr at 250°C did not cause disintegration of the oxide film, and essentially no corrosion occurred over the entire velocity range. No pretreatments were attempted with the type CD4MCu specimens.

An all-titanium pump loop was constructed to study the chemical stability of uranyl sulfate fuel solutions and the corrosion resistance of various materials at temperatures and pressures up to 370°C and 3000 psia. Preliminary runs with water and simulated reactor fuel solutions showed that the loop and control systems functioned properly. In the latter runs, at least a part of the heavy phase that formed at temperatures greater than the two-liquid-phase temperature was separated by the hydroclone. As the temperature of the system was increased beyond the two-liquid-phase temperature, the salt concentration of the light phase decreased, and the acid concentration increased. The mole ratios of uranium to sulfate, uranium to copper, and uranium to nickel decreased in the same proportion in the temperature range 330 to 365°C. Corrosion of titanium and Zircaloy-2 specimens was negligibly small.

Corrosion tests with Coors aluminum oxide in water at 100 and 300°C and in a simulated fuel solution at 100°C showed the material to have good corrosion resistance in water at both temperatures and poor resistance to the fuel solution at 100°C. Rates between 20 and 30 mils/yr were observed in the fuel solution. Specimens in which aluminum oxide was brazed to titanium with zirconium-base alloys showed reasonably good corrosion resistance to a simulated fuel solution at 100°C and to oxygenated water at 300°C during 1500-hr tests. Neither corrosion nor thermal cycling resulted in the aluminum oxide being detached from the titanium.

Corrosion tests of aluminum alloys in water for ten-day periods at temperatures from 170 to 290°C and at water flow rates between 20 and 107 fps were conducted. At temperatures from 170 to 200°C, aluminum alloys 1100, 5154, 6061, and X8001 exhibited similar behavior, with corrosion rates increasing with coolant velocity. At 230°C, no localized attack, except occasional shallow pits, was observed, and at flow rates below 67 fps, rates were similar to those observed at the lower temperatures. At 260°C, the corrosion rate of type X8001 alloy was nearly independent of flow rate below 67 fps; many specimens of other alloys showed significant localized attack. Only type X8001 was free from catastrophic corrosion at 290°C. Any of the alloys could be used in ten-day service if the average temperature of the oxide film were below 230°C and coolant flow rate were below 65 fps. None of the alloys would be useful at 100 fps at any temperatures tested.

The influence of water temperature, pH, and velocity on corrosion and on corrosion-product formation on the surface of aluminum alloys subjected to a very high heat flux was determined. At a heat flux of 1.5×10^6 Btu hr⁻¹ ft⁻² and with cooling-water temperatures and velocities in the ranges of 131 to 223°F and 32 to 48 fps, respectively, a tightly adherent layer of corrosion products (α -Al₂O₃ · H₂O) formed on the surface of the aluminum specimens at a linear rate during ten-day tests. The rate at which the corrosion product formed (and the rate of temperature increase in the aluminum) was markedly influenced by the pH of the coolant. With high-purity water as the coolant, oxide films as thick as 1.5 to 2.0 mils formed in ten days. When the pH of the cooling water was adjusted to 5 with nitric acid, oxide films less than 0.5 mil formed under the same conditions. From measured oxide thicknesses and temperature drops across the corrosion-product films, a thermal conductivity of 1 Btu hr⁻¹ ft⁻² (°F)⁻¹ ft was calculated for the aluminum oxide film. The rate of oxide formation was independent of the alloy and the velocity in the range investigated. The temperature of the cooling water was a significant factor; the lower the water temperature, the slower the rate of film formation. Because of the manner in which the specimens were fabricated, quantitative corrosion measurements were not possible. However, it was qualitatively established that corrosion was not severe, and, except in one case, evidence of localized attack was not found. It was concluded that under the conditions expected to exist during operation of the High Flux Isotope Reactor, aluminum would be a suitable material for cladding fuel elements.

15. Corrosion by Solutions Under Irradiation

The large amount of data obtained at ORNL on corrosion of Zircaloy-2 in uranyl sulfate has been reviewed and correlated. A model for this corrosion has been developed. The data can be well correlated by the equation

$$\frac{1}{R} = \frac{K_1}{K P^\alpha} + \frac{1}{K},$$

where R is the corrosion rate, P is the fission power density in solution, α is the factor by which the effective power density at the corroding surface exceeds that in solution, and K_1 and K are constants which are evaluated from the experimental data.

The program of testing zirconium alloys in uranyl sulfate solutions in in-pile loop assemblies has been augmented by use of facilities in the ORR. With this reactor, maximum fluxes were obtained which were greater by about 1.5 than those previously available in the LITR. Tests to ascertain the effects of surface treatments of Zircaloy-2, the effect of stagnant films of solution on portions of the surface, and the behavior of special zirconium alloys have been conducted in a D_2O solution of uranyl sulfate. Surfaces which were chemically polished, overground, or sandblasted and chemically polished corroded to about equal extents, surfaces exposed after sandblasting with no further treatment performed less well. Substantially greater corrosion rates were observed on surfaces which were covered during the exposure, values for α may have been as high as 15 for these surfaces exposed to a nearly stagnant film of solution.

The apparatus for the electrochemical measurement of corrosion rates was modified to permit measurements to be made above $250^\circ C$. The potential-time and current-potential behaviors are similar to previous observations on the Firth-Sterling Zircaloy-2 at $208^\circ C$. The rate-time results obtained gave further support to the logarithmic oxidation kinetics for Zircaloy-2.

The value of α in equations which predict the corrosion behavior of zirconium alloys under irradiation is almost certainly dependent on sorption of uranium in the corrosion film. Accordingly, sorption of uranium from aqueous uranyl sulfate solutions on zirconium oxides has been investigated. Most of the work employed a $110^\circ C$ -air-dried (AF) material of high surface area, but some data obtained with a material of lower surface area autoclaved in water at $300^\circ C$ (WF) are also reported. In tests at $280^\circ C$, the AF material showed a loss of surface area and marked decreases in uranium and sulfate sorption per gram of ZrO_2 during the first 2 to 4 hr exposure. Little or no time dependence on area or sorption was noted with the WF material. Sorption isotherms with the AF oxide show uranium sorption on a per-gram-of- ZrO_2 basis to be 30 to 40% greater at $280^\circ C$ than at $250^\circ C$. Data at 300 and $325^\circ C$ show uranium sorption in about the same amounts as that found at $250^\circ C$. Elution of oxide residues from sorption tests with aqueous reagents indicates that the WF oxide can be readily washed free of uranium, whereas the AF oxide retains significant amounts.

A rocking-autoclave experiment was performed in which a D_2O solution of uranyl nitrate (0.032 m) with $Cu(NO_3)_2$ and excess DNO_3 was exposed in Zircaloy-2. Exposure at $280^\circ C$ to the full reactor

power was made in five periods, the total irradiation time being 134 hr. The value of K_{Cu} (225°C) was estimated to be 1600 to 1700 liters mole⁻¹ hr⁻¹; that of G_{D_2} was estimated to be 1.3 to 1.4. The various pertinent pressure and analytical data were not completely interconsistent but allow an estimated range of Zircaloy-2 corrosion rates of 6 to 12 mils/yr (mpy) during most of the exposure. The corrosion rate appeared to increase during the last 30 hr of exposure, and the final rate was probably 30 mpy or more. From various features of the pressure data, estimates of G_{N_2} of 2×10^{-3} to 2.5×10^{-2} were made, which are 7 to 70 times larger than reported values from fission-fragment irradiations of $Ca(NO_3)_2$ solution. Recombination of nitrogen and oxygen was indicated, the apparent rate corresponding to a vapor-phase recombination with a G_{NO_3} value of 1 to 3, which is within the range of values for vapor-phase fixation previously reported by others.

16. Slurry Corrosion and Blanket Materials Tests

A variety of empirical test procedures, including exposure in static and rocking autoclaves, ball mills, spouted beds, and fluidized beds, have been developed and applied to evaluation of thorium pellets prepared by several methods.

Corrosion of Zircaloy-2 and other alloys, as well as efficiency of the palladium recombination catalyst, has been studied in in-pile autoclave tests with thorium-uranium slurries. In-pile tests to date have been of short duration largely because of difficulty in plugging capillary leads to auxiliary equipment. A new and more effective filter assembly to prevent this difficulty has been developed. In tests to date no effect of radiation on corrosion has been observed.

Hydriding of zirconium-base alloys has been shown to occur when the alloys are exposed to thorium-uranium slurries circulating under conditions of slug flow in toroids. Under these quite severe test conditions, hydride formation does not occur at 200°C but is important at 280°C and above. At 280°C the extent of hydriding decreases with flow velocity; at 330°C, hydride formation is apparent even under an overpressure of oxygen and is observable on exposure to D_2O without slurry particles.

Specimens exposed in in-pile autoclaves under a variety of conditions, however, show little effect of atmosphere or irradiation on hydrogen pickup of Zircaloy-2.

An in-pile loop assembly was developed and was operated with a thorium-uranium slurry for more than 2200 hr in the LITR. Operation of the stainless steel loop was at 280°C with flow rates of 6 to 8 fps in the piping and with oxygen overpressure. The loop assembly, sampling system, and auxiliary equipment were quite satisfactory, and the experiment was terminated according to plan. Postexposure examination is incomplete in many regards; a substantial degradation of the slurry during the exposures was observed.

PART III. SUPPORT FOR HIGH-TEMPERATURE SOLID-FUELED REACTORS

17. Transport of Noble Gases in Graphites

A mutual-diffusion coefficient for argon and helium in a relatively porous graphite has been obtained from experiments at 25 and 100°C and at uniform total pressures from 1 to 6 atm. The controlling diffusion mechanism was classical; surface diffusion and Knudsen diffusion effects were negligible. The ratio of over-all diffusion rates of helium and argon was inversely proportional to the square roots of the atomic weights.

Diffusion of argon through a relatively porous septum opposed by a flow of helium through the septum has been examined experimentally. Some contribution from the Knudsen diffusion mechanism was observed at high values for pressure differential across the septum. However, at low flow rates of helium through the graphite, behavior is successfully predicted by relatively simple equations.

Interdiffusion of argon and helium in low-permeability graphites has been shown to follow mechanisms very similar to those obtained with more porous materials.

Surface diffusion has been shown to be negligible by experiments at +30, 0, and -65°C with argon at 1.5 to 4 atm.

Routine testing of porosity and permeability of moderator graphites and coated and uncoated fuel-element sleeves of interest to the Gas-Cooled Reactor Project has been performed.

18. Evolution of Gas from Graphite

The amounts and compositions of gases and their rates of evolution from moderator graphite materials have been determined experimentally to temperatures as high as 2000°C. A very approximate correlation of gas content and analysis with ash content of the graphite is observed. Rates of evolution for most specimens fit the equation

$$V = A \log t + B ,$$

where V is the volume per 100 cm³ of graphite, t is in minutes, and A and B are constants. Some graphites, whose ash is high in calcium oxide, evolve considerable CO₂ at 600°C. For these cases the gas evolution rate is initially high at this temperature and drops abruptly, after CO₂ evolution ceases, to values similar to those for graphites which evolve little CO₂.

19. Measurement of Temperature in Reactor Environments

Selective oxidation of the Chromel-P wire is responsible for large negative errors in emf of Chromel-P-Alumel thermocouples in mildly oxidizing environments. For example, selective attack in the region at about 800°C has been demonstrated with bare wire thermocouples whose hot junctions were at 1000°C in a stagnant helium atmosphere. Alloys such as Geminol-P, Chromel-A, and Chromel-AA, which are 80% Ni-20% Cr, do not generate erroneous emf's under these conditions.

Abnormal emf readings have been obtained when Chromel-P-Alumel couples sheathed in stainless steel were exposed at high temperatures to helium contaminated with gases desorbed from graphites. The errors are again associated with selective attack on the Chromel-P wire at a certain critical temperature interval. Couples sheathed with types 310 and 347 stainless steel were less susceptible than those sheathed with type 304.

Preliminary studies have not been sufficient to show correlation of thermocouple emf with predicted oxidation of Chromel-P in H_2O-H_2 mixtures.

An IBM 704 program has been prepared by the MIT Engineering Practice School for calculation of theoretical error in thermocouple assemblies due to loss of insulation resistance at high temperatures. Preliminary calculations have given satisfactory results for simple assemblies. The program will be modified to allow calculation of errors in more complicated applications.

Calculations and experimental study of corrections for the cooling action of gas on thermocouples used to measure the temperatures of gas-cooled surfaces were continued. Experimental study has included the effects of the length of the lead wire and of a dimension (effective diameter) of the coolant channel. From these tests it is possible to predict the accuracy of attached thermocouples under various cooling conditions expected in nuclear reactors.

The changes in composition produced by transmutation in six pairs of thermocouple materials have been calculated for a thermal neutron flux of 10^{14} *nv* and for periods up to 20 years. The results indicate that Chromel-Alumel should be the most stable thermocouple, with iron-Constantan the next most satisfactory combination. Copper-Constantan, Pt vs Pt-10% Rh, tungsten-rhenium, and W vs W-26% Re thermocouples are expected to undergo composition changes which would seriously affect the output emf.

20. Removal of Radioactive Gaseous Fission Products from Other Gases

Studies were conducted on the removal of iodine vapor from air-steam mixtures at 75 to 118°C, from air at 100°C, and from helium at 300, 320, and 430°C. At 100°C in tests 2 hr in duration, radioiodine was removed from air by activated charcoal $\frac{3}{4}$ in. deep with efficiencies of 99.95%, somewhat less efficiently than at room temperature (99.99%). Similar tests with air-steam mixtures resulted in efficiencies of 99.9%, somewhat less than the efficiency in air alone at the same temperature. The efficiency was further reduced at higher velocities, such as 290 fpm.

In other tests, at 300 to 430°C, activated charcoal exhibited high initial efficiency for removal of radioiodine from helium, but with continued gas flow the iodine migrated slowly through the charcoal adsorber bed. A wide variation in iodine retention was found among different charcoals. Whetlerite charcoal, which is designed for use in gas masks for protection against war gases and which contains salts of copper, silver, and chromium, removed and retained more than 99.99% of the iodine for at least 216 hr at 325°C in a bed only $\frac{1}{4}$ in. thick. These results may be applied in the design of systems for removal of radioiodine from recirculating helium streams without reducing the temperature of the helium.

Dynamic adsorption measurements were made for krypton on charcoal in helium up to 420 psig. The dynamic adsorption coefficient, *k*, decreased only slightly with increased helium pressure, while the

number of theoretical plates per foot decreased appreciably. In other dynamic adsorption studies, no large differences in behavior were observed among several different charcoal types. In low-temperature tests, k increased from about $55 \text{ cm}^3/\text{g}$ at 25°C to about $500 \text{ cm}^3/\text{g}$ at -33°C . Static adsorption measurements have been made on a variety of materials with krypton and xenon at various temperatures. The results of these experiments provide a convenient means for obtaining xenon adsorption information, since the xenon tracer is not as conveniently available as that of krypton. The static adsorption isotherms were fitted to the Freundlich equation.

Transport of noble gases by gas-phase diffusion assumes importance at low carrier gas velocities. Diffusion measurements were made by using radiokrypton in activated charcoal beds filled with stagnant helium, effective diffusion coefficients for krypton were measured over the temperature range 0 to 60°C . These coefficients were approximately inversely proportional to the slopes of the adsorption isotherms, since the quantity of krypton available for gaseous diffusion is determined by the extent of adsorption. No significant difference was observed between the different adsorbents studied.

Adsorption measurements were made for determining the amount of radioactive noble gas contamination which will be released when Linde molecular sieves, types 4A and 5A, are regenerated after use in the removal of water and carbon dioxide from reactor coolants. Measurable adsorption of noble gases occurred in type 5A containing H_2O or CO_2 and in type 4A alone, indicating that provision for radioactive decay may be required prior to venting regeneration gases to the atmosphere. In measurements of the adsorption of xenon alone, on Linde molecular sieve type 4A, the adsorption at 60°C was greater than that at 25°C . Since the equilibration times were relatively long, it appears that the rate of approach to equilibrium is the controlling factor.

A number of proposed fission gas or iodine adsorption systems were reviewed for technical feasibility and safety. These systems have included the emergency iodine adsorption system for the NS "Savannah," and the gas cleaning systems for the High Flux Isotope Reactor, the Molten-Salt Reactor Experiment, the Low-Intensity Test Reactor, and several in-pile experiments.

21. Release of Fission Products on In-Pile Melting of Reactor Fuels

A program has been initiated to determine the release of fission products when oxide fuels are melted by nuclear heating. The in-pile facility has been designed and fabricated and was installed in the ORR. It was tested during measurement of the gamma heat profile. The first material to be tested will be a stainless-steel-clad UO_2 fuel specimen in a helium atmosphere. Operation of the first experiment has been approved by the various safety committees, the experiment is expected to be inserted shortly.

22. Effect of Radiation on Beryllium Oxide

Irradiation of cylindrical specimens (0.6 to 1.0 in. in diameter) of BeO to integrated fast-neutron dosages of 10^{21} nvt has been accomplished in the Engineering Test Reactor at Arco, Idaho. Hot-cell examination of these materials is quite incomplete.

Specimens receiving an exposure of 7×10^{20} *nvt* exhibited cracks, and severe deterioration was observed in materials receiving heavier dosages. The capsule cladding of 400 series stainless steels increased in dimension up to 3%; BeO irradiated at lower temperatures tended to enlarge more than that at higher temperatures for similar dosages. Thermal conductivity apparently decreases with increased dosage. While the major cause of the damage is not yet known, it is apparent that additional information is required before BeO can be used with confidence in long-lived reactors.

PART IV. PREPARATION AND PROPERTIES OF REACTOR MATERIALS

23. Chemistry of Organic Moderators and Coolants

A program has been initiated to determine the chemical kinetics of the pyrolytic and radiolytic decomposition of potential moderators and/or coolants. Initial studies will be limited to pyrolysis of biphenyl, under conditions of low conversion to allow determination of intermediates.

24. Preparation of Refractory Oxides from Molten Salts

Reaction with water vapor admitted at low partial pressure to the vapor space above molten salt mixtures has been used to precipitate single crystals of BeO and UO_2 from solutions of their fluorides. Uranium dioxide prepared in this way shows a unit-cell parameter a_0 of 5.472 ± 0.002 Å and corresponds to $\text{UO}_{2.00 \pm 0.003}$. Precipitation from solutions containing both BeF_2 and UF_4 produces some UO_2 which is completely encased in BeO.

25. Preparation of Pure Beryllium Compounds by Solvent Extraction

A liquid-liquid extraction process has been developed for preparation of extremely pure beryllium hydroxide for conversion to the oxide or to other compounds. Distribution coefficients for many contaminant ions have been evaluated, and several gram-size preparations more pure than the available spectrographic standards have been prepared.

CONTENTS

SUMMARY

iii

PART I MOLTEN-SALT REACTOR PROGRAM

1. HIGH-TEMPERATURE PHASE EQUILIBRIUM STUDIES	3
Systems for Use as Nuclear Reactor Fuels	3
The System $\text{LiF} \cdot \text{BeF}_2 \cdot \text{ThF}_4 \cdot \text{UF}_4$	3
The System $\text{LiF} \cdot \text{BeF}_2 \cdot \text{ZrF}_4 \cdot \text{ThF}_4 \cdot \text{UF}_4$	4
The System $\text{CrF}_2 \cdot \text{CrF}_3$	4
Immersion Oils with High Indices of Refraction	5
Crystal Properties and Crystal Structure	5
The Compounds $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{ThF}_4$ and $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{UF}_4$	5
Crystal Structure of LiSbF_6	6
X-Ray Diffraction Study of LiBrO_3	6
2. PRECIPITATION OF OXIDES FROM MOLTEN FLUORIDES	8
Precipitation of Oxides from MSRE Fuel	8
Recovery of Uranium and Protactinium from Molten Fluoride Systems by Precipitation as Oxides	9
3. SOLUBILITY OF GASES IN MOLTEN SALTS	12
Boron Trifluoride as a Soluble Poison in Molten Fluoride Reactor Fuels	12
Solubility of BF_3 in Simulated MSRE Fuel	12
Retention of BF_3 on Graphite	13
The Solubility of HF in Molten Fluorides	13
4. XENON POISONING IN MOLTEN-SALT REACTORS CONTAINING GRAPHITE	15
5. THERMODYNAMIC STUDIES IN MOLTEN SALTS	17
Experimental and Theoretical Study of Molten Reciprocal Salt Solutions	17
Electromotive Force Measurements in the System AgNO_3 and NaCl in Molten Equimolar Mixtures of NaNO_3 and KNO_3 and Their Comparison with the Quasi-Lattice Theory	17
A Critical Evaluation of Association Constants in Reciprocal Salt Systems	19
Freezing-Point Depressions in Sodium Fluoride	20
Effect of Ion Size	20
Effect of Cation Charge	21
Effects Related to Polarization	21
Heat of Fusion of $3\text{LiF} \cdot \text{ThF}_4$	23
Calculation of Densities of Molten Fluoride Systems	24
6. RADIOTRACER TECHNIQUES IN THE STUDY OF INOR-8 CORROSION BY MOLTEN FLUORIDES	26
7. BEHAVIOR OF FISSION PRODUCTS IN A GRAPHITE-MOLTEN SALT SYSTEM	29
8. PURIFICATION AND HANDLING OF MOLTEN SALTS	31

PART II. AQUEOUS REACTOR PROGRAM

9. AQUEOUS SYSTEMS AT ELEVATED TEMPERATURE.....	35
Solid-Liquid Equilibria in Sulfate-Based Systems: 300–350°C.....	35
Investigations on the System $\text{UO}_3\text{-CuO-SO}_3\text{-H}_2\text{O}$	35
Investigations on the System $\text{CuO-SO}_3\text{-D}_2\text{O}$	36
Investigations on the System $\text{NiO-SO}_3\text{-H}_2\text{O}$ Above 300°C	37
Liquid-Liquid Immiscibility and Solubility in the Supercritical Fluid in the System $\text{UO}_3\text{-CuO-SO}_3\text{-D}_2\text{O}$ and Its Three-Component Subsystems, $\text{UO}_3\text{-SO}_3\text{-D}_2\text{O}$ and $\text{CuO-SO}_3\text{-D}_2\text{O}$	39
Aqueous Homogeneous Reactor Fuel Studies	41
Estimation of Minimum Temperatures of Second Liquid Phase Formation in Homogeneous Reactor Fuel Concentrates: Use of the Acidity Ratio	41
The pH of Solutions Containing UO_2SO_4 , CuSO_4 , NiSO_4 , H_2SO_4 , H_2O , and D_2O : Its Use in the Determination of Free Acid in Homogeneous Reactor Fuels	44
Three-Dimensional Models for Representation of Solubility Equilibria	45
Solid-Liquid Equilibria in Nitrate-Based Systems	47
The System $\text{UO}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ from 25 to 350°C	47
The System $\text{ThO}_2\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ at 200 and 300°C	47
Electrolytic Conductance of Aqueous Solutions and Supercritical Fluids to High Temperature and Pressure.....	50
10. REACTIONS IN AQUEOUS SOLUTIONS	53
Decomposition of Peroxide in Uranyl Nitrate Solutions	53
Dissolution of Inorganic Solids in HRE-2 Fuel	54
Removal of Protactinium and Uranium from Thorium Nitrate–Nitric Acid Solutions.....	56
Aqueous Recovery of Pa^{231} from a Fluoride Mixture	58
Solubility of H_2 in H_2O and D_2 in D_2O	60
Characterization of Thorium Peroxides	61
Decomposition of H_2O_2 in Acid at Elevated Temperatures	62
11. AN INVESTIGATION OF URANIUM(VI) HYDROLYSIS AT ELEVATED TEMPERA- TURES, USING THE GLASS ELECTRODE	64
12. ISOPIESTIC STUDIES AT ELEVATED TEMPERATURES	66
13. SURFACE CHEMISTRY OF THORIA IN DILUTE AQUEOUS ELECTROLYTIC SOLUTIONS.....	70
Ionic Adsorption Equilibria	70
Calorimetric Studies	72
14. CORROSION BY SOLUTIONS	74
Corrosion in UO_2SO_4 Solutions of High Acidity.....	74
Chemical Equilibria and Corrosion in Uranyl Sulfate Solutions at Temperatures to 365°C	75
Corrosion of Aluminum Oxides in Aqueous Solutions	77

Corrosion of Aluminum by Water	78
Effect of Heat Flux on Corrosion of Aluminum by Water	79
Corrosion of Aluminum Alloys in High-Velocity Water at 170 to 290°C	80
Service Corrosion Testing for Other Divisions	83
Corrosion Testing in Support of Power Reactor Fuel Element Processing	83
Testing in Cooling-Water Systems	83
Tests in the Oak Ridge Research Reactor	84
Acceptance Tests	84
15. CORROSION BY SOLUTIONS UNDER IRRADIATION	85
Review and Correlation of Zircaloy-2 Radiation Corrosion Data	85
Corrosion of Zirconium Alloys in In-Pile Loops	86
Electrochemical Studies of Zircaloy-2 Corrosion	88
Sorption of Uranium from UO_2SO_4 Solutions on Hydrous Zirconia	90
Effect of Exposure Time on Sorption	90
Effect of Temperature	92
Elution of Sorbed Uranium	93
Behavior of Uranyl Nitrate Solutions	93
16. SLURRY CORROSION AND BLANKET MATERIALS TESTS	96
Thoria-Pellet Test Program	96
Test Methods	97
Evaluation of Experimental Pellets	98
Loop Tests of Thoria Pellets	99
Corrosion by Slurries in In-Pile Autoclaves	100
Operation and Examination of Irradiated Assemblies	100
Development of Al_2O_3 Slurry Capillary Filter	103
Hydriding of Zirconium-Base Alloys	103
Out-of-Pile Testing in Toroids	103
In-Pile Testing in Autoclaves	105
Operation of In-Pile Slurry Loop	105
Design and Prototype Testing	105
In-Pile Operation	108
Conclusions	110
PART III. SUPPORT FOR HIGH-TEMPERATURE SOLID-FUELED REACTORS	
17. TRANSPORT OF NOBLE GASES IN GRAPHITES	113
Uniform Pressure Interdiffusion of Helium and Argon in a Large-Pore Graphite	113
A Diffusion Model for Large-Pore Graphites	114
Interdiffusion Superposed on Forced Flow	117
Interdiffusion of Noble Gases in a Low-Permeability Graphite	119
Surface Diffusion in Large-Pore Graphite	121
Forced-Flow Characteristics of EGCR Graphites	121
18. EVOLUTION OF GAS FROM GRAPHITE	125

19. MEASUREMENT OF TEMPERATURE IN REACTOR ENVIRONMENTS	128
Behavior of Chromel-P-Alumel Thermocouples	128
Behavior of Sheathed Thermocouples in Graphite Assemblies.....	131
Oxidation of Chromel-P in H ₂ O-H ₂ Mixtures.....	133
Calculation of Thermocouple Error Due to Insulation-Leakage Current.....	134
Thermocouples for the Measurement of Surface Temperatures of Nuclear Fuel Elements	135
Calculated Radiation-Induced Changes in Thermocouple Composition.....	135
20. REMOVAL OF RADIOACTIVE GASEOUS FISSION PRODUCTS FROM OTHER GASES	138
Removal of Radioiodine Vapor	138
Removal of Iodine from Air-Steam Mixtures	138
Removal of Iodine from Air at 25°C	140
Removal of Iodine from Helium at High Temperatures	142
Removal of Radioactive Noble Gases from Carrier Gases	144
Dynamic Adsorption of Krypton	144
Equilibrium Adsorption of Krypton and Xenon.....	145
Diffusion of Krypton in Charcoal	146
Retention of Krypton and Xenon by Linde Molecular Sieves Used for Water and Carbon Dioxide Adsorption.....	146
Heat Effects During Adsorbent Pressurization	147
Assistance to Other Programs.....	147
21. RELEASE OF FISSION PRODUCTS ON IN-PILE MELTING OF REACTOR FUELS	149
22. EFFECT OF RADIATION ON BERYLLIUM OXIDE	153
PART IV. PREPARATION AND PROPERTIES OF REACTOR MATERIALS	
23. CHEMISTRY OF ORGANIC MODERATORS AND COOLANTS.....	157
24. PREPARATION OF REFRACTORY OXIDES FROM MOLTEN SALTS	158
25. PREPARATION OF PURE BERYLLIUM COMPOUNDS BY SOLVENT EXTRACTION....	159
PUBLICATIONS	161
PAPERS PRESENTED AT SCIENTIFIC AND TECHNICAL MEETINGS.....	163

Part I
MOLTEN-SALT REACTOR PROGRAM

1. HIGH-TEMPERATURE PHASE EQUILIBRIUM STUDIES

R. E. Thoma

H. Insley¹

J. H. Burns

C. F. Weaver

T. N. McVay¹

H. A. Friedman

G. M. Hebert

B. J. Sturm

The phase behavior of fused-salt materials of possible interest in high-temperature reactors is the subject of a continuing program of study.^{2,3}

The experimental data from which phase diagrams have been derived were obtained from thermal gradient quenching experiments, thermal analysis of melts using both heating and cooling cycles, and visual observation of phase changes during heating and cooling. Phases in samples from all these experiments were identified by use of the optical microscope and the x-ray diffractometer.

SYSTEMS FOR USE AS NUCLEAR REACTOR FUELS

The System $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$

The Molten-Salt Reactor Experiment will be a one-region reactor designed to demonstrate reliable operation of such a high-temperature, low-pressure system and, at the same time, provide appreciable conversion of Th^{232} to U^{233} . The fuel solvent is to be a mixture of LiF and BeF_2 with the lithium enriched in Li^7 . As a consequence of these decisions, the quaternary system has been carefully evaluated over the concentration ranges of reactor interest.

Examinations of all the contained binary and ternary systems have been completed. Phase diagrams for the $\text{LiF}-\text{UF}_4$,⁴ $\text{LiF}-\text{ThF}_4$,⁵ $\text{LiF}-\text{BeF}_2$,² $\text{BeF}_2-\text{ThF}_4$,⁶ BeF_2-UF_4 ,^{2,7} UF_4-ThF_4 ,⁸ $\text{LiF}-\text{ThF}_4-\text{UF}_4$,⁸ $\text{LiF}-\text{BeF}_2-\text{UF}_4$,^{2,9} $\text{LiF}-\text{BeF}_2-\text{ThF}_4$,⁶ and $\text{BeF}_2-\text{UF}_4-\text{ThF}_4$ ^{10,11} systems have been published elsewhere.

Phase equilibria in the $\text{LiF}-\text{BeF}_2-\text{UF}_4-\text{ThF}_4$ system have been described¹² in detail for mixtures having compositions within the regions (55–72 mole % LiF , 0–18 mole % ThF_4 , and 0–5 mole % UF_4)

¹Consultant.

²*Phase Diagrams of Nuclear Reactor Materials* (ed. by R. E. Thoma), ORNL-2548 (Nov. 2, 1959).

³R. E. Thoma *et al.*, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, p. 3.

⁴C. J. Barton *et al.*, *J. Am. Ceram. Soc.* **41**(2), 63–69 (1958).

⁵R. E. Thoma *et al.*, *J. Phys. Chem.* **63**, 1266 (1959).

⁶R. E. Thoma *et al.*, *J. Phys. Chem.* **64**, 865 (1960).

⁷T. B. Rhinehammer, P. A. Tucker, and E. F. Joy, *Phase Equilibria in the System BeF_2-UF_4* , MLM-1082, to be published.

⁸C. F. Weaver *et al.*, *J. Am. Ceram. Soc.* **43**, 213 (1960).

⁹L. B. Jones *et al.*, *Phase Equilibria in the $\text{LiF}-\text{BeF}_2-\text{UF}_4$ Ternary System*, MLM-1080 (Aug. 24, 1959).

¹⁰R. E. Thoma *et al.*, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, chap. 1.

¹¹C. F. Weaver *et al.*, *J. Am. Ceram. Soc.* **44**, 146 (1961).

¹²C. F. Weaver *et al.*, *Phase Equilibria in Molten Salt Breeder Fuels, I. The System $\text{LiF}-\text{BeF}_2-\text{UF}_4-\text{ThF}_4$* , ORNL-2896 (Dec. 27, 1960).

of potential use as molten-salt breeder reactor fuels. The phase behavior of the systems limiting the quaternary system $\text{LiF}-\text{BeF}_2-\text{UF}_4-\text{ThF}_4$ was reviewed.

Liquidus temperatures in the quaternary system at the fixed $\text{LiF}-\text{BeF}_2$ concentrations 65-25, 67.5-17.5, 70-6, and 70-10 (mole %) were below 550°C and were nearly linear functions of the thorium/uranium concentration ratio.¹² In each of these composition sections the ThF_4 -containing end member exhibited the maximum liquidus temperature.

Implications of the extensive solid solutions occurring in the limiting systems were discussed, and experimental information supporting the conclusions was presented.¹² Crystallographic properties of the phases occurring in the various related systems were tabulated. Characteristic phase transitions were described in detail for specific salt mixtures which have special utility in the reactor development program.

The System $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4-\text{UF}_4$

Uncertainties regarding possible precipitation of UO_2 through contamination of the fuel system by oxide ion has led to incorporation of ZrF_4 in the fuel mixture (see Chap. 2). This inclusion of ZrF_4 in appreciable quantities greatly complicates the problem of a complete and systematic representation of the phase behavior of the system. The problem is, fortunately, somewhat alleviated by the similarity of ZrF_4 , UF_4 , and ThF_4 .

Studies of this quinary system and of its included simpler systems are still in progress. The following conclusions are supported by the studies performed to date.

Incorporation of 5 mole % ZrF_4 , as in $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4-\text{UF}_4$ (70-23-5-1-1 mole %), has a slight beneficial effect on the liquidus temperature over the region of probable interest as MSRE fuel. The composition shown above, which is probably close to the fuel composition, melts at $442 \pm 3^\circ\text{C}$. When mixtures of this composition are permitted to freeze slowly, the first two phases which precipitate contain no UF_4 or ThF_4 ; one of these phases does contain ZrF_4 . When the fuel freezes completely (under near-equilibrium conditions), much of the UF_4 and ThF_4 appears as solid solution in a familiar phase whose stoichiometry is $7\text{LiF} \cdot 6(\text{U,Th})\text{F}_4$. The UF_4/ThF_4 ratio in the solid solution is lower than that in the equilibrium liquid; a reliable estimate for the UF_4 content of the first $7\text{LiF} \cdot 6(\text{U,Th})\text{F}_4$ which precipitates is 15 mole %.

The phase diagram, complicated by the existence of a ternary compound of LiF , BeF_2 , and ZrF_4 , can be elucidated only after much additional study. It appears, however, that phase behavior of the quinary system will be suitable for use in the MSRE.

The System $\text{CrF}_2-\text{CrF}_3$

The chemistry of chromium fluorides is of particular relevance to the technology of molten-salt reactors, because molten-salt-fluoride reactor fuels must be contained in alloys, such as INOR-8,

which contain substantial percentages of chromium. The corrosion of these alloys appears to be limited by the rate at which chromium diffuses through the metal to the metal-salt interface.¹³ The thermodynamic behavior of CrF_2 in molten fluorides has been the object of considerable investigation.¹⁴ In the study of methods for preparing pure fluorides of chromium for such investigations, a new compound, of the composition $3\text{CrF}_2 \cdot 2\text{CrF}_3$, was disclosed to contain both Cr(II) and Cr(III) .^{15,16}

The system CrF_2 - CrF_3 was brought under investigation in order to provide more information concerning the behavior of chromium in fluoride media. As a first step, the temperature-composition characteristics of the solid-liquid equilibria were delineated. The melting point of the component CrF_2 was determined as $894 \pm 6^\circ\text{C}$; that of CrF_3 was estimated to be above 1400°C . A single eutectic point was found at approximately 830°C and 30 mole % CrF_3 . The single intermediate compound $3\text{CrF}_2 \cdot 2\text{CrF}_3$ was found in the system. At a peritectic invariant point ($1000 \pm 4^\circ\text{C}$), it melts incongruently to CrF_3 and liquid. Crystals of the compound yield a reproducible x-ray diffraction pattern and are characteristically twinned, biaxial negative, with $2V = 55^\circ$, $N_\alpha = 1.518$, and $N_\gamma = 1.534$.

IMMERSION OILS WITH HIGH INDICES OF REFRACTION¹⁷

Stable homogeneous mixtures of perfluorotributylamine and polymers of chlorotrifluoroethylene have been compounded for use as immersion oils for refractive-index measurements in the range 1.292 to 1.411. These liquid mixtures possess convenient viscosities, maintain constant indices of refraction for long periods of use and storage, are noncorrosive to glass equipment, and are nontoxic. Surface-tension, viscosity, and vapor-pressure problems encountered with immersion oils, previously described in the literature, are essentially absent with these mixtures.

CRYSTAL PROPERTIES AND CRYSTAL STRUCTURE

The Compounds $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{ThF}_4$ and $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{UF}_4$ ¹⁸

The ternary compounds $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{ThF}_4$ and $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{UF}_4$ were prepared by reaction of the anhydrous components at high temperature and isolated as pure solid phases. Their characteristic optical properties, x-ray diffraction data, and melting-freezing relationships were determined. Crystals of these compounds are uniaxial positive, with $N_\omega = 1.544$ and 1.598, and $N_e = 1.552$ and 1.608 respectively. These ternary compounds are isostructural with each other and have tetragonal unit cells,

¹³ *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, chap. 4.

¹⁴ C. M. Blood, W. R. Grimes, and G. M. Watson, "Activity Coefficients of Ferrous Fluoride and of Nickel Fluoride in Molten Sodium Fluoride-Zirconium Fluoride Solutions," presented before the Division of Physical and Inorganic Chemistry, 132nd National Meeting of the American Chemical Society, New York, September 1957.

¹⁵ B. J. Sturm, "Synthesis of Chromium(II) and Chromium(II,III) Fluorides," paper presented at the 136th Meeting of the American Chemical Society, Atlantic City, N.J., September 1959.

¹⁶ *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, p 186.

¹⁷ *Am. Mineralogist* **45**, 469 (1960).

¹⁸ *J. Am. Ceram. Soc.* **43**, 608 (1960).

of the dimensions $a_0 = 11.82$ Å, $c_0 = 10.29$ Å for $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{ThF}_4$, and $a_0 = 11.61$ Å, $c_0 = 10.12$ Å for $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{UF}_4$.

The composition-temperature relationships of these ternary compounds have been described by the $\text{NaF}-\text{BeF}_2-\text{ThF}_4$ and $\text{NaF}-\text{BeF}_2-\text{UF}_4$ phase diagrams. The compound $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{ThF}_4$ melts semicongruently to a ThF_4 solid solution and liquid at 745°C . The compound $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{UF}_4$ melts semicongruently to UF_4 and liquid at 548°C .

Crystal Structure of LiSbF_6

As a result of the study of solvents for rare-earth and alkali fluorides, a new compound was produced by addition of LiF to a solution of 20% SbF_5 in HF .¹⁹ The formula was established by chemical analysis to be LiSbF_6 . The crystal-structure investigation was undertaken because this compound provides a means of comparing the configuration of fluoride ions about the cation in LiSbF_6 with that in NaSbF_6 (ref 20) and in the hexafluoroantimonates of Tl^+ , NH_4^+ , Rb^+ , and Cs^+ (ref 21) with which the lithium-containing compound is not isostructural.

The unit-cell dimensions and space-group symmetry of this compound were determined by a single-crystal x-ray diffraction study. The unit cell is rhombohedral, with

$$a_R = 5.43 \text{ Å}, \quad \alpha = 56^\circ 58'.$$

The corresponding hexagonal triply primitive cell has the following dimensions:

$$a_H = 5.18 \text{ Å}, \quad c_H = 13.60 \text{ Å}.$$

If the unit rhombohedron contains one formula weight of LiSbF_6 , the crystal density is 3.83 g/cm^3 . The Laue symmetry is $\bar{3}m$. Three space groups, $R3m$, $R32$, and $R\bar{3}m$, not distinguishable by diffraction, are consistent with the systematic extinctions.

The infrared absorption spectrum suggests that the crystals of LiSbF_6 contain Li^+ and SbF_6^- ions. A strong absorption band was observed at approximately 675 cm^{-1} for this compound in KBr . A value of 660 cm^{-1} for the γ_3 vibration of the SbF_6^- octahedron has been previously reported.²²

X-Ray Diffraction Study of LiBrO_3

X-ray diffraction measurements of lithium bromate were made in order to obtain data from which the crystal "free space" could be estimated. This parameter is needed for calculations in the study of radiolysis of alkali-metal bromates.²³ Single-crystal and powder diffraction methods were employed in the determination.

¹⁹D. O. Campbell, Chemical Technology Division, personal communication.

²⁰N. Schrewelius, *Z. anorg. u. allgem. Chem.* **238**, 241 (1938).

²¹N. Schrewelius, *Arkiv. Kemi, Mineral. Geol.* **16B**, No. 7 (1942).

²²P. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.* **1959**, 2762.

²³G. E. Boyd, personal communication.

The results of the measurements were interpreted as follows: LiBrO_3 is primitive orthorhombic with the following unit-cell dimensions:

$$a = 6.000 \pm 0.01 \text{ \AA} ,$$

$$b = 7.845 \pm 0.01 \text{ \AA} ,$$

$$c = 5.055 \pm 0.01 \text{ \AA} .$$

Systematic absences indicate that the probable space group is D_{2h}^{16} -Pnma. A determination of the approximate density by a pycnometric method using xylene as the liquid gave a value of 3.62 g/cm^3 , corresponding to the presence of four formula weights per unit cell (calculated density: 3.76 g/cm^3).

X-ray reflections of the general hkl type were observed to be strong only when $h + l$ is even and k is even; this observation requires that the bromine and lithium atoms occupy unit-cell positions analogous to those of iodine and sodium in NaIO_3 (ref 24) (with which LiBrO_3 appears to be isostructural). The determination of the exact positions of the bromine atoms and of the oxygens would require quantitative measurement of the x-ray intensities.

²⁴I. Naray-Szabo and J. Neugebauer, *J. Am. Chem. Soc.* **69**, 1280 (1947).

2. PRECIPITATION OF OXIDES FROM MOLTEN FLUORIDES

PRECIPITATION OF OXIDES FROM MSRE FUEL

J. E. Eorgan J. H. Shaffer R. E. Thoma
 H. A. Friedman G. M. Hebert C. F. Weaver

The ease of precipitation of UO_2 upon the addition of BeO , H_2O , or other reactive oxides to $\text{LiF-BeF}_2\text{-UF}_4$ mixtures has been described,¹ and the following section describes a potentially useful separation scheme based on such precipitation. However, in the operation of the Molten-Salt Reactor Experiment with a fuel of $\text{LiF-BeF}_2\text{-ThF}_4\text{-UF}_4$, precipitation of UO_2 by inadvertent contaminants might result in unstable reactor operation and, possibly, in localized hot spots if UO_2 deposits formed in the core. Oxide contamination could result from (1) impurities in the cover gas used in the reactor, (2) incompletely removed oxide films on the reactor metal, and, especially, (3) gases desorbed from the moderator graphite. Precipitation of oxides from the system $\text{LiF-BeF}_2\text{-ZrF}_4\text{-ThF}_4\text{-UF}_4$ by addition of reactive oxides has been studied to determine whether inadvertent precipitation of UO_2 could be avoided by the addition of ZrF_4 .

Equilibration of $\text{LiF-BeF}_2\text{-ZrF}_4\text{-UF}_4$ mixtures with BeO and careful examination of the products has established that a ZrF_4/UF_4 ratio in excess of 3 prevents precipitation of UO_2 ; from such melts the precipitate is ZrO_2 uncontaminated by UO_2 . From the results of these studies it was recommended that the MSRE be fueled with $\text{LiF-BeF}_2\text{-ZrF}_4\text{-ThF}_4\text{-UF}_4$ (70-23-5-1-1 mole %). Experimentation with this mixture demonstrates that a ZrF_4/UF_4 ratio of 3 or more prevents the formation of UO_2 ; when sufficient BeO is added to adjust the ZrF_4/UF_4 ratio to unity (by precipitation of ZrO_2), precipitation of UO_2 occurs. Addition of BeO in an amount calculated to precipitate all the UO_2 and ZrO_2 did not cause precipitation of ThO_2 .

Subsequent experiments have been performed in larger-scale equipment to verify this behavior of uranium and zirconium in the MSRE fuel. Addition of BeO in increments to such a melt with subsequent equilibration and filtration of samples for analysis gave the results shown in Fig. 2.1. These data indicate that the uranium and zirconium coprecipitate as oxides when the $\text{Zr}^{4+}/\text{U}^{4+}$ ratio falls to about 1.5. Further studies are in progress to evaluate the effect of temperature and of solution composition on this selective precipitation.

It is anticipated that the MSRE system can be cleaned sufficiently well to prevent precipitation of any oxide within the system. It appears from this study, however, that the relatively safe precipitation of small quantities of ZrO_2 can be readily substituted for the precipitation of UO_2 .

¹J. H. Shaffer *et al.*, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, p 84.

Fig. 2.1. The Behavior of ZrF_4 and UF_4 in LiF-BeF_2 (63-37 mole %) in Reacting with BeO at 700°C .

RECOVERY OF URANIUM AND PROTACTINIUM FROM MOLTEN FLUORIDE SYSTEMS BY PRECIPITATION AS OXIDES²

J. H. Shaffer

G. M. Watson

D. R. Cuneo

J. E. Strain

M. J. Kelly

In the conceptual two-region molten-salt breeder reactor, fissionable U^{233} will be recovered from the blanket as the decay product of Pa^{233} . Because of half-life and neutron absorption cross-section values, equilibrium concentrations of Pa^{233} in the blanket mixture would result in appreciable parasitic neutron absorptions. Therefore, if the thermal breeding potential of a molten-salt nuclear reactor is to be exploited, a method for removing protactinium as well as uranium from the blanket is desirable. A method of precipitating uranium and protactinium as oxides from solution in a molten fluoride solvent has been examined for application to the molten-salt reactor program.

Small-scale experiments clearly indicated that it is possible to remove protactinium from molten fluoride solutions by what appears to be surface precipitation of protactinium on beryllium oxide or thorium oxide particles. In these experiments, protactinium was repeatedly removed from molten mixtures of $\text{LiF-BeF}_2\text{-ThF}_4$ (67-18-15 mole %) by the addition of 1 to 2 wt % solid beryllium or thorium oxides. Typical results of these experiments are shown in Figs. 2.2. and 2.3. The removal was equally successful when the initial concentration of protactinium varied from tracer levels (1-2 ppb) to macro levels (50-75 ppm).

Similar procedures were successful in the removal of uranium from solution in molten fluorides. For example, Fig. 2.4 illustrates the effective removal of approximately 2000 ppm uranium from

²J. H. Shaffer *et al.*, paper presented at the First Conference on Nuclear Reactor Chemistry, Gatlinburg, Tenn., Oct. 12-14, 1960.

Fig. 2.2. Removal of Protactinium (Pa^{231} Labeled with Pa^{233}) from Solution in $\text{LiF}\cdot\text{BeF}_2\cdot\text{ThF}_4$ (67-18-15 mole %) by Reaction with BeO at 650°C .

Fig. 2.3. Removal of Protactinium (Pa^{231} Labeled with Pa^{233}) from Solution in $\text{LiF}\cdot\text{BeF}_2\cdot\text{ThF}_4$ (67-18-15 mole %) by Reaction with ThO_2 at 650°C .

Fig. 2.4. Extraction of Uranium from $\text{LiF}\cdot\text{BeF}_2\cdot\text{ThF}_4$ (67-18-15 mole %) at 650°C .

solution in molten $\text{LiF-BeF}_2\text{-ThF}_4$ (67-18-15 mole %) by the addition of 3 wt % beryllium oxide. Comparable results were obtained by using ThO_2 as the solid oxide precipitant.

Mixtures of protactinium and uranium dissolved in the molten fluoride solvent $\text{LiF-BeF}_2\text{-ThF}_4$ (67-18-15 mole %) demonstrated a dissimilar behavior in reacting with beryllium oxide. While these results, illustrated in Fig. 2.5, showed a coprecipitation of protactinium and uranium, a consideration of the magnitudes of the initial concentrations of these ions in solution suggests that the solubility of protactinium oxide may be much less than that of UO_2 . A subsequent experiment, see Fig. 2.6, illustrated the ability of UO_2 to displace or precipitate protactinium dissolved in the molten fluoride solvent.

By using concentrations comparable with those contemplated for uranium and protactinium in the proposed blanket of a two-region molten-salt breeder reactor, the experimental results demonstrate the application of oxide precipitation reactions to the molten-salt breeder reactor program. Of further interest to this program was the experimental observation that protactinium was precipitated from solution in the presence of approximately 1000 to 2000 ppm uranium. In addition to illustrating the removal of uranium and protactinium from salt mixtures containing high concentrations of thorium, the experimental results show that protactinium can also be separated from uranium by these oxide precipitation reactions.

Fig. 2.5. Reaction of BeO with Protactinium and Uranium Dissolved in $\text{LiF-BeF}_2\text{-ThF}_4$ (67-18-15 mole %) at 650°C .

Fig. 2.6. Reaction of Pa^{231} (Labeled with Pa^{233}) with UO_2 in $\text{LiF-BeF}_2\text{-ThF}_4$ (67-18-15 mole %) at 650°C .

3. SOLUBILITY OF GASES IN MOLTEN SALTS

BORON TRIFLUORIDE AS A SOLUBLE POISON IN MOLTEN FLUORIDE REACTOR FUELS

G. M. Watson

Control of a reactor by adjusting the concentration of some neutron absorber which can be readily added and removed has, for years, been an attractive possibility. Such chemical control of a molten-salt reactor might be obtained by use of BF_3 (enriched in B^{10} if necessary), the concentration of BF_3 in the molten fluoride fuel solution could be controlled by controlling the partial pressure of this gas over a free surface of the circulating system.

To assess the possible use of this material in the Molten-Salt Reactor Experiment, and molten-salt reactors generally, the solubility behavior of BF_3 has been determined in a simulated reactor fuel mixture, and the extent of reaction of BF_3 with moderator graphite has been examined.

Solubility of BF_3 in Simulated MSRE Fuel

J. H. Shaffer

The solubility of BF_3 in the molten fluoride mixture was determined by a method very similar to that described¹ for determination of the solubility of HF . The melt, which consisted of LiF - BeF_2 - ZrF_4 - ThF_4 - UF_4 (65-28-5-1-1 mole %), was saturated by sparging with BF_3 at a predetermined temperature (500–700°C) and pressure (1.2–1.9 atm BF_3). A measured portion of the saturated liquid was transferred, by melting a frozen seal, to an isolated section of the apparatus, where the dissolved BF_3 was recovered by sparging with helium. The recovered BF_3 was absorbed in aqueous NaCl solution and was measured by the Analytical Chemistry Division using a method described by Booth and Martin.²

The solubility of BF_3 was shown to obey Henry's law and to decrease with increasing temperature. The solubilities, in moles of BF_3 per liter of salt per atm of BF_3 , are 0.267, 0.132, 0.083, and 0.035 at 500, 550, 600, and 700°C respectively. From the temperature dependence of solubility it is seen that the enthalpy of solution is independent of temperature and equal to -15.1 kcal/mole.

These relatively high values would permit a B/U^{235} ratio of 0.4 in the MSRE fuel at the higher reactor temperature with 1 atm of BF_3 , it should be possible to achieve the desired reactor control, therefore, at quite modest pressures of BF_3 .

Intrusion of gaseous BF_3 into the void volume in the unclad graphite moderator of the MSRE would complicate use of this poison. The solubility of BF_3 in the liquid is sufficient, however, so that, if the physical adsorption of BF_3 on graphite is negligible and if equilibrium distribution

¹J. H. Shaffer, W. R. Grimes, and G. M. Watson, *J. Phys. Chem.* **63**, 1999 (1959).

²H. S. Booth and D. R. Martin, *Boron Trifluoride and Its Derivatives*, chapt. VII, Wiley, New York, 1949.

of BF_3 between moderator pores and the molten fuel is maintained, 85% of the boron content of the core will be in the molten fuel.

Additional information concerning reversible adsorption of BF_3 by graphite, rates of diffusion of BF_3 in graphite pores, and rates of solution of BF_3 in flowing salt streams will be required before this method of chemical control can be recommended.

Retention of BF_3 on Graphite

A. R. Saunders

The extent of reaction of BF_3 with moderator graphite or of irreversible sorption of BF_3 by graphite has been examined³ as a step in the evaluation of this gas as a chemical poison for the Molten-Salt Reactor Experiment.

The test specimens were Speer No. 2 reactor-grade graphite. The samples were degassed by heating to 2000°C in an induction furnace under a pressure of 0.1 μ over a 16-hr period and were then cooled under helium gas. After insertion into the test apparatus, with a short unavoidable exposure to the atmosphere, they were again degassed in a current of helium at 800°C. Specimens were then exposed to BF_3 at 10 to 15 psig for 2 hr at temperatures of 600 to 800°C. After exposure, the BF_3 was stripped from the specimens by sweeping with dry helium gas at atmospheric pressure for a 2-hr period. Boron content of the specimens was determined by spectrographic analysis and, in some cases for which B^{10}F_3 had been used, by measurement of neutron cross section with the pile oscillator.⁴

The experimental data obtained indicate a mean residual boron content of 10 ppm in the graphite after treatment, this retention is independent of exposure temperature and BF_3 pressure over the small pressure range studied. It is clear that no appreciable reaction of BF_3 with graphite occurs, the small quantity of boron retained may be by chemisorption on the active surfaces or, possibly, by reaction with small quantities of adsorbed water not removed by the final degassing treatment.

THE SOLUBILITY OF HF IN MOLTEN FLUORIDES

J. H. Shaffer

G. M. Watson

As part of a systematic study of gas solubilities in molten fluoride mixtures, the solubility of HF in molten $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4-\text{UF}_4$ (65-28-5-1-1 mole %) was determined. By simulating the MSRE fluoride fuel mixture, the HF solubility data should indicate the distribution of HF in the

³A. R. Saunders, *Retention of Boron Trifluoride on Graphite in a Molten Salt Reactor*, ORNL CF-60-11-21 (Nov. 4, 1960).

⁴ORSORT Reactor Physics Laboratory Manual, TID-5262 (July 1955).

polythermal reactor fuel circuit. In addition, a comparison of these data with the solubility behavior of HF in other fluoride solvents^{1,5} might be useful to the understanding of the liquid state of molten fluoride systems.

The solubility of HF, measured over the temperature and pressure ranges 500 to 700°C and 1.4 to 2.4 atm, respectively, was found to obey Henry's law and to decrease with increasing temperatures. Henry's law constants, expressed in moles of HF per cc of solution per atm, were found to be 17.0×10^{-6} , 13.3×10^{-6} , 10.8×10^{-6} , and 8.0×10^{-6} at temperatures of 500, 550, 600, and 700°C respectively. The temperature dependence of the Henry's law constants illustrates that the enthalpy of solution is constant and equal to approximately -5.65 kcal/mole over the temperature range studied.

⁵J. H. Shaffer and G. M. Watson, *Reactor Chem. Div. Ann. Progr. Rept. Apr. 29, 1960*, ORNL-2584, p 31.

4. XENON POISONING IN MOLTEN-SALT REACTORS CONTAINING GRAPHITE

R. B. Evans III

Since the Molten-Salt Reactor Experiment will be moderated with unclad graphite which is to be in contact with the fuel, the possibility exists that appreciable poisoning of the reactor will occur through diffusion of fission product xenon into the pores of the moderator. Burch, Watson, and Weeren, who examined this problem,¹ concluded that such poisoning could be avoided if a gas-expansion dome (of roughly half the volume of the fuel) were included in the circulating system. Spiewak² has pointed out, however, that the case will be considerably different in the MSRE, where the flow of fluid through the pump bowl will be less than 10% of the total flow through the reactor system. Accordingly, estimates have been made of the xenon poisoning to be expected in a hypothetical molten-salt reactor operating at steady-state conditions near those proposed for the MSRE.³

Xenon transport rates were considered for various combinations of generation, burnout, decay, removal via helium stripping, and diffusion into graphite. Particular attention was given to a discussion of the graphite porosity, permeability, and xenon diffusion coefficient. These parameters govern the rate of xenon diffusion into the graphite moderator.

Figure 4.1 shows a family of curves for poison fraction as a function of recycle rate (i.e., percentage of flow which is equilibrated with a stripping gas such as helium) and $D\lambda$. For orientation

¹W. D. Burch, G. M. Watson, and H. O. Weeren, *Xenon Control in Fluid Fueled Reactors*, ORNL CF-60-2-2 (July 6, 1960).

²I. Spiewak, ORNL interoffice correspondence, Oct. 7, 1960.

³G. M. Watson and R. B. Evans III, *Effects of Xenon Absorption in Molten Salt Reactors Containing Graphite*, ORNL CF-61-2-59 (Feb. 15, 1961).

Fig. 4.1. Poison Fraction vs Stripping Rate.

with these curves the estimated $D\lambda$ values for CEY and AGOT graphites are 5×10^{-6} and 6×10^{-4} cm/sec respectively. For $D\lambda$ values within this region, increasing the recycle rate is by far the most effective method of decreasing the poison fraction. Figure 4.1 clearly indicates that decreasing $D\lambda$ from 6×10^{-4} to 5×10^{-6} offers no real advantage when the recycle rate is kept below 10%.

Incorporation of a facility to permit stripping of a large fraction of the total flow coupled with graphite of low permeability effectively removes the xenon poisoning problem. However, the problem cannot be effectively solved by improved graphite alone.

5. THERMODYNAMIC STUDIES IN MOLTEN SALTS

EXPERIMENTAL AND THEORETICAL STUDY OF MOLTEN RECIPROCAL SALT SOLUTIONS

A. R. A. Funes¹

M. Blander

J. Braunstein²

D. G. Hill³

Additional theoretical and experimental studies were made of the thermodynamic properties of molten salt systems containing at least two cations and two anions (reciprocal salt systems). Theoretical calculations,⁴ based on the quasi-lattice model for dilute solutions of A^+ and C^- ions in the solvent BD, were made for the associations

where the ionic binding is nondirectional. They provided the association constants K_1 , K_2 , and K_{12} for the respective associations:

$$K_1 = Z(\beta_1 - 1), \quad (1)$$

$$K_1 K_2 = \frac{Z(Z-1)}{2} (\beta_1 \beta_2 - 2\beta_1 + 1), \quad (2)$$

$$K_1 K_{12} = \frac{Z(Z-1)}{2} (\beta_1 \beta_{12} - 2\beta_1 + 1), \quad (3)$$

where Z is a coordination number, $\beta_1 = \exp(-\Delta A_i/RT)$, in which ΔA_i is a specific bond free energy.⁵ For associations in which the change of the internal degrees of freedom of the ions involved is negligible, $\Delta A_i \approx \Delta E_i$ and is independent of temperature.

Electromotive Force Measurements in the System AgNO_3 and NaCl in Molten Equimolar Mixtures of NaNO_3 and KNO_3 and Their Comparison with the Quasi-Lattice Theory⁶

Using a concentration cell which has been described previously,^{7,8} measurements of the activity coefficients of AgNO_3 , γ_{AgNO_3} , in dilute solutions of AgNO_3 and NaCl in an equimolar mixture of

¹ Fellow of the Consejo Nacional de Investigaciones Cientificas y Tecnicas of Argentina.

² On sabbatical leave from the University of Maine, Orono, Maine.

³ Duke University, Durham, N. C., consultant to the Reactor Chemistry Division, summer 1960.

⁴ M. Blander, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, p 43.

⁵ M. Blander, *J. Chem. Phys.* **34**, 432 (1961).

⁶ D. G. Hill and M. Blander, to be submitted to the *Journal of Physical Chemistry*.

⁷ M. Blander, F. F. Blankenship, and R. F. Newton, *J. Phys. Chem.* **63**, 1259 (1959).

⁸ J. Braunstein and M. Blander, *J. Phys. Chem.* **64**, 10 (1960).

$\text{NaNO}_3\text{-KNO}_3$ were made at five temperatures ranging from 233 to 528°C. The concentration dependence of $\log \gamma_{\text{AgNO}_3}$ was compared with the results of calculations based on the asymmetric approximation and led to the values of K_1 and ΔE_1 listed in Table 5.1 for values of $Z = 4, 5$, and 6. These values probably cover the entire range of possible coordination numbers. The values of ΔE_1 for any one value of Z are constant at all temperatures within the estimated experimental error. This further demonstrates over much wider ranges of temperatures and values of K_1 the fact, observed previously in the pure NaNO_3 and pure KNO_3 solvents,⁴ that Eq. (1) with a constant value of ΔA_1 (ΔE_1) leads to a correct prediction of the temperature dependence of K_1 .

Table 5.1. Values of ΔE_1 and K_1 for the Association of Ag^+ and Cl^- in an Equimolar Mixture of NaNO_3 and KNO_3 as Obtained from the Comparison of the Data with the Theory

Temperature (°K)	$-\Delta E_1$ (kcal/mole)			K_1 [(moles/mole solvent) ⁻¹]
	$Z = 4$	$Z = 5$	$Z = 6$	
506	5.6	5.4	5.2	1051
551	5.57	5.33	5.13	644
658	5.67	5.38	5.15	302
752	5.72	5.40	5.13	180
801	5.6 ₂	5.2 ₈	5.0 ₀	133

The solvent effect on K_1 is illustrated in Table 5.2. The calculated values of ΔE_1 in Table 5.1 for the mixture are the averages of the values for pure NaNO_3 and KNO_3 and conform to the expression

$$\Delta E_1 (\text{NaNO}_3\text{-KNO}_3) = N_{\text{Na}} \Delta E_1 (\text{NaNO}_3) + N_{\text{K}} \Delta E_1 (\text{KNO}_3). \quad (4)$$

Table 5.2. Comparison of the Values of K_1 and ΔE_1 for the Association of Ag^+ and Cl^- in NaNO_3 , $\text{NaNO}_3\text{-KNO}_3$ (50-50 mole %), and KNO_3 at 385°C

	NaNO_3	$\text{NaNO}_3\text{-KNO}_3$ (50-50 mole %)	KNO_3
K_1 [(moles/mole solvent) ⁻¹]	205	302	456
$-\Delta E_1$ (kcal/mole)			
$Z = 4$	5.17	5.67	6.18
$Z = 5$	4.88	5.38	5.89
$Z = 6$	4.65	5.15	5.68

For values of β_1 appreciably larger than unity a linear relation of a type first suggested by Flood and co-workers,⁹

$$\ln K_1 (\text{NaNO}_3\text{-KNO}_3) = N_{\text{Na}} \ln K_1 (\text{NaNO}_3) + N_{\text{K}} \ln K_1 (\text{KNO}_3), \quad (5)$$

is consistent with the results.

A Critical Evaluation of Association Constants in Reciprocal Salt Systems¹⁰

A method was developed to evaluate stepwise association constants at infinite dilution. It consisted of the expansion of the activity coefficient of a component in powers of the stoichiometric concentrations of the solutes in a series in which the coefficients were combinations of the accumulative association constants, K_i ,

$$-\ln \gamma_{\text{AgNO}_3} = K_1 R_{\text{KX}} + (K_1 K_2 - \frac{1}{2} K_1^2) R_{\text{KX}}^2 + (2K_1 K_{12} - K_1^2) R_{\text{KX}} R_{\text{AgNO}_3} + \dots, \quad (6)$$

and were also the coefficients of a MacLaurin expansion of $-\ln \gamma_{\text{AgNO}_3}$. Thermodynamic association constants were obtained by extrapolation of the derivatives of the experimental activity coefficients to infinite dilution of the solutes and comparing these with the coefficients of Eq. (6). Precise data at low concentrations of the solutes were required for this extrapolation. Association constants in molten salts reported previously by other authors show large discrepancies. The method used here makes it clear that these discrepancies probably arise because of the lack of data at sufficiently low concentrations to permit a reliable evaluation of the association constants at infinite dilution of all solutes.

For the association of Ag^+ and Cl^- ions in molten KNO_3 , for example, the stepwise constants for the formation of AgCl , AgCl_2^- , and Ag_2Cl^+ at 385° were found to be $K_1 = 456 \pm 10$, $K_2 = 169 \pm 20$, and $K_{12} = 70 \pm 15$ (moles/mole KNO_3)⁻¹ respectively. For the association of Ag^+ and Br^- ions in KNO_3 , K_1 and K_{12} were evaluated and compared with Eqs. (1) and (3). The results of the comparison are shown in Table 5.3. The constancy within the estimated experimental

⁹H. Flood, T. Forland, and K. Grjotheim, *Z. Anorg. u. Allgem. Chem.* **276**, 289 (1954).

¹⁰J. Braunstein, M. Blander, R. M. Lindgren, and A. R. A. Funes, submitted to XVIII IUPAC Montreal, Canada - written in conjunction with the University of Maine.

Table 5.3. Values of K_1 and K_{12} , ΔE_1 and ΔE_{12} , for the Association of Ag^+ and Br^- Ions in KNO_3

$T(^{\circ}\text{K})$	K_1	$-\Delta E_1$ (kcal/mole)			K_{12}	$-\Delta E_{12}$ (kcal/mole)		
		$Z = 4$	$Z = 5$	$Z = 6$		$Z = 4$	$Z = 5$	$Z = 6$
675	925	7.3 ₁	7.0 ₁	6.7 ₇	289	7.0 ₇	6.7 ₀	6.3 ₉
711	772	7.4 ₄	7.1 ₂	6.8 ₇	210	7.0 ₀	6.5 ₉	6.2 ₈
725	737	7.5 ₃	7.2 ₀	6.9 ₄	208	7.1 ₂	6.7 ₁	6.3 ₉
747	598	7.4 ₄	7.1 ₁	6.8 ₅	174	7.0 ₇	6.6 ₅	6.3 ₃
773	540	7.5 ₄	7.2 ₀	6.9 ₃	145	7.0 ₄	6.6 ₁	6.2 ₇

error of the values of ΔE_1 and ΔE_{12} for any one value of Z demonstrates the potential usefulness of the theoretical expressions in predicting the temperature coefficients not only of K_1 but also of K_{12} .

FREEZING-POINT DEPRESSIONS IN SODIUM FLUORIDE

S. Cantor

This work is part of a general program whose purpose is to establish the effects of structural parameters on the thermodynamic properties of fused fluoride solutes. Many binary fluoride mixtures containing more than 75 mole % of sodium fluoride yield pure crystalline NaF as the primary phase on cooling from the liquid state. Accordingly, structural differences among several families of fluoride solutes can be deduced from their effects on the freezing point of sodium fluoride. Studies of the effects of alkaline-earth fluorides and the 3d transition metal difluorides (MnF_2 , FeF_2 , CoF_2 , NiF_2 , ZnF_2) have been reported previously.¹¹ The present work reports studies of effects related to ion size, cation charge, and polarization.

Effect of Ion Size

When the isostructural tetravalent fluorides, in concentrations up to 15 mole %, were dissolved in NaF, the freezing-point lowering followed the order $\text{ThF}_4 > \text{UF}_4 > \text{HfF}_4 = \text{ZrF}_4$; the depressions of the freezing point were less than would be consistent with ideal behavior. This behavior is consistent with the assumptions that eightfold coordination of the tetravalent cation exists in solution (as it does in the crystalline state) and that the cation size determines the extent to which all eight fluoride ions are in contact with the cation. As the tetravalent ion size increases, more fluoride ions will be in contact, and, therefore, greater work will be required for the sodium ions to attract fluorides and establish long-range order, that is, crystallize. In fact, it is only in the case of Th^{4+} that all eight fluorides can have points of contact.

The nature of the relationship between the depression of the freezing point of NaF and the tetravalent cation radius is shown in Fig. 5.1. A test of whether this linear relationship holds when two tetravalent fluorides are in solution at the total concentration for which the lines are drawn is indicated in Fig. 5.2, in which the radius for the pair was taken as an arithmetic average of the two cationic radii. At the higher concentration (15 mole % solute) the two tetravalent cations appear to have a synergistic effect for fluoride attraction; that is, the freezing point of NaF is lower than expected.

¹¹S. Cantor, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, p 48; paper submitted to *Journal of Physical Chemistry*.

Fig. 5.1. Freezing Points of NaF vs Ionic Radius of M^{4+} .

Effect of Cation Charge

Three fluorides whose interionic distances approximate that of NaF are CaF_2 , YF_3 , and ThF_4 . The significant structural difference among these solutes lies in their cationic charge. It is clear from the results indicated in Fig. 5.3 that the larger the cation charge of the solute, the greater its freezing-point depression. Stated differently, the stronger the electric field of the solute cation, the greater will be its attraction for fluoride ions, which, in turn, will make the establishment of long-range order for NaF (crystallization) more difficult. In addition it would seem from the data that the excess freezing-point depression caused by the trivalent fluoride is approximately half way between those of the divalent and tetraivalent fluorides.

Effects Related to Polarization

If a set of solute cations have the same charge and size, the cation with the greater polarizing power would be expected to have a greater fluoride affinity, thereby causing a greater freezing-

Fig. 5.2. Freezing Points of NaF in NaF-MF₄ Systems as a Function of Solute Ionic Radius.

Fig. 5.3. Freezing-Point Depressions in NaF Caused by CaF₂, YF₃, and ThF₄.

point lowering of NaF. For MgF₂ and ZnF₂, whose cation sizes and charges are about the same, a significant structural difference is the greater polarizing power of the d^{10} electronic configuration (Zn²⁺) over that in the inert-gas configuration (Mg²⁺). Re-examination of the data¹¹ shows that, indeed, as revealed by Fig. 5.4, ZnF₂ does depress the NaF freezing point somewhat significantly more than does MgF₂.

Fig. 5.4. Freezing-Point Depressions in NaF Caused by MgF₂ and ZnF₂.

HEAT OF FUSION OF $3\text{LiF} \cdot \text{ThF}_4$

R. A. Gilbert¹²

R. E. Thoma

As part of the continuing program of research on the chemistry of fused salts, the phase diagrams of many binary systems of the $\text{AX} \cdot \text{MX}_4$ type [A = alkali metal, M = heavy metal (Th , U , Zr , Hf)] have been determined.¹³ Within these diagrams, many intermediate congruently melting compounds have appeared. While melting points and some information on crystal structure are usually available, little is known about the thermodynamic properties of these intermediate compounds. This information would be of value in calculating ideal phase diagrams for comparison with experiment results. In making such thermodynamic calculations for binary fused salt mixtures, Chu and Egan¹⁴ were forced to estimate entropies of fusion because such data were not available.

As the first stage in such a thermodynamic study, the heat of fusion of the compound $3\text{LiF} \cdot \text{ThF}_4$ was determined using the Bunsen ice calorimeter. The material chosen for study was $3\text{LiF} \cdot \text{ThF}_4$ because of its relatively low melting point (approx 570°C) and because no solid decomposition occurs below the melting point. Figure 5.5 presents the experimental data, along with equations for the

¹²Chemistry Division.

¹³*Phase Diagrams of Nuclear Reactor Materials*, ORNL-2548 (Nov. 6, 1959).

¹⁴*Ann. N.Y. Acad. Sci.* **79** (Art. 11), 908 (1960).

Fig. 5.5. Heat of Fusion of $3\text{LiF} \cdot \text{ThF}_4$.

solid and liquid lines. Over the relatively short temperature ranges shown, the heat capacities of the solid and liquid can be considered constant within the experimental precision; linear equations can therefore be used.

It is evident from the data in Fig. 5.5 that a small amount of premelting has occurred, probably because of the presence of some impurities in the sample. Thus, the melting point is seen to be in the range 568 to 569°C. Because the solid and liquid lines are so nearly parallel, the effect of this 1° uncertainty on the heat of fusion is negligible; at 568°C the calculated value is 13,938 cal and at 569°C, 13,942 cal.

When all uncertainties are taken into account, the heat of fusion is considered to be $13,940 \pm 50$ cal/mole.

CALCULATION OF DENSITIES OF MOLTEN FLUORIDE SYSTEMS

P. B. Bien

S. Cantor

F. F. Blankenship

As part of the larger general problem of understanding and predicting the thermodynamic properties of fused fluorides, the experimentally determined densities of the systems LiF-BeF₂,¹⁵ NaF-BeF₂,¹⁶ LiF-BeF₂-UF₄,¹⁷ and NaF-BeF₂-UF₄^{16,17} were examined. The specific objective was to derive equations for these systems relating density or molar volume to composition. It was hoped that these equations might be useful (with suitable modifications) for calculating the densities of related systems.

Plots of the molar volumes in LiF-BeF₂ and NaF-BeF₂ melts revealed a linear relationship with mole fraction, expressed by the equation

$$V_t = N_1 V_1 + (1 - N_1) V_2, \quad (1)$$

where V_t is the molar volume at temperature t (°C), V_1 and V_2 are the molar volumes of pure liquid alkali fluoride and BeF₂, respectively, at temperature t , and N_1 is the mole fraction of the alkali fluoride. The assumption that the volume contribution of BeF₂ in these melts is only associated with its fluoride ions (because the Be²⁺ ion is relatively small) allows the molar volume to be equated to mole fraction and ion volume:

$$V_t = N_1 V_{A^+} + (2 - N_1) V_{F^-}, \quad (2)$$

where V_{A^+} and V_{F^-} are the volumes of a gram ion of alkali and fluoride ions respectively (herein after referred to as "ionic molar volumes"). The ionic molar volumes were calculated from the

¹⁵B. C. Blanke *et al.*, MLM-1086 (December 1956).

¹⁶B. C. Blanke *et al.*, MLM-1079 (April 1956).

¹⁷B. C. Blanke *et al.*, MLM-1076 (April 1956).

literature values for the alkali fluorides¹⁸ and BeF_2 ¹⁹ and are expressed by the following equations:

$$\begin{aligned} V_{\text{F}^-} &= (10.32 + 2.25 \times 10^{-3}t) \text{ cm}^3, \\ V_{\text{Na}^+} &= (5.48 + 3.55 \times 10^{-3}t) \text{ cm}^3, \\ V_{\text{Li}^+} &= (0.046 + 1.53 \times 10^{-3}t) \text{ cm}^3. \end{aligned} \quad (3)$$

At 600 and 800°C, volumes calculated from Eqs. (2) and (3) deviated from the observed results by an average of 2%.

When the same assumption made for BeF_2 was applied to UF_4 , that is, when the volume contribution was assigned to the fluoride ions alone, then it was a simple matter to derive an equation analogous to (2). If the mole fractions of alkali fluoride and UF_4 are N_1 and N_3 , respectively, then the equation for the ternary melt (containing BeF_2) is given by

$$V_t = N_1 V_{\text{A}^+} + V_{\text{F}^-} (2 + 2N_3 - N_1). \quad (4)$$

Molar volumes in the ternary systems calculated by means of Eqs. (3) and (4) differed from the observed molar volumes by an average of 2.5%.

An equation similar to (2) was also derived for the molar volume of the MSRE fuel system, $\text{LiF}-\text{BeF}_2-\text{UF}_4-\text{ZrF}_4-\text{ThF}_4$, under the assumption that the partial molar volumes for all three tetravalent fluorides are due to fluoride ions alone. This volume equation for MSRE fuel (70-23-5-1-1 mole % $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{UF}_4-\text{ThF}_4$) gave a value which corresponds to a density expression, $d = 2.77 - 6 \times 10^{-4}t$; this is in good agreement with the experimental equation $d = 2.84 - 5.6 \times 10^{-4}t$ (ref 20).

The relatively good agreement between calculated and observed densities provides confidence in the soundness of the assumptions. The significance of the agreement is that densities of fluoride melts are predictable if the components are sufficiently similar to those treated in this study.

¹⁸F. M. Jaeger, *Z. anorg. Chem.* **101**, 177-78 (1917).

¹⁹J. D. MacKenzie, *J. Chem. Phys.* **32**, 1150 (1956).

²⁰S. S. Kirsliis, *MSRP Quart. Progr. Rept.* Feb. 28, 1961 (to be published).

6. RADIOTRACER TECHNIQUES IN THE STUDY OF INOR-8 CORROSION BY MOLTEN FLUORIDES^{1,2}

G. M. Watson

J. H. DeVan³

R. B. Evans III

When INOR-8 (nominal composition: 7% Cr, 16% Mo, bal Ni) is exposed to a molten fluoride mixture containing reducible material, chromium is selectively oxidized and removed from the alloy. When FeF_2 serves as the oxidant in a polythermal test system the corrosion reaction

is essentially complete at all practical temperatures; use of FeF_2 as the oxidant removes chromium from all portions of the system. The rate of corrosion is controlled by rates of diffusion of chromium within the alloy since the other metals are not oxidized.

The self-diffusion coefficients for chromium in Inconel and INOR-8 and the applicability of these values to alloys under corrosive conditions have been evaluated by use of radiotracer Cr^{51} .

Over-all coefficients have been obtained by measuring the total radioactivity of exposed alloy specimens and that of the salt to which they were exposed.⁴ In addition, coefficients were obtained from measurement of tracer concentration profiles through successive electropolishings of

¹A portion of this summary is an abstract which appears in *Intern. J. Appl. Radiation and Isotopes* 9, 170 (1960).

²Complete tabulation of the experimental INOR-8 data is given in the following: J. H. DeVan, a thesis, *Effect of Alloying Additions on the Corrosion Behavior of Nickel-Molybdenum Alloys in Fused Fluoride Mixtures*, pp 74-106, Department of Chemical and Metallurgical Engineering, University of Tennessee, August 1960.

³Metallurgy Division.

⁴R. B. Evans III, J. H. DeVan, and G. M. Watson, *Self-Diffusion of Chromium in Nickel-Base Alloys*, ORNL-2982 (Jan. 20, 1961).

Fig. 6.1. Self-Diffusion Coefficients for Chromium-51 in INOR-8, Loop 1248.

the metal specimens.⁵ The over-all coefficients and those obtained from electropolishing experiments show reasonable agreement at all temperatures, as shown in Fig. 6.1.

Duplicate polythermal loops of INOR-8 were used to circulate a noncorrosive fluoride melt containing Cr^{51} (as CrF_2). One of these loops was sacrificed to evaluate takeup of Cr^{51} by the alloy, which led to the data mentioned above; the second was used to circulate a melt containing FeF_2 to obtain measurable removal of chromium from the alloy, as shown by the voids present in Fig. 6.2. Good agreement between observed behavior and that predicted from the measured diffusion

⁵G. M. Watson *et al.*, *Reactor Chem. Div. Ann. Progr. Rept.*, Jan. 31, 1960, ORNL-2931, pp 52-63.

Fig. 6.2. Corrosion of INOR-8 Induced by Exposure to Salt Containing FeF_2 . Salt composition, NaF-ZrF_4 (53-47 mole %); FeF_2 concentration, 4000 ppm as Fe^{2+} . Reduced 15%.

coefficients was obtained (as demonstrated by Fig. 6.3). This agreement suggests that the self-diffusion coefficient for chromium can be used to predict corrosion rates – even when the content in the affected portions of the INOR-8 is drastically altered.

Fig. 6.3. Per Cent of Tracer Remaining as a Function of Depth Removed from Specimen Surface.

7. BEHAVIOR OF FISSION PRODUCTS IN A GRAPHITE-MOLTEN SALT SYSTEM

R. E. Adams

W. E. Browning, Jr.

A graphite specimen from experiment 47-2, conducted by personnel from the Reactor Division, was examined in the hot cells at Battelle Memorial Institute. This specimen of graphite (type S4A) had been irradiated in the MTR at about 1300°F for 1600 hr in contact with LiF-BeF₂-ThF₄-UF₄ (67-18.5-1.5-13 mole %). The graphite-salt assembly was contained in a flexible capsule of INOR-8, and the contents of the capsule were maintained under 100 psia through external pressure transmitted through the liquid sodium in the bath surrounding the capsule.

Weight-change data indicated that the graphite specimen had absorbed molten salt to the extent of 0.9 vol %; this value agrees well with that obtained for similar specimens out of pile. Optical examination of the graphite (at magnifications up to 34X) showed the surface to be unaffected; a small amount of molten salt adhered to the bottom surface of the specimen.

The graphite specimen was sectioned in several places, and an autoradiographic study was made of each of the cut faces. The high radiation levels of the graphite sections, which had contact readings in the range of 50 to 100 r/hr, required special autoradiographic techniques to be developed. All evidence, from both the autoradiographs and the core-drilling tests to be described later, indicates that the interior regions of high activity were not merely on the cut diametral surfaces, but extended longitudinally through the graphite. It is postulated that the graphite specimen contained planes of high porosity (visible in cross sections as chords) which had channels to the circumference and possibly to the bottom, into which molten-salt fuel intruded.

Core-drilling apparatus, consisting of a Dumore high-speed bench drill and modified No. 16 hypodermic-needle drills, were used to obtain samples of graphite in specific areas selected from observation of the autoradiographs. Because of the high level of radioactivity it was necessary to conduct the drilling remotely in a hot cell.

Samples were taken along the high-activity chord and along a number of radii for the measurement of activity as a function of distance from the circumference. An enlarged autoradiograph of the drill face is shown in Fig. 7.1. Upon completion of drilling, the specimen was again autoradiographed; a definite reduction in total radioactivity was noted, especially along the chord.

The cores were removed from the drill needles, weighed, and their relative gross gamma activities determined. There was a great variation in unit activities among these cores, which, however, correlated quite well with the location of the hole and activity of the region. With the radial cores, activity increased rapidly as the periphery of the graphite was approached. Interior cores, when located in areas shown by the autoradiograph to be relatively free of activity, were characteristically low, 2000 to 6000 counts min⁻¹ mg⁻¹.

Several typical cores were analyzed with a multichannel gamma spectrometer. Peripheral cores showed principal peaks indicating Ce¹⁴¹-Ce¹⁴⁴, Pa¹³³, Ru¹⁰³-Ru¹⁰⁶, and Zr⁹⁵-Nb⁹⁵, similar to those exhibited by the fused-salt fuel. Cores from the high-activity chord showed

Part II
AQUEOUS REACTOR PROGRAM

9. AQUEOUS SYSTEMS AT ELEVATED TEMPERATURE

W. L. Marshall

E. U. Franck¹

J. E. Savolainen

J. S. Gill

R. Slusher

E. V. Jones

F. J. Smith²

Investigations of phase equilibria in systems suitable for use in aqueous homogeneous reactors have continued. A major part of these investigations deals with the definition of solubility equilibria in the five-component system $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-D}_2\text{O}$ and its accessory four- and three-component systems at temperatures between 300 and 374°C, an upper temperature range of current interest for aqueous homogeneous reactors. Other phase-equilibrium work included the determination of the solubility of UO_3 and ThO_2 at high temperature in solutions of HNO_3 and H_2O . A new program was initiated for the determination of electrolytic conductances of aqueous systems to 800°C and 4000 atm of pressure. Most of the investigations reported have been discussed in homogeneous reactor progress and laboratory reports over the past year.^{3,4} These studies are reviewed briefly in this section.

SOLID-LIQUID EQUILIBRIA IN SULFATE-BASED SYSTEMS: 300–350°C

Investigations on the System $\text{UO}_3\text{-CuO-SO}_3\text{-H}_2\text{O}$

Previous work had established the simultaneous solubility of $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{H}_2\text{O}$ and $\text{CuO}\cdot 3\text{UO}_3$ at 300°C as a function of concentration of total sulfate in the system $\text{UO}_3\text{-CuO-SO}_3\text{-H}_2\text{O}$.⁵ The intent of this present work was to determine simultaneous solubilities for these two solids in this system at 325 and 350°C in order to establish the magnitude of the temperature coefficient of solubility. These experiments have been described in detail elsewhere.⁶ Results at 325 and 350°C are compared in Fig. 9.1 with a curve at 300°C extrapolated from values at higher concentrations of sulfate. These data, plotted in terms of the saturation molal ratios, UO_2^{2+} :total sulfate and Cu^{2+} :total sulfate, appear to indicate an almost undetectable change in solubility between 300 and 350° for the two solids, $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{H}_2\text{O}$ and $\text{CuO}\cdot 3\text{UO}_3$, in concentrations of total sulfate between 0.02 and 0.03 *m*.

¹On leave from the University of Göttingen, Germany, March to November, 1960.

²Summer employee, 1960. Now at Louisiana State University, Baton Rouge.

³H. F. McDuffie *et al.*, *HRP Quart. Progr. Repts.*; Jan. 31, 1960, ORNL-2920, pp 53–75; April 30, 1960, ORNL-2947, pp 47–59; July 31, 1960, ORNL-3004, pp 45–60; Nov. 30, 1960, ORNL-3061, pp 50–60.

⁴W. L. Marshall and E. V. Jones, *Temperatures of Second Liquid Phase Formation for Two Aqueous Homogeneous Reactor Compositions and Their Concentrates*, HRP-60-142 (1960); W. L. Marshall and J. E. Savolainen, *HRP Quart. Progr. Rept.* Jan. 31, 1960, ORNL-2920, pp 62–63.

⁵W. L. Marshall and J. S. Gill, *Investigation of the System $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-H}_2\text{O}$ at 300°C*, ORNL CF-59-12-60, rev 1 (December 1959); *HRP Quart. Progr. Rept.* Jan. 31, 1960, ORNL-2920, pp 64–68.

⁶W. L. Marshall and J. S. Gill, *HRP Quart. Progr. Rept.* Apr. 30, 1960, ORNL-2947, pp 58–59.

Fig. 9.1. Molal Ratios, CuO/SO_3 and UO_3/SO_3 , in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ Solutions at 300, 325, and 350°C, Saturated with $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{H}_2\text{O}$ and $\text{CuO}\cdot 3\text{UO}_3$.

Investigations on the System $\text{CuO-SO}_3\text{-D}_2\text{O}$

The solubility of $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{H}_2\text{O}$, antlerite, was determined previously at 300°C in solutions varying from 0.0025 to 2.0 m in total sulfate.⁵ The present investigation extended the study to the analogous D_2O system at 300, 325, and 350°C and attempted to locate the points of intersection between the solid-liquid region and the region of liquid-liquid immiscibility. The solubilities were determined by the method of direct sampling and subsequent analysis used previously.⁵ In Fig. 9.2, the results at 300°C for the solubility of deuterated antlerite, $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{D}_2\text{O}$, in D_2SO_4 solution are compared with the results obtained in the H_2O system.⁵ The saturation molal ratio, Cu^{2+} : total sulfate, is plotted against the molality of total sulfate on a logarithmic scale to show its variation over a wide range of concentration. The fact that $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{D}_2\text{O}$ in the D_2O system showed a greater solubility than in the corresponding H_2O system is analogous to the behavior of $\text{NiSO}_4\cdot\text{D}_2\text{O}$ and $\text{NiSO}_4\cdot\text{H}_2\text{O}$ at 300°C in $\text{D}_2\text{SO}_4\text{-D}_2\text{O}$ and $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions.

Several saturation molal ratios, Cu^{2+} : total sulfate, were found to have an approximate value of 0.34 at a 0.0014 molality of total sulfate, although the initial solution compositions contained widely different concentrations of D_2SO_4 , all greater than 0.0014 m . This point is believed to constitute an isothermal invariant at which solution, $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{D}_2\text{O}$ solid, and an unidentified solid are stable

phases. Going to lower concentrations than 0.0014 *m* total sulfate, that is, moving from the invariant point, would be expected to eliminate antlerite as a stable solid.

The absence of change within experimental error in saturation molal ratio, as the temperature is raised to 325°C, is shown in Fig. 9.3. These solubility data are compared with the previously determined values at 300°C. The invariant point for the simultaneous existence of the unidentified solid and $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{D}_2\text{O}$ appears to be nearly the same at 300 and 325°C. At 350°C the second liquid phase is believed to exist at high concentrations of solutes and may intersect the ternary *L* + *S* curve in the vicinity of 0.06 to 0.1 *m* total sulfate. At this point, two liquid phases and $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{D}_2\text{O}$ solid would be in equilibrium.

Fig. 9.2. The Solubility of $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{D}_2\text{O}$ in $\text{D}_2\text{SO}_4\text{-D}_2\text{O}$ Solutions at 300°C; Comparison with Analogous H_2O System.

Fig. 9.3. The Solubility of $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{D}_2\text{O}$ in $\text{D}_2\text{SO}_4\text{-D}_2\text{O}$ Solutions at 300, 325, and 350°C.

The saturation molal ratio, Cu^{2+} :total sulfate, at constant molality of total sulfate over the range of concentration in which $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{D}_2\text{O}$ is a stable solid, shows very little decrease as the temperature is raised from 300 to 325°C. As the second liquid phase appears, the decrease in the molal ratio with temperature is considerably greater.

Investigations on the System $\text{NiO-SO}_3\text{-H}_2\text{O}$ Above 300°C

Another important subsystem of the multicomponent system $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-H}_2\text{O}$ is $\text{NiO-SO}_3\text{-H}_2\text{O}$. Solid-liquid equilibria were previously investigated from 10^{-4} to 3 *m* total sulfate at temperatures as

high as 300°C.⁷ No second liquid phase was found. In view of the existence of heavy liquid phases in the $\text{UO}_3\text{-SO}_3\text{-H}_2\text{O}$ and $\text{CuO-SO}_3\text{-H}_2\text{O}$ systems, it was desirable to know whether, under saturation vapor pressure, and at higher temperatures, a second liquid phase might be found in the $\text{NiO-SO}_3\text{-H}_2\text{O}$ system.

Experimental data were obtained by using a synthetic method which entailed sealing in a silica tube a solution of known concentration, inserting the tube in a variable-temperature salt bath, mixing the solution by a vibration technique, and visually observing phase changes.⁸ The results of the earlier study on the nickel system⁷ suggested that the molal ratio, Ni^{2+} :total sulfate, would have to be kept below approximately 0.3 in order to achieve stability much above 300°C. The over-all experimental results are shown in Fig. 9.4, plotted as saturation molal ratio, Ni^{2+} :total sulfate vs temperature, for several concentrations of total sulfate. Included as terminal points in the figure are critical temperatures for solutions of H_2SO_4 in H_2O obtained previously by Stuckey and Secoy.⁸ The present results must extrapolate to the values of the earlier work as the molal ratio, Ni^{2+} :total sulfate, approaches zero. The combined data show that no two-liquid-phase region was observed. It was found, however, that the solubility of NiO in the supercritical fluid extended to molal ratios,

⁷ W. L. Marshall, J. S. Gill, and R. Slusher, *HRP Quart. Progr. Rept. July 31, 1958*, ORNL-2561, pp 308-11.

⁸ J. E. Stuckey, *Critical Phenomena in Binary Aqueous Solutions in the System $\text{SO}_3\text{-H}_2\text{O}$* , Ph.D dissertation, University of Oklahoma, Norman, 1957.

Fig. 9.4. System $\text{NiO-SO}_3\text{-H}_2\text{O}$ Above 250°C; Solubility in Supercritical Fluid and Solid-Liquid Equilibria.

Ni^{2+} : total sulfate, a little greater than 0.1, at least for solutions from 0.5 to 2 *m* in total sulfate. The location of the point of intersection of the critical curve with the solid-liquid curve suggests that the solubility of NiO is greater than 0.2 *m* but less than 0.3 *m* in a supercritical fluid 2 *m* in total sulfate.

Application of these findings to the multicomponent system $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-H}_2\text{O}$ suggests that there must be a portion of the system, adjacent to the $\text{NiO-SO}_3\text{-H}_2\text{O}$ edge, which is saturated with a nickel-containing solid phase; consequently, no complete definition of the five-component system at saturation vapor pressure in terms of liquid-liquid-vapor equilibria appears possible.

**LIQUID-LIQUID IMMISCIBILITY AND SOLUBILITY IN THE SUPERCRITICAL FLUID
IN THE SYSTEM $\text{UO}_3\text{-CuO-SO}_3\text{-D}_2\text{O}$ AND ITS THREE-COMPONENT SUBSYSTEMS,
 $\text{UO}_3\text{-SO}_3\text{-D}_2\text{O}$ AND $\text{CuO-SO}_3\text{-D}_2\text{O}$**

The determination of liquid-liquid immiscibility boundaries and critical temperatures in the systems $\text{UO}_3\text{-CuO-SO}_3\text{-D}_2\text{O}$, $\text{UO}_3\text{-SO}_3\text{-D}_2\text{O}$, and $\text{CuO-SO}_3\text{-D}_2\text{O}$ forms a part of the over-all study of the five-component system $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-D}_2\text{O}$ at temperatures above 300°C. A previous study presented information up to 300°C on solid-liquid equilibria in the system $\text{NiO-SO}_3\text{-H}_2\text{O}$,⁷ another important subsystem of the five-component system, and in its D_2O analog.⁹ The investigation of the system $\text{NiO-SO}_3\text{-H}_2\text{O}$ above 300°C, reported in this section, indicated the temperatures at which supercritical fluids are formed (i.e., the temperature at which the meniscus between the vapor and liquid phases disappears) and presented evidence of the solubility of the NiO component in the supercritical fluid. Other studies showed the nature and composition of the heavy-liquid phases in equilibrium with the light-liquid phases in the system $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-D}_2\text{O}$ and its four- and three-component subsystems at 285, 300, 325, and 350°C.¹⁰ A desirable goal of this work is the development of an equation to express the two-liquid-phase and critical-temperature boundaries as a function of the concentrations of the various solution components.

In this investigation, using a synthetic method previously described,¹¹ critical temperatures and the temperatures of formation of a second liquid phase were determined for a set of solution compositions containing CuSO_4 , UO_2SO_4 , D_2SO_4 , and D_2O in which the molal ratio, $\text{Cu}^{2+}:\text{UO}_2^{2+}$, was kept at unity. The set of solutions was divided into several series; the molal concentration of total sulfate was held constant for each series, and the molal ratio $[(\text{Cu}^{2+} + \text{UO}_2^{2+}):\text{total sulfate}]$, *R*, was varied from 0 to 1. This procedure was used since in previous work *R* values for the formation of a second liquid phase for any series appeared to be nearly linear with temperature. The results are displayed in Fig. 9.5 and show approximately linear relationships.

⁹W. L. Marshall, J. S. Gill, and R. Slusher, *HRP Quart. Progr. Rept. Apr. 30, 1959*, ORNL-2743, pp 235-37.

¹⁰E. V. Jones and W. L. Marshall, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, pp 100-103.

¹¹C. J. Barton, G. M. Hebert, and W. L. Marshall, *Liquid-Liquid Immiscibility Above 300°C in the System $\text{UO}_3\text{-SO}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$* , ORNL CF-59-11-64 (November 1959); *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, p 111.

Fig. 9.5. Liquid-Liquid Immiscibility and Critical Phenomena in the System $\text{UO}_3\text{-CuO-SO}_3\text{-D}_2\text{O}$; $\frac{m \text{ Cu}^{2+}}{m \text{ UO}_2^{2+}} = 1$.

The two-liquid-phase regions in the subsystems $\text{UO}_3\text{-SO}_3\text{-D}_2\text{O}$ and $\text{CuO-SO}_3\text{-D}_2\text{O}$ were investigated by using the same experimental methods and techniques. These data are presented in Figs. 9.6 and 9.7.

The results in Figs. 9.5, 9.6, and 9.7 show considerable solubility for both UO_2^{2+} and Cu^{2+} ions in the supercritical fluid region, as might have been expected from previous preliminary observations in the system $\text{UO}_3\text{-SO}_3\text{-H}_2\text{O}$.¹² If hydrodynamic pressures greater than the critical pressures of liquid phases having a low molal ratio, metal oxide: total sulfate, are maintained on fuel systems at lower temperature and the temperature is raised, the solution phases may be phase stable to temperatures somewhat above 400°C. Critical phenomena, that is, disappearance of the meniscus, are not observed in these cases since a pressure greater than the critical pressure never allows the existence of a vapor phase. On a long-range basis, this means that a sulfate-based reactor fuel might be available for aqueous homogeneous reactors operating at temperatures above 400°C.

¹²W. L. Marshall and G. M. Hebert, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, pp 100-103.

Fig. 9.6. Liquid-Liquid Immiscibility and Critical Phenomena in the System $\text{UO}_3\text{-SO}_3\text{-D}_2\text{O}$.

Fig. 9.7. Liquid-Liquid Immiscibility and Critical Phenomena in the System $\text{CuO-SO}_3\text{-D}_2\text{O}$.

AQUEOUS HOMOGENEOUS REACTOR FUEL STUDIES

Estimation of Minimum Temperatures of Second Liquid Phase Formation in Homogeneous Reactor Fuel Concentrates: Use of the Acidity Ratio

The temperatures for the appearance of a second liquid phase were determined for two aqueous homogeneous reactor fuel compositions (series A and B) and for three sets of solutions of UO_2SO_4 , CuSO_4 , and D_2SO_4 in D_2O (series C) and their concentrates. In series C the molal ratio, $\text{UO}_2^{2+}:\text{Cu}^{2+}$, was kept constant at 1.0. The data are intended to supplement those given previously.¹³ Comparison of the results herein with those previously presented suggests a more general criterion for estimation of the minimum liquid-liquid immiscibility temperatures for homogeneous reactor fuel concentrates.

The experimental details have been reported elsewhere.¹⁴ Temperatures for the appearance of liquid-liquid immiscibility were determined by visual observations in the conventional manner.¹¹

¹³W. L. Marshall, R. E. Moore, and J. S. Gill, *Two Liquid Phase Temperature Limits for the Homogeneous Reactor Fuel Solution and Its Concentrates*, ORNL CF-59-8-41 (August 1959) and ORNL CF-59-11-27 (November 1959); *Reactor Chem. Div. Ann. Progr. Rept.* Jan. 31, 1960, ORNL-2931, pp 103-5.

¹⁴W. L. Marshall and E. V. Jones, *Temperatures of Second Liquid Phase Formation for Two Aqueous Homogeneous Reactor Compositions and Their Concentrates*, HRP-60-142 (1960); W. L. Marshall and J. E. Savolainen, *HRP Quart. Progr. Rept.* Jan. 31, 1960, ORNL-2920, pp 62-63.

Experimental results are plotted in Fig. 9.8 for series A and B and in Fig. 9.9 for series C. The concentration factor x , when multiplied by the concentration of a component at $x = 1$, gives the molar (at 25°C) concentration of that component in the concentrate. This concentration factor was converted to unity at approximately 0.0258 M (or the equivalent 0.0218 m UO_2^{2+}) for comparison with results presented previously.¹³ Molar concentrations (at 25°C) at $x = 1$ are given in Table 9.1. A solution of series A at $x = 1$ corresponds closely to a homogeneous reactor fuel composition used recently, whereas in series B the relative concentration of free acid is a little higher.

In Fig. 9.10 the lowest temperature for the appearance of liquid-liquid immiscibility upon concentration of a fuel composition is plotted against the molal ratio, D_2SO_4 :total sulfate. Figure 9.11 shows the variation in the molar concentration factor at the minimum temperature as a function of this

Fig. 9.8. The Temperature of Appearance of Liquid-Liquid Immiscibility as a Function of Dilution and Concentration of Two HR Fuel Compositions. $x = 1$ at 0.0258 M (25°C) UO_2SO_4 (D_2O solutions).

Fig. 9.9. The Temperature of Appearance of Liquid-Liquid Immiscibility of Several Solutions of UO_2SO_4 , CuSO_4 , D_2SO_4 , and D_2O as a Function of Concentration Factor.

Table 9.1. Molar Concentrations of Solution Components at $x = 1$ for Solution Series A, B, and C

Species	Molarity (at 25°C)				
	A	B	Set 1	Set 2	Set 3
UO_2SO_4	0.0258	0.0258	0.025	0.025	0.025
CuSO_4	0.0131	0.0134	0.025	0.025	0.025
NiSO_4	0.00852	0.00878	0	0	0
D_2SO_4	0.0247	0.0347	0.025	0.037	0.050
Total sulfate	0.0721	0.0827	0.075	0.087	0.100

Fig. 9.10. Minimum Temperature for Appearance of Liquid-Liquid Immiscibility in Aqueous Homogeneous Reactor Fuel Concentrates.

Fig. 9.11. Concentration Factor at Minimum Temperature for Appearance of Liquid-Liquid Immiscibility in Aqueous Homogeneous Reactor Fuel Concentrates.

same molal ratio, hereafter called the acidity ratio. For these curves, prepared from data in ref 13, the molal ratio, $\text{UO}_2^{2+}:\text{Cu}^{2+}:\text{Ni}^{2+}$, is 1:0.492:0.232, as compared with 1:0.506:0.330 for series A and 1:0.519:0.340 for series B. The two-liquid-phase minimum temperatures obtained from the curves in Fig. 9.8 are 1°C lower for series A and 2°C lower for series B than the curve in Fig. 9.10 would indicate at the corresponding acidity molal ratios (D_2SO_4 : total sulfate) of 0.343 and 0.420. Doubling

the relative concentration of Cu^{2+} and eliminating Ni^{2+} to give a molal ratio, $\text{UO}_2^{2+}:\text{Cu}^{2+}:\text{Ni}^{2+}$, of 1:1:0 (series C, Fig. 9.9) raised the temperature at the minimum by only 8, 6, and 4°C at acidity molal ratios (D_2SO_4 :total sulfate) of 0.33, 0.43, and 0.50 respectively. These latter changes in temperature are small, considering that the relative Cu^{2+} concentration was increased by 100% and Ni^{2+} was eliminated.

Large differences in temperature for small changes in the acidity ratio, D_2SO_4 :total sulfate, and small differences in temperature for moderately large changes in molal ratios, $\text{Cu}^{2+}:\text{UO}_2^{2+}$ and $\text{Ni}^{2+}:\text{UO}_2^{2+}$, substantiate the belief that relative acidity is the most important variable in the range of current homogeneous reactor fuel compositions. As secondary effects, an increase in the molal ratio, $\text{Ni}^{2+}:\text{UO}_2^{2+}$, appears to lower by a small amount the temperature for occurrence of immiscibility, whereas an increase in the molal ratio, $\text{Cu}^{2+}:\text{UO}_2^{2+}$, for most ranges of composition raises this temperature (see Fig. 9.9 and ref 15).

As a first approximation, the curve in Fig. 9.10 may be used to estimate two-liquid-phase minimum temperatures within 2 or 3°C for solution concentrates of current homogeneous reactor fuel compositions showing moderate variations in molal ratios, $\text{Cu}^{2+}:\text{UO}_2^{2+}$ and $\text{Ni}^{2+}:\text{UO}_2^{2+}$, and large variations in the acidity ratio, D_2SO_4 :total sulfate.

The pH of Solutions Containing UO_2SO_4 , CuSO_4 , NiSO_4 , H_2SO_4 , H_2O , and D_2O : Its Use in the Determination of Free Acid in Homogeneous Reactor Fuels

The precise measurement of pH of intensely radioactive homogeneous reactor fuel solutions by use of glass electrodes is difficult because of the detrimental effect of radiation on glass. The glass electrode must be replaced frequently, a procedure which may become difficult, since the electrodes and part of the equipment are used in "hot cells." However, if the intensely radioactive solution were diluted considerably with H_2O , it was believed the pH of the resulting solution of lowered radioactivity might be measured with less difficulty. A study was made for determining the pH at 25°C of various dilutions of solutions simulating the HRT fuel composition and of similar solutions containing varying concentrations of the major fuel components.

Hopes for the ultimate usefulness of the method were predicated on the expectation that the pH measurements of diluted fuel solutions would, to a close approximation, give values the same as those for sulfuric acid at the same concentration as that of the free acid in the test solutions, that is, that the diluted UO_2SO_4 , CuSO_4 , and NiSO_4 would have little effect on the pH of the diluted H_2SO_4 . Moreover, dilution by H_2O of solutions initially in D_2O would convert the measured solutions to dilute H_2O solutions and substantially eliminate any effect on pH due to D_2O .

The experimental technique was similar to that used for the determination of free nitric acid in uranyl nitrate solutions, reported previously.¹⁶ Five aliquots from each of four stock solutions A, B,

¹⁵F. E. Clark *et al.*, *J. Chem. Eng. Data* 4, 12-15 (1959).

¹⁶W. L. Marshall and R. Slusher, *HRP Quart. Progr. Rept. Oct. 31, 1959*, ORNL-2879, pp 119-21.

C, D, containing in A, 0.025 M UO_2SO_4 , 0.0125 M CuSO_4 , and 0.006 M NiSO_4 ; in B, 0.025 M UO_2SO_4 , 0.025 M CuSO_4 , and 0.006 M NiSO_4 ; in C, 0.025 M UO_2SO_4 , 0.0125 M CuSO_4 , and 0.12 M NiSO_4 ; and in D, 0.05 M UO_2SO_4 , 0.0125 M CuSO_4 , 0.006 M NiSO_4 , were made 0.01, 0.02, 0.03, 0.04, and 0.05 M in D_2SO_4 respectively. The measured pH's for these 20 solutions, each diluted 1:10, 1:100, and 1:1000, have been reported.¹⁷ These values are plotted in Fig. 9.12 vs the known concentration of free acid present in each dilution. It is obvious that the original expectation was justified except for the 1:1000 dilutions of solutions which initially had low concentrations.

Fig. 9.12. The pH of Dilutions of UO_2SO_4 , CuSO_4 , NiSO_4 , and D_2SO_4 in D_2O Solution; pH vs Free D_2SO_4 (Dilutions with H_2O).

Three-Dimensional Models for Representation of Solubility Equilibria

Three-dimensional models representing the solubility relationships in the system $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-D}_2\text{O}$ at 300°C were constructed for solutions having total sulfate concentrations of 0.06, 0.10, 0.20, 0.30, and 0.50 m . The results of previously reported solubility studies¹⁸ were used to establish the location of the surfaces of saturation for the several solid and liquid phases which appear at the boundary limits of the region of unsaturated solutions. The particular saturating phases shown in these models are the solids $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{D}_2\text{O}$, $\text{NiSO}_4\cdot\text{D}_2\text{O}$, $\text{UO}_3\cdot\text{UO}_2\text{SO}_4\cdot 5\text{D}_2\text{O}$, $\text{CuO}\cdot 2\text{UO}_2\text{SO}_4\cdot 7\text{D}_2\text{O}$, $\text{CuO}\cdot 3\text{UO}_3$, $\text{NiO}\cdot 3\text{UO}_3$ and a second liquid phase of variable composition.

All five models are shown in Fig. 9.13 for comparison. The unit of length, $m_{\text{metal oxide}}/m_{\text{total sulfate}}$, on all axes is the same for all models; therefore, dimensional changes as a function of sulfate concen-

¹⁷W. L. Marshall and R. Slusher, *HRP Quart. Progr. Rept. Jan. 31, 1960*, ORNL-2920, pp 68-70.

¹⁸W. L. Marshall and J. S. Gill, *Investigation of the System $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-H}_2\text{O}$ at 300°C* , ORNL CF-59-12-60, rev 1 (December 1959); *HRP Quart. Progr. Rept. Jan. 31, 1960*, ORNL-2920, pp 64-68.

Fig. 9.13. Three-Dimensional Models Representing System $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-D}_2\text{O}$ at 300°C ; 0.06, 0.1, 0.2, 0.3, and 0.5 Molal in Total Sulfate.

tration are directly comparable. A series of these models shows the change in surface area for saturating solid phases as the total sulfate concentration is varied. In general, there appear to be several concentration ranges over which different types of solids are stable. At very low sulfate concentrations, hydroxides and oxides are stable – the areas of saturation may become independent of anionic solvating species and should appear the same in a nitrate as well as in a sulfate system. At moderately low concentrations of total sulfate, oxysulfates appear, for example, $2\text{NiO} \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$, $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{D}_2\text{O}$, and $\text{UO}_3 \cdot \text{UO}_2\text{SO}_4 \cdot 5\text{D}_2\text{O}$, whereas at higher concentrations the stoichiometric salts, such as the solid $\text{NiSO}_4 \cdot \text{D}_2\text{O}$ or the liquid pseudosalt $\text{UO}_2\text{SO}_4 \cdot \text{D}_2\text{O}$, engulf the oxysulfate surfaces. At the highest concentrations, the acid salts should appear.

These models are useful for selecting fuel compositions for homogeneous reactors and for anticipating solid phases which may precipitate from solution if boundaries of saturation are violated. They form a background of information from which to make further studies.

SOLID-LIQUID EQUILIBRIA IN NITRATE-BASED SYSTEMS

The System $\text{UO}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ from 25 to 350°C

Investigations on the system $\text{UO}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ were essentially completed.¹⁹ Figures 9.14 and 9.15 show the over-all collection of data for this system. Both figures include new information at 325 and 350°C at very low and very high concentrations. In Fig. 9.15 the curves taken from the data in Fig. 9.14 are shown on the same scale for saturation molal ratio, UO_2^{2+} : total nitrate vs logarithm of the molality of the total nitrate at the various temperatures.

The System $\text{ThO}_2\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ at 200 and 300°C

Investigations of the thermal and hydrolytic stability of $\text{Th}(\text{NO}_3)_4$ in H_2O solution at elevated temperature were among the first solubility studies to be made on the Aqueous Homogeneous Reactor Project.²⁰ These earlier investigations were carried out in sealed tubes, using the synthetic method. The renewed interest in $\text{Th}(\text{NO}_3)_4\text{-DNO}_3\text{-D}_2\text{O}$ solutions as a breeder blanket suggested that the earlier investigations of the $\text{ThO}_2\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ system be extended.

Pressure vessels used for the study of solution-solid equilibria in other systems were employed.¹⁸ These vessels were equipped with capillary tubes for direct sampling to permit analysis of the liquid. They were charged with selected levels of nitrate and an excess of thorium, either by the use of $\text{Th}(\text{NO}_3)_4$ solutions or mixtures of ThO_2 and nitric acid solutions. The vessels were then sealed and rocked at 200 or 300°C for 2-, 20-, 24-, and 48-hr periods. After each period the rocker was stopped, the excess solid allowed to settle, and the solution sampled. The solution sample was analyzed for its Th^{4+} and NO_3^- content. Experimental results are shown graphically in Fig. 9.16. The solid ThO_2

¹⁹W. L. Marshall and R. Slusher, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, pp 108–10.

²⁰W. L. Marshall, J. S. Gill, and C. H. Secoy, *HRP Quart. Progr. Rept. Nov. 30, 1950*, ORNL-925, pp 279–90.

Fig. 9.14. The Solubility of $\text{UO}_3 \cdot \text{H}_2\text{O}$ in $\text{HNO}_3\text{-H}_2\text{O}$ Solutions, 25 to 350°C; Set A.

Fig. 9.15. The Solubility of $\text{UO}_3 \cdot \text{H}_2\text{O}$ in $\text{HNO}_3\text{-H}_2\text{O}$ Solutions, 25 to 350°C; Set B.

Fig. 9.16. Solubility of ThO_2 in $\text{HNO}_3\text{-H}_2\text{O}$ Solutions at 200 and 300°C.

used in these experiments was selected from three different batches of the oxide, each prepared by precipitation from thorium nitrate solution as the oxalate and then calcined at a different temperature. The data are listed below:

ThO ₂ Product	ORNL Pilot Plant No.	Calcination Temperature (°C)
A	DT-58-650	650
B	DT-58-1100	1100
C	DT-15-1600	1600

These three batches of oxide, having different surface areas and chemical reactivities as a result of the differences in calcination temperatures, were tested to establish whether equilibrium conditions were truly being established in the solubility experiments. The results in Fig. 9.16 show that at 300°C, the HNO₃-H₂O solutions were saturated at the end of the runs to approximately the same extent by all three different preparations of ThO₂. Furthermore, in the majority of runs, the solutions became saturated or precipitated solid to reach a stable saturation concentration after a 2-hr period at both 200 and 300°C.

Examination of the solubility data for ThO₂ in HNO₃-H₂O at 300°C showed a sharp decrease in the saturation molal ratio, Th⁴⁺:total nitrate, at concentrations of NO₃⁻ below 10.0 M (25°C molarity), whereas for the analogous system, UO₃-N₂O₅-H₂O, the decrease was very much less (see previous part on system UO₃-N₂O₅-H₂O). At 200°C, this very sharp decrease in saturation molal ratio was not evident, but the studies have not been extended to very low concentrations of NO₃⁻. The analogous D₂O systems should show relatively little difference in solubility relationships from the H₂O systems.

The rapid rate at which the various forms of refractory ThO₂ dissolved in HNO₃-H₂O solution at 200 and 300°C may be of considerable interest. At temperatures up to 100°C the dissolving rate is very low; consequently, in the chemical reprocessing of ThO₂ fuel elements, a small amount of HF is customarily added to HNO₃ to promote the dissolution. In these studies, no HF or other complexing agent was present, but the rates of solution were fast. Methods by which refractory ThO₂ or other refractory oxides can be rapidly dissolved in pressure vessels at 200°C, 300°C, or higher should be of general interest in chemical processing.

ELECTROLYTIC CONDUCTANCE OF AQUEOUS SOLUTIONS AND SUPERCRITICAL FLUIDS AT HIGH TEMPERATURE AND PRESSURE

The construction of cells for the measurement of electrolytic conductance of aqueous solutions and supercritical fluids at high temperature and pressure and associated high-pressure generating equipment was completed. The electrolytic conductivities for a 0.01 *m* KCl solution were determined at

pressures up to 4000 atm at 800°C as well as at lower temperatures. Some preliminary results at 800°C are shown in Fig. 9.17, plotted as conductance, $1/R$, against the pressure. The cell constant was estimated as 0.32 ($\pm 4\%$) from conductance measurements of the 0.01 *m* KCl solution at the ambient temperature $27 \pm 2^\circ\text{C}$. A constant-temperature bath, which was not available for the preliminary work, will be used later for the accurate determination of the cell constant. The conductivity values are to be converted to equivalent conductivities by making use of estimated densities of the supercritical KCl-H₂O fluid and a precisely measured cell constant.

Fig. 9.17. Conductance Readings of 0.01 Molal KCl in H₂O Solution at 800°C and up to 4000 atm.

The construction of the apparatus shown in Fig. 9.18 and preliminary measurements were carried out under the direction of E. U. Franck. These measurements are believed to be the first made at 800°C and 4000 atm. The previous record, conductance measurements at 700°C and 2500 atm, was achieved by Franck in Göttingen.

Fig. 9.18. Apparatus for Electrical Conductivity Studies at Elevated Temperatures and Pressures.

10. REACTIONS IN AQUEOUS SOLUTIONS

DECOMPOSITION OF PEROXIDE IN URANYL NITRATE SOLUTIONS

M. J. Kelly

M. D. Silverman

G. M. Watson

A study was made for determining whether the decomposition of peroxide in uranyl nitrate solutions was sufficiently rapid to support consideration of uranyl nitrate solutions as potential aqueous homogeneous reactor fuels.¹ The experimental work was restricted to uranium concentrations of 0.034 M, but both H₂O and D₂O were tested as solvents, and several possible catalysts and promoters were studied within the temperature range 40 to 100°C. Most studies were made in solutions containing 0.05 M excess HNO₃.

The problems caused by the radiolytic production of peroxide in reactor fuel solutions, the equilibrium between H₂O₂ and uranium peroxide, and the relatively low solubility of uranium peroxide have been discussed in connection with studies of the kinetics of the decomposition of peroxide in uranyl sulfate solutions.^{2,3}

In all previous work the decomposition of peroxide in uranyl solutions was found to be first-order with respect to peroxide; most of the results of this study followed the same pattern. Experimental data and figures showing the effects of temperature, acidity, and catalysts have been reported.⁴

The effect of promoters (mixed iron and copper salts) was studied in more detail than in previous work.² The results obtained show that:

1. Promotion increased with increasing copper concentration, reaching a plateau or saturation value at about 0.0005 M Cu²⁺ (30 ppm). These results are shown in Fig. 10.1, where, for fixed-iron concentrations, values of k (the decomposition rate constant) are plotted vs the copper concentration.
2. The rate of decomposition was first-order (with respect to H₂O₂) only at low copper concentrations but became complex at high concentrations.
3. The activation energy of the "promoted" system was the same as that of the original process, approximately 25,000 cal/mole, suggesting that the mechanism of decomposition is probably the same and lending strong argument to the belief that minute amounts of iron are responsible for the catalysis in "purified" solutions.
4. The promotion factor, $\Delta k/k_0$, seemed to decrease with increasing iron concentration (see Fig. 10.2).

¹W. L. Marshall, *Consideration of UO₂(NO₃)₂·HNO₃·H₂O (D₂O) as a High Temperature Homogeneous Reactor Fuel*, ORNL CF-59-5-100 (May 26, 1959).

²M. D. Silverman, G. M. Watson, and H. F. McDuffie, *Ind. Eng. Chem.* **48**, 1238 (1956).

³L. O. Gilpatrick and H. F. McDuffie, *HRP Quart. Progr. Rept.* July 31, 1958, ORNL-2561, p 313.

⁴M. J. Kelly, M. D. Silverman, and G. M. Watson, *HRP Quart. Progr. Rept.* Apr. 30, 1960, ORNL-2947, p 47.

Fig. 10.1. Effect of Copper as a Promoter for Iron-Catalyzed Peroxide Decomposition: Nitrate System.

Fig. 10.2. Copper Promotion Factors in Iron-Catalyzed Peroxide Decomposition: Nitrate System.

Extrapolation of these results to higher temperatures suggests that peroxide decomposition rates should prove adequate under hypothetical reactor conditions for systems based on uranyl nitrate.

DISSOLUTION OF INORGANIC SOLIDS IN HRE-2 FUEL

M. J. Kelly
D. R. Cuneo L. O. Gilpatrick M. D. Silverman

A study was made for determining the dissolution rates of solids in simulated HRE-2 fuel in well-stirred autoclaves at $\sim 250^\circ\text{C}$. This study was limited to those solids which could conceivably have existed within the HRE-2 core as a consequence of off-design operation. The solids tested were UO_3 , UO_2 , U_3O_8 , $\text{CuO} \cdot 3\text{UO}_3$, and reactor-solution solids prepared by drying simulated fuel solution and calcining at 500°C . Under the test conditions these solids dissolved rapidly, generally following apparently first-order kinetics. The experimental details are discussed elsewhere.⁵

In every experiment the rate of solution of the solid was fast, the apparent half-life varied from less than 0.5 min to 2.5 min.

⁵M. D. Silverman *et al.*, HRP Quart. Progr. Rept. July 31, 1960, ORNL-3004, p 45.

Experiments using UO_3 and solids prepared by evaporating simulated reactor fuel and calcining these solids at 500°C showed rates of solution so rapid that calculation of the rate constant was impractical. Experiments using $\text{CuO} \cdot 3\text{UO}_3$ as the initial solid seemed to indicate that the uranium and copper dissolved at different rates. The apparent half-life was less than 2.0 min for both components, with uranium returning to solution more quickly

The most refractory components in this group of solids (U_3O_8 and UO_2) were investigated more thoroughly. Figure 10.3 shows a plot of the results, based on the assumption of a first-order process.

The results suggest that the solids tested, if formed in the reactor, should redissolve promptly under conditions of good agitation such as have been provided by the present modifications to the HRE-2. This conclusion is predicated upon the availability of excess acid and oxygen at the reaction site. Since all these solids are rich in uranium, the local area of high fission density and,

Fig. 10.3. Dissolution of Solids U_3O_8 and UO_2 in $0.003 \text{ M } \text{UO}_2\text{SO}_4 + \text{Excess } \text{H}_2\text{SO}_4$.

therefore, high temperature created by the solid could result in an inability of the solution to make contact with the solid particle as long as it remained in a high-intensity neutron flux.

REMOVAL OF PROTACTINIUM AND URANIUM FROM THORIUM NITRATE-NITRIC ACID SOLUTIONS

M. J. Kelly

G. L. Johnson⁶

D. R. Cuneo

Successful use of thorium nitrate as a breeder blanket component would be dependent, in part, on the continuous removal of protactinium to maintain a low steady-state concentration in the blanket solution. This would prevent excess neutron loss by capture and allow decay of the Pa^{233} to U^{233} , a fissionable product.

Previous work on the removal of protactinium from molten salts⁷ by precipitation on thorium oxide suggested the investigation of the adsorption of protactinium on thorium. At low ($<0.5\text{ M}$) concentrations of thorium nitrate adsorption did occur. Increasing the thorium concentration or the addition of nitric acid caused this effect to disappear.

The most promising alternate seemed to be the coprecipitation of protactinium and uranium with a thorium compound.⁸ Coprecipitation with thorium peroxide appeared feasible⁹ and provides so many advantages that it was the second system investigated. The experimental procedures are reported in some detail elsewhere.¹⁰

A clear-cut example of the success of the technique in removing protactinium from solution is shown in Fig. 10.4. The shaded area represents that fraction of the total peroxide which was in the form of thorium peroxide precipitate and had been removed from the supernatant fluid by centrifugation. Based on a 2-to-3 correspondence between hydrogen peroxide and thorium peroxide it was calculated that some 2% of the total thorium had been precipitated. At the same time, nevertheless, 96% of the tracer protactinium had been removed!

When the soluble peroxide level fell below 0.2 M (at $\sim 275\text{ min}$) the protactinium began to return to solution, it appears likely that enforcement of a steady-state level of 0.225 M soluble peroxide would have also effectively precipitated the protactinium.

The effect of temperature on the rate of peroxide decomposition is shown in Fig. 10.5. The energy of activation calculated from these data corresponds to $22 \pm 2\text{ kcal/mole}$, a value which is very close to those for the catalyzed decomposition of peroxide in uranium solution systems.

⁶Research participant from Duke University.

⁷J. H. Shaffer *et al.*, *The Recovery of Uranium and Protactinium from Molten Fluoride Systems by Precipitation as Oxides*, paper 37 presented at First Conference on Nuclear Reactor Chemistry, Gatlinburg, Tenn., Oct. 12-14, 1960.

⁸T. F. Connolly, *Bibliography on Nuclear Reactor Fuel Reprocessing and Waste Disposal*, ORNL-2971, vol 2 (Sept. 19, 1960).

⁹L. I. Katzin (ed.), *Production and Separation of U^{233}* , TID-5223, part 1, pp 318-47.

¹⁰M. J. Kelly, G. L. Johnson, and D. R. Cuneo, *HRP Quart. Progr. Rept.*, Oct. 30, 1960, ORNL-3061, p 43.

Fig. 10.4. Coprecipitation of Pa²³³ Tracer with Thorium Peroxide.

Fig. 10.5. Effect of Temperature on Peroxide Decomposition.

It was noted that increasing the acidity, with all other conditions constant, caused an increase in the rate of reaction. This result was contrary to the usual experience in uranium systems.

The concentration of peroxide necessary for precipitation apparently varied with the ratio of thorium to acid. For 2 M thorium solutions the threshold level of peroxide for precipitation was a function of the stoichiometric acid concentration, as shown in Table 10.1. The small change between the 0.922 M value and the stoichiometric value may be rationalized by the comment that the measured pH of 2.0 M thorium nitrate solution was approximately zero.

Table 10.1. Threshold Level of Peroxide for Precipitation

Solution: 2 M $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$
 Temperature: 55°C

Acid Concentration (M)	Peroxide Concentration for Precipitation (M)
0.00	0.085 ± 0.01
0.922	0.105 ± 0.01
1.892	0.20 ± 0.01
3.544	0.40 ± 0.02

Whenever sufficient peroxide was added to cause precipitation of particulate material which could be satisfactorily centrifuged from the solution, the protactinium was removed with the precipitate. The protactinium did not reappear in solution so long as any observable precipitate was present. It seems reasonable to assume that the protactinium peroxide is more insoluble than the thorium peroxide and that quantities greater than 5 ppm could be removed by precipitating a very small quantity of the thorium. Protactinium-231 is available for experiments to test this assumption.

A single experiment was run at 48.9°C with 2 M thorium nitrate, 2 M HNO_3 , and ~75 ppm uranium, using the technique described above. Uranium was *not* removed from the solution when a portion of the thorium was precipitated. Another experiment, identical to this one except for the initial addition of protactinium tracer, showed that the protactinium was removed as successfully in the presence of uranium as in the experiments with no uranium present.

The results seem to indicate that protactinium could be held at an arbitrarily low steady-state concentration in a thorium nitrate-nitric acid breeder blanket solution. This could be accomplished by coprecipitating the protactinium together with a small percentage of the thorium by means of peroxide addition in a side-stream operation. The peroxide remaining in solution will decompose, leaving no undesirable contaminants in the blanket solution.

AQUEOUS RECOVERY OF Pa^{231} FROM A FLUORIDE MIXTURE

M. J. Kelly

D. R. Cuneo

J. E. Strain¹¹

Following studies of protactinium removal from the mixture $\text{LiF-BF}_2\text{-ThF}_4$ (67-18-15 mole %),¹² attempts were made to recover the Pa^{231} which had been added to the mixture to simulate the concentration range of Pa^{233} formed in a breeder blanket.

¹¹Analytical Chemistry Division.

¹²See chap 2, this report.

The protactinium removal studies were concluded, leaving a mixture of $\text{LiF}\cdot\text{BeF}_2\cdot\text{ThF}_4\cdot\text{UO}_2\cdot\text{UF}_4$ plus some 50 ppm of Pa^{231} and a trace amount of Pa^{233} . As a first step in Pa^{231} recovery, the melt described above was hydrofluorinated to convert all constituents to their fluorides and then exposed to either BeO or ThO_2 in the form of small pellets contained in a wire-mesh screen. The gamma activity of the melt before and after such exposure indicated this to be a valid method of removing the protactinium from the multicomponent system to a smaller volume of a single compound, that is, either BeO or ThO_2 . Successive exposures of the melt to fresh oxide reduced the protactinium content, as indicated by gamma counting, to a relatively low level.

The oxides containing the protactinium were added to a water-soluble KF melt to which sufficient BeF_2 had been added to reduce the melting point to below 750°C . The system was then hydrofluorinated to remove the oxide. The fluoride salts formed were treated with fuming sulfuric acid to remove the fluoride. Complete removal of the fluoride was impractical, so AlCl_3

Table 10.2. Material Balance for Protactinium Recovery as Determined by Pa^{233} Gamma Activity
Activity of initial salt mixture: $21.5 \times 10^4 \text{ counts min}^{-1} \text{ g}^{-1}$

	Activity (counts/min)
	$\times 10^7$
Total activity of salt sample used ^a	8.49
Activity removed by sampling	2.99
Theoretical activity remaining in reaction vessel	5.50
Activity lost on exterior of sample sticks and in samples not returned to vessel (only more active material returned)	3.75
Activity after returning portion of sampled material to vessel (available for recovery by BeO , ThO_2)	4.74
Activity left in reaction vessel after BeO , ThO_2 contacted with melt	0.88
Activity available for aqueous recovery attempts (contained in 218 g of salt)	3.86
Activity recovered by aqueous processing [contained in 51 mg of solids - chiefly as $\text{Pa}_2(\text{SO}_4)_5$]	3.01
Summary of Pa^{231} usage:	
Physically recovered	35.5%
Lost in aqueous recovery	10
Left in reaction vessel	10.4
No attempt to recover - left in samples and other portions of removal experimentation	44.2
	<hr/> 100.1%

^aComposition: $\text{LiF}\cdot\text{BeF}_2\cdot\text{ThF}_4$ (67-18-15 mole %) plus trace amounts of Pa^{233} added via irradiated ThO_2 plus ~50 ppm Pa^{231} added as the oxide fused with $\text{NH}_4\text{F}\cdot\text{HF}$.

was added to complex the remaining fluoride ion. An extraction with diisobutyl carbinol followed. When repeated contacting of the salt solution yielded little more Pa^{233} activity into the organic phase, the $\text{Pa}^{231,233}$ was stripped from the organic phase with 18 N H_2SO_4 containing a small amount of HF. Repeated extractions and strippings yielded some 79% of the protactinium believed to be in the system at the start of the aqueous recovery attempts.

Table 10.2 presents a summary of the protactinium content and recovery at various stages.

SOLUBILITY OF H_2 IN H_2O AND D_2 IN D_2O

L. O. Gilpatrick

H. H. Stone

The recombination reactions existing in the homogeneous reactor require precise data on gas solubilities so that these will not be exceeded under particular reactor operating conditions. Some data are available,¹³ but they are not of sufficient scope to supply information either for a wide range of reactor operating conditions or for the precise calculations required to delineate the mechanism of the recombination reaction.

This study was initiated to supply the data needed. The solubility of gases of interest over a wide range of chemical systems and temperatures is being determined. The data reported here were obtained to test the feasibility and precision of the technique, but they are of sufficient interest to warrant reporting them at this time. The experimental details are reported elsewhere.¹⁴

The results obtained to date are shown in Table 10.3. The H_2 - H_2O data are in essential agreement with that of Wiebe and Gaddy¹⁵ below 100°C and with the data of Pray *et al.*¹⁶ above 100°C. The D_2 - D_2O data vary by several per cent from those reported by Stephan *et al.*¹³

¹³E. F. Stephan *et al.*, *The Solubility of Gases in Water and in Aqueous Uranyl Salt Solutions at Elevated Temperatures and Pressures*, BMI-1067 (Jan. 23, 1956).

¹⁴L. O. Gilpatrick and H. H. Stone, *HRP Quart. Progr. Rept.* Oct. 30, 1960, ORNL-3061, p 47.

¹⁵R. Wiebe and V. L. Gaddy, *J. Am. Chem. Soc.* 56, 76 (1934).

¹⁶Pray *et al.*, *Ind. Eng. Chem.* 44, 1146-51 (1952).

Table 10.3. Solubility of H_2 in H_2O and D_2 in D_2O

Temperature (°C)	H_2 - H_2O System		D_2 - D_2O System	
	Number of Samples	Solubility (std cc g ⁻¹ atm ⁻¹)	Number of Samples	Solubility (std cc g ⁻¹ atm ⁻¹)
		× 10 ⁻²		× 10 ⁻²
25	5	1.766 ± 0.014	6	1.816 ± 0.011
40	5	1.690 ± 0.021	3	1.683 ± 0.006
50	3	1.676 ± 0.019	3	1.631 ± 0.006
60	27	1.689 ± 0.027	5	1.621 ± 0.008
70	13	1.693 ± 0.018	3	1.653 ± 0.011
80	5	1.735 ± 0.007	6	1.667 ± 0.010

Table 10.3 (continued)

Temperature (°C)	H ₂ -H ₂ O System		D ₂ -D ₂ O System	
	Number of Samples	Solubility (std cc g ⁻¹ atm ⁻¹)	Number of Samples	Solubility (std cc g ⁻¹ atm ⁻¹)
		× 10 ⁻²		× 10 ⁻²
90	8	1.795 ± 0.028	3	1.727 ± 0.001
100	6	1.863 ± 0.024	5	1.802 ± 0.012
110	10	1.933 ± 0.031	3	1.881 ± 0.010
120	5	2.065 ± 0.036	3	1.981 ± 0.002
130	6	2.196 ± 0.035	3	2.096 ± 0.013
140	9	2.365 ± 0.023	10	2.188 ± 0.020
150	26	2.491 ± 0.054	13	2.343 ± 0.026
160	10	2.688 ± 0.017	5	2.515 ± 0.020
170	3	2.848 ± 0.013	4	2.691 ± 0.016
180	5	3.109 ± 0.022	3	2.930 ± 0.004
190	6	3.385 ± 0.017	3	3.165 ± 0.018
200	3	3.865 ± 0.051	4	3.449 ± 0.016
210	2	3.975 ± 0.014	4	3.763 ± 0.025
220	3	4.266 ± 0.009	2	4.074 ± 0.010
230	5	4.802 ± 0.020	3	4.540 ± 0.074
240	5	5.301 ± 0.034	6	4.976 ± 0.037
250	9	5.892 ± 0.067	4	5.492 ± 0.046

These data compared favorably with available literature values. With the technique used it was possible to obtain data of an internal consistency better than that reported by others. The bulk of the data on the D₂-D₂O system is not available from the work of others.

CHARACTERIZATION OF THORIUM PEROXIDES

M. J. Kelly D. R. Cuneo

The removal of protactinium from thorium solutions by peroxide precipitation aroused questions concerning the nature of the precipitate. Hamaker and Koch¹⁷ have reported an approximate composition of Th(O⁻)_{3.2}(A⁻)_{0.5}(O²⁻)_{0.15} · 2.5H₂O, where A⁻ stands for the anion of the original solute, for peroxides formed from several soluble salts of thorium. Their results seemed subject to some ambiguities, therefore, experiments to resolve those questions were initiated.

¹⁷Hamaker and Koch, pp 318-47 in *Production and Separation of U²³³*, ed. by L. I. Katzin, TID-5223, part 1.

Precipitations of the peroxy salts of thorium nitrate, sulfate, and chloride were made with H_2O_2 from solutions which were neutral or acid. A more easily filterable precipitate was formed when excess acid was present. In the case of thorium chloride without excess acid a gel was formed. Precipitates formed in unacidified sulfate and nitrate solutions required washing with acetone for satisfactory filtering. Precipitates formed with excess acid were filterable but were sometimes dehydrated with acetone to speed the filtration and washing steps. All samples were vacuum-dried for several hours.

In every system the ratio of two thorium atoms to three titratable (direct titration with ceric ion) peroxide molecules was observed. In every case the original solution anion was present in the solid, dried precipitate. The anion, regardless of charge, was close to the stoichiometric ratio $\text{Th}_2(\text{OO})_3(\text{A}^{n-}) \cdot x\text{H}_2\text{O}$.

DECOMPOSITION OF H_2O_2 IN ACID AT ELEVATED TEMPERATURES

M. J. Kelly

D. R. Cuneo

The formation and subsequent decomposition reactions of peroxide in aqueous homogeneous reactors continue to be of considerable interest. Work at elevated temperatures (i.e., above 100°C) on the simple system $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ with the decomposition reaction catalyzed by added iron has shown an interesting anomaly occurring at 190 to 210°C .

Equipment used for recombination studies¹⁸ was adapted so that small quantities of 30% H_2O_2 could be injected rapidly into the reaction bombs and samples withdrawn serially; this made it possible to follow the course of the decomposition reaction. After peroxide injection and the establishment of equilibrium, sampling was begun. A 1-ml sample drawn through a 20-mil capillary, surrounded by a cold trap, could be taken in less than a second. Samples could be withdrawn within 10 sec of each other. Cooling by the cold trap reduced the decomposition rate so that standard analytical techniques could be used for the peroxide determination without the introduction of appreciable error.

Figure 10.6 shows the only significant results to date. It should be noted that thermal decomposition of the peroxide does occur in the titanium reaction bombs without added iron. The slope shown in Fig. 10.6 for the experimental points at 220°C and above corresponds to the slope observed for the uncatalyzed process. This is probably a heterogeneous decomposition process occurring by wall catalysis. At the temperatures of the experiment a finite amount of added iron is required to override this process. The addition of 2.8 ppm of iron changes the activation energy observed to the 23 to 25 kcal/mole considered normal for the catalyzed homogeneous solution decomposition. As the reaction temperature is increased, a significant reduction from the

¹⁸H. F. McDuffie *et al.*, *J. Phys. Chem.* **62**, 1030 (1958).

expected rate is observed. This transition zone shown in Fig. 10.6 may be explained by the loss of iron activity, probably by hydrolytic action which destroys its ionic character. This assumption is strengthened by the experimental points at 210°C and above where the addition of more added iron does not increase the rate of reaction.

Fig. 10.6. Temperature Dependence of k , the Rate Constant for Decomposition of H_2O_2 in 0.025 M H_2SO_4 , with Varying Concentrations of Iron.

11. AN INVESTIGATION OF URANIUM(VI) HYDROLYSIS AT ELEVATED TEMPERATURES, USING THE GLASS ELECTRODE¹

C. F. Baes, Jr.

N. J. Meyer²

The hydrolysis of uranium(VI) in 0.5 *m* nitrate solution has been investigated at temperatures up to 148°C, using the glass electrode emf cell and the vibrating-reed electrometer measuring circuit described previously.³

Results at 25 and 94°C (which were obtained over the uranium concentration ranges 0.001–0.02 *m* and 0.002–0.02 *m*, respectively, and from nearly zero hydrolysis to, or near to, the precipitation points) indicate the following equilibria to be the first and second hydrolysis steps:

Table 11.1 lists values of the corresponding equilibrium quotients Q_1 and Q_2 , and the quotient Q_d (equal to Q_2/Q_1^2) for the dimerization reaction

Table 11.1. Equilibrium Quotient Values

	At 25°C	At 94°C
Q_1	$(2.5 \pm 1) \times 10^{-6}$	$(7 \pm 1) \times 10^{-5}$
Q_2	$(1.1 \pm 0.1) \times 10^{-6}$	$(3.2 \pm 0.2) \times 10^{-5}$
Q_d	1×10^5	$(7 \pm 2) \times 10^3$

The value of Q_2 found at 25°C is in adequate agreement with various previous room-temperature determinations in the literature⁴ (which fall in the range 0.7 to 1.5×10^{-6}). The value of Q_1 is difficult to determine accurately at room temperature because of the small contribution of equilibrium (1) to uranium(VI) hydrolysis. Other investigators have reported Q_1 values in the range 0.8×10^{-6} to 2×10^{-5} (refs 4 and 5).

¹Presented in preliminary form at the First Conference on Nuclear Reactor Chemistry, Gatlinburg, Tenn., Oct. 12–14, 1960.

²ORINS research participant from Bowling Green State University, Bowling Green, Ohio.

³C. F. Baes, Jr., *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, p 130.

⁴J. Bjerrum, G. Schwarzenbach, and L. Sillen, *Stability Constants; Part II. Inorganic Liquids*, p 9, Chemical Society, London, 1958.

⁵R. L. Gustafson, C. Richard, and A. E. Martell, *J. Am. Chem. Soc.* **82**, 1526 (1960).

Preliminary results at 148°C confirm this increase in uranium(VI) hydrolysis with temperature (giving $Q_2 = 1$ to 2×10^{-4}); however, the accuracy of these measurements was limited by appreciable leaching of alkali-metal oxides from the glass electrodes used.

The decrease of the dimerization quotient Q_d with increasing temperature indicates increased stability of the monomeric hydrolysis product UO_2OH^+ , compared with the dimeric $\text{U}_2\text{O}_5^{2+}$. It is hoped that more extensive measurements at 148°C, using glass electrodes of greater chemical resistance, will permit a more accurate determination of the temperature dependence of equilibrium (3).

From the values of Q_1 and Q_2 listed above, the following enthalpies, free energies, and entropies of reaction are estimated at 25°C:

Reaction	ΔH (kcal)	ΔF (kcal)	ΔS (cal/°K)
(1)	10.5 ± 1.5	7.6 ± 0.2	10 ± 5
(2)	10.6 ± 0.5	8.13 ± 0.05	8.4 ± 2

Equilibria (1) and (2) account adequately for the observed hydrolysis behavior up to hydrolysis numbers (i.e., the formal number of OH^- ions per UO_2^{2+} ion) of about 0.2. At higher hydroxyl numbers (which reach a maximum value of 1.5 at 25°C and 0.6 at 94°C) it is clear that additional, more hydrolyzed species are formed. Ahrland, Hietanen, and Sillen⁶ were able to account reasonably well for the previous extensive room-temperature measurements of Ahrland⁷ by the assumption that these further hydrolysis products are members of the "core-links" series

However, the present measurements show systematic deviations (which were less clearly apparent in Ahrland's results) from the behavior required by this assumption. These deviations are too large to be explained by experimental error, activity coefficient variation, or liquid-junction potential effects.

While the general interpretation of the present results is not yet complete, preliminary examination suggests that the principal reaction subsequent to equilibrium (2) is

[The species $(\text{UO}_2)_3(\text{OH})_5^+$ was proposed some years ago by Sutton.⁸] If no additional equilibria prove to be of comparable importance, it appears that the present results will permit the evaluation of the equilibrium quotient for this reaction at 25 and 94°C with useful accuracy.

⁶S. Ahrland, S. Hietanen, and L. Sillen, *Acta Chem. Scand.* 8(10), 1907 (1954).

⁷S. Ahrland, *Acta Chem. Scand.* 3, 374 (1949).

⁸J. Sutton, *J. Chem. Soc. (suppl No. 2)*, S-275 (1949).

12. ISOPIESTIC STUDIES AT ELEVATED TEMPERATURES

B. A. Soldano

C. S. Patterson¹

The high-temperature isopiestic apparatus used to study the osmotic behavior of aqueous electrolytes² has been modified. To improve the reliability of the internal weighing system, the original electrical microformer circuitry was replaced by a direct optical system. In the new design the null point of the balance is established by the observation of a collimated light beam, reflected from a corrosion-resistant Stellite mirror, mounted on the balance. The light beam enters and leaves the apparatus through a specially designed quartz window. Figure 12.1 shows the general arrangement of this optical system. The experimental precision has been very good: in no case was the difference between duplicate equilibrium molalities greater than 0.8%; in over 60% of the cases the duplicates agreed to within 0.4% in molality; and in many cases the duplicates agreed to within 0.1% in molality.

UNCLASSIFIED
ORNL-LR-DWG 56719

Fig. 12.1. Schematic Drawing of the Optical System for the Isopiestic Unit.

Studies with the modified apparatus were made at temperatures between 100 and 142°C, over concentration ranges from 0.5 *m* up to saturation, and for representative electrolytes of the 1-1, 2-1, 2-2, and 1-2 types. Special emphasis was placed upon the concentration-dependent behavior at 121.1°C.

The experimental data were converted to values of the isopiestic ratio *R*, the ratio of the osmotic coefficient of the test salt to that of NaCl, chosen as the working standard. Although at present there do not exist any generally accepted primary standards for water activities in salt solutions above 100°C,

¹Summer employee; present address: Furman University, Greenville, S.C.

²W. J. Hamer (ed.), pp 224–35 in *The Structure of Electrolyte Solutions*, Wiley, New York, 1959.

the results of Smith³ on the boiling points of sodium chloride solutions from 25 to 100°C were extrapolated to 121.1°C in order to obtain estimated values of the osmotic coefficients for NaCl.

Table 12.1 presents experimental values of the isopiestic ratios for seven salts at 121.1°C, together with estimated values for the osmotic coefficient of NaCl. As shown by Fig. 12.2, the osmotic coefficients for the 1-1 electrolytes show a concentration dependence at 121.1° which is quite similar to that found at 25° by Robinson and Stokes.⁴

³R. P. Smith, *J. Am. Chem. Soc.* **61**, 500 (1939); R. P. Smith and D. S. Hirtle, *J. Am. Chem. Soc.* **61**, 1123 (1939).

⁴R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 1955.

Table 12.1. Isopiestic Ratios at 121.1°C

Molality	Osmotic Coefficient of NaCl (estd)	Ratio (to NaCl) for Electrolyte Listed						
		LiCl	KCl	CsCl	Na ₂ SO ₄	BaCl ₂	MgSO ₄	UO ₂ SO ₄
Experimental								
0.500	0.911							
0.5014						0.8722		
0.594					0.7363			
0.636		1.031						
0.676			0.9704					
0.6858				0.9565				
Interpolated								
1.00	0.930	1.045	0.9620	0.943	0.697	0.899		
1.25					0.678	0.912		
1.50		1.062	0.952	0.928	0.662	0.923		
1.56							0.4205	
1.65								0.397
1.75					0.649	0.929		
2.00	0.976	1.077	0.943	0.918	0.638	0.931	0.434	
2.25					0.627	0.932		
2.50		1.091	0.935	0.908	0.616	0.932	0.488	
2.70					0.607			
2.75						0.931		
3.0	1.041	1.105	0.927	0.898		0.926	0.560	0.460
3.5		1.120	0.919	0.888			0.628	0.491
4.0	1.089	1.134	0.910	0.878			0.694	0.521
4.5		1.149	0.902	0.869			0.755	0.548
5.0			0.894	0.859			0.808	0.572
5.1							0.817	
5.5								0.594
6.0								0.614
6.5								0.633

Fig. 12.2. Comparative Osmotic Coefficients for Rounded Molalities at 25°C and 121.1°C.

Table 12.2 presents data showing the change in isopiestic ratio with temperature for the seven salts at concentrations selected to permit measurements at all temperatures from 25 to 142°C. For the 1-1 electrolytes, the ratios (to NaCl, also a 1-1 electrolyte) appear to be almost independent of temperature. The 12% change between these temperatures for LiCl, while not large, nevertheless reflects the previously noted anomalous behavior of lithium ions.

Table 12.2. Variation of Osmotic Ratios with Temperature at Fixed Molality

Salt	Molality	Osmotic Ratio (to NaCl std)			
		25.0°C	99.6°C	121.1°C	142.0°C
LiCl	(1.40)	1.120	1.020	1.059	1.047
MgSO ₄	3.04	0.881	0.635	0.542	0.482
UO ₂ SO ₄	3.42	0.804	0.550	0.487	0.429
KCl	1.55	0.9440	0.9445	0.9446	0.9446
BaCl ₂	1.12	1.011	0.915	0.905	0.873
Na ₂ SO ₄	1.54	0.648	0.6655	0.660	0.634
CsCl	1.59	0.892	0.9385	0.926	0.920

Figure 12.3 shows the much more pronounced linear temperature dependence of the isopiestic ratio for the 2-1 and 2-2 electrolytes. It was interesting that the isopiestic ratios for sodium sulfate, at a concentration of 1.54 m , showed very little temperature dependence. In this respect it behaved more like a 1-1 electrolyte.

Fig. 12.3. Representative Isopiestic Ratios Relative to NaCl as a Function of Kelvin Temperature at Fixed Molality.

The significance of charge type is apparent when the slopes for the temperature dependence of 1-1, 2-1, 1-2, and 2-2 electrolytes are compared. Studies with other electrolytes, with mixtures, and at lower concentrations are in process to provide additional information concerning the behavior of aqueous solutions at elevated temperatures.

14. CORROSION BY SOLUTIONS

	J. C. Griess	H. C. Savage
J. L. English	L. L. Fairchild	P. D. Neumann
J. M. Baker	D. N. Hess	J. G. Rainwater ²
S. E. Bolt ¹	T. H. Mauney	L. Rice
	J. F. Winesette	

CORROSION IN UO_2SO_4 SOLUTIONS OF HIGH ACIDITY

Most corrosion testing in the Aqueous Homogeneous Reactor Program has been conducted with uranyl sulfate solutions 0.025 *m* in H_2SO_4 , since it was generally believed that this acid concentration would be adequate for solution stability in the HRT. In general, however, the higher the acid concentration, the more stable the fuel system; moreover, chemical analyses of HRT fuel solutions during run 21 suggested that additional acid would be desirable. Accordingly, the corrosion behavior of type 347 and of type CD4MCu stainless steel at 250 and 300°C has been examined in solutions containing 0.04 *m* UO_2SO_4 , 0.025 *m* CuSO_4 , and 0.05 *m* H_2SO_4 . Attempts were made to determine the critical solution velocity and the extent of corrosion at velocities below the critical velocity for each alloy.

Type 347 stainless steel specimens, when exposed at 250°C, showed a critical velocity of about 10 fps. Even at velocities slightly below 10 fps, about 0.002 in. of metal corroded before a protective oxide film formed. Exposure of specimens to oxygenated water at 280°C for 48 hr prior to exposure to the uranyl sulfate solution at 250°C for 270 hr resulted in a critical velocity of 15 to 20 fps. At flow rates less than the critical velocity, about 0.001 in. of metal corroded during formation of the protective film. When the specimens were given the pretreatment in high-temperature water and exposed to the uranyl sulfate solution at 300°C for 319 hr, a critical velocity of 45 to 50 fps was observed and only 0.0001 to 0.0003 in. of metal corroded at flow rates less than the critical velocity. The same specimens that were exposed at 300°C were then exposed (without descaling) to the uranyl sulfate solution at 250°C for 560 hr; no further corrosion occurred at velocities up to 50 fps. It is obvious from these experiments that pretreatment of the specimens is beneficial, at least for relatively short periods of time; in some previous cases pretreatment films have lasted for many hundreds of hours.³ However, it must be realized that films developed below the critical velocity have been demonstrated to be metastable when exposed at flow rates above the critical velocity. Thus, although the specimens exposed at 300°C resisted attack when exposed above the critical velocity at 250°C, the protective film probably would eventually deteriorate if flow velocities were maintained at above 10 fps.

¹Reactor Division.

²Summer research participant from the University of Arkansas.

³J. C. Griess *et al.*, HRP Quart. Progr. Rept. Jan. 31, 1957, ORNL-2272, pp 80-81.

The less extensive tests with type CD4MCu stainless steel have been performed with specimens machined from a single casting of the material and without pretreatment of the specimens. In tests with this material a critical velocity of less than 10 fps was observed at 250°C. In the velocity range of 10 to 14 fps the metal corroded to an average depth of 0.005 in. during a 275-hr run. At 300°C the critical velocity was about 30 fps, and 0.0005 to 0.001 in. of metal was removed during the formation of a protective oxide film. At both temperatures an unusual form of localized attack was observed. At 250°C preferential attack occurred on the grains themselves. The grain boundaries were raised, giving the specimen a very rough surface. At 300°C a similar attack was observed, although the grain boundaries were less well defined. In addition, relatively large areas showed very minor attack. It is clear that the cast type CD4MCu stainless steel has a lower critical velocity than the wrought type 347 stainless steel. This result is consistent with previous data which showed that cast type 347 stainless steel usually has a lower critical velocity in a given environment than does the wrought material.⁴

CHEMICAL EQUILIBRIA AND CORROSION IN URANYL SULFATE SOLUTIONS AT TEMPERATURES TO 365°C

The chemical stability of uranyl sulfate solutions at elevated temperatures has been the subject of a large number of investigations in the Aqueous Homogeneous Reactor Program. Such studies have been conducted in pressurized autoclaves of several types and in loops in which the solution is circulated by means of pumps. Though they are more expensive, in general, the pump-loop tests have many advantages over those using autoclaves. Reactor conditions of fluid flow, temperature, and dissolved-gas concentration (i.e., oxygen) can be more nearly duplicated in the pump loops, and samples of fuel solution can be routinely removed for chemical analyses. By use of the loops, corrosion specimens can be exposed to the circulating solution for evaluation, and the effect of heated and cooled metal surfaces on solution stability and corrosion can be investigated.

A disadvantage of such loop tests in the past has been the inability of the available loops to operate at temperatures above 330°C and at pressures above 2000 psia. Accordingly, a loop, similar in design to the HRP in-pile loops, has been constructed to operate at temperatures and pressures of 370°C and 3000 psia. This assembly permits evaluation of solution stability and material corrosion to temperatures near the critical temperature of water.

The loop, shown schematically in Fig. 14.1, is constructed of titanium, which is far superior to type 347 stainless steel in resistance to corrosion by acid uranyl sulfate solutions. A 5-gpm canned-rotor pump circulates the solution through the 1/4-in. main-loop piping, which contains a combination heater-cooler unit to control the main-stream temperature. Corrosion-test specimens are placed in the main-loop stream. A horizontally mounted pressurizer is used to provide steam pressurization and expansion volume when heating the solution to elevated temperatures. For continuous removal

⁴J. C. Griess *et al.*, *HRP Quart. Progr. Rept. Jan. 31, 1955*, ORNL-1835, p 83.

Fig. 14.1. Titanium Loop System for Use at 370°C and 3000 psia.

of solids or heavy-phase material which might be formed during operation at elevated temperatures, part of the circulating solution is passed through a hydroclone.⁵ Auxiliary apparatus for removing samples of the fuel solution from the main-loop stream and the hydroclone underflow pipe can be operated while the loop is operating at temperature and pressure.

The loop has been cleaned and calibrated and used in three relatively short tests (up to 75 hr) of the stability and corrosivity of a D_2O solution containing 0.044 M UO_2SO_4 , 0.022 M $CuSO_4$, 0.0149 M $NiSO_4$, and 0.038 M D_2SO_4 at temperatures up to 365°C. [The temperature for separation of this solution into two liquid phases is 327°C (ref 6).]

The temperature of the main circulating stream was maintained about 5°C below that in the pressurizer and was increased in steps. After increasing the temperature and allowing the system to reach equilibrium, a solution sample was withdrawn from the circulating stream and occasionally from the

⁵P. A. Haas, *Hydraulic Cyclones for Application to Homogeneous Reactor Chemical Processing*, ORNL-2301 (Nov. 18, 1957).

⁶W. L. Marshall, private communication.

underflow pot of the hydroclone. It was presumed that the solution withdrawn from the circulating stream at temperatures above which an extra liquid phase formed contained only the light phase and that the solution taken from the underflow pot contained a mixture of light and heavy phases.

As the temperature of the system was increased beyond 327°C, all constituents of the light phase except free acid decreased in concentration. With a pressurizer temperature of 365°C and the circulating stream at 360°C, the concentration of U, Cu, Ni, and SO_4^{2-} in the light phase was 0.01, 0.014, 0.005, and 0.071 M respectively. The mole ratios of copper to nickel, nickel to sulfate, and copper to sulfate were essentially constant from room temperature to the highest temperature investigated.

Solution samples removed from the underflow pot of the hydroclone at temperatures greater than 327°C contained more salts than did samples removed from the line. However, the concentrations of salts indicated that not all the heavy-phase material collected at that location. It is highly probable that a substantial amount of the heavy phase collected in the pressurizer, where temperatures were slightly higher.

Corrosion specimens made from Ti-75A and from a Zircaloy-2 weldment showed negligible attack during the 153 hr of the run. The titanium specimens developed a dark blue-gray color and exhibited weight gains of about 0.03 mg/cm². The Zircaloy-2 specimens were covered with a black film, which appeared to be transforming to a white film at a few isolated areas. Weight gains of about 0.1 mg/cm² were observed.

The performance of the loop was very satisfactory. It should be a useful tool for studying solution stability and corrosion at temperatures nearly as high as the critical temperature of water.

CORROSION OF ALUMINUM OXIDES IN AQUEOUS SOLUTIONS

Specimens of aluminum oxide have been tested for corrosion resistance to establish suitability for use of the material as a nonconducting liner in magnetic flowmeters. Specimens, supplied by the Coors Porcelain Company, were of two grades: one grade contained 93 to 95% Al_2O_3 , and the second contained a minimum of 98%.

Both grades showed excellent resistance to corrosion in oxygenated distilled water boiling under atmospheric pressure for 1500 hr, and both were satisfactory (less than 3 mils/yr, from weight-loss measurements) in oxygenated distilled water at 300°C for the same time interval. Attack by aerated simulated fuel solution (0.04 M UO_2SO_4 , 0.02 M H_2SO_4 , and 0.005 M CuSO_4) on boiling at atmospheric pressure for 1000 hr, however, was much more severe; corrosion rates of 21 to 31 mils/yr which were demonstrated are probably too high for the service proposed.

Specimens, consisting of alumina brazed to Ti-75A, have been tested for corrosion resistance to establish suitability for use in valves and flowmeters. Specimens were vacuum-brazed at about 1000°C with four different brazing alloys. Test conditions, alloy composition, and observed weight loss data are shown in Table 14.1.

Attack on titanium metal is negligible under these conditions. Brazed areas exposed to the boiling reactor solution showed no visible evidence of attack; those exposed to 300°C water were

Table 14.1. Observed Weight Losses on Brazed Aluminum Oxide-Titanium Specimens Exposed for 1500 hr in Various Media

Medium	Temperature (°C)	Brazing Alloy Composition (wt %)	Weight Loss (mg/cm ²) ^a
Oxygenated distilled water	300	95 Zr, 5 Be	7.1
		80 Zr, 15 Fe, 5 Be	7.5
		48 Zr, 48 Ti, 4 Be	9.0
		47 Zr, 47 Ti, 3 V, 3 Be	5.3
Reactor fuel solution ^b	100	95 Zr, 5 Be	15.2
		80 Zr, 15 Fe, 5 Be	6.7
		48 Zr, 48 Ti, 4 Be	38.8
		47 Zr, 47 Ti, 3 V, 3 Be	11.8

^aBased on combined areas of aluminum oxide and braze alloy only.

^bAn air-aerated, simulated reactor fuel solution containing 0.04 M UO₂SO₄, 0.02 M H₂SO₄, and 0.005 M CuSO₄.

dull and covered with black corrosion products. Neither corrosion nor the thermal cycling detached the alumina from the metallic titanium.

CORROSION OF ALUMINUM BY WATER

The High Flux Isotope Reactor (HFIR) for the production of transplutonium elements is to be built at ORNL. To achieve the high neutron flux necessary to produce significant quantities of the transplutonium elements, a compact, relatively small core of high power density is necessary. The reactor core^{7,8} will be an integral unit composed of a flux trap surrounded by two concentric rings of involute fuel plates. Each plate has a thickness of 0.050 in., which includes the uranium-aluminum alloy fuel and 0.010 in. of an aluminum alloy cladding on each side. The plates are separated by a 0.050-in. channel through which light water flows at about 40 fps. This high flow rate is necessary to remove the heat from the fuel plates, since heat fluxes as high as 1.5×10^6 Btu hr⁻¹ ft⁻² will exist during reactor operation. Under normal conditions, cooling water will enter the reactor at a temperature of 120°F (49°C) and will rise 70°F (39°C) in passing through the core.

Because of the very high power density in the HFIR core, fuel loadings must be removed after about ten days for reasons of neutron economy. Corrosion rates of the aluminum fuel cladding which are considerably in excess of those suitable for conventional power reactors can, therefore, be tolerated. Since, however, data on corrosion of aluminum in water under conditions of very high heat flux do not exist, experimental study of the corrosion problem and the effect of corrosion products on heat transfer was necessary. Alternative fuel element designs, which would require coolant flow

⁷J. A. Lane et al., *High-Flux Isotope Reactor: Preliminary Design Study*, ORNL CF-59-2-65 (Mar. 20, 1959).

⁸T. E. Cole, *High-Flux Isotope Reactor: A General Description*, ORNL CF-60-3-33 (Mar. 15, 1960).

rates of 100 fps, have been considered for this reactor. Accordingly, the effect of very high coolant flow rates on commercially available aluminum alloys has been examined.

Effect of Heat Flux on Corrosion of Aluminum by Water

The equipment and methods of preparation of test specimens, which have been described elsewhere,^{9,10} are, briefly, the following. The specimens were prepared by pressing an aluminum tube 8.3 in. long with a 0.100-in.-thick wall onto a mandrel to form a rectangular channel of 0.050- by 0.500-in. cross section through which the coolant flowed. The corners and narrow edges of the center 6.5-in. portion of the specimen were then machined to a wall thickness of 0.025 in. to reduce the heat generation in that region. The 1-in. length at each end was welded into large aluminum electrodes to which electrical leads from the transformer were attached and by means of which the specimen was flanged into a bypass line of the 100-gpm pump loop which provided the flow of water through the specimen. In all tests the specimen was mounted vertically, with water entering at the bottom.

Heat was generated by passing 60-cycle current at 8500 to 10,000 amp through the specimen. The power (about 16 kw) so produced corresponded to a nominal heat flux of 1.5×10^6 Btu hr⁻¹ ft⁻² across the water-aluminum interface under the 0.100-in.-thick part of the specimen and 0.5×10^6 Btu hr⁻¹ ft⁻² across the rest of the surface. The heat fluxes were held constant at the above values within $\pm 5\%$.

Thermocouples were spot-welded to the outside of the specimen, and close-fitting Mycalex, which served as thermal and electrical insulation, surrounded the specimen. The Mycalex was backed up with heavy stainless steel plates so that the thin specimen could withstand the internal pressure (up to 900 psi) used in the tests.

Heat was removed by circulation of water at 34 to 48 fps through the specimens. The quality of the cooling water in the loop was maintained as desired by use of a mixed-bed demineralizer (for high-purity water) or a cation exchanger (to provide water of pH below 7) in a bypass circuit. Aliquots of water were removed from the loop periodically for determination of quality. When the mixed-bed ion exchanger was used, the pH of the water varied between 6.0 and 6.5, and the resistivity of the water in the loop varied between 1 and 2×10^6 ohm-cm. Control of the pH of the water at values less than 7 by means of the cation exchanger was usually good to ± 0.1 pH unit; resistivity of the water at pH 5 was approximately 2×10^5 ohm-cm.

Two aluminum alloys have been tested in a total of ten experiments in the high-heat-flux facility; the compositions of these alloys, types 1100 and 6061, are shown in Table 14.2. Data obtained during

⁹J. C. Griess, H. C. Savage, et al., *Effect of Heat Flux on the Corrosion of Aluminum by Water. Part I. Experimental Equipment and Preliminary Test Results*, ORNL-2939 (Apr. 29, 1960).

¹⁰J. C. Griess, H. C. Savage, et al., *Effect of Heat Flux on the Corrosion of Aluminum by Water. Part II. Influence of Water Temperature, Velocity, and pH on Corrosion-Product Formation*, ORNL-3056 (Feb. 10, 1961).

these tests and from metallographic examination of the test specimens after exposure justify the following conclusions.

1. The corrosion of aluminum under conditions expected to exist in the HFIR leads to the formation of an adherent, nearly transparent, corrosion-product oxide which has a thermal conductivity of about $1 \text{ Btu hr}^{-1} \text{ ft}^{-2} (\text{°F})^{-1} \text{ ft}$. As the corrosion product forms, the temperature of the aluminum increases under constant test conditions.

2. At a heat flux of $1.5 \times 10^6 \text{ Btu hr}^{-1} \text{ ft}^{-2}$, the rate at which the oxide forms on aluminum surfaces is dependent on the pH of the coolant. The use of high-purity water or water adjusted to pH values of 4 or less with nitric acid or carbon dioxide causes more rapid film formation than does water adjusted to a pH of 5 with nitric acid.

3. The rate at which oxide forms on the water-cooled aluminum surface depends on the temperature of the coolant. For the coolant temperatures used, 131 to 223°F, the higher the temperature of the coolant, the greater was the rate at which the oxide film formed.

4. In the range of 34 to 48 fps there appears to be no effect of coolant velocity on the rate at which corrosion products build up on the water-cooled surfaces.

5. With sufficiently thin layers of corrosion product (usually less than 0.001 in. thick) thermal cycling of the aluminum produces no apparent loss of oxide. Thermal cycling usually causes the loss of some oxide from the surface when the oxide is much in excess of 0.001 in. thick.

6. Although quantitative corrosion rates of types 1100 and 6061 aluminum alloys have not been determined, the appearance of the specimens at the conclusion of these tests indicated that corrosion damage was not severe.

7. Under the conditions expected to exist during operation of the HFIR, aluminum will probably be a successful cladding material. Corrosion damage does not appear to be a serious problem; by adjusting the pH of the water to 5 with nitric acid, excessive fuel-element temperatures should not occur during the ten-day fuel cycle.

Corrosion of Aluminum Alloys in High-Velocity Water at 170 to 290°C

The corrosion tests described were carried out as the first phase of a program to determine whether commercial aluminum alloys could be used to clad fuel elements for the HFIR. Because of the very high heat fluxes which will exist during HFIR operation, and in spite of the relatively low temperature of the coolant water, temperatures in the aluminum fuel cladding will be high. The aluminum temperature will be further increased by the fact that corrosion products which adhere, at least partially, to the surface have low thermal conductivity. It has been shown (see above) that, under conditions of rapid heat transfer, the temperature at the oxide-metal interface or the mean temperature in the corrosion-product film determines the corrosion rate;^{11,12} isothermal tests must,

¹¹D. R. DeHalas, *A Study of Heat-Transfer Effects on Aluminum Corrosion, Part I*, HW-42585 rev. (Apr. 19, 1956).

¹²R. J. Lobsinger and J. M. Atwood, *Corrosion* 13, 582t-84t (1957).

as a consequence, be conducted at temperatures expected to exist in the corrosion-product scale. Thus the tests described in this report were conducted in the temperature range of 170 to 290°C.

The corrosion of aluminum and its alloys by high-temperature flowing water has been the subject of a number of investigations. Tests have usually been conducted under conditions of moderate flow rate, 15 to 30 fps, and high temperature, 250 to 360°C. For most reactors the rate of fuel burnup is such that fuel elements remain in a reactor for relatively long periods. Consequently, low corrosion rates must be achieved if thin aluminum cladding is to retain its integrity.

The results of previous investigations have shown that aluminum, and most of the commercial alloys, suffer heavy corrosion damage in high-purity water at 200°C and above.^{13,14} Alloying aluminum with many different elements has little, if any, effect in reducing the rate of attack.¹⁵ However, the addition of small amounts of nickel to aluminum substantially increases its corrosion resistance, and the addition of a small amount of iron to the above alloy produces a further beneficial effect.¹⁶ (An alloy containing about 1% nickel and 0.5% iron is commercially available and is designated X8001.) Recent data have shown that the presence of silicon in the alloy is detrimental to its corrosion resistance in high-temperature water. By reducing the silicon content of the alloy to very low values, a further lowering of the corrosion rate can be achieved.¹⁷ The beneficial effect of the low silicon content, however, is only significant at temperatures of 300°C and above;¹⁸ at temperatures of about 250°C all alloys of this class show comparable corrosion rates.

Corrosion tests were conducted with commercially available type 1100, 5154, 6061, and X8001 alloys in water at flow rates between 20 and 107 fps and at temperatures between 170 and 290°C. Compositions of these alloys are shown in Table 14.2. In addition, several experimental alloys containing a variety of concentrations of iron, nickel, and silicon were tested. These isothermal tests, which were of ten days duration, were conducted in 100-A pump loops in which heat was supplied to the aluminum test specimens by the coolant water. After the test, the specimens were examined for gain in weight and were subjected to metallographic examination to assess extent of attack.

The major results obtained from these studies can be summarized as follows.

1. During ten-day tests in the temperature range of 170 to 200°C, aluminum alloy types 1100, 5154, 6061, and X8001 exhibited essentially the same corrosion behavior. At water flow rates of 20 to 107 fps, corrosion rates generally increased with increase in coolant velocity.

¹³J. E. Draley and W. E. Ruther, *Corrosion* 12, 441t-48t (1956).

¹⁴P. O. Strom and M. H. Boyer, *Static Corrosion of Aluminum Alloys at 350°F and 480°F in Distilled Water*, LRL-64 (October 1953).

¹⁵M. H. Brown, R. H. Brown, and W. W. Binger, "Aluminum Alloys for Handling High-Temperature Water," paper presented at the Sixteenth Annual Conference, National Association of Corrosion Engineers, Dallas, Texas, March 14-18, 1960.

¹⁶J. E. Draley and W. E. Ruther, *Corrosion* 12, 480t-90t (1956).

¹⁷J. E. Draley, "Aqueous Corrosion of 1100 Aluminum and of Aluminum-Nickel Alloys," paper presented at the International Conference on Aqueous Corrosion of Reactor Materials, Brussels, Oct. 14-16, 1959.

¹⁸J. E. Draley, private communication.

Table 14.2. Composition of Commercial Aluminum Alloy Test Materials

Alloy Designation	Composition ^a (wt %)									
	Fe	Si	Cu	Mn	Zn	Mg	Cr	Ti	Ni	Al
1100	(1.0 Fe + Si)		0.20	0.05	0.10					99.00 ^b
5154	(0.45 Fe + Si)		0.10	0.10	0.20	3.1-3.9	0.15-0.35	0.20		bal
6061	0.7	0.40-0.80	0.15-0.40	0.15	0.25	0.15	0.15-0.35	0.15		bal
X8001	0.45-0.70	0.17	0.15						0.9-1.3	bal

^aMaximum, unless shown as range.^bMinimum.

2. At 230°C, types 1100 and X8001 aluminum alloys (the only alloys tested at this temperature) behaved similarly. At flow rates of 20 to 67 fps the corrosion rates of these alloys at 230°C were nearly the same as observed at 170 and 200°C. At temperatures up to and including 230°C none of the alloys showed localized attack except for occasional shallow pits.

3. At 260°C many of the types 1100 and 6061 aluminum specimens underwent significant localized attack in the form of subsurface void formation, whereas others were unaffected. Had the tests lasted longer than ten days, all specimens of these alloys might have been seriously damaged by this type of attack. On the other hand, specimens of type X8001 aluminum were completely free of localized attack except for a few shallow pits. The corrosion rate of type X8001 specimens was nearly independent of flow rate between 20 and 67 fps.

4. Of the commercial alloys tested, only type X8001 did not suffer catastrophic attack at 290°C. In fact, at the three highest velocities, the corrosion rate of type X8001 aluminum appeared to be slightly lower at 290°C than at 260°C.

5. At 260°C and at coolant flows of 20 to 95 fps, type X8001 aluminum corroded fairly rapidly during the first 100 to 200 hr of test and then corroded at constant and lower rates; at the highest velocity tested, the corrosion rate was independent of time. The observed linear corrosion rates (in mils/yr) after the initial 100- to 200-hr period were: 5 mpy at 20 to 31 fps; 10 mpy at 31 to 44 fps; 15 mpy at 44 to 67 fps; 60 mpy at 67 to 95 fps; and 200 mpy at 95 to 107 fps.

6. Highly polished specimens of type X8001 aluminum corroded at approximately the same rate in water at 260°C as specimens with a machined finish, but specimens pretreated in water at 250 or 300°C for 24 hr in an autoclave were significantly more resistant to attack in water flowing at 20 to 47 fps than were the "as-machined" specimens; at higher flow rates the pretreatment was not effective.

7. Several experimental alloys containing various concentrations of iron, nickel, and silicon appeared to be no more resistant to attack at 260°C and 42 fps than did the X8001 alloy.

From the results of these tests and since the HFIR fuel elements will be in the reactor only ten days, any of the alloys tested could be used as cladding so long as the average temperature of the

oxide film (i.e., the temperature that controls the rate of corrosion under conditions of heat flux) did not exceed 230°C and the flow rate of the coolant was less than 65 fps. At higher temperatures only the type X8001 alloy and the experimental alloys could be used. None of the alloys tested could be used successfully at 100 fps at any of the temperatures tested.

SERVICE CORROSION TESTING FOR OTHER DIVISIONS

Corrosion Testing in Support of Power Reactor Fuel Element Processing

These tests support the development program concerned with the power reactor fuel element processing (aqueous) and waste disposal conducted by the Chemical Technology Division. The corrosion resistance of metals and alloys that might be suitable for container materials for various dissolution processes and storage containers is determined under conditions simulating those that would exist in a processing plant. Because of the nature and variety of the development programs, many different materials are tested under many different conditions.

During the past year, tests have been carried out in solution simulating those that would exist in the following processes, either developed or under development by the Chemical Technology Division: Thorex, Sulfex, Zircex, Zirflex, and waste calcination. The pertinent results obtained from this testing program are considered an integral part of the development work on the various processes and as such are included in the reports issued by the Chemical Technology Division.

Testing in Cooling-Water Systems

Experimental testing programs are being conducted in the secondary side of the HRT heat exchangers and in the core and cooling systems of the ORR. In addition, consultation on various cooling-water systems is supplied as requested.

Water Treatment for HRT Steam Generators. — Treatment of the boiler water for the HRT is complicated by the fact that oxygen (and hydrogen) is generated in the water by the radioactive fuel solution passing through the tubes. Since the heat-exchanger tubes are made of type 347 stainless steel, the presence of oxygen leads to stress-corrosion cracking problems with only trace concentrations of chloride ions in the water. Furthermore, oxygen in the steam causes excessive corrosion of the shell of the heat exchanger and the piping in the steam system, both of which are made of carbon steel. A method of water treatment which has resulted in trouble-free operation of the HRT steam generators has been developed.¹⁹ In brief, the method uses potassium phosphate to maintain the pH of the water in the range 10.5 to 11.5 and hydrazine to remove the oxygen from the system. The chloride concentration of the water is also controlled to less than

¹⁹P. D. Neumann, *Water Treatment in Aqueous Homogeneous Reactors, Experience in HRE-2*, ORNL CF-61-1-19 (Jan. 4, 1961).

1 ppm. Although this water treatment appears to be adequate for the HRT, the cost would be prohibitive for a large utility plant powered by aqueous homogeneous reactors. The incorporation of an intermediate heat-exchange cycle in the reactor or the use of other materials not susceptible to corrosion by oxygen might be more economical than chemical scavenging of the oxygen.

Tests in the Oak Ridge Research Reactor

Since operation of the ORR began, a testing program to determine the corrosion rates of various aluminum alloys used in the construction of the reactor has been conducted. Some of the corrosion results obtained to date have been reported.^{20,21} These results indicate that with the water treatment practiced at the ORR all the aluminum alloys used in the system can be expected to give satisfactory results for many years. Based on the observed generalized corrosion rates alone, one would expect 40 to 50 years of service life. However, since occasional localized attack more severe than indicated by the generalized rates has been observed (rarely), minor repairs will almost certainly be required before that time.

Acceptance Tests

As a routine service, standard acceptance tests for austenitic stainless steels are conducted. These tests include the boiling 65% HNO₃ test (ASTM-A262-55T), the oxalic acid test (ASTM-A262-55T), and the Strauss test (ASTM-A393-55T).

²⁰P. D. Neumann, *Secondary-Side Water Treatment for Corrosion Control in Aluminum Heat Exchangers; Practices and Results at the Oak Ridge Research Reactor*, ORNL CF-59-8-5 (Aug. 12, 1959).

²¹P. D. Neumann, *Corrosion in the Oak Ridge Research Reactor, Core Cooling System*, ORNL CF-60-4-97 (Apr. 25, 1960).

15. CORROSION BY SOLUTIONS UNDER IRRADIATION

G. H. Jenks

H. C. Savage

A. L. Bacarella

S. J. Ball¹

R. A. Lorenz

J. E. Baker

S. E. Bolt²

A. J. Shor

J. M. Baker

R. J. Davis

S. H. Wheeler

V. A. DeCarlo²

REVIEW AND CORRELATION OF ZIRCALOY-2 RADIATION CORROSION DATA

Many of the data obtained at ORNL for the in-pile corrosion of Zircaloy-2 in uranyl sulfate solution have been reviewed and correlated, and a report of the work has been prepared.³ The correlations are based on the following equation for the relationship between corrosion rate (R) and fission power density in solution (P):

$$\frac{1}{R} = \frac{K_1}{K P \alpha} + \frac{1}{K}, \quad (1)$$

where α is a factor by which the effective power density at the corroding surface is greater than that in the solution, because of uranium sorption on the surface; and K_1 and K are constants which are evaluated from the experimental data. A model for the radiation effects on Zircaloy-2 corrosion which leads to this equation is also described and discussed in this report.

The work had the purpose of evaluating the applicability of the general equation as well as the data review and correlation.

The basic postulates for the model are described by Eqs. (2) through (5), as follows: (1) The corrosion rate is assumed to be directly proportional to the concentration of radiation defects N in the metal or protective oxide. (2) The defects are formed at a rate proportional to $P\alpha$ and are removed by radiation annealing at a rate proportional to $P\alpha N$ and by thermal or corrosion annealing at a rate proportional to N . (3) A steady-state concentration of defects is reached. (4) Substitution of the expression for N_s in Eq. (2) gives an expression similar to that of Eq. (1):

$$R = aN, \quad (2)$$

$$dN/dt = K''P\alpha - K^0 P\alpha N - K'N, \quad (3)$$

$$N_s = \frac{K''P\alpha}{K^0 P\alpha + K'}, \quad (4)$$

$$\frac{1}{R_s} = \frac{K'/K^0}{a(K''/K^0)P\alpha} + \frac{1}{aK''/K^0}. \quad (5)$$

¹Instrumentation and Controls Division.

²Reactor Division.

³G. H. Jenks, *Review and Correlation of In-Pile Zircaloy-2 Corrosion Data and a Model for the Effect of Irradiation*, ORNL-3039 (to be published).

The results of the correlations of the experimental data obtained at 280°C show that a relationship of the general form of Eq. (1) is obeyed within the power density range tested (up to 110 w/ml) and that the values of K are essentially independent of solution composition. They also indicate that the value of the factor K_1 is independent of solution composition. The experimental information for temperatures other than 280°C is not sufficient to establish the validity of the general relationship at other temperatures. However, if the reasonable assumption is made that the relationship is obeyed and that α does not change or changes slowly with temperature, the data are sufficient to establish a range of K values at 250 and 300°C and also to establish that over the temperature range investigated, 225 to 330°C, the data are reasonably well expressed by Eq. (6):

$$\frac{1}{R} = \frac{2.3}{P\alpha} + 2.25 \times 10^{-11} \exp \left(\frac{11,500}{T} \right), \quad (6)$$

where T is the temperature in °K. As expressed by the equation, maximum corrosion rates of 12, 40, and 84 mils/yr are expected at 250, 280, and 300°C respectively.

The value for α prevailing during exposure depends upon the solution composition and the velocity of solution flow past a surface. Some values for α in solutions of several different compositions and at several different velocities are shown below (these values are considered applicable to convergent and to straight-channel type of flow).

1. Solution: 0.04 m UO_2SO_4 , 0.005 to 0.0075 m CuSO_4 , and 0.02 to 0.03 m H_2SO_4 , in H_2O and D_2O (tests at 280 and 300°C). Best estimates of α at velocities up to about 25 fps are given by the expression

$$\alpha = \frac{4.8}{v^{0.6}} + 1.$$

2. Solution: 0.17 m UO_2SO_4 , 0.02 to 0.03 m H_2SO_4 , in H_2O (tests at 280°C). Values of α are 2.5 to 3.5 at velocities of about 0.8 fps; the value is unity at 10 fps and above (to ~45 fps).

3. Solution: 0.17 m UO_2SO_4 with 0.15 m CuSO_4 and 0.4 m H_2SO_4 or with 0.02 m CuSO_4 , 0.1 m H_2SO_4 , and 0.2 m Li_2SO_4 , in H_2O (tests at 280°C). At all velocities to about 45 fps, the α value was unity.

CORROSION OF ZIRCONIUM ALLOYS IN IN-PILE LOOPS

In a continuation of in-pile studies to establish corrosion behavior of possible materials of construction for aqueous homogeneous reactors, a variety of zirconium alloy specimens have been exposed in an in-pile loop experiment (designated 0-1-25) at 280°C to a D_2O solution containing 0.04 m UO_2SO_4 , 0.016–0.035 m H_2SO_4 , and 0.006 m CuSO_4 .

The loop was constructed of type 347 stainless steel and was similar in design to loops previously described.⁴ The core section contained two tapered-channel specimen holders in which solution velocity ranged from 10 to 23 fps with included angles in the channels from ± 4 to 0° . Additional

⁴H. C. Savage *et al.*, *In-Pile Corrosion Test Loops for Aqueous Homogeneous Reactor Solutions*, ORNL-2977 (Nov. 10, 1960).

specimens were arranged in regions around the core channels; solution velocity past these annulus specimens was about 1.5 fps. Specimens were mounted in a manner such that appreciable fractions of the surface were covered by the holder or by adjacent specimens; the covered surfaces were not sealed from the circulating solution but were in contact with an essentially stagnant thin film of solution. In this study, specimens having different ratios of exposed to covered surface were included to better establish differences in corrosion behavior.

Exposure was performed in beam hole HN-1 of the ORR for 2741 hr during which time the reactor generated 36,895 Mwhr of energy. The loop was fully inserted in the reactor for nearly 80% of this interval.

The exposed specimens were examined for weight loss, induced activity, and composition of materials retained on surfaces. Examinations by metallographic techniques were also performed on these materials.

Results obtained in this study have been reported in some detail⁵ elsewhere; a summary of the conclusions is presented below.

Studies with Zircaloy-2 at 280°C show that the factor K [see Eq. (1), this chap.] is the same for D_2O solutions of UO_2SO_4 as for H_2O solutions, the same for machined as for chemically polished surfaces, and the same for material fabricated to give random orientations as for that with preferred orientations.

For a given set of conditions, surfaces of Zircaloy-2 which were chemically polished, overground, or sandblasted followed by chemical polishing corroded to about equal extents. Sandblasting alone had a deleterious effect on the corrosion resistance of Zircaloy-2 at some power-density levels.

The corrosion on covered Zircaloy-2 surfaces was substantially greater than that on surfaces exposed to flowing solution. The value of α on the covered surfaces may have been as high as 15; that on the exposed surfaces was as low as 1.5 to 2 under some flow conditions. The value of α for the covered surfaces was appreciably greater than the value of 6 to 8 deduced from the results of previous experiments which employed H_2O solutions of UO_2SO_4 .

Specimens of weld and air-contaminated weld materials corroded at about the same rate as stock Zircaloy-2.

Zirconium-1% chromium alloy suffered radiation-induced corrosion in about the same amount as Zircaloy-2.

The results for two specimens of crystal-bar zirconium indicate a K value of about 20 mils/yr for this material, a value in near agreement with that determined in previous experiments. Uranium sorption on crystal-bar zirconium, as measured by the value of α , was greater than that on Zircaloy-2.

Specimens of Zr-15% Nb, Zr-15% Nb-2% Mo, and Zr-15% Nb-1% Cu in the beta-quenched condition showed better corrosion resistance than Zircaloy-2. However, specimens of these materials heat-treated at 400 to 500°C for one to two weeks showed poorer corrosion resistance than Zircaloy-2. The results provide evidence that uranium sorption plays an important role in the in-pile corrosion of

⁵G. H. Jenks, H. C. Savage, *et al.*, HRP Quart. Progr. Rept. July 31, 1960, ORNL-3004, p 65.

these materials just as it does for Zircaloy-2 and zirconium. It is possible that the performance of some of the heat-treated alloys was poorer than that of Zircaloy-2 because of a difference in the uranium sorption.

ELECTROCHEMICAL STUDIES OF ZIRCALOY-2 CORROSION

The measurement of corrosion rates by the linear polarization technique⁶ was extended to temperatures above 250°C. The apparatus was modified to permit the temperature of the Teflon seals to be held near 25°C while the system operated at the higher test temperature. This modification required that a new method be developed for attaching the test sample to the external measuring instruments. The best results were obtained when the zirconium wire was Heliarc-welded to a machined tip on the test sample. However, there is still some question in the interpretation of the results obtained with this method of attachment, because the rate of attack on the welded areas was apparently higher than on the other areas (white oxide was formed).

Rate-time measurements were performed on a machined Zircaloy-2 specimen (obtained from Allegheny-Ludlum) in 0.05 *m* H₂SO₄, 300 ppm O₂ (25°C), at 258°C. The results for the first 1600 min can be satisfactorily expressed by an equation of the form:

$$1/R = 1/A + Bt,$$

where *R* is the corrosion rate in μg of oxygen per cm² per min, *A* is a constant, 0.57, *B* is a constant equal to 0.37 cm² per μg of oxygen, and *t* is the time in minutes. From 1600 to 3600 min the rate decreased to a steady-state rate of 0.14 mil/yr (mpy) (0.0014 μg of oxygen per cm² per min) and remained constant at this rate until the experiment was terminated at 18,000 min. The value of *A* is not reliable (as an initial rate) because of uncertainty in the initial exposure time.

The area of the welded section which exhibited the white oxide was estimated to be 0.06 cm² or about 1% of the total area. Its contribution to the corrosion current for the major portion of the experiment was probably negligible. However, at the steady state, it is conceivable that the welded section could have been generating a significant part of the measured corrosion current.

The potential-time behavior for this specimen at 258°C was similar to that previously observed⁶ for the Firth-Sterling alloy at 208°C. However, at these higher temperatures, the observed potential changes occur in a much shorter time interval, and the steady-state potential was observed to be -1.150 ± 0.100 v, compared with -0.550 ± 0.100 v at 208°C.

The current-potential behavior for the anodic and cathodic reactions on the Zircaloy-2 specimen is presented in Fig. 15.1. The Tafel slope for oxygen reduction is 0.220 v, and the calculated $\alpha_c Z_c = 0.48$. A one-point estimate for the anodic Tafel slope was performed and gave a value of $b_a = 1.060$ v, with $\alpha_a Z_a = 0.1$. An extrapolation of the cathodic curve to the open-circuit potential, *E*, gave a value for the corrosion current of 3.3×10^{-7} amp/cm² (0.13 mpy). About the same value,

⁶G. H. Jenks and A. L. Bacarella, *HRP Quart. Progr. Rept. Jan. 31, 1959*, ORNL-2696, pp 144-46.

Fig. 15.1. Experimental Current-Potential Plot for Machined Zircaloy-2 Specimen in 0.05 m H₂SO₄, 250 psi O₂(25°C), 258°C, Time = 10,000 min.

3.6×10^{-7} amp/cm² (0.14 mpy), was obtained for the corrosion current from a small-current polarization measurement, $(d\eta/dI)_{\eta \rightarrow 0}$, using the equation

$$I_{\text{corr}} = \frac{RT/F}{(\alpha_a Z_a + \alpha_c Z_c)(d\eta/dI)_{\eta \rightarrow 0}},$$

where $\alpha_a Z_a + \alpha_c Z_c = 0.58$.

At these higher temperatures the rate of film growth is greatly accelerated, and since the potential is a function of the oxide thickness, the potential changes would be expected to occur in a much shorter time interval, as observed. Furthermore, the lower steady-state potential observed at 258°C is consistent with the greater amount of oxide formed.

It can be concluded that this modification of the equipment yields satisfactory results. The welded junction, which led to some question in the interpretation of the results, will be eliminated in future measurements.

SORPTION OF URANIUM FROM UO_2SO_4 SOLUTIONS ON HYDROUS ZIRCONIA

Changes in rate of corrosion of zirconium alloys with solution composition under irradiation (see "Review and Correlation of Zircaloy-2 Radiation Corrosion Data," above) are believed to result from changes of the amounts, or the relative importance, of sorbed uranium on the alloy surface; the factor α in the corrosion equations is a function of the sorbed uranium. Accordingly, investigations of the sorption of uranium from uranyl sulfate solutions on hydrous zirconia have been conducted at elevated temperatures.

Sorption experiments have been performed with light-water solutions of uranyl sulfate containing $0.02 \text{ } m \text{ H}_2\text{SO}_4$. Exposures have been made in a titanium autoclave equipped with a centrifuge cone for solid-liquid separation at test temperature. The autoclave was charged with 5 ml of solution and 0.5 g of oxide in each case.

Most experiments were made with a zirconium oxide preparation from City Chemical Company which was pretreated by a 2-hr heating to 110°C in air before storage in capped bottles. This material, referred to as AF oxide, contained about 55 wt % H_2O and 1.7 wt % sulfate; the surface area before use was $275 \text{ m}^2/\text{g}$ by nitrogen adsorption. The surface decreased on autoclaving with water or the test solution; values from 85 to $220 \text{ m}^2/\text{g}$ have been observed for the exposed and dried (but unwashed) AF material.

Some sorption experiments have been made with material prepared by autoclaving the City Chemical oxide in water for 4 hr at 300°C and drying at 110°C in air before storage in capped bottles. This material (designated WF oxide) contains about 5% H_2O and 3.6% sulfate; the surface area of this oxide is about $76 \text{ m}^2/\text{g}$. The WF oxide changes relatively little on exposure to the test solutions.

Effect of Exposure Time on Sorption

Sorption experiments were performed at 280°C in which autoclaving time was varied from 10 min to 17 hr. One series of tests used AF oxide and uranyl sulfate solution with 45 g of uranium per liter, while the second used WF oxide and solution containing 30 g of uranium per liter. Sorption of uranium and sulfate ion, pH of the solution at conclusion of the test, and surface area of oxide residues are shown in Fig. 15.2.

Tests with the WF oxide indicate a small decrease in acidity of the solution during the first 4 hr with an equal increase between the 4th and 17th hr. No change in surface area, or in sorption of uranium or sulfate, was observed after the first 30 min.

The AF oxide shows significant changes with time in each of the parameters studied, although, except for solution pH, the values are essentially constant after 2 to 4 hr at temperature.

Fig. 15.2. Sorption on Air-Dried and Water-Autoclaved Oxides at Various Exposure Times at 280°C.

These data for AF oxide are in general agreement with those from previous studies⁷⁻⁹ which have shown that sorption by similarly treated oxide was similar in magnitude to that in in-pile films and scales on Zircaloy-2 as inferred from corrosion data and from analysis of the scales. These changes in sorption with time for AF material are almost certainly a result of sintering and dehydration of the preparation during exposure.

Effect of Temperature

Results obtained in 2- to 4-hr exposures to solutions of varying uranium concentration at temperatures from 250 to 325°C are shown in Fig. 15.3.

⁷J. C. Banter and S. H. Wheeler, *Adsorption of Uranium on Hydrated Zirconium Oxide from Uranyl Sulfate Solutions at Elevated Temperatures*, ORNL CF-61-3-94 (in press).

⁸G. Goldstein, *Sorption of Uranium on Zirconium Oxide*, ORNL report (to be published).

⁹G. H. Jenks *et al.*, *HRP Quart. Progr. Rept. May 1-Oct. 31, 1959*, ORNL-2879, pp 148-49.

Fig. 15.3. Sorption Isotherms at 250, 280, 300, and 325°C.

Amounts of uranium sorbed on the AF oxide were similar at 250, 300, and 325°C, while somewhat higher values were obtained at 280°C. The amount of sulfate sorbed (values include the original sulfate in the oxide) showed a less marked dependence on concentration. The sorption isotherm at 250°C agrees well with an older study when both are expressed as quantity sorbed per gram of dry ZrO_2 .¹⁰

The limited study of WF oxide showed much smaller absolute values of sorbed uranium but considerably greater effect of increasing temperature from 250 to 280°C.

Elution of Sorbed Uranium

Elution studies, both in batch and in column experiments, have been performed with AF and WF oxides on which uranium had been sorbed from solutions at 280°C.

Nearly all the sorbed uranium is washed from WF oxide by water, and essentially complete recovery is obtained with 0.02 *m* H_2SO_4 or 0.1 *m* HCl . A considerable fraction of the uranium sorbed on AF oxide remains after extended washing with 0.1 *m* HCl or KCl solutions and after treatment with 1.8 *M* H_2SO_4 . This difference in behavior may be due to occlusion of uranium caused by sintering of the AF oxide on exposure. This retention of uranium on the oxide is similar to that observed by films and scales formed on Zircaloy-2 in in-pile experiments.^{11,12}

BEHAVIOR OF URANYL NITRATE SOLUTIONS^{13,14}

The possibility of using $\text{UO}_2(\text{NO}_3)_2$ fuel solutions in aqueous homogeneous reactors has recently been reconsidered by Marshall.¹⁵ He points out that the nitrate system shows some advantage over the sulfate with respect to high-temperature stability toward two-liquid-phase and solid-phase formation. Direct experimental information regarding the radiation decomposition of the nitrate ion in $\text{UO}_2(\text{NO}_3)_2$ fuel solutions was not available, but from considerations of the data of Boyle and Mahlman¹⁶ it was suggested that radiation decomposition of nitrate may be negligible in the dilute $\text{UO}_2(\text{NO}_3)_2$ solutions which would be employed in reactors.

In an effort to obtain experimental information of the nitrate stability and of other factors which are of importance in the evaluation of a fuel solution, an in-pile autoclave experiment with a $\text{UO}_2(\text{NO}_3)_2$

¹⁰G. H. Jenks *et al.*, *HRP Quart. Progr. Rept.* Jan. 31, 1960, ORNL-2920, p 79.

¹¹G. H. Jenks *et al.*, *HRP Quart. Progr. Rept.* Oct. 31, 1957, ORNL-2432, p 123.

¹²B. E. Dearing, "Adsorption and Fixation of Uranium on Zircaloy in Autoclave Tests," p 5 in *Uranium Surface Contamination on Nuclear Reactor Fuel Elements* (ed. By W. M. Cashin), KAPL-2061 (Oct. 23, 1959).

¹³G. H. Jenks, H. C. Savage, *et al.*, *HRP Quart. Progr. Rept.* Apr. 30, 1960, ORNL-2947, p 60.

¹⁴R. J. Davis *et al.*, report in preparation.

¹⁵W. L. Marshall, *Consideration of $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O(D}_2\text{O)}$ as a High Temperature Reactor Fuel*, ORNL CF-59-5-100 (May 26, 1959).

¹⁶J. W. Boyle and H. A. Mahlman, *Nuclear Sci. and Eng.* 2, 492-500 (1957).

solution has been carried out. The other factors investigated were: radiolytic gas formation and copper-catalyzed recombination, and Zircaloy-2 radiation corrosion in the nitrate solution. No information has been reported previously on the radiation corrosion of Zircaloy-2 in $\text{UO}_2(\text{NO}_3)_2$ solutions. Recombination of H_2 and O_2 and D_2 and O_2 catalyzed by copper has been investigated out-of-pile by Kelly *et al.*^{17,18} The activation energy found was similar to that in sulfate systems. The K_{Cu} values for light-water nitrate solutions were about half those for similar sulfate solutions. D_2O as solvent reduced the K_{Cu} by approximately another factor of 2. As mentioned, Boyle and Mahlman report values of G_{N_2} in rather concentrated $\text{Th}(\text{NO}_3)_4$ solutions [$\sim 0.3\text{--}3\text{ }m\text{ Th}(\text{NO}_3)_4$]. For fission fragments, G_{N_2} was considerably higher than for fast neutrons or gamma rays, and it decreased rapidly with decreasing concentration of $\text{Th}(\text{NO}_3)_4$. Some N_2O was found; it was about 10% of the amount of N_2 . Sowden and Lynde¹⁹ subjected $\text{Ca}(\text{NO}_3)_2$ solutions (0.21 to $4\text{ }M\text{ NO}_3^-$) to fission recoils and reported $G_{\text{N}_2} = 0.004 (\text{NO}_3^-)^{1.5}$ for the entire concentration range. The G_{N_2} values of Boyle and Mahlman for nitrate concentration within the indicated limits are expressed fairly well by this equation as are, also, the G_{N_2} values reported²⁰ for $\text{UO}_2(\text{NO}_3)_2$ ($\sim 1\text{ }M$) in Los Alamos water boilers. Gas phase recombination of nitrogen with oxygen has been studied.^{21,22} The G_{NO_2} values increase with the ratio of oxygen to nitrogen and with the addition of water vapor, and are considerably higher at elevated temperatures than at room temperature. Values of G_{NO_2} from 0.3 to 5 were reported. Varying amounts of N_2O were also formed, the average being about half the amount of NO_2 . Values of G_{H_2} were also measured by Sowden and Lynde, and these results were expressed by $G_{\text{H}_2} = 2.0 - [0.8(\text{NO}_3^-)^{1/3}]$.

In the present work, the autoclave and the coupon specimens were made of Zircaloy-2. The initial composition of the solution was $0.032\text{ }m\text{ UO}_2(\text{NO}_3)_2$, $0.008\text{ }m\text{ Cu}(\text{NO}_3)_2$, $0.072\text{ }m$ excess DNO_3 , and $0.17\text{ }m\text{ NO}_3^-$ in D_2O , and the autoclave was about 85% full at the maximum exposure temperature of 280°C . Barton and Hebert²³ tested the stability of this solution in a quartz tube, and it appeared to be stable to 327°C . During exposure to full reactor power the solution temperature was 280°C .

Pretreatment was done at 280°C for 185 hr. The exposure to full reactor power irradiation was performed in five successive periods. The first three and the last were of about one day each, and the

¹⁷M. J. Kelly *et al.*, *The Effectiveness of Cupric Ion as a Homogeneous Catalyst in the $\text{UO}_3\text{--HNO}_3\text{--H}_2\text{O}$ System for the Recombination of Hydrogen and Oxygen Produced by Radiolytic Decomposition*, ORNL CF-59-9-15 (Sept. 3, 1959).

¹⁸M. J. Kelly, private communication.

¹⁹R. G. Sowden and Elizabeth M. Lynde, *The Effect of Fission Recoil Energy on Calcium Nitrate Solutions*, A.E.R.E. C/R-2480 (February 1958).

²⁰R. M. Bidwell, L. D. P. King, and W. R. Wyckoff, *Nuclear Sci. and Eng.* **1**, 452 (1956).

²¹C. G. Edwards and F. Moseley, *The Production of Chemicals from Reactors. Part 1. The Fixation of Atmospheric Nitrogen by Fission Fragments*, A.E.R.E. C/R-2710 (October 1958).

²²P. Hartek and S. Dondes, *Nucleonics* **14**(7), 22–25 (1956).

²³C. J. Barton and G. M. Hebert, private communication.

fourth period was of about two days duration. The usual pressure-temperature data were obtained. Between the irradiation periods the experiment was retracted, in most cases with the reactor operating. Prior to the first and to the last irradiation periods, a series of radiolytic-gas buildup curves was obtained by short exposures at 225°C and with the reactor at 20% of full power. The initial exposure of this type was at 235°C.

After completion of the exposure, the autoclave was immediately cooled and vented, and about three weeks later was opened for examination. The solution, the autoclave rinse water, and the large amount of suspended solid material were chemically analyzed. The specimens were visually examined, then weighed. Some of them were defilmed, and others were pickled to remove a surface sample for analyses. After further pickling, two samples were used for Zr^{95} activity analysis and estimation of thermal neutron flux.

The results of this experiment, which do not make the use of uranyl nitrate solutions look especially promising, are summarized as follows:

All the data are consistent with the occurrence of nitrate decomposition during radiation exposure. The results of pressure measurements during the initial 225 to 235°C exposures and during the initial 280°C exposure provide evidence that the initial nitrate decomposition rate was greater than that predicted by the reported results of Sowden and Lynde by factors of from about 7 to 70.

A back reaction of the nitrate decomposition products is indicated by the results of the first 280°C radiation exposure and by the results of the initial 225 and 235°C exposures. The $G_{\text{NO}_3^-}$ value of about 1 to 3 for gas-phase recombination, estimated from these results by assuming that NO_3^- is the sole product of recombination, is within the range of values which have been reported by others. It should be noted, however, that the conditions of pressure, temperature, and gas phase composition in this experiment differ from those employed in the other reported studies, and the $G_{\text{NO}_3^-}$ for this present experiment cannot be accurately predicted from the other studies.

The initial K_{Cu} values (225°C) are about three times as large as those found out-of-pile by Kelly *et al.* The initial G_{D_2} value of 1.3 is near agreement with the value of about 1.5 found for nitrate solutions by other workers. The apparent decreases in K_{Cu} and G_{D_2} throughout the exposure can be ascribed to a loss of uranium and copper from solution.

The Zircaloy-2 corrosion rates during the initial 100 hr of radiation at 280°C were probably in the range 6 to 12 mils/yr (mpy). A corrosion rate in the same range would be expected for uranyl sulfate solutions of similar concentrations. During the final 34 hr, the rate was greater than 12 mpy and was probably as high as 30 or more. The large amount of sorbed uranium (0.16 mg/cm²) indicates that a high effective power density prevailed in the system and probably accounts for the high rate near the end of the exposure.

16. SLURRY CORROSION AND BLANKET MATERIALS TESTS

E. L. Compere

H. C. Savage

J. M. Baker

W. J. Leonard¹

S. A. Reed

S. E. Bolt

R. A. Lorenz

A. J. Shor

V. A. DeCarlo

R. E. McDonald¹

A. J. Taylor²

R. B. Gallaher

R. A. McNees²

L. F. Woo

M. L. Picklesimer¹

THORIA-PELLET TEST PROGRAM

The use of thoria pellets as a possible blanket material in a two-region breeder reactor was investigated at ORNL in 1953-54 in a series of preliminary tests using fluidized beds of ThO₂ cylinders and washers.³ Recent renewed interest in a pellet blanket⁴ has stimulated a more comprehensive investigation of methods for preparing suitable thoria compacts and of development of tests for estimating the attrition of the pellets under simulated reactor conditions.

In one proposed 400-Mw breeder reactor⁴ the blanket would contain ~27 metric tons of thoria pellets. If the pellets were attrited at the maximum acceptable rate⁵ of 0.06%/day as a result of periodic agitation of the beds, thermal ratcheting, etc., ~16 kg/day of fine material would result. If pellets are moved only a few times during the course of their exposure, losses due to pellet attrition as a consequence of movement from one reactor region to another are probably momentarily higher but are much less frequent. Such movement may be accomplished by fluidization, jet-pumping, or other schemes.

The size distribution and chemical behavior of the degradation products are of considerable interest since these properties will control disposition of the fines within the reactor system. While in the reactor system, the nature, extent, and locality of their accumulation will be important, since they may be the cause of hot spots, reduced heat transfer, maintenance problems, etc. Procedures for removal of these degradation products are of interest, in addition, because of potential processing advantages.

Efforts during the year have been devoted to development of test procedures for characterization of pellet preparations and to examination of experimental preparations from a variety of sources. Many of the preparations were prepared by the Chemical Technology Division or by the Ceramics Group of the Metallurgy Division. Samples have, in addition, been obtained from Davison Chemical Company, American Lava Corporation, Norton Company, and Nuclear Materials and Equipment Corporation.

¹Metallurgy Division.

²Ceramics Group, Metallurgy Division.

³I. Spiewak and J. A. Hafford, *Abrasion Test of Thoria Pellets*, ORNL CF-54-3-44 (Mar. 9, 1954).

⁴I. Spiewak *et al.*, *HRP Quart. Progr. Rept. Apr. 30, 1960*, ORNL-2947, p 32.

⁵R. B. Briggs, ORNL HRP-60-132 (Oct. 20, 1960).

The experimental pellets, which were calcined in the range 1000 to 1750°C, included 0.2-in.-diam spheres and right cylinders and cylinders with hemispherical ends, ~0.2 in. in diameter by 0.2 in. in length. Major fabrication variables included pellet density, calcination temperature, initial thoria calcination temperature and particle size, additives (CaO, Al₂O₃), pressing pressures, die lubricants, and binders.

Test Methods

Autoclave Tests. — Specimens from all preparations were exposed to pure water at 260°C in static autoclave tests of 17 to 350 hr duration. The effect on the preparations was evaluated from weight changes, dimensional changes, differences in general appearance as observed with an optical microscope, and by chemical analysis of the supernatant liquid for leachable additives originally in the samples.

When sufficient specimens were available, a portion of them was also subjected to 24-hr rocking-autoclave tests in 260°C water, using the same post-run examinations. The 2.5-liter autoclave was rocked $\pm 60^\circ$ at 38 cycles/min. Rocking-autoclave tests served to indicate susceptibility to attrition due to pellet agitation as well as leaching in high-temperature water. Low values on this test would be expected to imply satisfactory handling qualities for reactor exposure.

Ball-Mill Tests. — Ball-mill tests have served as one rapid and reproducible method for determining the relative integrity of thoria^{6,7} and urania⁸ experimental pellet preparations.

A systematic study of the effect of several pertinent ball-mill-test variables on rate of attrition of the pellets and on the size distribution of the particles which were rubbed from the pellets has been conducted.

These tests revealed that weight-loss rates increased with increasing speed of rotation of the mill and with increase in number of pellets charged to the mill. Rates of attrition were nearly independent of ball-mill length or quantity of water in the mill.⁷ Examination of fines produced by wet-milling the pellets⁷ showed a mean particle diameter of 2 μ with 80% of the material less than 6 μ in diameter.

The grain size of thoria used in preparing these pellets was 7 μ , and some grain growth would be expected during firing of the specimens; accordingly, it appears that attrition is due to wear of material from pellet surface rather than dislodgment of thoria grains on gross chipping of the specimens. These findings are in agreement with similar studies elsewhere with pellets of UO₂.⁹

⁶E. L. Compere *et al.*, *HRP Quart. Progr. Rept.* Apr. 30, 1960, ORNL-2947, p 92.

⁷E. L. Compere *et al.*, *HRP Quart. Progr. Rept.* July 31, 1960, ORNL-3004, p 89.

⁸M. R. Scheve, *Liquid Fluidized Bed Study*, MND-LFBR-2303, p 10 (February 1960).

⁹E. L. Compere *et al.*, *Report on Trip to the Martin Company, Baltimore, Maryland, August 31, 1960*, ORNL CF-60-9-63 (Sept. 14, 1960).

Spouted-Bed Tests. — The spouted-bed test has been generally applied to pellet preparations as a rapid screening test to indicate susceptibility to attrition under agitation. The method consisted in consecutive 1-hr exposures at room temperature using ten pellets in a bed jetted to produce pellet trajectories of a given height, for example, with a superficial liquid velocity of 0.2 fps and a jet velocity of 24 fps. Quality of the pellets was determined after each 1-hr exposure by measuring weight loss and dimensional changes and by microscopic examination. Rates of attrition during these tests have ranged from 30 to 0.13%/hr, after various exposure times on various preparations. Of 12 preparations in one series, for example, six displayed rates of 1%/hr or less. After ten consecutive 1-hr exposures (25 were used in a few cases), attrition rates were frequently a factor of 3 to 4 lower than the initial 1-hr rate, but subsequently appeared to become relatively steady in value. This was attributed to pellet surfaces becoming rounded and smoother.

Fluidized-Bed Tests. — In a few cases for which a sufficient number of pellets were available, the pellet preparations have been tested in fluidized beds. A typical test is one in which 1500 pellets (744 g), which formed an 8-in. settled bed in a 2-in. Pyrex pipe, were fluidized at 0.7 fps superficial velocity, resulting in a bed expansion of 40 to 50%. The pellets were fluidized for four 2-hr test periods. Quality of the pellets was ascertained as in the spouting-bed tests.

Evaluation of Experimental Pellets

The considerable quantity of empirical data developed in this program has been reported in detail to the groups concerned with preparation of the materials and to HRP personnel. Accordingly, no attempt will be made to present or to summarize the data in this document. The following brief description presents data and conclusions typical of those obtained in a large number of examinations.

Examination of Pellets from Batch P-39. — Pellet preparation P-39 consisted of 0.2-in. cylinders with hemispherical ends, prepared from pure thoria with the addition of 5% aluminum stearate (equivalent to 0.3% Al_2O_3 in the pellet) as lubricant. After pressing, the material was fired at 1750°C to a density (mercury immersion) of 9.7. This material, which was used for evaluation of the ball-milling and spouted-bed procedures described above, performed as follows:

Static autoclave, 260°C	0.0005–0.0012%/hr
Rocking autoclave, 260°C	1.2%/hr
Fluidized bed, 25°C	0.2–0.1%/hr
Ball mill, 25°C	2.3–1.1%/hr
Spouted bed, 25°C	1.4–3%/hr (first hr) 0.8%/hr (steady)

Examination of Preparations from D-40 Thoria Powder. — A series of evaluation tests⁷ has been made for determining the integrity and relative attrition rates of a group of 24 experimental pellet preparations which were fabricated by the Ceramics Group of the Metallurgy Division.¹⁰ The group

¹⁰A. Taboada *et al.*, HRP Quart. Progr. Rept. Apr. 30, 1960, ORNL-2947, p 32.

of pellets resulted from a systematic study of composition and fabrication variables associated with the manufacture of pellets from a specific preparation (batch D-40) of thoria powder.

The group was comprised of both flat-ended and spherical-ended pellets ($\sim 0.2 \times 0.2$ in.) which were made from ThO_2 precalcined at three temperatures, 800, 1200, and 1425°C . Final calcination of all pellet preparations was at 1650°C . Twelve of the preparations contained ~ 0.5 wt % CaO. By chemical analysis, it was found that the group of pellets to which no CaO was intentionally added contained calcium in an amount equivalent to ~ 0.05 wt % CaO. Half of the samples had been tumbled after final firing to remove easily abraded projections.

Average 2-hr weight-loss rates of pellets in the ball-mill test ranged from 0.22 to 4.65%/hr. The highest rate was shown by a round-end, nontumbled, CaO-free preparation which was compacted from 800°C -calcined ThO_2 . The lowest rate was displayed by a preparation which was made from 1425°C -calcined ThO_2 powder with 0.5 wt % CaO that had rounded ends and had been tumbled after final calcination at 1650°C .

Average 2-hr rates of pellets exposed in initial spouted-bed tests ranged from 0.13 to 2.80%/hr. The same preparations which displayed the highest and the lowest average rates in the ball-mill tests were worst and best in the spouted-bed tests. The average weight-loss rate (0.90%/hr) of pellets containing no additive was a factor of about 1.5 greater than the average rate (0.64%/hr) of pellets containing CaO additive.

With flat-ended pellets, attrition rates in both ball-mill and spouted-bed tests increased as the ThO_2 precalcination temperature was increased from 800 to 1425°C ; conversely, the attrition rates of cylinders with rounded ends decreased as the ThO_2 precalcination temperature was increased.

In 72-hr static autoclave tests, weight-loss rates varied between 3×10^{-5} and $600 \times 10^{-5}\%$ /hr. Some calcium was leached from all preparations containing CaO as additive; two preparations which displayed the highest weight losses were those which lost the highest percentages of calcium. During subsequent exposure in spouted-bed tests, several pellets of both preparations disintegrated during the first hour of exposure. In general, preparations from which the highest percentages of calcium were leached displayed the highest deterioration rates during the post-autoclave spouted-bed tests. Thus the quality of the pellets was changed significantly due to the reaction of high-temperature water and the additive.

For the group of pellets containing no CaO as additive, the preparations which were tumbled after final calcination at 1650°C displayed rates in spouted-bed tests approximately twofold higher after autoclaving. No trend in rates of nontumbled pellets was observed.

LOOP TESTS OF THORIA PELLETS

A few tests have been conducted with the pellets exposed to D_2O at 260°C in a 100-A loop assembly using N_2 as the cover gas. A typical test of this series was made with an old preparation

of 0.1-in. cylindrical pellets (American Lava Corporation¹¹) which contained 0.5 wt % CaO as additive. Static autoclave tests at 260°C on single pellets gave weight-loss rates which ranged between 0.0002 and 0.02%/hr. Two consecutive 24-hr rocking-autoclave tests gave attrition rates which averaged 0.7%/hr.

For the loop test, pellets were exposed in a horizontal, randomly packed static bed and in a vertical column in which the pellets were fluidized. With uniform cylindrical pellets, under geometries such as that of the experiment, a pulsating action may develop in fluidized beds; such a pulsation was observed in this experiment. The superficial velocity through the horizontal bed was 1.3 fps, and a velocity of 0.2 fps was maintained through the pulsating fluidized bed. A television x-ray unit was used periodically to observe that there was constant movement of the pellets in the vertical bed.

During the 288-hr test at 260°C, the attrition rate in the horizontal bed was 0.008%/hr. In the fluidized bed the rate was 0.02%/hr. Seventy-seven per cent of the material lost from cylinders in the horizontal bed remained as fines within the bed. No fines remained in the fluidized bed. Approximately 7% of the calcium was leached from the pellets. Although 26 g of ThO₂ and 0.2 g of calcium were released from the beds, only trace quantities of the material were detected in the circulating D₂O. The bulk of the attrition products was deposited in the loop piping. The material was recovered by a circulating rinse of the loop, using 5% nitric acid at 200°C.

CORROSION BY SLURRIES IN IN-PILE AUTOCLAVES

Operation and Examination of Irradiated Assemblies

Corrosion by slurries of metals of interest to the Homogeneous Reactor Program is under examination in a continuing program of testing using in-pile autoclave assemblies of Zircaloy-2. Two such experiments were irradiated in the HB-5 facility of the LITR and examined during the report period.^{12,13}

Each assembly contained a thorium-uranium slurry in D₂O with palladium to catalyze recombination of D₂ and O₂. Concentrations of slurry were such that with the autoclave in the fully inserted position the fission power density was 34 and 43 w/ml, respectively, at 280°C. In-pile exposures were of relatively short duration in both cases; Table 16.1 indicates operating conditions and exposure times for these experiments.

Stepwise heating (in 30°C increments) with rocking of the assembly between each heating cycle was necessary to maintain the slurry suspended during out-of-pile heatup to 280°C.

¹¹I. Spiewak and J. A. Hafford, *Abrasion Test of Thorium Pellets*, ORNL CF-54-3-44 (Mar. 9, 1954).

¹²E. L. Compere *et al.*, *HRP Quart. Progr. Rept. Apr. 30, 1960*, ORNL-2947, p 99.

¹³E. L. Compere *et al.*, *HRP Quart. Progr. Rept. July 31, 1960*, ORNL-3004, p 93.

Table 16.1. Radiation Corrosion of Coupon Specimens in Zircaloy-2 Autoclave Experiments

	Experiment L5Z-152S	Experiment L5Z-153S
Temperature, °C	280	280
Concentration of slurry, g of Th per kg of D ₂ O	1080	820
Wt % enriched U, with respect to Th	7.9	13.2
Concentration of catalyst, m of Pd	0.0006	0.019
Atmosphere	Excess O ₂	Excess O ₂
Hours at temperature out-of-pile	673	261
Total hours at temperature	738	422
Hours irradiated	42	136
Effective fraction of full irradiation time, fully inserted flux	0.151	0.101
Estimated flux, neutrons cm ⁻² sec ⁻¹ (in the fully inserted position)	1.2×10^{13}	1.2×10^{13}
Maximum power density, w/ml, at 280°C	34	43
Average power density while irradiated, w/ml, at 280°C	5.1	4.3
Autoclave generalized corrosion, ^a μin.		
Out-of-pile	51	52
Total	54	53
Coupon-specimen corrosion, ^b μin.		
Zircaloy-2 ^c	13, 17	13, 19
Type 347 SS	28	84
Titanium-75A	29	39

^aBased on oxygen measurements.

^bCorrosion of the first three Zircaloy-2, stainless steel, and titanium specimens based on weight loss; corrosion of the last Zircaloy-2 specimen based on weight gain.

^cIn a number of experiments Zircaloy-2 has been observed to gain in weight as a result of in-pile exposure. Consequently, the results from the first three Zircaloy-2 coupons represent the least amount of corrosion that could have occurred.

The first of these experiments (designated L5Z-152S) was operated at 280°C for 673 hr out-of-pile before insertion; after operation for 17 hr in the fully retracted position (3% of flux at fully inserted position) the experiment was moved to the maximum flux position. After 5 hr of smooth operation it was necessary to retract the assembly because of a temperature rise which suggested deposition of slurry around the thermowell. The experiment was terminated after some exploratory exposures (to 15% of maximum flux) because of a partial plug in the capillary tubing between the autoclave and the pressure sensing equipment.

The second experiment (designated L5Z-153S) was operated out-of-pile for 250 hr before insertion; because of excessive buildup of radiolytic gas at the maximum flux position (corresponding to 43 w/ml) the assembly was retracted to a lower flux (7% of maximum) for continuous irradiation.

This experiment was also terminated (after 162 hr in-pile) because of partial plugging of the capillary pressure leads.

Performance of the palladium catalyst was quite different on the two experiments. When the increased concentration of palladium in L5Z-153S is considered, the catalyst efficiency was less by more than a factor of 100 in the second experiment.

Generalized corrosion in these experiments was followed by decrease in oxygen pressure measured at 25°C during reactor shutdowns.^{14,15} Both experiments showed a rapid initial consumption of oxygen during initial out-of-pile operation (perhaps due to some oxidation of uranium in the slurry), followed by a slow decrease, which is linear with time, corresponding to corrosion at perhaps 0.4 mil/yr. The behavior of experiment L5Z-153S is shown in Fig. 16.1. In neither case was the effect of the irradiation exposure observable.

¹⁴E. L. Compere *et al.*, *HRP Quart. Progr. Rept. Jan. 31, 1958*, ORNL-2493, p 113.

¹⁵K. S. Warren and R. J. Davis, *In-Reactor Autoclave Corrosion Studies - LITR. 1. Outline of Methods and Procedures*, ORNL CF-57-5-110 (May 22, 1957).

Fig. 16.1. Radiation Corrosion of Zircaloy-2 Autoclave by Thoria-Urania Slurry.

The results obtained from the corrosion specimens in these experiments are shown in Table 16.1. As in some previous experiments, corrosion of Zircaloy-2 coupon specimens (especially in experiment L5Z-153S) based on weight changes (<0.5 mg) agreed poorly with the value predicted from oxygen consumption data. Techniques for the adequate removal of zirconium oxide corrosion films have not yet been developed. Since an indeterminate amount of film may be lost in the experiment, corrosion results based on weight-change data will tend to have lower values than those based on oxygen consumption.

Development of Al_2O_3 Slurry Capillary Filter

Difficulties, described above, in operation of in-pile autoclaves have necessitated development of a filter to prevent plugging of the capillary pressure leads by slurry agglomeration.

An Al_2O_3 filter for application between Zircaloy-2 slurry autoclaves and the attached water-filled capillary lines leading to pressure instruments has been fabricated following the development of Al_2O_3 -Zircaloy-2 brazing procedures. A porous, 100% Al_2O_3 (Coors Porcelain Company, AP-100 body) tube, 0.13 in. OD $\times$ 0.07 in. ID $\times$ 0.25 in., was pretested by exposure in a static autoclave for eight weeks to 280°C water, with a resultant weight loss of 0.24%. Subsequently, one end of the tube was brazed coaxially with the 0.052-in. hole to the pressure capillary tap in the Zircaloy-2 autoclave closure. A Zircaloy-2 cover was brazed to the other end of the Al_2O_3 tubing. The brazing (by the HRP Metallurgy Section and the Welding and Brazing Laboratory of the Metallurgy Division, Fabrication Section) was carried out in a vacuum furnace, using an alloy containing 48% zirconium, 48% titanium, and 4% beryllium.

The brazed filter assembly satisfactorily separated slurry from water, with no visible solids carry-over and no evidence of plugging. Exposure of the assembly to 280°C water for 64 hr did not result in attack of the joint or any appreciable corrosion. Further testing is being carried out, using the filters as components in slurry autoclave experiments.

HYDRIDING OF ZIRCONIUM-BASE ALLOYS

Out-of-Pile Testing in Toroids

Previous investigations¹⁶ of the variables associated with hydriding of zirconium-base alloys during exposure to circulating (slug flow) aqueous slurries in toroids were concerned with the relative effects of (1) thoria or thoria-urania preparation variables, (2) operating atmospheres, (3) amount of gas overpressure, and (4) zirconium-alloy composition. Recent studies have been directed toward evaluating the effects of slurry flow velocity and of operating temperatures on the severity of hydriding.

To determine the relative effects of flow velocity, a group of four tests was made at 10 fps to compare with previous runs made at 26 fps. Other test conditions duplicated those of several

¹⁶E. L. Compere *et al.*, HRP Quart. Progr. Rept. Oct. 31, 1959, ORNL-2879, p 191.

earlier runs.¹⁶ Slurries of two mixed thorium-uranium oxide preparations (6 and 9% uranium based on thorium) were circulated at a concentration of 500 g of thorium-uranium per kg of D₂O in 300-hr tests at 280°C. Four pin specimens of Zircaloy-2, item 569, were exposed in each test. Deuterium gas was charged to the toroids to provide total pressures of 10 psig in two toroids and 50 and 100 psig, respectively, in the other two toroids.

In previous tests conducted at 26 fps, specimens of item-569 Zircaloy-2 were grossly hydrided in 300-hr periods with 100 psi deuterium overpressure, and specimens picked up significant quantities of deuterium in tests in which 10 to 50 psi overpressure of D₂ was used.¹⁶

Gross hydriding of the type previously observed in the runs at higher flow velocity was not observed in the tests at 10 fps. Metallographic examinations revealed a concentration of zirconium hydride needles on the upstream areas of the pins to a depth of ~15 mils. The same effect, which extended to a depth of ~8 mils, was noted on the downstream areas of the specimens.

The extent of attack as well as the degree of hydriding was less at the lower velocity; for example, weight losses of scrubbed specimens exposed at 10 fps ranged from nil to 0.3 mg/cm², as compared with losses of 4.8 to 7 mg/cm² for specimens exposed at 26 fps. Thus the severity of hydriding appeared to be directly related to the flow velocity, presumably as a result of more severe attack at the higher velocity under slug-flow conditions in the toroids.

Examination of specimens from toroid tests at 200°C revealed no evidence of hydriding of zirconium alloys, whereas frequent and sometimes severe hydriding of the alloys occurred when the same slurries were used in tests at 280°C.¹⁶ Recently, specimens from two batches of Zircaloy-2 (items 569 and 611) were examined for evidence of hydriding after they had been exposed at 330°C in 300-hr tests at 26 fps.

Two tests used a slurry of (batch DT-18) thoria-0.5% urania at a concentration of 400 g of Th per kg of D₂O, with an atmosphere of 90 psig (room temperature) of D₂ in one toroid and of O₂ in another toroid. Comparison tests were made with the same overpressures of D₂ and O₂ but with only D₂O in the toroids.

Metallographic examination revealed some hydrogen pickup by all specimens. The two specimens exposed in oxygenated D₂O displayed an increase in apparent hydrogen content to a depth of 2 to 6 mils in isolated areas under defects in the oxide corrosion film. Specimens exposed in D₂O with deuterium atmosphere displayed a shallow penetration of hydride needles around the total circumference of the pins extending to a depth of about 5 mils on the upstream portions. No increase in hydride was noted in the interior of the pins.

More defects were noted in the oxide corrosion film of specimens exposed in slurry with an oxygen atmosphere. A thin layer containing hydride needles was detected around the circumference of the specimens. In slurry tests with a deuterium atmosphere a general increase in hydride needles was found throughout the pins, with heaviest formation on the upstream (~15 mils in depth) and downstream (~7 mils) areas.

Based on these findings, it appears that increased temperature promoted hydride needle formation in aqueous systems and that the effect was intensified under hydrogen atmosphere with slurry in slug flow in the toroids.

In-Pile Testing in Autoclaves¹⁶

Specimens of Zircaloy-2 from five in-pile autoclave tests in which thoria or thoria-urania slurries were irradiated in previous years have been examined to ascertain the effect of irradiation on hydrogen uptake by this alloy. Data obtained from this study are shown, along with irradiation conditions, in Table 16.2. Zircaloy-2 generally acquires 20 to 100 ppm of hydrogen on out-of-pile exposure to high-temperature water. No effect of atmosphere or of irradiation on hydrogen pickup is shown by the data from these specimens.

OPERATION OF IN-PILE SLURRY LOOP

During the past year final component development and out-of-pile mockup tests were completed, the construction of the in-pile loop and out-of-pile demonstration of the assembly were completed, and satisfactory in-pile operation of the loop was accomplished. This important effort, which has been described in some detail elsewhere,¹⁷⁻¹⁹ is discussed briefly.

Design and Prototype Testing

The final in-pile loop, designated L-2-27S and shown in Fig. 16.2, is the result of a considerable component development and mockup testing program in which more than 4000 hr of out-of-pile operation of prototype loops was accomplished.

The core section of coiled $\frac{1}{2}$ -in. sched-40 pipe was designed to provide sufficient volume (300 cc) to expose 35% of the slurry inventory to maximum neutron flux, to provide space for corrosion test specimens, and to afford flow velocities of ~ 6 fps to prevent settling of the slurry. A mockup of this core section was tested for 1500 hr in an out-of-pile prototype loop.

The 5-gpm canned-rotor pump with bearings and journal bushings of aluminum oxide, used on the in-pile loop, was identical to those used in in-pile solution loops.^{20,21} Before use in the in-pile loop, such a pump was tested for 3500 hr on the prototype loop; a portion of this time the pump was operated without a bearing purge so that thoria was able to enter the bearing region; no difficulty was encountered.

¹⁷H. C. Savage *et al.*, *HRP Quart. Progr. Rept.* Apr. 30, 1960, ORNL-2947, p 101.

¹⁸H. C. Savage *et al.*, *HRP Quart. Progr. Rept.* July 31, 1960, ORNL-3004, p 96.

¹⁹H. C. Savage *et al.*, *HRP Quart. Progr. Rept.* Nov. 30, 1960, ORNL-3061, p 89.

²⁰H. C. Savage, *Sintered Alumina as a Pump Bearing and Journal Material*, ORNL CF-57-11-122 (Nov. 26, 1957).

²¹H. C. Savage *et al.*, *In-Pile Corrosion Test Loops for Aqueous Homogeneous Reactor Solutions*, ORNL-2977 (Nov. 10, 1960).

Table 16.2. Hydrogen Pickup in Zircaloy-2 Autoclaves

Experiment	Thorium (g per kg of D ₂ O)	Uranium (g per kg of D ₂ O)	Atmosphere	Hours at Temperature	Hours Irradiated	Average Fission Power Density (w/ml)	Total Corrosion Based on Gas Measurement (μ in.)	Zircaloy-2 Specimen	Zircaloy-2 Item No.	Specimen Corrosion (μ in.)	Hydrogen After Exposure (ppm) ^a	Hydrogen Pickup (ppm) ^a
L6Z-122S	990	5	O ₂	1074	765	0.8	105	L	1212	35	120	60
								M	1212	44	130	70
L6Z-125S	950	5	D ₂	1232	1044	0.7	62	L	1212	118	160	100
								M	1212	94 ^b	120	60
L6Z-126S	980	50	D ₂	314	140	2.5	53	L	1212	55	130	70
								M	1212	40 ^b	170	110
L6Z-127S	400	20	O ₂	1122	732	1.2	100	M ₁	1215D	104	150	40
								M ₂	1215D	8 ^b	140	30
Y6Z-128S	410	20	O ₂	1143	0	0	33	M ₁	1215D	6 ^c	160	50
								M ₂	1215D	0 ^c	130	20
L6Z-129S	1090	54	O ₂	1660	1260	4.5	175	S ₂	1215G	145 ^b	210	90

^aHydrogen content expressed as ppm H with no distinction between H and D atoms.^bUndeformed specimen.^cSpecimen corrosion based on weight loss here, all others based on weight gain.

Based on these findings, it appears that increased temperature promoted hydride needle formation in aqueous systems and that the effect was intensified under hydrogen atmosphere with slurry in slug flow in the toroids.

In-Pile Testing in Autoclaves¹⁶

Specimens of Zircaloy-2 from five in-pile autoclave tests in which thoria or thoria-urania slurries were irradiated in previous years have been examined to ascertain the effect of irradiation on hydrogen uptake by this alloy. Data obtained from this study are shown, along with irradiation conditions, in Table 16.2. Zircaloy-2 generally acquires 20 to 100 ppm of hydrogen on out-of-pile exposure to high-temperature water. No effect of atmosphere or of irradiation on hydrogen pickup is shown by the data from these specimens.

OPERATION OF IN-PILE SLURRY LOOP

During the past year final component development and out-of-pile mockup tests were completed, the construction of the in-pile loop and out-of-pile demonstration of the assembly were completed, and satisfactory in-pile operation of the loop was accomplished. This important effort, which has been described in some detail elsewhere,¹⁷⁻¹⁹ is discussed briefly.

Design and Prototype Testing

The final in-pile loop, designated L-2-27S and shown in Fig. 16.2, is the result of a considerable component development and mockup testing program in which more than 4000 hr of out-of-pile operation of prototype loops was accomplished.

The core section of coiled $\frac{1}{2}$ -in. sched-40 pipe was designed to provide sufficient volume (300 cc) to expose 35% of the slurry inventory to maximum neutron flux, to provide space for corrosion test specimens, and to afford flow velocities of ~ 6 fps to prevent settling of the slurry. A mockup of this core section was tested for 1500 hr in an out-of-pile prototype loop.

The 5-gpm canned-rotor pump with bearings and journal bushings of aluminum oxide, used on the in-pile loop, was identical to those used in in-pile solution loops.^{20,21} Before use in the in-pile loop, such a pump was tested for 3500 hr on the prototype loop; a portion of this time the pump was operated without a bearing purge so that thoria was able to enter the bearing region; no difficulty was encountered.

¹⁷H. C. Savage *et al.*, *HRP Quart. Progr. Rept. Apr. 30, 1960*, ORNL-2947, p 101.

¹⁸H. C. Savage *et al.*, *HRP Quart. Progr. Rept. July 31, 1960*, ORNL-3004, p 96.

¹⁹H. C. Savage *et al.*, *HRP Quart. Progr. Rept. Nov. 30, 1960*, ORNL-3061, p 89.

²⁰H. C. Savage, *Sintered Alumina as a Pump Bearing and Journal Material*, ORNL CF-57-11-122 (Nov. 26, 1957).

²¹H. C. Savage *et al.*, *In-Pile Corrosion Test Loops for Aqueous Homogeneous Reactor Solutions*, ORNL-2977 (Nov. 10, 1960).

The sintered stainless steel filter ($8\text{-}\mu$ mean-pore diameter) which provided thorium-free filtrate for the pressurizer and the pump bearing purge was operated successfully for 4200 hr in prototype loops with thorium slurries containing up to 1400 g of ThO_2 per kg of D_2O and at temperatures to 280°C .

The sampling system, capable of removing 15 ml of slurry from the main loop stream and replacing D_2O to maintain a constant volume in the loop, consisted of sample holdup and carrier tanks interconnected through capillary tubing and valves with the loop. The system was tested by drawing 21 samples from the prototype loop; no difficulty in operation was observed.

Before operation of the in-pile loop, extensive out-of-pile testing of loop corrosion was performed in prototype loops. Over-all corrosion during three runs totaling 2100 hr of operation at 280°C at flow rates of ~ 8 fps of slurry containing 450 to 1400 g of ThO_2 per kg of D_2O was shown to be (by chromium analysis of the slurry and by oxygen uptake of the system) less than 0.7 mil/yr (mpy).

A sample of the thorium-uranium slurry from batch D-22 subsequently used in the in-pile loop was circulated for 700 hr at 280°C in the prototype loop. Slurry samples removed during this operation reduced the $\text{ThO}_2\text{-UO}_2$ concentration from 1400 to 700 g per kg of D_2O ; analysis of these samples indicated that all slurry in the loop was in circulation, and periodic radiographic examination of the core section revealed no thorium deposition. The mean particle size of the slurry was decreased during the 700 hr from 1.9 to $1.6\text{ }\mu$.

Activity and stability of the palladium catalyst for $\text{D}_2\text{-O}_2$ recombination were evaluated in the prototype loop tests. The palladium in slurry from batch D-22 was shown to require 600 hr of circulation at 280°C to lose half its activity.

In-Pile Operation

Satisfactory performance of the in-pile loop L-2-275 and its auxiliary equipment was demonstrated in more than 900 hr of out-of-pile circulation of slurry at 280°C . The loop was then installed in beam hole HB-2 of the LITR. The circulating slurry at the start of the irradiation contained 1350 g of Th per kg of D_2O (980 g of Th per liter at 280°C); the slurry contained 0.4% by weight of enriched uranium (based on thorium content) and 0.019 m palladium. The loop was operated at 280°C with velocities in the piping of 6 to 8 fps with the slurry maintained under an oxygen atmosphere. The experiment was completed after 3115 hr of slurry circulation, of which 2220 hr was continuous in-pile operation and 1839 hr was with the LITR at 3 Mw. Withdrawal of six samples during irradiation reduced the circulating concentration to 960 g of Th per kg of D_2O (735 g of Th per liter at 280°C). Six terminal samples involving a tracer experiment to verify the circulating inventory were also withdrawn. Sampling was accomplished without difficulty.

Before removal from the reactor, the thorium oxide remaining in the loop (450 g of Th per kg of D_2O) was flushed to a slurry holdup tank located in a shielded, external equipment chamber. Radiation measurements of the loop during removal from the reactor indicated that practically all the thorium oxide and associated fission products had been removed by the flushing operation. These

measurements and the ease with which the slurry was removed indicated that there was no caking of the slurry on the inside surface of the loop.

Fission and gamma heating measurements, as well as observations of pumping power required, gave no evidence of loss of thorium from circulation during operation. Since no significant changes in the temperature of the core-section piping were observed, no deposits were formed in the maximum-flux region. Radioactivity observed in the filter region on withdrawal of the assembly from the reactor was slightly greater than that on adjacent piping and pressurizer regions; the difference represented only very slight deposits.

A slow decrease in core outlet temperature (2 to 4°C over a period of days) was frequently observed. The original spread between inlet and outlet temperature returned during reactor shutdowns; the spread was also restored in one case by increasing slurry flow rate. The decrease may have been due to a slight accumulation of solids as a sludge which decreased heat transfer to the thermocouple.

From measurements of increase in iron content of the slurry solids, the generalized rate of corrosion of the loop system was 0.4 mpy during 820 hr of preirradiation operation and 0.4 mpy during the next 1279 hr, which included 1042 hr of irradiation at full power. Measurements of chromium content (soluble CrO_4^{2-}) of the slurry and oxygen uptake by the system indicate a somewhat greater amount of metal attacked; however, these values include a substantial but unknown contribution by the internal surface of the filter system and the pressurizer.

Forty-eight specimens of Zircaloy-2, titanium, and type 347 stainless steel ($\frac{1}{4} \times \frac{5}{8} \times \frac{1}{16}$ in.) were placed in similar arrays in the nose and rear of the core and in the rear of the loop. Specimen holders were such as to permit flow at 8 and 22 fps at each location. Corrosion of these specimens is presently under examination.

Radiolytic gas pressure remained below 10 psi during the exposure. Recombination by gamma radiation was estimated to be sufficient to account for the production rate of $0.08 \text{ mole liter}^{-1} \text{ hr}^{-1}$ (ref 22), assuming a G value²³ of 5 molecules of D_2 per 100 ev.

A substantial degradation of particle size of the slurry occurred as irradiation proceeded. The average diameter decreased from the original value of 1.7μ prior to irradiation to 0.3μ after 1460 hr of irradiation (2716 hr of slurry circulation). The surface area of the slurry increased from 1.5 to over $25 \text{ m}^2/\text{g}$. These effects, see Fig. 16.3, seem to have started with initiation of irradiation and had not necessarily ceased when irradiation was terminated. Degradation of slurry particles by pumping alone has been observed in many test runs.^{24,25} It now appears, however, that radiation acted in combination with the pumping as a definite cause of slurry degradation.

²²E. L. Compere *et al.*, HRP Quart. Progr. Rept. July 31, 1960, ORNL-3004, p 97.

²³C. J. Hochanadel, *The Radiation Induced Reaction of Hydrogen and Oxygen in Water at 25° to 250°C*, ICP UAE, P/739, rev 1 (1955).

²⁴E. L. Compere *et al.*, HRP Quart. Progr. Rept. Oct. 31, 1959, ORNL-2654, p 139.

²⁵H. C. Savage *et al.*, HRP Quart. Progr. Rept. Jan. 31, 1960, ORNL-2920, p 111.

Fig. 16.3. Effect of Irradiation and Circulation on Slurry Particle-Size Distribution and Surface Area.

Settling rates of the slurry samples decreased as irradiation proceeded and the solids content of the settled bed diminished. Their behavior implies that the slurry became more flocculated under irradiation and subsequently settled under highly hindered conditions.

Conclusions

Operation of the in-pile slurry loop was extremely satisfactory in so far as reliability of all components was concerned. It appears that a powerful tool for definitive study of slurries in irradiation fields has been demonstrated.

Part III

SUPPORT FOR HIGH-TEMPERATURE SOLID-FUELED REACTORS

17. TRANSPORT OF NOBLE GASES IN GRAPHITES

R. B. Evans III

The objectives of the studies of diffusion of noble gases through graphites are (1) to obtain empirical diffusion data for a variety of graphites, (2) to present the data in terms of acceptable models, (3) to develop flow equations and to establish flow mechanisms to predict the behavior of similar systems, and (4) to perform routine permeability measurements in direct support of immediate EGCR programs.

Diffusion models, applicable to gas-graphite systems, may be classified in terms of three basic mechanisms. These are Knudsen flow, mutual diffusion, and combined Knudsen and mutual diffusion. The combined mechanism is intermediate with respect to Knudsen flow, which depends on wall collisions – at low pressures – in small passages, and mutual diffusion, which depends on intermolecular collisions – at high pressures – in large passages. The diffusion rates encountered under a pure Knudsen mechanism are several orders of magnitude lower than those encountered under a mutual diffusion mechanism. Thus, materials which fall into the Knudsen classification represent the most desirable materials from the standpoint of reactor applications.

Although the need for performing evaluation experiments with Knudsen materials is apparent, it is also clear that the intermediate mechanisms offer a relatively fertile area for fundamental studies – particularly since Knudsen theories are well advanced as compared with theories for the intermediate mechanisms. The approach employed in this program has been to study mutual diffusion mechanisms and then to apply the knowledge gained to the intermediate case. It is interesting to note that none of the materials subjected to experimentation during the last year have exhibited a pure Knudsen mechanism, although work is now being conducted with materials with permeability coefficients as low as 10^{-5} to 10^{-6} cm²/sec.

Questions such as the effect of coatings on the applicability of some of the conclusions are yet to be answered. Such studies form the basis for plans for future investigations.

UNIFORM PRESSURE INTERDIFFUSION OF HELIUM AND ARGON IN A LARGE-PORE GRAPHITE¹

J. Truitt

A mutual diffusion coefficient for argon and helium in a large-pore graphite (22 vol % porosity) has been determined.² The coefficient reported is based on two series of steady-state diffusion experiments conducted at uniform total pressures ranging from 1 to 6 atm. One series was performed at room temperature (about 25°C), the other at 100°C. The controlling diffusion mechanism

¹ Abstract of manuscript submitted for publication in *J. Chem. Eng. Data*.

² R. B. Evans III, J. Truitt, and G. M. Watson, *Interdiffusion of Helium and Argon in a Large Pore Graphite*, ORNL CF-60-11-102 (Nov. 23, 1960).

was classical in nature, and surface and Knudsen diffusion effects were shown to be negligible. The coefficients exhibited classical temperature and pressure dependencies, as shown in Fig. 17.1.

Fig. 17.1. Mutual Diffusion Coefficient for Helium-Argon in AGOT Graphite.

As a result of the presence of sources and sinks for the gases in the diffusion system employed for the measurements, a net-drift effect was observed. The ratio of the over-all helium diffusion rate to that of argon was inversely proportional to the square root of the ratio of the atomic weight of argon to that of helium for all uniform total pressure experiments. It was found that the same coefficient could be determined when the pressure of the gases within the graphite was not uniform, although the individual rates were appreciably altered. Comparison of the "free-space" coefficient with the measured coefficient indicates that the tortuosity factor for this graphite is 5.08.

A DIFFUSION MODEL FOR LARGE-PORE GRAPHITES

R. B. Evans III E. A. Mason³

A model, which may be helpful in future studies, has emanated from considerations given to the net-drift phenomenon mentioned above. The drift is directly related to the technique⁴ employed

³Consultant, Department of Physics, University of Maryland.

⁴E. Wicke and R. Kallenbach, *Kolloid-Z.* 97, 135 (1941).

in the diffusion experiments. A brief description of this technique may be presented with the aid of Fig. 17.2, which shows, from bottom to top, the argon outlet (with thermocouple), the container, the diffusion septum (graphite cylinder) with container cap, and the inner helium-flow guide. Helium is forced past the inside graphite surface; argon is forced past the outside surface. The experimental diffusion rates are based on steady-state measurements of the effluent rates and compositions of the sweep streams. The total pressure and temperature on each side of the septum are held equal. The diffusion rate, J_i (particles $\text{sec}^{-1} \text{ cm}^{-2}$), of each gas is constant at any point along the flow path.

UNCLASSIFIED
PHOTO 36002

Fig. 17.2. Diffusion Cell and Graphite Septum.

The ultimate goal is the acquisition of an equation of the form:^{5,6}

$$J_i = -D_{i,\text{eff}} \nabla n_i + \delta x_i J, \quad \begin{array}{ll} \delta = 0, & \text{flow is Knudsen,} \\ \delta = 1, & \text{diffusion is classical,} \end{array} \quad (1)$$

where

$$J \text{ is the net flux, } ^7 \sum_{i=1}^{\nu} J_i \text{ (particles } \text{cm}^{-2} \text{ sec}^{-1}\text{),}$$

⁵R. D. Present, *Kinetic Theory of Gases*, p 49, McGraw-Hill, New York, 1958.

⁶J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, p 519, Wiley, New York, 1954.

⁷ $AJ_i = \dot{n}_i \cdot N$, where A (cm^2) is the area normal to flow and N is Avogadro's number. The flow is expressed in terms of $\dot{n}_i$ in Fig. 17.3.

$D_{i,\text{eff}}$ is the apparent coefficient (cm^2/sec),

n_i is the particle density of the i th component,

n is the total density, $\sum_{i=1}^{\nu} n_i$ (particles/ cm^3),

x_i is the particle fraction of the i th component.

Equation (1) is a series resistance formula and is an accepted relationship for diffusion of binary mixtures when $\delta = 1$. The variable δ is defined over the interval $0 < \delta < 1$, δ increases as the ratio of the average pore radius to the mean free path (a/λ) increases. When flow is Knudsen, $\delta x_i J = 0$. Furthermore, $\nabla n_1 = -\nabla n_2$ (for a binary mixture) when $\Delta P = 0$. The well-known results:

$$J_1/J_2 = -D_{1,\text{eff}}/D_{2,\text{eff}} = -(m_2/m_1)^{1/2} \quad (2a)$$

and

$$J = J_1 [1 - (m_1/m_2)^{1/2}] = J_2 [1 - (m_2/m_1)^{1/2}] \quad (2b)$$

follow by the previous definitions.

The present discussion deals primarily with similar relationships under the same conditions when $\delta \rightarrow 1$. An important clue is offered by the treatment of Waldmann⁸ of the interdiffusion of a ternary system composed of two gases and a dust suspension. Since the dust was successfully treated as being a third gas component in previous work, the same approach is followed with respect to the interdiffusion of a binary mixture in a porous medium. The graphite is visualized as being a large number of carbon particles suspended in the diffusion path. The particles are subject to forces which tend to cause them to move, however, they are fixed ($J_d = 0$) and exhibit a concentration profile which is constant with position ($\nabla x_d = 0$). A combination of these conditions, Waldmann's expression⁸ for $D_{i,d}$ (where $m_d \gg m_i$ and the radii r are such that $r_d \gg r_i$), and suitable diffusion equations [see Hirschfelder's Eq. (8.1-3), ref 6] lead to the expression:

$$\sum_{i \neq d} J_i (m_i)^{1/2} (1 + \frac{\pi}{8} \alpha_i) = 0. \quad (3)$$

The subscript i refers to the two gases, and subscript d refers to the carbon dust particles. When the accommodation coefficients α_i of the two gases are equal, Eqs. (3) and (2a) are identical. This is somewhat surprising because no direct restrictions (except those mentioned in connection with m_d and r_d) regarding a/λ or δ were applied to derive Eq. (3).

Other investigators⁹⁻¹² have developed Eq. (2a) (for $\delta \rightarrow 1$) using the incorrect premise that the net force on the graphite septum is zero since $\nabla P = 0$. The latter is merely a condition that

⁸L. Waldmann, *Z. Naturforsch.* 14a, 589 (1959).

⁹R. B. Evans III, J. Truitt, and G. M. Watson, *Interdiffusion of Helium and Argon in a Large Pore Graphite*, ORNL CF-60-11-102 (Nov. 23, 1960).

¹⁰J. Hoogschagen, *J. Chem. Phys.* 21, 2096 (1953).

¹¹E. Wicke, private communication, November 1960.

¹²H. A. Kramers and J. Kistemaker, *Physica* 10, 699 (1943).

Poiseuille flow does not exist. Actually, the cell *tends* to move under the conditions of the experiment in a manner discussed by Waldmann.⁸

It is apparent from the use of diffusion equations for a ternary mixture in the derivation of Eq. (3) that Eq. (1) is merely a phenomenological expression — particularly when $1 > \delta > 0$. Equation (1) is a convenient means of obtaining integrated rate expression in terms of $D_{i,\text{eff}}$. It will be necessary to define $D_{i,\text{eff}}$ and δ in terms of D_{id} , D_{12} , and D_{21} . The AGOT data appear to be a limiting case where $\delta \rightarrow 1$ and $D_{1,\text{eff}} \rightarrow D_{12} = D_{21}$, the latter being subject to corrections for the internal geometry of the graphites.

INTERDIFFUSION SUPERPOSED ON FORCED FLOW

J. Truitt

A study of diffusion of argon through a graphite septum opposed to a forced flow of helium through the septum has been completed for two relatively permeable graphites, Moderator No. 1 from Speer Carbon Company and AGOT from National Carbon Company. The flow problems involved are of direct interest to gas-cooled reactor designs that attempt to remove fission products which diffuse from the fuel by purging an annular volume between the fuel element and a porous sleeve. The objective of these experiments was to demonstrate a method for predicting such superposed flow from diffusion and permeability data from separate and simple experiments.

The equation of interest is the integrated form of Eq. (1) (see "A Diffusion Model for Large-Pore Graphites," immediately preceding), where $\delta = 1$ and $D_{12,\text{eff}} \nabla x_1 = -D_{21,\text{eff}} \nabla x_2$. The equation is

$$\exp\left(\frac{\mathbf{J}L}{nD_{12,\text{eff}}}\right) = \frac{\mathbf{J}_1 - \mathbf{J}_{x_1}(L)}{\mathbf{J}_1 - \mathbf{J}_{x_1}(0)}, \quad (4)$$

which holds for steady-state linear flow (diffusion and forced flow). The symbol L (cm) represents the specimen thickness. The total flux $\mathbf{J}$ for the superposed case is the vector sum of the uniform-pressure $\mathbf{J}'$ and the forced-flow flux $\mathbf{J}_f$; that is,

$$\mathbf{J} = \mathbf{J}' + \mathbf{J}_f. \quad (5)$$

The forced-flow component, as defined by $\mathbf{J}_{fi} = -(K_i/kT) \cdot \Delta P$, where $P = nkT$, is discussed elsewhere.⁹ The symbol K (cm^2/sec) denotes the permeability coefficient. It is pertinent to note that K varies with P , T , and x_i . To obtain K_{mix} for the superposed calculations, it was necessary to integrate $(K)^{-1}$ with respect to L (actually x_i), utilizing literature values of the viscosity of the two gases involved (helium and argon) and the uniform-pressure concentration profiles. The results of a typical experiment, conducted at low $\mathbf{J}_f = \dot{n}_f N/A$ values (with AGOT), are shown in Fig. 17.3. The nonzero $\mathbf{J}_i$ values when $\nabla P = 0$ (actually $\dot{n}_i'$ at $\Delta P = 0$ on the plots) are clearly demonstrated by these data. A comparison of the predicted and experimental values reveals the

Fig. 17.3. Results of Diffusion Experiments at 100°C.

accuracy with which Eqs. (4) and (5) describe superposed flow. It is interesting that Eq. (5) successfully relates two entirely different modes of flow. This suggests that the carbon-dust model might be applicable to superposed flow and even to forced flow.

Although the results with the Speer graphite – using both pure gases and mixtures at the 0 and L positions – were essentially the same as the AGOT results, an additional group of experiments

conducted at high forced-flow rates revealed that Eqs. (4) and (5) will not give an accurate estimate of contamination resulting from back diffusion. Under the conditions of these experiments, which are $J = J_{He} \sim J_f$ and $x_{Ar}(0) = 0$, Eqs. (4) and (5) may be written as:

$$\log_{10} \left(- \frac{J_{Ar}}{J_{He}} \right) = \frac{K_{He}}{2.303 D_{12,eff}} \frac{\Delta P}{P} + \log_{10} N_{Ar}(L). \quad (6)$$

The experimental data and the curves representing Eq. (6) appear in Fig. 17.4. The divergence of the experimental curve and the theoretical curve at high ΔP values suggests the presence of a Knudsen (small passage) contribution that was completely masked by the mechanism which controls the rates near $\Delta P = 0$. The deviation is too great to be attributed to pressure diffusion. Thus, under the conditions of these experiments, the assumption of $\delta = 1$ (no Knudsen contribution) implied in Eq. (4) is no longer tenable. Similar studies are planned for low-permeability graphites.

Fig. 17.4. Comparison of Predicted and Experimental Values at High Helium Sweep Rates.

INTERDIFFUSION OF NOBLE GASES IN A LOW-PERMEABILITY GRAPHITE

R. B. Evans III

Considerable attention has been given to techniques of determining the permeability coefficients of graphites which exhibit low values of porosity and forced-flow rates.¹³ In addition, the apparatus for studying interdiffusion behavior has been modified such that very low diffusion rates can be measured under steady-state conditions. The results of several diffusion experiments

¹³W. T. Ward and N. V. Smith, *GCR Quart. Progr. Rept. Dec. 31, 1960*, ORNL-3049, p 297.

which were conducted at uniform total pressure are presently available for the helium-argon-CEY graphite system. The CEY graphite was in the form of a coated pipe (1 $\frac{1}{4}$ in. OD, $\frac{7}{8}$ in. ID, 5 in. long). This material is manufactured by the National Carbon Company.

Based on the permeability data alone, it was tentatively concluded (as a first approximation) that the diffusion mechanism would be of the Knudsen type and that Eq. (1) (see "A Diffusion Model for Large-Pore Graphites," this report) with $\delta = 0$ would describe the diffusion mechanism. The diffusion coefficients were calculated on this basis; that is, the concentration profiles were taken to be linear, since $\delta = 0$. Plots of $(D_{i,\text{eff}})^{-1}$ vs P_m were prepared to test the initial conclusions. Curves of this type are straight lines. Also, the slopes of the curves are indicative of the type of mechanism under study: if the slope is zero, the mechanism is Knudsen flow; if the slope is positive and the intercept is zero, classical diffusion prevails. The results plotted in this manner are shown on Fig. 17.5.

Fig. 17.5. Reciprocal Transport Coefficients for Helium and Argon in Coated CEY Graphite Pipe.

It is apparent from the curves that the permeability and diffusion coefficients became identical as $P_m \rightarrow 0$ or $a/\lambda = 0$. This is precisely what one would predict on the basis of established theory. As the pressure is increased, however, $(K)^{-1}$ decreases slightly and $(D_{i,\text{eff}})^{-1}$ increases markedly. The difference between the two values would be very large at reactor pressures, and the contribution of the intercept (Knudsen flow) to the total flow resistance would be small. Thus, the tentative conclusions regarding Knudsen flow were incorrect. Even though the values of the CEY permeability coefficients are low – as well as variations of the permeability coefficient with pressure – it appears that the mechanisms exhibited by the CEY are very similar to those observed with the permeable graphites such as AGOT and Speer No. 1.

SURFACE DIFFUSION IN LARGE-PORE GRAPHITE

P. S. Spangler

During the initial stages of the program, considerable attention was given to the relative magnitudes of pore-diffusion rates and surface-diffusion rates. The absence of appreciable Knudsen diffusion in large-pore graphites was established through pore-size distribution data, permeability data, and the behavior of measured diffusion rates with respect to temperature and pressure. However, definite conclusions regarding surface-diffusion effects could not be drawn on the basis of available data. To circumvent this difficulty, a special group of experiments was conducted at low temperatures, where adsorption and surface diffusion effects (of argon) would be magnified.

An AGOT graphite specimen, for which surface area, porosity, and xenon adsorption characteristics were known,¹⁴ was subjected to a series of argon-adsorption experiments. The work was coordinated and reported by W. T. Ward;¹⁴ the determinations were conducted at ORGDP. Based on this information, estimates of the surface rates were made by use of techniques developed by Gilliland *et al.*¹⁵ These estimates revealed that the surface-diffusion rates would be several orders of magnitude less than the gaseous diffusion which would take place in the pore volumes under experimental conditions, and, also, that surface diffusion of noble gases would not constitute a problem at reactor temperatures.

These conclusions were verified by a series of interdiffusion experiments conducted concurrently (but with a different AGOT specimen) with the experiments discussed previously. The experiments were conducted at +30, 0, and -65°C at total pressures ranging from 1.5 to 4 atm. Within the precision of the experiments, Eq. (4) (see "Interdiffusion Superposed on Forced Flow," this report) and the normalization formula shown in Fig. 17.1 were followed. No surface-diffusion effects were detected.

FORCED-FLOW CHARACTERISTICS OF EGCR GRAPHITES

N. V. Smith J. Truitt W. T. Ward

A considerable effort¹⁶⁻¹⁸ has been devoted to routine determination of porosity and permeability of commercial graphites considered for use as components of the EGCR. The graphites of most interest have been (1) uncoated fuel-element sleeves, (2) fuel-element sleeves coated with pyrolytic carbon or with silicon carbide, and (3) moderator graphite. Special attention has been given to the uniformity of these materials with respect to permeability and to type of flow to be expected within these materials at EGCR operating conditions.

¹⁴M. C. Cannon *et al.*, *Adsorption of Xenon and Argon on Graphite*, ORNL-2955 (Nov. 21, 1960).

¹⁵E. R. Gilliland, R. F. Baddour, and J. L. Russell, *A.I.Ch.E. Journal* 64, 1162 (1960).

¹⁶GCR Quart. Progr. Rept. June 30, 1960, ORNL-2964, pp 202-6.

¹⁷GCR Quart. Progr. Rept. Sept. 30, 1960, ORNL-3015, pp 137-42.

¹⁸GCR Quart. Progr. Rept. Dec. 31, 1960, ORNL-3049, pp 297-302.

Fig. 17.6. Specimen Components for EGCR Sleeve Permeability Tests.

Tests of permeability of the sleeves were generally performed on 3-ft-long specimens of the 4-in.-diam pipe (see Fig. 17.6). Uncoated specimens from Speer Carbon Company showed the lowest permeability constants, specimens from Great Lakes Carbon Company were intermediate, and National Carbon Company AGOT specimens showed the highest permeability constants.¹⁹

Coatings of pyrolytic carbon were found to be more effective in reducing permeability of the sleeve material than those of SiC. However, the EGCR will use sleeves coated with SiC, since these afford greater resistance to oxidation in the event of a serious air leak into the reactor system.

Details of the EGCR design require graphite-to-graphite joints of the sleeve material to form the fuel channel. Tests of such closures (see Fig. 17.7) indicate that such joints will be responsible for a large fraction of the leakage from the sleeves.

Permeability of possible moderator materials was evaluated from small plugs machined from the large pieces supplied. A variety of tests have been used to assess the possible effect of

¹⁹N. V. Smith and J. Truitt, *EGCR Graphite Permeability Tests: Results of Forced Flow Experiments on EGCR Fuel Element Sleeves and Sleeve Materials*, ORNL CF-60-7-101 (July 29, 1960).

Fig. 17.7. Small Plug Permeability Apparatus.

specimen preparation on the observed permeability. No serious error was introduced (by plugging of the surface pores, for example) by the preparation procedures. Permeability of the moderator graphite (AGOT from National Carbon Company) varies considerably with position of the specimen within the manufactured block and with direction of gas flow relative to the extrusion axis. Values of permeability range from 20 to 160 millidarcys for this material; the average permeability constant for the moderator graphite is 90 millidarcys ($K \sim 6 \text{ cm}^2/\text{sec}$).

From the data from several types of experiments it may be predicted that the gas flow within the EGCR moderator will be in the viscous rather than turbulent region.

18. EVOLUTION OF GAS FROM GRAPHITE

L. G. Overholser

J. P. Blakely

Studies of the degassing behavior of reactor-grade graphites have been continued.¹ Special attention has been given to graphites prepared from needle coke, in view of the projected use of this type of graphite in the EGCR. The needle-coke graphites are being used as moderators at high temperatures because of their greater dimensional stability in the presence of high neutron fluxes. The projected use at the high temperatures, however, does aggravate the compatibility problems arising from the possible interaction of the gas released by the graphite with other components of the reactor. The studies²⁻⁴ have been made for determining the quantity and composition of the gas evolved by the various graphites at the temperatures of interest, as well as for acquiring information concerning the rates at which the gas may be released.

Selected data are presented in Table 18.1 to show differences in the behavior of the various graphites upon degassing to 1800°C by use of induction heating. The designated temperatures represent the temperatures at which gas collections were made. The volume corresponding to the particular temperature is the volume of gas collected between this temperature and the next lower temperature (room temperature is initial temperature), the bulk of the gas being collected, however, at the designated temperature. A very approximate correlation of the gas content with the total ash content is evident. It should be noted, however, that other graphites with an ash content of <20 ppm have been found to evolve 40 to 50 cm³ of gas per 100 cm³ of graphite. Other factors such as the atmosphere during letdown in the furnace and subsequent exposure conditions frequently make it difficult to establish the true effect of the impurities present.

Data have been obtained for other graphites prepared under such conditions that the effect of letdown atmosphere, method of purification, and particle size of the coke mix could be evaluated. No important differences in the gas content were observed when either Ar or N₂ was used as the letdown atmosphere or when purification was effected by thermal or gas processes. Variations of the particle size of the coke mix also produced no significant effect on the gas content. All these graphites, however, had an ash content of < 100 ppm.

Rates of evolution of gas at 300, 600, and 1000°C, along with analyses of the collected gas, have been determined for a total of 18 varieties of moderator graphite.²⁻⁴ The data obtained in most cases fit the equation

$$V = A \log t + B, \quad (1)$$

where V is the volume of gas evolved in cm³ (at standard temperature and pressure) per 100 cm³ of graphite, and t is time in minutes.

¹Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960, ORNL-2931, pp 139-48.

²GCR Quart. Progr. Rept. June 30, 1960, ORNL-2964, p 190.

³GCR Quart. Progr. Rept. Sept. 30, 1960, ORNL-3015, p 125.

⁴GCR Quart. Progr. Rept. Dec. 31, 1960, ORNL-3049, p 287.

Table 18.1. Volume and Composition of Gas Evolved by Various Graphites at 1000, 1400, and 1800°C

Graphite	Ash (ppm)	Temperature (°C)	Volume (cm ³ per 100 cm ³ of graphite)	Vol % of Constituents in Evolved Gas					
				H ₂	Hydrocarbons	H ₂ O	CO ₂	N ₂	CO
SP-22B	<20	1000	10.1	78	1	0.4	0.4		28
		1400	7.2	66	0.4	2		4	28
		1800	8.3	17	0.1		0.3	6	76
			25.6	14 ^a	0.1 ^a	0.1 ^a		0.8 ^a	10.3 ^a
GLC	290	1000	14.1	56	2	0.4	1.4	0.4	40
		1400	14.9	48	0.6	0.1	0.2	3	48
		1800	10.0	69	1		0.1	10	28
			39.0	22 ^a	0.5 ^a	0.1 ^a	0.2 ^a	1.5 ^a	15 ^a
AGOT-LS	400 ^b	1000	39.8	44	0.5	0.4	0.3	1	54
		1400	6.8	14	0.3	2	0.3	20	63
		1800	2.1	7	0.2		0.4	33	58
			48.7	19 ^a	0.2 ^a	0.3 ^a	0.1 ^a	2.6 ^a	27 ^a
NCN	560 ^b	1000	62.0	64	1	0.2	0.1	1	35
		1400	26.1	60	1	0.2	0.1	7	31
		1800	16.2	73	1		0.1	5	21
			104.3	67 ^a	0.9 ^a	0.2 ^a	0.1 ^a	3.2 ^a	33 ^a
AGOT-VCB	350 ^b	1000	35.9	30		0.4	1.0	1	68
		1400	6.6	18	1	1	0.9	18	60
		1800	3.1	71	0.5		0.3	17	10
			45.6	14 ^a	0.1 ^a	0.2 ^a	0.5 ^a	2	29 ^a
EGCR	300	1000	29.2	37	1	0.3	0.2	1	60
		1400	10.3	69	1	0.5	0.3	3	26
		1800	6.2	45	0.6	0.5	0.1	5	49
			45.7	21 ^a	0.4 ^a	0.2 ^a	0.1 ^a	1 ^a	23 ^a

^aTotal volume of constituent, cm³ per 100 cm³ of graphite.^bHigh calcium.

Gas evolved at 300°C consists mainly of H₂, N₂, and a mixture of hydrocarbons. Values of *A* in Eq. (1) have ranged from 0.1 to 0.29 for the graphites tested.

The behavior at 600°C falls into two general classes. In the simpler case, the gas evolved at this temperature is primarily H₂O, hydrocarbons, and CO; the degassing rate is given by Eq. (1), with a slope of 0.36 to 1.0 for the 15 cases examined. In one case (the EGCR moderator), considerable SO₂ was evolved at this temperature. For a few graphites, however, considerable CO₂ is evolved in early stages of the heating; for such graphites the rate curve has a large initial slope which decreases abruptly to a value similar to that shown by graphites of the first class.

These large initial slopes must be due to rapid release of surface oxide as CO_2 ; this behavior may be a consequence of the high calcium content shown by most graphites of this class.

The rate data collected for most of the graphites at 1000°C obey an essentially linear relationship for a plot of volume vs $\log t$ for times up to ~ 1000 min. For some graphites, however, the curves show a definite change in slope over extended periods of heating. The cause of the change in slope for these cases is not clearly understood. It is known that in some instances the concentration of H_2 increases and that of CO decreases as the degassing proceeds at 1000°C . The evidence is not conclusive enough, however, to state that these changes are solely responsible for the increase in slope. The slopes found for the various graphites for periods up to 1000 min are in fair agreement.

19. MEASUREMENT OF TEMPERATURE IN REACTOR ENVIRONMENTS

G. W. Keilholtz

W. T. Rainey
R. L. Bennett

W. E. Browning
H. L. Hemphill

BEHAVIOR OF CHROMEL-P-ALUMEL THERMOCOUPLES

Temperature measurements in the gas circuit of the Experimental Gas-Cooled Reactor are to be made with Chromel-P-Alumel thermocouples. Since these couples have been observed¹ to show large though slow decreases in emf on long exposure at 1000°C under special atmospheres, a program of testing of such couples has been required.

Results of preliminary experiments² indicated that, when Chromel-P-Alumel couples are exposed in flowing air or helium, only small increases in emf occur during extended exposures at 1000°C. Cross comparison³ with wires of platinum indicates that both wires become more positive during the exposure but that most of the change is in the Chromel. Exposure of such couples in capsules to which finely divided chromium, type 347 stainless steel, polyethylene, or Refrasil insulation are added reveals that contaminations from these materials are not primarily responsible for the effects.

Large negative drifts in emf (3 mv) have been observed when Chromel-P-Alumel couples are exposed in stagnant helium at 1000°C; however, evacuation of the capsule for the initial 18 hr at temperature prevented the decrease in emf.

When test thermocouples whose hot junctions have been at 1000°C for periods in excess of 100 hr are withdrawn in 1-in. steps from the furnace, the error in temperature indication varies considerably with past performance. Couples which have shown no drift or slight positive drift in output show relatively small (less than 1 mv) error at all positions. However, couples which have shown appreciable negative drifts (see Fig. 19.1) show pronounced error. It appears that the abnormality is located in that portion of the wires which lay during testing in the 800–900°C region of the furnace. Similar measurements with cross comparisons vs platinum wires show the effect to be due to the Chromel-P wire alone.

When Chromel-P wires were heated in stagnant helium, an immediate and progressive brightening, which started at the hot junction and moved toward the cooler region, was observed.⁴ Longer heating resulted in disappearance of the bright film except in the region where sharp thermal gradients occurred in the wire. Figure 19.2 shows a portion of wire exposed in the gradient region which was still covered by the loose metal film over an oxide layer. Analysis showed the metal film to contain more than 99% nickel.

¹J. F. Potts, Jr., and D. L. McElroy, *Thermocouple Research to 1000°C – Final Report*, ORNL-2773, p 104–13 (Jan. 16, 1961).

²Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960, ORNL-2931, p 166.

³GCR Quart. Progr. Rept. Mar. 31, 1960, ORNL-2929, p 217.

⁴GCR Quart. Progr. Rept. Sept. 30, 1960, ORNL-3015, p 151.

Fig. 19.1. Chromel-P vs Alumel Thermal Gradient Profile.

Fig. 19.2. Surface Appearance of Chromel-P Wire from Thermal Gradient Region of Furnace After 120 hr Heating. 21X. Reduced 8%.

When Chromel-P wires were introduced into a 1000°C zone, a sudden evolution of gas occurred during the first minute of heating, followed by a slower release of gas which persisted for 10 to 15 min. Careful cleaning by organic solvents reduced the initial gas release, and bright-annealed Chromel-P wires gave only a trace of gas. Mass spectrographic analysis of the gas indicated the presence of CO_2 , $(\text{N}_2 + \text{CO})$, H_2 , and a trace of H_2O . After exposure of Chromel-P wire for 40 hr, analysis of the gas showed the remainder to be predominantly H_2 with a small amount of $(\text{N}_2 + \text{CO})$.

Analyses of Chromel-P wires after various periods of heating showed a progressive loss of oxygen and carbon from the wires in the 1000°C region, with a corresponding increase in oxygen and carbon contents of the wires in the thermal-gradient region. Metallographic examination reveals a very heavy intergranular oxidation of the chromium in the region from 800 to 900°C; no intergranular oxidation is detected in sections at other temperatures.

The principal mechanism involved in the negative-emf-drift phenomenon seems to be this selective oxidation of chromium, which occurs only in a limited temperature range and in rather critical limits of oxidizing potential.

The oxidation of Chromel-P-type alloy at temperatures other than 800 to 900°C and in atmospheres richer in oxidizing agent appeared to be a nonselective surface effect. The high-chromium alloys, such as Geminol-P and Chromel-A, do not develop negative emf drifts under these conditions.

When using dull (oxidized) wires, sufficient oxygen and/or carbon can be furnished by the wires alone to cause selective oxidation at certain temperatures. Therefore, dull-finish wires should be used only in applications allowing an adequate supply of oxygen, such that only nonselective oxidation occurs. Only bright-annealed wires should be used in those applications in which the wires are not in contact with oxidizing atmospheres.

BEHAVIOR OF SHEATHED THERMOCOUPLES IN GRAPHITE ASSEMBLIES

Chromel-P-Alumel thermocouples will be exposed, in service in the EGCR, to flowing helium containing gases desorbed from moderator graphite. Accordingly, thermocouples, in stainless steel sheaths such as have been specified for the EGCR, have been given stringent tests in such an environment.

The thermocouples were inserted into a cylindrical block of AGOT graphite (National Carbon Company) which was contained in a vessel of stainless steel. A pressure of 3 psig of helium was maintained within the vessel. The hot end of the graphite block was at 870°C. Control couples of each type were exposed in thermowells of stainless steel which extended into the graphite cylinder.

UNCLASSIFIED
ORNL-LR-DWG 55956

Fig. 19.3. Thermal Gradient Profiles for Chromel-P/Alumel Sheathed Thermocouples After Graphite-Helium Exposure.

Thermocouples sheathed with types 304, 310, and 347 stainless steel were tested in such assemblies. In cases where the gases desorbed from the graphite were kept in the system, thermocouples sheathed with type 310 and 347 stainless steel showed virtually no drift in emf over exposure periods up to 83 days, while couples sheathed with type 304 stainless steel showed negative drifts of up to 30°C. Control couples in air showed slight positive drifts on these exposures.

Tests in which the desorbed gases were allowed to dissipate or to react with the stainless steel portions of the apparatus before insertion of the thermocouples indicated that sheathing of type 304 stainless steel was adequate.

Measurement of thermal-gradient emf profile was made by comparison with a standard couple on stepwise withdrawal from the assembly; this gave values shown in Fig. 19.3. The results suggest that the thermocouple sheathed with type 304 stainless steel was attacked in the region (at 750°C) about 10 in. from the hot junction. Comparison with a platinum wire indicated that the Chromel-P wire was responsible for virtually all the difficulty. Metallographic examination of the wires at 1-in. intervals reveals (see Fig. 19.4) severe intergranular attack on the Chromel-P wire in the region

UNCLASSIFIED
Y-39729

Fig. 19.4. Chromel-P/Alumel Thermocouples Sheathed in Type 304 Stainless Steel.

about $10\frac{1}{2}$ in. from the hot junction; this section of the Chromel-P wire was found to be magnetic, indicating a loss of chromium from the alloy.

It is not clear why thermocouples sheathed with types 310 and 317 stainless steel have been satisfactory nor why those with sheaths of type 304 (from two manufacturers) have proved unsatisfactory. It appears, however, that gaseous materials desorbed from the graphite play an important role in this attack. Gastight sheaths must, accordingly, be recommended for such applications.

OXIDATION OF CHROMEL-P IN H_2O-H_2 MIXTURES

Selective reaction, by oxidation or carburization, of chromium in the Chromel wire has been suggested as being responsible for shifts in thermal emf of the Chromel-Alumel thermocouple in gaseous environments. Accordingly, a systematic study of oxidation of chromium in such alloys and its effect on thermocouple output has been initiated.

Preliminary studies have followed the work of Moreau and Benard,⁵ who selectively oxidized chromium in nickel-chromium alloys by high-temperature treatment with hydrogen and water vapor. In these experiments, Chromel wires in a long tube were maintained in a thermal gradient from 25 to $1300^\circ C$ and were exposed to flowing H_2-H_2O atmospheres. After exposure the wires were joined to platinum and tested by stepwise withdrawal from a standard furnace assembly as described under "Behavior of Chromel-P-Alumel Thermocouples," this chapter.

From available thermodynamic data and the assumption of ideal solid solution for the Chromel-P alloy, the behavior of this alloy in H_2-H_2O mixtures at various temperatures is expected to follow that shown in Fig. 19.5. The limited data obtained to date seem to be in accord with this expected behavior.

⁵J. Moreau and J. Benard, *J. chim. phys.* 53, 787 (1956).

Fig. 19.5. Equilibrium Oxidation Temperature as a Function of Water-Hydrogen Ratio.

Additional data, in combination with studies of the diffusion-controlled rate of reaction, will be required to establish the relationship between thermal emf and selective oxidation of the chromium. A satisfactory method for the experimental study seems to have been demonstrated.

CALCULATION OF THERMOCOUPLE ERROR DUE TO INSULATION-LEAKAGE CURRENT

In the development of high-temperature measurement techniques using electrical methods, the variations in electrical resistance of insulation with temperature become important. The resistivities of the common ceramic materials decrease almost exponentially with temperature. Therefore, it is possible for leakage currents to become significant at high temperatures. In thermocouple systems using ceramic spacing between wires, the leakage currents result in voltage division of the output signal, with corresponding error in indicated temperature. The resultant error is a function of several variable parameters as well as the geometry of the system.

A program was prepared by MIT Engineering Practice School students for calculation of the theoretical error in thermocouple assemblies.⁶ This program was based on a simplified model of the assembly, as shown in Fig. 19.6. This model assumed junctions of two dissimilar wires *a* and

Fig. 19.6. Equivalent Circuit of Insulated Thermocouple and Measuring Circuit.

b at temperatures T_1 and T_2 with absolute emfs of E_1 and E_2 . The temperature at T_1 was that to be measured against the reference temperature T_2 , and the emf output of the system was dependent upon $T_1 - T_2$. The emf applied by the potentiometer to give zero current through the galvanometer G was E_0 . The resistivities of the wires were represented by R_{1a} , R_{1b} , R_{2a} , and R_{2b} , and that of the insulator by R_3 . Absolute emf's of junctions between insulator and wires *a* and *b* were E_3 and E_4 respectively. The temperatures T_3 , T_4 , and T_5 were intermediate temperatures dependent upon the thermal gradient of the system.

⁶G. K. Moeller, B. R. Bronfin, and P. W. Whitmarsh, *Error Determination in High Temperature Thermocouple Measurements*, KT-552 (Nov. 30, 1960).

Sample calculations have given expected results for rather simple systems. However, further calculations will be made on practical installations. In addition, the program will be modified to allow for calculation of errors in sheathed assemblies.

THERMOCOUPLES FOR THE MEASUREMENT OF SURFACE TEMPERATURES OF NUCLEAR FUEL ELEMENTS

When thermocouples are used to measure the temperatures of gas-cooled surfaces, corrections must be made for the cooling action of the gas on the thermocouple. In a previous report,⁷ methods of fabrication of thermocouples having small and reproducible cooling corrections were described. Methods of measuring cooling corrections were given and theoretical heat transfer calculations were developed. It was reported that the variation of thermocouple-cooling corrections with gas velocity could be predicted with the theory.

This work has been extended to include the effects of the length of the lead wire and of a dimension (effective diameter) of the coolant channel.⁸ From tests conducted under a small number of cooling conditions, it is possible to predict the accuracy of attached thermocouples under various cooling conditions encountered in measuring the temperatures of components of nuclear reactors.

CALCULATED RADIATION-INDUCED CHANGES IN THERMOCOUPLE COMPOSITION⁸

Thermocouples used for measurement of temperatures in nuclear reactors may undergo transmutations on exposure to neutrons which change the composition of the thermoelements, such a change in composition will generally result in a change in the thermocouple calibration. In practical radiation fields the magnitude of composition change can be substantial. To determine the extent to which these composition changes take place, an IBM 704 computer program has been devised which computes the modified composition of a thermocouple alloy as a function of time and of radiation dose received.

This computer program has been used to evaluate the expected composition changes in Chromel-Alumel, iron-Constantan, copper-Constantan, Pt vs Pt-10% Rh, tungsten-rhenium, and W vs W-26% Re thermocouples. The products of the nuclear reactions of each isotope in a particular element were calculated. The product isotopes were then summed into product elements for each time period to establish the modified composition. The calculations were made for irradiations in a flux of 1×10^{14} thermal neutrons $\text{cm}^{-2} \text{sec}^{-1}$ for periods up to 20 years.

Table 19.1 gives comparisons of the original compositions of the thermocouple materials and the compositions after ten years of irradiation. The changes indicated in the table are the absolute changes in composition.

⁷Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960, ORNL-2931, p. 159.

⁸Temperature, Its Measurement and Control in Science and Industry, Fourth Symposium, March 27-31, 1961, Reinhold, New York (to be published).

Table 19.1. Comparisons of Thermocouple-Material Compositions Before and After Ten Years of Irradiation

Thermocouple Material	Irradiation Time	Percentage Composition by Elements									
		Al	Si	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Chromel	0		0.36	0.00	9.58				89.87	0.00	
	10		0.36	0.14	9.43				89.76	0.10	
	Change			+0.14	-0.15				-0.11	+0.10	
Alumel	0	1.60	0.74			3.35	0.02	0.33	95.20	0.04	
	10	1.59	0.75			2.21	1.16	0.22	95.19	0.14	
	Change	-0.01	+0.01			-1.14	+1.14	-0.11	-0.01	+0.10	
Iron	0					0.00	100	0.00			
	10					0.22	99.77	0.01			
	Change					+0.22	-0.23	+0.01			
Copper	0								0.00	100	0.00
	10								5.04	89.92	5.02
	Change								+5.04	-10.08	+5.02
Constantan	0		0.05			0.96	0.20		45.01	55.10	0.00
	10		0.05			0.63	0.53		47.73	49.59	2.77
	Change					-0.33	+0.33		+2.72	-5.51	+2.77
		Rh	Pd	W	Re	Os	Pt	Au	Hg		
Platinum	0						100	0.00	0.00		
	10						98.15	0.32	0.92		
	Change						-1.85	+0.32	+0.92		
Pt-10% Rh	0	10.0	0.00				90.0	0.00	0.00		
	10	0.12	9.88				88.33	0.29	0.83		
	Change	-9.88	+9.88				-1.67	+0.29	+0.83		
Tungsten	0			100	0.00	0.00					
	10			81.02	6.51	12.37					
	Change			-18.98	+6.51	+12.37					
Rhenium	0				100	0.00					
	10				8.83	91.15					
	Change				-91.17	+91.15					
W-26% Re	0			74.0	26.0	0.00					
	10			59.95	7.12	32.93					
	Change			-14.05	-18.88	+32.93					

Chromel is quite stable to composition changes through transmutation reactions, because nickel, the major constituent in Chromel, undergoes very little transmutation.

Alumel is also primarily of nickel, but the other elements in the alloy (manganese, iron, cobalt, and copper) all change significantly. The greatest change is in iron, which increases from 0.02 to 1.16%.

Iron is stable to radiation transmutation. During a ten-year irradiation period the only significant change is the growth of 0.2% manganese in the pure iron wire.

Copper undergoes a significant change in composition; 5% nickel and 5% zinc grow in during the postulated ten-year irradiation.

Constantan is composed primarily of copper and nickel. Since nickel is stable, the effects of the copper transmutation are significant, though not as great as in pure copper.

Platinum is relatively stable and shows only 2% conversion to gold and mercury over a ten-year period.

The Pt-10% Rh alloy is not stable to radiation transmutation. Essentially all the rhodium is converted to palladium over a ten-year period. Fifteen per cent of the rhodium is converted to palladium in the first five months.

Tungsten is also not stable to radiation transmutation. During the ten-year period, 19% of the tungsten is converted to rhenium and osmium.

Rhenium is the least stable of the thermocouple materials considered. Ninety-one per cent of the rhenium is converted to osmium during the ten-year period.

Since neither tungsten nor rhenium is stable, it can be expected that W-26% Re also will not be stable. Thirty-three per cent of the weight is converted to osmium at the expense of both tungsten and rhenium.

20. REMOVAL OF RADIOACTIVE GASEOUS FISSION PRODUCTS FROM OTHER GASES

W. E. Browning

R. D. Ackley

R. E. Adams

Problems associated with the removal, containment, and disposal of gaseous radioactive fission products present in dynamic gas systems are becoming more demanding as the nuclear industry undergoes expansion. A considerable portion of the radioactive by-products of uranium fission appears as iodine, krypton, and xenon, which by virtue of their volatility are difficult to retain in many types of fuel elements. This behavior has a marked influence on the design, location, and operation of nuclear reactors and fuel reprocessing plants and in the design and operation of in-pile experiments. Either by design or by accident, large amounts of gaseous fission products can be present in the off-gas or ventilation systems discharging into the atmosphere adjacent to the installation. To avoid serious biological hazards it is frequently necessary to provide facilities to reduce the concentration of radioactive gases to acceptable values before discharge of the carrier gas into the atmosphere. This study is directed toward the solution of problems associated with the removal, containment, and disposal of radioactive iodine, krypton, and xenon from gas streams according to the needs of reactor development programs.

REMOVAL OF RADIOIODINE VAPOR

The study of adsorption of radioiodine from gas streams¹ has been extended to removal of this element from air and air-steam mixtures at elevated temperatures and from helium streams at temperatures from 300 to 430°C.

Removal of Iodine from Air-Steam Mixtures²

This study was undertaken at the request of the Oak Ridge Operations Office of AEC in support of the hazards evaluation program for the Small Pressurized Water Reactor (SPWR) under consideration by the AEC for location at Jamestown, New York. The study was designed to duplicate, as closely as possible, conditions which would occur following a reactor accident postulated by the AEC hazards evaluation team. The accident was assumed to result in loss of the coolant and subsequent meltdown of the reactor core. The brief pressure surge would cause leaks in the reactor pressure shell, and escape of fission products from these leaks would occur for about 1 hr, which is the time required for the pressure differential to become negligible. The release of iodine vapor in such an accident would require a removal system through which air could be recirculated within the containment vessel to reduce the quantity of iodine discharged to the atmosphere. Tests were, accordingly, conducted to study the removal of iodine vapor by activated charcoal from air with varying concentrations of water vapor at temperatures from 70 to 120°C.

¹W. E. Browning, R. D. Ackley, and R. E. Adams, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, pp 170-81.

²R. E. Adams and W. E. Browning, *Removal of Radioiodine from Air-Steam Mixtures*, ORNL CF-60-11-39, to be issued.

The experimental assembly, shown in Fig. 20.1, was constructed from glass pipe with external heating provided by flexible heating tapes to a point just downstream of the experimental charcoal trap. Thermocouples were provided to monitor temperatures at various points on the glass pipes; one thermocouple was located immediately downstream from the test adsorber within the vessel

UNCLASSIFIED
ORNL-LR-DWG 57720

Fig. 20.1. Experimental System for Steam-Air Experiments.

to monitor the temperature of the steam-air mixture. Wall temperatures of the glass pipe were maintained equal to or, in some cases, slightly greater ($1-2^{\circ}\text{C}$) than the temperature of the steam-air mixture. Drains were provided to permit collection of the condensate during an experiment. Metered air and steam were mixed and supplied to the apparatus through a heated metal system. Difficulty in accurate metering of small quantities of steam was avoided by use of a heated and insulated rotameter as a qualitative monitoring device during operation of the experiment. At the end of the test, a final calculation of the steam injection rate was made, based on the temperature history and the amount of condensate collected. Iodine vapor (I^{127} containing I^{131}) was injected by passing a small portion of air through a glass U-tube containing elemental iodine crystals. Iodine vapor which passed the test adsorber was retained on the CWS-6 filter downstream, on the silver-copper packing of the water-cooled condenser, on the final room-temperature charcoal adsorber, or in the condensate drained at intervals from the system. No radioiodine was found in gases exhausted from the system. Iodine adsorption efficiency of the test specimen was determined by comparison of the iodine on the adsorber with that obtained from a complete material balance (by radioassay) of iodine in the downstream sections of the assembly.

The test adsorber was designed to simulate a small section of a commercial charcoal canister;³ one canister was cut open and the charcoal (8–14 mesh) and the perforated metal cylinders were used to construct the test adsorber. A bed depth of 0.75 in. of charcoal was used in these tests.

Two experiments were performed with the system at about 100°C, with the iodine added in laboratory air to which no water was added. These experiments, which were of 2 hr duration, used superficial air velocities of 50 fpm past the charcoal and resulted in iodine removal efficiencies of 99.93 and 99.98%; the efficiency of commercial Dorex H-42 canisters at 25°C for iodine removal from laboratory air is 99.99%.⁴

The removal of iodine from steam-air mixtures was tested in six experiments at gas velocities from 23.9 to 75 fpm and temperatures from 75 to 118°C, and in a single experiment at 105°C with a gas velocity of 290 fpm. The results of these tests are shown in Table 20.1.

Comparison with the data obtained without the addition of steam suggests a slight deleterious effect of water vapor on the adsorption process. This effect could occur by the blocking action of water vapor adsorbed on the charcoal surface, thus preventing the iodine vapor from efficient and rapid contact with the surface. This effect coupled with the short bed depth of 0.75 in. would allow some iodine molecules to pass through the charcoal mass without contact with a charcoal surface.

The effect of superficial gas velocity on adsorption efficiency appears negligible or very small at velocities up to 75 fpm; the iodine adsorption efficiency dropped significantly, however, at a velocity of 290 fpm. The difference (99.8+ vs 99.5+%) would be important in many applications. Activated charcoal exhibits a high efficiency for iodine vapor removal from steam-air mixtures for periods up to 2.75 hr with gas velocities less than 75 fpm. From these tests, charcoal appears entirely suitable for application in the SPWR iodine removal system.

Removal of Iodine from Air at 25°C

A small effort has been devoted to testing the removal of iodine, from air streams at room temperature, by specially treated cloth and paper filter media. Valuable applications for such materials would include (1) composite filters for removal of particulate matter as well as iodine vapor, (2) tapes for instruments for continuous monitoring of radioiodine, and (3) removal of iodine from air streams where low pressure drops and reasonable efficiencies are required.

Table 20.2 shows the results obtained on several commercially available materials of possible value for such applications. The retention of iodine by these materials varies widely, but two of the materials appear promising.

³Dorex H-42, available from Connor Engineering Corp., Danbury, Conn.

⁴R. E. Adams and W. E. Browning, *Removal of Radioiodine from Air Streams by Activated Charcoal*, ORNL-2872 (Mar. 17, 1960).

Table 20.1. Efficiency of Removal of Iodine from Steam-Air Mixtures on Charcoal from Dorex H-42 Canisters

Test Condition	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
Steam, % saturated ^a	96.3	101.9	98.9	56.4	82.9	73.2	98.7
System pressure, psig	0	0	0	1.25	1.0	6.5	1.25
Steam-air temperature, °C, at charcoal trap	75	87	96	118	102	118	105
Ratio I ₂ /charcoal, mg/g	7.4×10^{-4}	2.2×10^{-1}	7.3×10^{-2}	9.2×10^{-2}	1.4×10^{-1}	1.2×10^{-1}	2.8×10^{-1}
Ratio I ₂ /gas, mg/liter	1.2×10^{-5}	9.3×10^{-3}	5.6×10^{-3}	4.0×10^{-3}	2.3×10^{-3}	5.9×10^{-3}	2.5×10^{-3}
Linear velocity of gas through charcoal, fpm	26.5	30.1	23.9	74.9	36.8	47.2	290.8
Duration of test, hr	2.75	1.0	2.0	2.0	2.0	2.0	2.5
Iodine removal efficiency, %	99.80	99.94	99.93	99.91	99.86	99.91	99.54

^aCalculated from amounts of steam and air injected and conditions of temperature and pressure. Percentages greater than 100 would indicate gas contains condensed water (e.g., fog). None of above percentages are significantly greater than 100.

Table 20.2. Removal of Iodine from Room-Temperature Air by Special Filter Media

Filter Media	Linear Velocity of Air (fpm)	I ₂ Concentration in Air (mg/liter)	Iodine Retention (%)	
			After 1 hr	After 3.7 hr
$\times 10^{-2}$				
Activated carbon paper tape, type 166 ^a	22.6	1.27	15.73	11.44
Activated carbon wool cloth, type 165 ^a	22.8	2.86	99.88	99.86
Activated carbon wool cloth, type 164 ^a	22.5	2.15	2.56	2.49
Nonwoven cloth containing 12% carbon, sample No. 1632 ^b	22.3	1.71	60.89	56.16
Charcoal-loaded filter paper ^c	22.5	1.93	99.73	99.50

^aManufactured by Barneby-Cheney Co., Columbus, Ohio.

^bObtained by H. Gilbert, Office of Health and Safety, AEC, Washington, D.C. Manufactured by Lantuck Division, West Point Manufacturing Co., West Point, Georgia.

^cManufactured by Wiggins Teape and Alex Pirie Ltd., Gateway House, 1 Watling Street, London, England.

Removal of Iodine from Helium at High Temperatures

A study^{5,6} of the efficiency of removal of radioiodine from helium streams at elevated temperatures is in progress in support of the Experimental Gas-Cooled Reactor Project. In these experiments, iodine vapor is injected into flowing helium for a short period of time and is adsorbed on the test material at elevated temperatures in the apparatus shown schematically in Fig. 20.2.

⁵GCR Quart. Progr. Rept. Dec. 31, 1960, ORNL-3049, pp 302-8.

⁶GCR Quart. Progr. Rept. Mar. 31, 1961, ORNL-3102, in preparation.

UNCLASSIFIED
ORNL-LR-DWG 57724

Fig. 20.2. Experimental System for Helium Experiments.

Helium, without added iodine, continues to flow for an extended period; desorption of iodine from the heated adsorber is monitored by counting the downstream room-temperature collectors. Upon termination of the experiment the I^{131} activity is determined in the test adsorber and in all downstream sections of the apparatus to permit an evaluation of adsorber efficiency.

Activated charcoals remove iodine vapor from helium streams with high efficiency at temperatures as high as 430°C for periods up to 3 hr, but continued helium flow slowly removes the iodine contained in the charcoal bed.⁵ Additional study revealed that a wide variation in iodine retention from high-temperature helium exists among the charcoals.

A moderately rapid test has been devised to reject worthless materials and to obtain data for a more detailed study of the mechanisms of iodine release. Iodine retention tests are now performed using test adsorber beds approximately 0.25 in. deep to give a rapid indication of the relative value of the adsorbent material. Table 20.3 lists the pertinent test conditions and results from this screening study.

Table 20.3. Retention of Iodine from Flowing Helium on Adsorbers at Elevated Temperatures

Adsorbent Material	Temperature (°C)	Bed Depth (in.)	Gas Velocity (fpm)	Duration of Test (hr)	Iodine Retention (%)
Pittsburgh BPL, 8-14 mesh	320	0.375	13.6-110.8	144	16.0
Columbia G, 8-14 mesh	320	0.25	13.6-110.8	166	94.7
Pittsburgh PCB, 6-16 mesh	325	0.25	14.9-117.4	168	97.6
Pittsburgh BPL, 12-30 mesh	325	0.25	13.6-75.6	168	30.2
Whetlerite ASC, ^a 12-30 mesh	325	0.25	13.4-44.1	216	99.99+
Silver-plated copper mesh, 10 wt % Ag	320	0.33	13.2-72.5	193	95.7

^aThis material is made by impregnating Pittsburgh BPL charcoal with salts of silver, copper, and chromium.

One type of charcoal, Whetlerite ASC, is noted to exhibit markedly superior iodine adsorption and retention characteristics. Whetlerite charcoal is prepared by impregnating Pittsburgh BPL charcoal with salts of copper, silver, and chromium. It is designed for use in gas masks for protection against war gases and is available in commercial quantities. The apparent value of the metal salts for iodine retention may be assessed by comparing the 30.2% iodine retention of Pittsburgh BPL, 12-30 mesh, with the 99.99+% iodine retention by Whetlerite ASC, 12-30 mesh, both at 320°C. Tests with this and other charcoals will be continued in an effort to obtain a more complete definition of the mechanism of adsorption and release of iodine from surfaces.

REMOVAL OF RADIOACTIVE NOBLE GASES FROM CARRIER GASES

The following studies, which are a continuation of work summarized previously,⁷ have been reported in greater detail in recent Gas-Cooled Reactor Project quarterly progress reports.⁸⁻¹² The method of krypton and xenon removal receiving the most emphasis is that based on physical adsorption; in this method the adsorber may delay the noble gases relative to the moving carrier gas, with resultant radioactive decay of short-lived isotopes in the adsorber, or the adsorber may act as a concentrator and collector. Therefore, the work is concerned mainly with obtaining basic experimental and theoretical data for predicting the behavior of noble gases in adsorbers operating under a variety of conditions and for optimizing adsorber design.

Dynamic Adsorption of Krypton

Experimentally, a gas-solid chromatographic technique has been extensively employed in this work. A pulse of radioactive krypton or xenon is injected into a flowing carrier gas at the entrance of a trap containing the adsorbent under study, and elution curves are obtained by using beta-counting equipment.

Mathematical analysis of the elution curves yields two important parameters, the dynamic adsorption coefficient k and the number of theoretical plates N . The coefficient k (cm^3/g), which is a direct measure of retention time, is determined from

$$k \approx \frac{t_{\max} F}{m},$$

where $t_{\max}$ (minutes) is the time at which maximum fission gas partial pressure occurs in the effluent, F (cm^3/min) is the volumetric flow rate at the carrier gas pressure in the adsorbent but at room temperature, and m is the mass of adsorbent (g). From a theoretical standpoint, this k value is numerically approximately equal to the slope of the linear equilibrium adsorption isotherm $V = k'P$ when the units of k' are $\text{cm}^3 \text{ g}^{-1} \text{ atm}^{-1}$. Omitting details of the calculation of N , this quantity is a function of the shape of the elution curve and is a direct measure of the ratio of a breakthrough time (arbitrarily defined) to $t_{\max}$.

In coolant purification loops for helium-cooled reactors, the helium carrier gas is usually at rather high pressures (e.g., ~ 300 psig). Consequently, knowledge of the effect of high-pressure helium on the quantities k and N is required. This effect was studied by obtaining krypton elution

⁷W. E. Browning, R. D. Ackley, and R. E. Adams, *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, pp 170-81.

⁸GCR Quart. Progr. Rept. Mar. 31, 1960, ORNL-2929, pp 221-23.

⁹GCR Quart. Progr. Rept. June 30, 1960, ORNL-2964, pp 210-12.

¹⁰GCR Quart. Progr. Rept. Sept. 30, 1960, ORNL-3015, pp 147-50.

¹¹GCR Quart. Progr. Rept. Dec. 31, 1960, ORNL-3049, pp 302-8.

¹²GCR Quart. Progr. Rept. Mar. 31, 1961, ORNL-3102, in preparation.

curves for helium carrier gas pressures up to about 420 psia with Columbia G activated carbon, 8–14 mesh, at 25°C as the adsorbent and with Kr⁸⁵ as the tracer. (Xenon behavior can be fairly well predicted, with the aid of auxiliary data, from that of krypton.) The results (Fig. 20.3) showed that under the experimental conditions employed, the dynamic adsorption coefficient k decreased only slightly with increased helium pressure and that the decrease in N with pressure, while appreciable, would not be serious from the standpoint of adsorber design.⁸

Fig. 20.3. Effect of Helium Pressure at 25°C on Dynamic Adsorption of Krypton by Charcoal.

In other studies the dynamic krypton adsorption measurements were extended to include some other types of charcoal and, also, a greater variety of operating conditions, some of which correspond to those of proposed designs for GCR-ORR loop experiment No. 2 traps. The charcoal types included were Columbia HCC 12/28X, Columbia ACC 6/14X, Pittsburgh PCB 12/30, and Pittsburgh PCA 12/30. The k and N values obtained indicated that there were no large differences between these materials. As the adsorbent temperature varies downward from 25 to -33°C, k increases from about 55 cm³/g to about 500 cm³/g. The number of theoretical plates, N , was observed to tend toward relatively small values at low carrier gas velocities. This is a result of transport of krypton by longitudinal diffusion becoming important relative to transport by convection.^{9,10,12}

Equilibrium Adsorption of Krypton and Xenon

Equilibrium (or static) krypton and xenon adsorption data are useful as a check on dynamic adsorption measurements and theory and, also, as a convenient means for obtaining xenon adsorption information, since the Xe¹³³ tracer for dynamic measurements is not as readily available as Kr⁸⁵. Such data, as adsorption isotherms, have been obtained at 0, 25, and 60°C for some of the charcoals of interest and for Linde molecular sieves. These data have been summarized in a

semiquantitative fashion.¹¹ In several instances, where comparable dynamic and equilibrium adsorption coefficients were available, good agreement was observed. More recently, the equilibrium data were statistically analyzed by means of an Oracle linear regression code. In these calculations, the isotherms were fitted to the Freundlich equation, $V = kP^{1/n}$, which gave a better fit, in general, than the Langmuir equation over the range of the data. The temperature dependence of the adsorption was represented by $k = Ae^{B/T}$, where k is an arbitrarily defined adsorption coefficient for the cases of nonlinear isotherms, A and B are evaluated constants, and T is absolute temperature. The detailed results of these calculations have been reported.¹³

Diffusion of Krypton in Charcoal

As mentioned under "Dynamic Adsorption of Krypton," this report, transport by diffusion assumes importance at low carrier gas velocities. Accordingly, a study of this mechanism was undertaken. Experimentally, natural krypton with Kr⁸⁵ tracer was injected into one end of a charcoal column (previously flooded with helium), and relative krypton concentration as a function of time, under the condition of no convection flow, was measured at the other end by means of a G-M counter tube. The data were analyzed in conjunction with the applicable solution of the diffusion equation, and effective or apparent diffusion coefficients were evaluated. The krypton diffusion coefficients obtained with Pittsburgh PCB 12/30 activated carbon at 0, 25, and 60°C, with stagnant helium at 1 atm as the predominant component of the gas phase, were 0.0021, 0.0057, and 0.0141 cm²/sec respectively. These coefficients are approximately inversely proportional to the corresponding slopes of the adsorption isotherms of krypton on Pittsburgh PCB charcoal. This relationship is a consequence of the relative quantity of krypton available for gaseous diffusion being determined by the extent of adsorption. Less extensive measurements were made for Pittsburgh PCB 6/16 and Columbia HCC 12/28X. No significant difference for krypton diffusion in the three adsorbents, PCB 12/30, PCB 6/16, and HCC 12/28X, was observed, but this is probably due to lack of resolution, since the effective diffusion coefficient should increase with charcoal grain size, other factors being constant.^{10,11,12}

Retention of Krypton and Xenon by Linde Molecular Sieves Used for Water and Carbon Dioxide Adsorption

Linde molecular sieves, types 4A and 5A, are being considered for use in removal of water and carbon dioxide from reactor coolants. If regeneration gases are to be vented to the atmosphere, the quantity of radioactive fission product gases associated with the sieves must be low. Type 4A appeared attractive since dynamic krypton adsorption results indicated that krypton adsorption was negligible. (Presumably, xenon adsorption would also be negligible since pores

¹³R. D. Ackley and W. E. Browning, *Adsorption of Krypton and Xenon on Activated Carbon and Linde Molecular Sieves*, ORNL CF-61-2-32 (Feb. 14, 1961).

inaccessible to krypton would be inaccessible to xenon.) In a further study of the behavior of type 4A sieves, equilibrium (or static) krypton and xenon adsorption data were obtained. Krypton adsorption was observed to be appreciable at 25°C, and xenon adsorption, while apparently negligible at 25°C, was measurable at 60°C. Times required for equilibration were relatively long. These long equilibration times are probably the explanation for the observations in the dynamic tests and for the apparently anomalous behavior of xenon at 60 and 25°C. Apparently, the pore diameter in 4A is so close to the molecular diameters for krypton and xenon that these gases can enter only at a slow rate, but the rate of approach to equilibrium increases with temperature. In a related study, which was performed by members of the MIT Practice School, dynamic retention of krypton by type 5A sieves was measured, at 25°C, as a function of the amount of loading with carbon dioxide and with water. They observed that relatively high loadings were required, as indicated by the dynamic adsorption coefficient k , to reduce krypton retention to negligible values. In view of these results, provision for radioactive decay in the sieves may be required prior to venting regeneration gases to the atmosphere.^{11,12,14}

Heat Effects During Adsorber Pressurization

During pressure testing of GCR-ORR loop traps with nitrogen, localized heating and bulging of the metal of one of the traps were observed. In an effort to explain these phenomena, equations were developed which expressed the temperature rise due to the heat of compression on sudden pressurization, and calculations were made of the expected temperature rise due to the heat of adsorption. Also, a few laboratory-scale tests were made under conditions simulating the pressure testing. The calculated and laboratory results were in fairly good agreement and were consistent with the observed localized heating in the loop traps when their geometry was taken into consideration. On the other hand, the bulging did not seem to have been due to this relatively mild heating but was apparently caused by the high pressure alone.^{10,11}

ASSISTANCE TO OTHER PROGRAMS

Personnel from this division have served in an advisory capacity in the design of iodine removal equipment for the off-gas systems of the NS "Savannah." Information concerning the iodine removal efficiency to be expected from proposed designs was provided, the off-gas system in the NS "Savannah" was inspected, and an oral report on the subject was delivered to the AEC Advisory Committee on Reactor Safeguards.

A proposed addition of an iodine vapor adsorber to the off-gas system of the LITR was evaluated in terms of atmospheric radiation doses to Laboratory personnel.¹⁵ This evaluation was

¹⁴E. E. Wright, Jr., and A. R. McLain, *Krypton Holdup in Molecular Sieves*, KT-548 (Nov. 8, 1960).

¹⁵R. E. Adams and W. E. Browning, *Evaluation of Iodine Vapor Adsorbers for the Low Intensity Test Reactor (LITR)*, in preparation.

made by comparing doses that could result in the event of a partial reactor core meltdown while utilizing the present off-gas system to those doses that would result if an iodine adsorber was installed. It was concluded that the addition of an iodine adsorber is needed to reduce the iodine hazard to a more acceptable level.

Consultation services have been and are being provided to project personnel responsible for the design of the off-gas system for the Molten-Salt Reactor Experiment. Calculations are in progress to predict temperature rises in the HRT off-gas adsorber system and to relate changes in HRT reactor power to adsorber temperature transients.

Data from the iodine adsorption experiments are being used in a review of the proposed off-gas systems of the HFIR. Calculations are being made for evaluating the expected performance of the off-gas systems, both in terms of amounts of fission gases penetrating the systems and the possible radiation hazards to personnel resulting from discharge of these fission gases to the atmosphere.

Assistance has been given to several experimental programs in the design and evaluation of off-gas systems connected with in-pile experimentation.¹⁶ These systems include provisions for preventing a gross release of gaseous fission products in the event of experiment failure or for continuous processing of off-gas during operation of the experiment.

¹⁶R. E. Adams and W. E. Browning, *Evaluation of Experiment Off-Gas System for the EGCR-LITR Capsule Experiment*, ORNL CF-60-9-8 (Sept. 2, 1960).

RP 149-152

NSIC-161

~~h 128~~

~~IV 312 402~~

21. RELEASE OF FISSION PRODUCTS ON IN-PILE MELTING OF REACTOR FUELS

R. P. Shields R. A. Lorenz
C. E. Miller C. J. Barton
W. E. Browning, Jr.

The most serious hazard from postulated accidents with nuclear reactors is generally associated with release of fission products from fuel elements which melt because of a nuclear excursion or because of loss of reactor coolant. The release of fission products when reactor fuels are melted by external heating is under study in the Chemistry Division.¹

The present series of experiments will determine the release of fission products when reactor fuels are melted by nuclear heating. Some of the parameters which may be important in this experiment are type of fuel material, coolant composition, quantity of fission products present, operating temperature prior to melting, specimen geometry, the rate of temperature rise, and the length of time the specimen remains molten. In-pile tests will permit these parameters to be studied under conditions resembling those of a nuclear accident.

In the initial in-pile experiment² an unirradiated stainless-steel-clad UO_2 fuel specimen will be placed in a reactor furnace (described below) and moved to a position close enough to the lattice of the ORR to build up traces of fission products. After 24 to 36 hr of irradiation the specimen will be further lowered to a position where the fission and gamma heat will cause the specimen to melt. Helium gas sweeping over the specimen will carry fission products to filters and traps, where the fission products will be separated and collected. At the end of the experiment, the furnace and associated tubing, filters, and traps will be removed for fission product analysis.

The details of the reactor furnace are shown in Fig. 21.1. The specimen is a stainless-steel-clad UO_2 cylinder 0.210 in. in diameter by 1 in. long. Its density is about 95% of theoretical, and 3% of the uranium is U^{235} . The specimen is mounted on a porous thoria pedestal which is supported by a porous zirconia base resting on a beryllia heat conductor. The thoria serves as a container for the molten UO_2 , and the thoria and zirconia both serve as heat insulators. The specimen is enclosed by a thoria cylinder having a thoria plug and is surrounded by a zirconia cylinder. These parts are all contained in a primary stainless steel container which is enclosed by a secondary stainless steel container. The top and bottom of the primary container both have aluminum-filled caps to transfer heat from the ends of the primary container to the side of the secondary container. Water flowing past the secondary container will cool the experiment. The integrity of the two systems is monitored by stagnant helium pressurized above reactor tank pressure. Leaks in either containment system will be detected by a drop in the helium pressure.

During the time the experiment is in the reactor, a flow of helium (see Fig. 21.2) will pass through the primary system and will carry particulate matter and fission products from the furnace

¹G. W. Parker *et al.*, *Fission Product Release from UO_2 by High Temperature Diffusion and Melting in Helium and Air*, ORNL CF-60-12-14 (Feb. 14, 1961).

²R. P. Shields *et al.*, *In-Pile Experiment for Measuring Release of Fission Products on Melting of Reactor Fuels*, ORNL-3087, to be issued.

UNCLASSIFIED
ORNL-LR-DWG 49981

Fig. 21.1. Reactor Furnace for Melt-Down Experiments.

through a stainless steel tube to three graded filters and a charcoal trap. The three graded filters provide information concerning the size of the particulate matter. The charcoal, maintained at reactor tank water temperature (120°F), will remove iodine and possibly other fission products from the gas stream. The sweep gas then will pass through a liquid-nitrogen-cooled charcoal trap located outside of the reactor pool. This charcoal will retain all the rare gases released from the irradiated fuel specimens. Radioactive gases in the inlet and exit lines to this trap will be monitored by ion chambers connected to recording electrometers in the experiment control room. From the cooled-charcoal trap the helium sweep gas will flow into the reactor off-gas system.

The facility tube (Fig. 21.3) enters the ORR top plate through the V-5 access flange and is bent to pass into the F-9 lattice position. The lower end of the facility tube fits into a lattice insert which is machined to fuel element dimensions. A hydraulic positioning mechanism is mounted

Fig. 21.2. Experiment Flow Diagram.

on the top of the facility tube for the purpose of lowering the furnace into the reactor lattice or raising it to a position above the lattice while the reactor is operating. This mechanism can move the experiment 36 in. up or down. Solenoid valves operated from the control panel direct the flow of process water which operates the mechanism, while manual valves adjust the water flow rate and permit regulation of travel speed for lowering the experiment to 2 in./min and for raising the experiment to 6 in./min.

A pipe which penetrates the top of the reactor tank through the flange supporting the facility tube permits tank water to be directed by a pair of mechanically linked valves either into the facility tube to provide a cooling medium for the experiment or through a pipe which runs to the bottom of the facility tube to operate a hydraulic plunger to close the cooling water outlet. When the mechanically linked valves are in the latter position the facility tube is isolated from the reactor tank, and the tube may be opened either to insert or to remove an experiment while the reactor is operating.

Fig. 21.3. F-9 Facility Flow Diagram.

The radial temperature profile of the experiment as a function of vertical position of the experiment in the reactor has been calculated by an Oracle program which was devised to solve heat transfer problems. Flux data for these calculations were obtained by direct measurement in the F-9 facility. The thermal neutron flux was measured by exposing a cobalt wire and was found to have a peak value of 9.4×10^{13} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. Measurement of the gamma heat is still in progress; the heat appears to be of the order of 3 w/g.

Operation of the first experiment has been approved by the Operations Division and the Reactor Experimental Review Committee; we expect to insert the experiment in March.

22. EFFECT OF RADIATION ON BERYLLIUM OXIDE

G. W. Keilholtz
R. P. Shields

J. E. Lee, Jr.
W. E. Browning, Jr.

Beryllium oxide, because of its excellent neutron cross section and moderating ability, has been proposed for use as a moderator in a variety of high-temperature nuclear reactors. In such usage, beryllium oxide must withstand irradiation by neutrons, both fast and thermal, and by gamma rays to high total dosages and must withstand the considerable stresses resulting from such irradiation. An experimental program¹ is in progress to determine the resistance of BeO to reactor irradiation as a function of specimen composition and dimensions, irradiation temperature, thermal stresses, and radiation dosages. This program is designed to determine the conditions under which BeO moderator material may be used without failure in nuclear reactors, to determine the effects of radiation on the important properties of this material, and to establish, if possible, the mechanism of failure under irradiation.

The experimental assembly has been described previously.¹⁻³ Each assembly consists of six capsules, each containing three specimens spaced inside an Inconel housing which provides an annulus through which a controlled helium-argon coolant mixture is circulated to control the specimen temperature. In any one experiment the dosage received by capsules at the top of the lattice is less by a factor of 3 or 4 than that received by those near the bottom of the lattice. The irradiation temperatures were varied from a maximum of 1100°C to a low of 120°C. The specimens contained in the capsules were 1 in. in length and from 0.428 to 0.800 in. in diameter. The beryllium oxide studied to date had a density of 2.9 g/cm³, fabricated by hot pressing, or 2.6 g/cm³, fabricated by isostatic pressing and sintering.

Five assemblies totaling 57 BeO sample specimens have been irradiated in the Engineering Test Reactor at Arco, Idaho. These assemblies, in which total dosages⁴ as high as 10^{21} nvt of fast neutrons have been accumulated, have been disassembled in hot cells,⁵ and the BeO specimens have been removed from the capsules. Severe physical damage was observed on materials receiving largest dosages in these tests.

Examinations are in progress to establish (1) possible changes in lattice parameters, (2) changes in grain size of the material, (3) changes in form or identity of species observed by metallographic techniques, (4) retention of gases formed as a consequence of irradiation, and (5) thermal conductivity of the irradiated specimens.

¹ *Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960*, ORNL-2931, p 157.

² *ANP Semmann. Progr. Rept. Sept. 30, 1958*, ORNL-2599, p 70.

³ *ANP Semmann. Progr. Rept. Oct. 31, 1959*, ORNL-2840, p 79.

⁴ These fluxes are in some cases estimates based on previous experience in the ETR facility. Flux monitors attached to these specific experiments are presently under examination. Values given here are believed accurate to $\pm 25\%$.

⁵ Disassembly and preliminary examinations were carried out at Battelle Memorial Institute, Columbus, Ohio.

An intensive study of these materials is still in progress. The following observations and conclusions, however, are apparent from inspections of all materials irradiated in this study.

1. Cracks begin to appear in the BeO specimens after an irradiation to fast-neutron dosages of approximately 7×10^{20} *nvt*.

2. The cladding (type 430 stainless steel) on the BeO specimens increases up to 2.5 to 3.0% in diameter, BeO irradiated at lower temperature seems to enlarge more than that at high temperature for similar dosages.

3. One capsule burst its cladding after an irradiation of approximately 10^{21} *nvt* at 120°C.

4. Specimens of BeO irradiated at 120°C for an estimated 10^{21} *nvt* seem to disintegrate slowly into powder when removed from the capsule and exposed to the atmosphere in the hot cell.

5. Irradiated BeO specimens apparently become more difficult to polish for metallographic study as the dosage increases.

6. Thermal conductivity apparently decreases with increased dosage as evidenced by progressive increases in measured thermal gradients in the specimens during irradiation. These changes amounted to greater than 30% for higher doses.⁶

A sixth irradiation assembly with somewhat larger pieces (1.2 in. in diameter) of the low-density BeO is being assembled for insertion into the ETR in March 1961. In addition, and since the results of the completed irradiations have clearly shown failure of BeO under the test conditions, design of a new series of irradiation assemblies to test systematically the effect of important parameters has been started.

⁶Pronounced changes (as much as a factor of 5) in thermal conductivity of BeO on irradiation of small specimens to 10^{21} *nvt* have been observed by French scientists, according to M. Salesse and R. Caillat, French AEC.

Part IV

PREPARATION AND PROPERTIES OF REACTOR MATERIALS

23. CHEMISTRY OF ORGANIC MODERATORS AND COOLANTS

W. T. Rainey L. B. Yeatts, Jr.

A research program has been initiated to determine the chemical kinetics of the pyrolytic and radiolytic decomposition of potentially useful organic moderators and/or coolants. The program to date has been concerned with survey of the literature, planning of experimental procedures, and the design, procurement, and assembly of equipment.

The initial research is to be a chemical kinetic investigation of the pyrolytic decomposition of biphenyl. Since the initial decomposition mechanism is of primary importance, the number and concentration of secondary reaction products will be limited by decomposing less than 0.5% of the biphenyl sample. For this study a quantity of highly purified biphenyl has been obtained. A chromatographic analysis shows only air, tetrahydrofuran solvent, and biphenyl. A pyrolysis furnace with a temperature-control unit which permits only minor temperature variations is available. A vacuum line to permit separation of the organic materials following pyrolysis has been assembled. The separation is to be made on the basis of boiling-point differences, with three fractions: first, permanent gases and low-boiling hydrocarbons; second, materials with boiling points ranging from room temperature to 260°C; finally, the high-boiling polymeric products. Vapor chromatographic equipment is being obtained for use in the identification of these decomposition products. A dimethyl-sulfolane column at 0°C in series with a Linde 5A molecular sieve column at 25°C will be used to analyze the mixture of permanent gases and low-boiling hydrocarbons. The intermediate-boiling compounds are to be identified through the use of a didecyl phthalate column and a silicone rubber column. The polymeric products will be analyzed on a molten-salt column which is useful up to 500°C; the stationary phase will be a eutectic mixture of lithium, sodium, and potassium nitrates supported on firebrick.

24. PREPARATION OF REFRACTORY OXIDES FROM MOLTEN SALTS

J. H. Shaffer
G. M. Watson

H. H. Stone
L. O. Gilpatrick

Refractory oxides of beryllium and uranium have been prepared from their fluoride salts, dissolved in molten-salt solvents at 800°C, by reactions with water vapor. Upon optical examination, these oxide particles were found to be high-purity single crystals of sizes ranging up to 200 μ . Because of these unique properties, further development of this relatively low-temperature method for preparing refractory oxides was desired.

Preparations of beryllium oxide were made by reacting water vapor with various concentrations of beryllium fluoride in lithium fluoride at 800°C. While the particle sizes of BeO obtained from each experiment were comparable (none over 100 μ), the apparent concentrations of impurities included in the crystalline oxide were found to diminish as the concentration of BeF₂ in the fluoride melt was decreased. Spectrographic analyses of various batches of BeO prepared by this technique showed typical total impurity concentrations of approximately 500 to 750 ppm. Of these impurities, approximately 80% was attributed to solvent and container-corrosion materials that were incompletely removed by the recovery process.

Uranium dioxide prepared by this water-vapor reaction technique demonstrated properties of near-stoichiometric UO₂. The unit-cell lattice parameter, a_0 , was found to be 5.472 ± 0.002 Å by x-ray diffraction measurements and corresponds to UO_{2.00 $\pm$ 0.003}. In addition, petrographic observations of the UO₂ product verified the presence of garnet-red single crystals of UO₂ that were free of inclusions. Of the total reportable impurities ($\sim$ 500 ppm) found in the prepared UO₂ by spectrographic analysis, approximately 95% of the contamination was from solvent and container materials. Preparations of UO₂ have been made from UF₄ dissolved in solvent mixtures of LiF-BeF₂, LiF-NaF, and LiCl-NaCl.

When water vapor was reacted with mixtures of UF₄ and BeF₂ dissolved in a molten-fluoride solvent, some of the UO₂ particles were completely coated with BeO. Subsequent experiments showed that single crystals of UO₂, added to a mixture of BeF₂ and LiF prior to the reaction with water vapor, could also be coated with BeO. However, petrographic examination of the oxide prepared by both techniques indicated that only UO₂ particles of sizes less than 20 μ were coated with BeO.

These results demonstrate that single crystals of refractory oxides can be prepared from molten salts at relatively low temperatures. Additional experimental techniques are being developed in an attempt to improve the purity of these oxides and to provide more economical methods for their production.

25. PREPARATION OF PURE BERYLLIUM COMPOUNDS BY SOLVENT EXTRACTION

R. E. Moore

Beryllium oxide of very much greater purity than that now commercially available may be of considerable value for special reactor applications.¹ A liquid-liquid extraction process is being developed for the preparation of ultrapure beryllium hydroxide which could be converted to the oxide or to other compounds. Discussions of the process and distribution coefficients for many impurities at various pH values are reported elsewhere.² Figure 25.1 shows the effect of pH on the distribution coefficient for beryllium and several typical impurities.

Fig. 25.1. Distribution-Coefficient Dependence on pH.

Several gram-size quantities of $\text{Be}(\text{OH})_2$ were prepared for spectrographic analysis by the extraction process. The starting material, $\text{Be}(\text{OH})_2$, contained at least 725 ppm metallic impurities, together with approximately 2000 ppm phosphorus and some fluoride. The purified product gave the following spectrographic analysis:

¹R. E. Moore, *Purification of Beryllium Compounds: A Literature Survey*, ORNL-2938 (June 1, 1960).

²ANP Project Semiann. Progr. Rept. Oct. 31, 1960, ORNL-3029, pp 56-58.

Element	Parts per Million Parts of BeO
Reportable impurities	
Mg	5
Si	10
Sn	5
V	5
B	5
Elements below present spectrographic standards	
Mo	< 50
Zn	< 25
Sr, Cr, Ni, Ti	< 20
Al, Ba, Ca, Fe, K, Li, Na	< 10
Co, Cu, Mn, Pb	< 5
Ag	< 0.5
P, F	Not detected

A comparison of the results of these analyses demonstrates the potential of this liquid-liquid extraction technique for obtaining ultrapure beryllium compounds. Accordingly, larger batches of ultrapure beryllium hydroxide are being prepared for primary use in developing improved spectrographic standards.

PUBLICATIONS

AUTHOR(S)	TITLE	PUBLICATION
Barton, C. J.	Solubility of Plutonium Trifluoride in Fused-Alkali Fluoride-Beryllium Fluoride Mixtures	<i>J. Phys. Chem.</i> 64 , 306 (1960)
Blander, M.	Quasi-Lattice Model of Reciprocal Salt Systems. A Generalized Calculation	<i>J. Chem. Phys.</i> 34 , 432 (1961)
Blander, M.	Some Calculations for a One-Dimensional Salt Mixture	<i>J. Chem. Phys.</i> 34 , 697 (1961)
Blankenship, F. F., R. E. Thoma, and M. A. Bredig	Fused-Salt Phase Equilibria	<i>McGraw-Hill Encyclopedia of Science and Technology</i> , McGraw-Hill, New York, 1960, pp 579-86
Browning, W. E., Jr.	Removal of Fission Product Activity from Gases. Part 1	<i>Nuclear Safety</i> 1 (3), 40-46 (1960)
Browning, W. E., Jr.	Removal of Fission Product Activity from Gases. Part 2	<i>Nuclear Safety</i> 1 (4), 47-53 (1960)
Burns, J. H., D. W. Osborne, and E. F. Westrum, Jr.	Heat Capacities of Uranium Tetrafluoride from 1.3° to 20°K and the Thermodynamic Functions to 300°K. Calorimeter for the Range 0.8° to 20°K (work done at Argonne National Laboratory)	<i>J. Chem. Phys.</i> 33 , 387 (1960)
Compere, E. L.	Thorium Oxide Suspensions	<i>Nucleonics</i> 18 , 12 (1960)
Friedman, H. A.	Analyses of Lithium Metal, Hydride, and Hydroxide for Nickel, Copper, Silicon, Iron, Chromium, Aluminum, and Hydroxide	<i>Anal. Chem.</i> 32 , 137 (1960)
Grimes, W. R., F. F. Blankenship, and G. W. Keilholtz	Chemical Aspects of Molten Fluoride Reactors	<i>Progr. in Nuclear Energy, Ser. IV</i> , 2 , 140 (1960)
Grimes, W. R., and D. R. Cuneo	Molten Salts as Reactor Fuels	chap. 17 in <i>Reactor Handbook</i> , 2d ed., vol I, <i>Materials</i> , Interscience, New York, 1960
Hill, D. G., J. Braunstein, and M. Blander	Electromotive Force Measurements in the System $\text{AgNO}_3\text{-NaCl-NaNO}_3$ and Their Comparison with the Quasi-Lattice Theory	<i>J. Phys. Chem.</i> 64 , 1038 (1960)
Insley, H., R. E. Thoma, H. Friedman, and C. F. Weaver	Ameliorations Des Methodes De Determination Des Equilibres De Phases a Haute Temperature Dans Les Systemes Ceramiques et Associes	<i>Bull. soc. franc. ceram.</i> , No. 48, 57-62 (1960)
Langer, S., and F. F. Blankenship	The Vapor Pressure of Uranium Tetrafluoride	<i>J. Inorg. & Nuclear Chem.</i> 14 , 26 (1960)
McDuffie, H. F., C. H. Secoy, C. J. Hochanadel, and J. P. McBride	Aqueous Fuel Systems	chap. 16 in <i>Reactor Handbook</i> , 2d ed., vol I, <i>Materials</i> , Interscience, New York, 1960
Patterson, C. S., L. O. Gilpatrick, and B. A. Soldano	The Osmotic Behavior of Representative Aqueous Salt Solutions at 100°C	<i>J. Chem. Soc.</i> 1960 , 2730-34
Thoma, R. E.	Book review of <i>Reactor Handbook 1, Materials</i> , 2d ed.	<i>J. Am. Ceram. Soc.</i> 44 (3), 79 (1961)

AUTHOR(S)	TITLE	PUBLICATION
Thoma, R. E., C. F. Weaver, H. A. Friedman, and L. A. Harris	The Compounds $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{ThF}_4$ and $\text{NaF} \cdot \text{BeF}_2 \cdot 3\text{UF}_4$	<i>J. Am. Ceram. Soc.</i> 43 (11), 608 (1960)
Thoma, R. E., H. Insley, H. A. Friedman, and C. F. Weaver	Phase Equilibria in the Systems BeF_2 - ThF_4 and LiF - BeF_2 - ThF_4	<i>J. Phys. Chem.</i> 64 , 865 (1960)
Ward, W. T., R. A. Strehlow, W. R. Grimes, and G. M. Watson	Rare Earth and Yttrium Fluorides. Solubility Relations in Various Molten NaF - ZrF_4 and NaF - ZrF_4 - UF_4 Solvents	<i>J. Chem. Eng. Data</i> 5 (2), 137 (1960)
Watt, W. J., and M. Blander	The Thermodynamics of the Molten Salt System KNO_3 - AgNO_3 - K_2SO_4 from Electromotive Force Measurements	<i>J. Phys. Chem.</i> 64 , 729 (1960)
Weaver, C. F., and T. N. McVay	Immersion Oils with Indices of Refraction from 1.292 to 1.411	<i>Am. Mineralogist</i> 45 , 469 (1960)
Weaver, C. F., R. E. Thoma, H. Insley, and H. A. Friedman	Phase Equilibria in the Systems UF_4 - ThF_4 and LiF - UF_4 - ThF_4	<i>J. Am. Ceram. Soc.</i> 43 (4), 213-18 (1960)
Weaver, C. F., R. E. Thoma, H. A. Friedman, and G. M. Hebert	Phase Equilibria in the System BeF_2 - UF_4 - ThF_4	<i>J. Am. Ceram. Soc.</i> 44 (3), 146 (1961)
Adams, R. E., and W. E. Browning, Jr.	Removal of Radioiodine from Air Streams by Activated Charcoal	ORNL-2872 (Mar. 17, 1960)
Cannon, M. C., W. T. Ward, G. M. Watson, and W. R. Grimes	Adsorption of Xenon and Argon on Graphite	ORNL-2955 (Nov. 21, 1960)
Evans, R. B., III, J. H. DeVan, and G. M. Watson	Self-Diffusion of Chromium in Nickel-Base Alloys	ORNL-2982 (Jan. 20, 1961)
Griess, J. C., H. C. Savage, T. H. Mauney, and J. L. English	Effect of Heat Flux on the Corrosion of Aluminum by Water: Part I. Experimental Equipment and Preliminary Test Results	ORNL-2939 (Apr. 29, 1960)
Griess, J. C., H. C. Savage, T. H. Mauney, J. L. English, and J. G. Rainwater	Effect of Heat Flux on the Corrosion of Aluminum by Water: Part II. Influence of Water Temperature, Velocity, and pH on Corrosion-Product Formation	ORNL-3056 (Feb. 10, 1961)
Moore, R. E.	Purification of Beryllium Compounds: A Literature Survey	ORNL-2938 (June 1, 1960)
Rosenthal, M. W., M. M. Yarosh, C. F. Baes, Jr., and R. C. Robertson	The Feasibility of an Unattended Nuclear Power Plant	ORNL-2985 (Aug. 30, 1960)
Savage, H. C., G. H. Jenks, and E. G. Bohlmann	In-Pile Corrosion Test Loops for Aqueous Homogeneous Reactor Solutions	ORNL-2977 (Nov. 10, 1960)
Weaver, C. F., R. E. Thoma, H. Insley, and H. A. Friedman	Phase Equilibria in Molten Salt Breeder Reactor Fuels. I. The System LiF - BeF_2 - UF_4 - ThF_4	ORNL-2896 (Dec. 27, 1960)

AUTHOR(S)	TITLE	PUBLICATION
Ackley, R. D., R. E. Adams, and W. E. Browning, Jr.	The Disposal of Radioactive Fission Gases by Adsorption	TID-7593, pp 199-216 (October 1960)

PAPERS PRESENTED AT SCIENTIFIC AND TECHNICAL MEETINGS

AUTHOR(S)	TITLE	PLACE PRESENTED
Adams,* R. E., and W. E. Browning	Removal of Radioactive Iodine Vapor from Air Streams	American Chemical Society, New York, N.Y., Sept. 11-16, 1960
Baes, C. F., Jr.	An Investigation of Uranyl Ion Hydrolysis at Elevated Temperatures Using the Glass Electrode	Nuclear Reactor Chemistry Conference, Gatlinburg, Tenn., Oct. 12-14, 1960
Barton, C. J., W. L. Marshall,* and G. M. Hebert	Liquid-Liquid Immiscibility Above 300°C in the System $\text{UO}_3\text{-SO}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$	American Chemical Society, Cleveland, Ohio, Apr. 5-14, 1960
Blander, M.	Vapor Phase Infrared Spectra of ZrF_4 and HfF_4	American Chemical Society, New York, N.Y., Sept. 11-16, 1960
Blander, M.	Vapor Phase Infrared Spectra of ZrF_4 and HfF_4	Gordon Research Conference, New Hampton, N.H., Aug. 22-26, 1960
Blood, C. M.	Solubility of NiF_2 and FeF_2 in Molten Fluoride Solutions	Southeastern Regional American Chemical Society Meeting, Birmingham, Ala., Nov. 3-5, 1960
Browning,* W. E., R. E. Adams, and R. D. Ackley	Removal of Volatile Fission Products from Gases	Nuclear Reactor Chemistry Conference, Gatlinburg, Tenn., Oct. 12-14, 1960
Cantor,* S., and T. S. Carlton	Cryoscopy in Sodium Fluoride; Effects of Tetravalent Fluorides	Southeastern Regional American Chemical Society Meeting, Birmingham, Ala., Nov. 3-5, 1960
Cantor, S.	Cryoscopy in Sodium Fluoride; Effects of Divalent Fluorides	American Chemical Society, New York, N.Y., Sept. 11-16, 1960
Franck, E. U.	Hydrolysis in Supercritical Steam (work done at Institute of Physical Chemistry, University of Göttingen, Germany)	American Chemical Society, New York, N.Y., Sept. 11-16, 1960
Franck, E. U.	Hydrolysis in Supercritical Steam (work done at Institute of Physical Chemistry, University of Göttingen, Germany)	Nuclear Reactor Chemistry Conference, Gatlinburg, Tenn., Oct. 12-14, 1960

*Denotes speaker.

AUTHOR(S)	TITLE	PLACE PRESENTED
Friedman,* H. A., Insley, R. E. Thoma, and C. F. Weaver	Improved Techniques and Apparatus for the Determination of Phase Equilibria in Fused Salt Systems at Elevated Temperatures	Southeastern Regional American Chemical Society Meeting, Birmingham, Ala., Nov. 3-5, 1960
Gill,* J. S., and W. L. Marshall	The Compound $\text{CuO} \cdot 3\text{UO}_3$	American Chemical Society, Cleveland, Ohio, Apr. 5-14, 1960
Gilpatrick,* L. O., and H. F. McDuffie	Free-Acid Determination Using Cation- Exchange Resins	American Chemical Society, New York, N.Y., Sept. 11-16, 1960
Griess, J. C., H. C. Savage,* T. H. Mauney, and J. L. English	The Corrosion of Aluminum Under Conditions of High Heat Flux	Nuclear Reactor Chemistry Con- ference, Gatlinburg, Tenn., Oct. 12-14, 1960
Grimes, W. R., G. M. Watson,* J. H. DeVan, and R. B. Evans III	Diffusion of Chromium in Nickel-Base Alloys	Nuclear Reactor Chemistry Con- ference, Gatlinburg, Tenn., Oct. 12-14, 1960
Grimes, W. R., J. H. Shaffer, R. A. Strehlow, W. T. Ward, and G. M. Watson*	Radioisotopes as Tracers for Reactions in Molten Fluoride Media	IAEA Conference on Uses of Radioisotopes in Physical Sci- ences and Industry, Copenha- gen, Denmark, September 1960
Grimes, W. R., G. M. Watson,* J. H. DeVan, and R. B. Evans III	Radiotracer Techniques in the Study of Cor- rosion by Molten Fluorides	IAEA Conference on Uses of Radioisotopes in Physical Sci- ences and Industry, Copenha- gen, Denmark, September 1960
Insley,* H., R. E. Thoma, H. A. Friedman, and C. F. Weaver	Improved Methods for Determining Phase Equilibria in Ceramic and Related Systems at Elevated Temperatures	French Ceramic Society Colo- quium, Paris, France, June 8-10, 1960
Jenks, G. H.	Radiation Corrosion of Zircaloy-2	Nuclear Reactor Chemistry Con- ference, Gatlinburg, Tenn., Oct. 12-14, 1960
Jones,* E. V., and W. L. Marshall	Compositions of Heavy- and Light-Liquid Phases in the System $\text{UO}_3\text{-SO}_3\text{-H}_2\text{O(D}_2\text{O)}$, 285-350°C; Distribution of Copper(II) Oxide and Nickel(II) Oxide	American Chemical Society, New York, N.Y., Sept. 11-16, 1960
Kelly, M. J., W. L. Marshall, and H. F. McDuffie*	Recent Developments in Aqueous Homogene- ous Reactor Fuel Solution Chemistry	Nuclear Reactor Chemistry Con- ference, Gatlinburg, Tenn., Oct. 12-14, 1960
Marshall,* W. L., and J. S. Gill	Investigation of the System $\text{UO}_3\text{-CuO-NiO-}$ $\text{SO}_3\text{-H}_2\text{O}$ at 300°C	American Chemical Society, Cleveland, Ohio, Apr. 5-14, 1960
McDuffie,* H. F., J. C. Griess, M. J. Kelly, and W. L. Marshall	Recent Progress in the Development of Aque- ous Homogeneous Reactor Fuel Solutions	American Nuclear Society, San Francisco, Calif., Dec. 12-14, 1960

*Denotes speaker.

AUTHOR(S)	TITLE	PLACE PRESENTED
Redman,* J. D., C. J. Barton, and R. A. Strehlow	Phase Relations in the Systems NaF-PuF ₃ and NaF-CeF ₃	Southeastern Regional American Chemical Society Meeting, Birmingham, Ala., Nov. 3-5, 1960
Reed, S. A.	Hydriding of Zirconium-Base Alloys During Exposure to Circulating Thoria-Urania Slurries	9th Annual AEC Corrosion Symposium, May 10, 1960
Secoy,* C. H., and H. F. Holmes	Electrokinetic Transport Properties of Thoria Surfaces in Dilute Aqueous Electrolytes	Nuclear Reactor Chemistry Conference, Gatlinburg, Tenn., Oct. 12-14, 1960
Shaffer,* J. H., G. M. Watson, and W. R. Grimes	Selective Precipitation of Oxides from Molten Fluorides	Southeastern Regional American Chemical Society Meeting, Birmingham, Ala., Nov. 3-5, 1960
Shaffer,* J. H., W. R. Grimes, G. M. Watson, D. R. Cuneo, J. E. Strain, and M. J. Kelly	The Recovery of Uranium and Protactinium from Molten Fluoride Systems by Precipitation as Oxides	Nuclear Reactor Chemistry Conference, Gatlinburg, Tenn., Oct. 12-14, 1960
Thoma,* R. E., H. A. Friedman, H. Insley, and C. F. Weaver	Phase Behavior of Molten Fluoride Fuels, Blankets, and Coolants	Nuclear Reactor Chemistry Conference, Gatlinburg, Tenn., Oct. 12-14, 1960
Thoma, R. E.	Fused Salt Phase Equilibrium Studies	Southeastern Regional American Chemical Society Meeting, Birmingham, Ala., Nov. 3-5, 1960
Thoma,* R. E., and F. F. Blankenship	Development of Fuels and Blankets for Molten-Salt Reactors	American Nuclear Society, San Francisco, Calif., Dec. 12-14, 1960
Weaver,* C. F., R. E. Thoma, H. A. Friedman, and H. Insley	Phase Equilibria in the System NaF-BeF ₂ -ThF ₄	American Chemical Society, New York, N.Y., Sept. 11-16, 1960

*Denotes speaker.

x

y

e

g

y

INTERNAL DISTRIBUTION

1. Biology Library	60. E. L. Compere
2. Reactor Division Library	61. J. C. Griess
3. ORNL - Y-12 Technical Library,
Document Reference Section	62. G. H. Jenks
4-6. Central Research Library	63. H. C. Savage
7-26. Laboratory Records Department	64. C. P. Keim
27. Laboratory Records, ORNL R.C.	65. M. Blander
28. C. E. Center	66. S. Cantor
29. A. M. Weinberg	67. J. H. Shaffer
30. J. P. Murray (K-25)	68. M. J. Kelly
31. R. G. Jordan (Y-12)	69. C. J. Barton
32. J. A. Swartout	70. W. L. Marshall
33. G. E. Boyd	71. C. F. Baes
34. W. R. Grimes	72. R. E. Thoma
35. R. B. Briggs	73. R. A. Strehlow
36. D. S. Billington	74. R. B. Evans III
37. F. F. Blankenship	75. G. W. Keilholtz
38. A. L. Boch	76. W. E. Browning
39. J. H. Frye, Jr.	77. W. T. Rainey
40. H. G. MacPherson	78. L. G. Overholser
41. J. C. White	79. G. C. Williams
42. W. D. Manly	80. Farrington Daniels (consultant)
43. C. H. Secoy	81. F. T. Miles (consultant)
44. E. G. Bohlmann	82. F. T. Gucker (consultant)
45. R. A. Charpie	83. Leo Brewer (consultant)
46. R. S. Cockreham	84. J. E. Ricci (consultant)
47. Esther Cohn	85. D. G. Hill (consultant)
48. F. L. Culler	86. G. W. Morey (consultant)
49. W. H. Jordan	87. Henry Eyring (consultant)
50. M. T. Kelley	88. M. G. Fontana (consultant)
51. J. A. Lane	89. R. M. Fuoss (consultant)
52. H. F. McDuffie	90. Norman Hackerman (consultant)
53. P. M. Reyling	91. H. S. Harned (consultant)
54. M. J. Skinner	92. E. A. Mason (consultant)
55. A. H. Snell	93. T. N. McVay (consultant)
56. E. H. Taylor	94. George Scatchard (consultant)
57. G. M. Watson	95. T. F. Young (consultant)
58. C. E. Winters	96. J. S. Dahler (consultant)
59. G. C. Warlick	97. J. W. Cobble (consultant)
	98. P. H. Emmett (consultant)

EXTERNAL DISTRIBUTION

- 99. Division of Research and Development, AEC, Washington
- 100. Division of Research and Development, AEC, ORO
- 101. Division of Reactor Development, AEC, Washington
- 102. Division of Reactor Development, AEC, ORO
- 103-694. Given distribution as shown in TID-4500 (16th ed.) under Chemistry category
(75 copies - OTS)