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ANNUAL PROGRESS REPORT
FOR PERIOD ENDING MAY 31, 1970

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
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REACTOR CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

For Period Ending May 31, 1970

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PART I. MOLTEN SALT CHEMISTRY

FLUORIDE SYSTEMS

THE ESTIMATION OF ACTIVITY COEFFICIENTS IN $LiF-BeF_2-ThF_4$ MELTS

C. F. Baes, Jr.

A polymer model, shown previously[1] to account for observed activity coefficients in the binary system $LiF-BeF_2$, has been extended to melts containing two additional components, MF_y and NF_z. In addition to the polymeric beryllium species $Be_aF_b^{(b-2a)-}$ previously assumed to be formed by sharing of F^- ions between tetrahedrally coordinated Be^{2+} ions, mononuclear species (e.g., $MF^{(y-1)+}$, $MF_2^{(y-2)+}$, . . .$MF_6^{(6-y)-}$) were assumed to be formed by the additional components. As previously, the entropy of mixing was based on volume fractions (actually fluoride fractions) rather than mole fractions. The model also includes heat of mixing terms for the six pairwise interactions of the four kinds of species F^-, $Be_aF_b^{(b-2a)-}$, $MF_b^{(b-y)-}$, and $NF_b^{(b-z)-}$.

Upon adjusting four parameters of the model which determine the stability and heat of mixing of the thorium species and the cerium species -- the corresponding parameters associated with the beryllium species were previously known from the binary system $LiF-BeF_2$ -- activity coefficients were generated for $LiF-BeF_2-ThF_4$ melts containing a small amount of CeF_3. These calculated coefficients agree quite well with the observed composition dependence of the reductive extraction of lithium and cerium from such melts by thorium in molten bismuth[2] and with the observed composition dependence of CeF_3 solubility.[3]

Activity coefficient curves could then be generated for all the components over the composition range $X_{LiF} = 0.5 - 0.8$, $X_{ThF_4} = 0-0.16$, and low CeF_3 concentrations. The activity coefficients of LiF, BeF_2, and ThF_4 were found to depend primarily on X_{LiF}.

[1] C. F. Baes, Jr., J. Solid State Chem. 1, 159 (1970).

[2] J. H. Shaffer, D. M. Moulton, W. R. Grimes, MSR Prog. Semiann. Progr. Rept., Aug. 31, 1968, ORNL-4344, p. 156.

[3] C. J. Barton, M. A. Bredig, L. O. Gilpatrick and J. A. Fredricksen, Inorg. Chem. 9, 307 (1970).

A RE-EXAMINATION OF THE LIQUIDUS IN THE SYSTEM $LiF-BeF_2$ FOR COMPOSITIONS BETWEEN 12 AND 60 MOLE PERCENT BeF_2

K. A. Romberger and J. Braunstein

Measurements of the emf with the molten salt concentration cell described above[1] were shown to permit determination of the liquidus in this system with unprecedented accuracy. The method is applicable also to other BeF_2-alkali fluoride systems and promises extension to other systems such as $LiF-ThF_4$ and possibly some ternary systems. The method depends on the response of the beryllium electrode to the chemical potential of beryllium fluoride; this gives rise to a discontinuity at a phase boundary of the slope of plots of (isothermal) EMF vs composition (X) or of EMF vs temperature (T). Not only does the discontinuity of dE/dX or dE/dT permit accurate location of the liquidus, but analysis of emf changes, at temperatures just below the liquidus, at compositions on both sides of an invariant point proivdes virtually unequivocal identification of the invariant point as a eutectic, peritectic, or congruent melting point. Previous applications of emf measurements to molten salt phase studies have not fully recognized or exploited the above quantitative and qualitative aspects.[2] We were able to establish, with this method, that the compound Li_2BeF_4 melts congruently (composition 0.3333 ± 0.0004 mole fraction BeF_2) at $459.1 \pm 0.2°C$, and that there is a eutectic of LiF and Li_2BeF_4 at 0.3280 ± 0.0004 mole fraction BeF_2 and $458.9 \pm 0.2°C$.

[1] K. A. Romberger and J. Braunstein, "EMF of Binary Molten Salt Concentration Cells," this report, p. 12.

[2] H. A. Øye, Acta Chem. Scand. 18, 361 (1964).

COMPILATION OF THERMODYNAMIC DATA FOR REACTIONS IN MSR FLUORIDES

C. F. Baes, Jr.

The chemical development which has been carried out, largely at ORNL, in support of the Molten Salt Breeder Reactor (MSBR) concept has produced a fairly quantitative description of the chemistry and thermodynamics of actinide, fission-product and structural metal fluorides in

molten $LiF-BeF_2$ solutions. This information has been summarized[1] (1) in terms of important heterogeneous chemical equilibria, many of which have been measured directly; (2) in terms of free energies of formation of solutes in molten 0.67 LiF-0.33 BeF_2 solutions; and (3) in terms of standard electrode potentials, some of which have been measured directly. This information may be applied to a variety of important aspects of molten salt reactor chemistry: The corrosion reactions between the Hastelloy-N container material (a nickel base alloy containing Fe, Cr, and Mo) and the fuel can be predicted from hydrogen reduction equilibria. Salt purification procedures can be specified for the removal of structural metal cations, oxides, and sulfides from a knowledge of the hydrofluorination equilibria which are employed. The stability of Th, Pa and U fluorides toward chemical reduction and toward precipitation by oxide similarly have been established by measurements of heterogeneous equilibria which include oxide solubility and oxide exchange reactions. The behavior of a large part of the yield of fission products can also be predicted on the basis of these studies and available thermochemical data. Finally, these chemical studies and the thermodynamic information which they have produced demonstrate the importance of the redox potential in controlling many features of MSBR fuel chemistry.

[1] C. F. Baes, Jr., Nuclear Metallurgy, 15, "Symposium of the Reprocessing of Nuclear Fuels," P. Chiotti, ed., USAEC-DTI, p. 617 (1969).

PHASE RELATIONS IN THE SYSTEM $KF-CeF_3$

L. O. Gilpatrick, H. Insley, C. J. Barton

The system $KF-CeF_3$ was investigated as a function of temperature and composition by thermal analysis, differential thermal analysis and gradient quenching. Results of a preliminary investigation of this system were reported earlier.[1] Crystalline phases in the quenched samples were identified principally by use of the polarizing microscope, but selected samples were examined by x-ray powder diffraction. Three compounds were identified: $3KF \cdot CeF_3$, $KF \cdot CeF_3$, and $KF \cdot 2CeF_3$ which melt incongruently at 675 $\pm$ 10°C, 755 $\pm$ 5°C, and 1135 $\pm$ 15°C, respectively.

Of these only $KF \cdot CeF_3$ is stable below 585°C. Three peritectic equilibria were observed corresponding to these incongruent melting points at 24, 32, and 63% CeF_3. The $KF \cdot 2CeF_3$ phase exhibits a substantial solid solubility for KF at temperatures above 795°C which results in a region of cubic solid solution whose properties vary over the composition range from 50 to 66-2/3 mole % CeF_3. The minimum liquidus temperature in the system is 620 ± 3°C at a composition of 19 mole % CeF_3.

A manuscript describing this work has been submitted to the Journal of Inorganic and Nuclear Chemistry for publication.

[1] C. J. Barton et al., Reactor Chem. Div. Ann. Prog. Rept. Dec. 31, 1966, ORNL-4076, p. 7.

CeF_3 SOLUBILITY IN MOLTEN MIXTURES OF LiF, BeF_2, and ThF_4

C. J. Barton, L. O. Gilpatrick, M. A. Bredig[1] and Judy A. Fredricksen[2]

Several compositions in this system have been examined in addition to those previously reported.[3] Comparison of these data with the results of previous investigations of the solubility of CeF_3 in LiF-BeF_2 melts[4] and of PuF_3 in similar compositions[5] points to the conclusion that the solubility of PuF_3 in the ternary mixtures will probably be adequate to fuel a reactor based on PuF_3 as the fissile agent.

The solubility of CeF_3 in eight LiF-BeF_2-ThF_4 and four LiF-ThF_4 mixtures was determined between 600° and 800°C by radiochemical and wet chemical analysis. Sintered copper filter sticks were used to remove filtered samples of the molten fluoride mixture that were saturated with CeF_3 tagged with ^{144}Ce. The data are well represented by straight lines in log solubility vs 1/T plots, the slopes of which yield the heat of solution of CeF_3 in the various solvents. These data together with published values permitted the formulation of relationships between solubility and solvent composition that could be rationalized in terms of charge size and the size of the ions involved.

This study has been completed and the results have been published.[6]

[1]Chemistry Division, Oak Ridge National Laboratory.

[2]Oak Ridge Associated Universities summer participant from St. Cloud State College, St. Cloud, Minn.

[3]J. A. Fredricksen, L. O. Gilpatrick, and C. J. Barton, "Solubility of Cerium Trifluoride in Molten Mixtures of LiF, BeF_2, and ThF_4, ORNL-TM-2335 (Jan. 1969).

[4]W. T. Ward et al., "Solubility Relations Among Rare-Earth Fluorides in Selected Molten Fluoride Solvents," ORNL-2749, Oct. 1959.

[5]C. J. Barton, J. Phys. Chem. 64, 306 (1960).

[6]C. J. Barton et al., Inorganic Chem. 9, 307 (1970).

PHASE EQUILIBRIA IN THE SYSTEM $LiF-BeF_2-CeF_3$

L. O. Gilpatrick, H. Insley, and C. J. Barton

Progress has been made in exploring the ternary fluoride salt system $LiF-BeF_2-CeF_3$ using the gradient quench technique. The solubility of CeF_3 in $LiF-BeF_2$ compositions were measured earlier[1] and correlated with other CeF_3 solubility measurements.[2] This system is of interest in part, because of its presumed analogy with the system $LiF-BeF_2-PuF_3$[3] which has some interest as a possible fuel composition for molten salt reactors.[4] Compositions were chosen to define the lower melting phase boundaries, resulting in the study of compositions containing less than 10 mole % CeF_3. The cerium fluoride primary phase field dominates the system as might be expected from its high melting point of 1460°C. This field approaches within 0.5 mole % of the low melting $LiF-BeF_2$ binary system in the range 33 to approximately 60 mole % BeF_2 where the melting temperatures of $LiF-BeF_2$ compositions are less than 460°C.[5] The ternary eutectic invariant point is apparently near the composition $LiF-BeF_2-CeF_3$ (46.5-53-0.5 mole %) and its melting point is currently estimated to be 358°C. The ternary eutectic in the sub-system $LiF-Li_2BeF_4-CeF_3$ is 455 ± 3°C, 5°C below the melting point of Li_2BeF_4 as reported by Thoma et al.[5]

Some evidence has been found for two immiscible liquids in equilibrium in a small region of this system which is rich in BeF_2 and near the CeF_3-BeF_2 eutectic composition at 5 ± 1 mole % CeF_3. This eutectic has a melting point of 537 ± 5°C. Equilibration times of three weeks or longer are needed to assure equilibrium in this part of the system due to the high viscosity of the melts. Further work will be needed to substantiate these findings and to define the boundary of the region of immiscibility.

[1] W. T. Ward, R. A. Strehlow, W. R. Grimes, and G. M. Watson, Solubility Relations Among Rare Earth Fluorides in Selected Molten Fluoride Solvents, ORNL-2749 (1959).

[2] C. J. Barton, M. A. Bredig, L. O. Gilpatrick, J. A. Fredricksen, Inorg. Chem. 9, 307 (1970).

[3] C. J. Barton, J. Phys. Chem. 64, 306 (1960).

[4] R. E. Thoma, Chemical Feasibility of Fueling Molten Salt Reactors with PuF_3, ORNL-TM-2256, (Jan. 20, 1968).

[5] R. E. Thoma, H. Insley, H. A. Friedman, and G. M. Hebert, J. Nucl. Matr. 27, 176 (1968).

METHOD FOR ESTIMATING ISOTHERMAL COMPRESSIBILITY OF MOLTEN SALTS

S. Cantor

The published molten-salt data (sonic velocity, density, isobaric heat-capacity)[1] from which isothermal compressibility can be rigorously calculated has been reviewed. We have found that the temperature dependence of compressibility for all salts fits the simple exponential relationship,

$$\beta_T = \beta_M \exp[b(T-T_M)] \qquad (1)$$

where β_T and β_M are the isothermal compressibilities at temperature T (in °K) and at the melting point, T_M; b is a constant for a given salt and seems to have the narrow range (for 35 salts) 1-2 x 10^{-3}/°K. β_M, the isothermal compressibility at the melting point, can be reasonably well predicted (with an uncertainty of 30% or less) by the equation

$$\beta_M = 9V_\ell/nU_\ell \qquad (2)$$

where V_ℓ is the molar volume at the melting point; U_ℓ is the cohesive energy of a mole of liquid (approximated by subtracting the heat of fusion from the Born-Haber crystal energy[2]); n is a constant dependent on an ion's position in the periodic table. The values of n were obtained empirically from compressibility data of the alkali and alkaline-earth halides:

Ion type	He	Ne	Ar	Kr	Xe
n	1.3	1.4	1.9	2.1	2.5

(For instance, Li^+ and Cl^- are, respectively, He and Ar ion types; therefore, n for LiCl is (1.3 + 1.9)/2 = 1.6). Equation (2) is merely a Born-Lande equation[2] originally derived for ionic crystals, and applied to ionic liquids.

With β_M estimated by eq. (2), β_T may be estimated from eq. (1) by: substituting an average empirical value for b of $1.5 \times 10^{-3}/°K$. A second method is to use a "corresponding-states" equation,

$$\beta_T/\beta_M = T/T_M \qquad (3)$$

Neither method greatly increases the error already present in the estimated value of β_M.

[1]G. J. Janz, Molten Salts Handbook, Academic Press, New York (1967).

[2]D. A. Johnson, Some Thermodynamic Aspects of Inorganic Chemistry, Cambridge Univ. Press (1968), pp. 20-23, 203-204.

METAL DILATOMETER FOR DETERMINING DENSITY OF VOLATILE LIQUIDS AT ELEVATED TEMPERATURE;[1] APPLICATION TO MOLTEN FLUORIDES OF REACTOR INTEREST

S. Cantor

In this apparatus, a metal probe detects the changes in liquid level in the neck of a volume - calibrated metal vessel. Vapor is prevented from escaping by a Teflon stopper, which also permits vertical displacement of the probe. When the probe contacts the liquid surface, a vacuum-

tube voltmeter changes from an open circuit reading to a detectable resistance. The probe height is measured to ± 0.02 mm with a cathetometer. Through a side arm in the neck of the vessel, an inert, insoluble gas can be introduced to suppress bubbles in the melt. The accuracy (± 0.3%) of the apparatus was established by measuring $NaNO_3$ and KNO_3, whose densities have been accurately determined by Archimedean techniques.

Densities of seven salt mixtures were determined by this method. The results are summarized below:

Composition (mole %)	Equation, $\rho(gcm^{-3})$ temp. range in °C	How Used
$64.7LiF,30.1BeF_2,5.2ZrF_4$	$\rho = 2.539-5.77x10^{-4}t$ 543 - 750°C	MSRE fuel carrier
$64.79LiF,29.96BeF_2,4.99ZrF_4,0.26UF_4$	$\rho = 2.533-5.62x10^{-4}t$ 524 - 761°C	MSRE fuel salt (carrier + UF_4)
$66LiF,34BeF_2$	$\rho = 2.280-4.88x10^{-4}t$ 515 - 820°C	MSRE coolant
$92NaBF_4,8NaF$	$\rho = 2.252-7.11x10^{-4}t$ 399 - 591°C	Intermediate coolant
$70.06LiF,17.96BeF_2,11.98ThF_4$	$\rho = 3.824-8.06x10^{-4}t$ 533 - 741°C	Single-fluid breeder solvent
$69.98LiF,14.99BeF_2,15.03ThF_4$	$\rho = 4.181-9.52x10^{-4}t$ 543 - 750°C	Blanket in two-fluid reactor
$70.11LiF,23.88BeF_2$ $6.01ThF_4$	$\rho = 3.112-6.71x10^{-4}t$ 555 - 707°C	Molten-salt converter reactor fuel salt

In all seven mixtures, measured densities were approximately equal to densities calculated from the additive volumes of the components.

Another interesting result exhibited by the last three listed mixtures was the approximately equal expansivity (fractional change of volume with temperature) for all three despite differences in concentrations of BeF_2 and of ThF_4. At 600°C, the expansivity for each of these three mixtures was $\simeq 2.5 \times 10^{-4}$/°C. This value may apply to all reactor fuel melts since they all contain about 70 mole % LiF.

[1]The apparatus is fully described in Rev. Sci. Instrum. 40, 967 (1969).

VISCOSITY OF MOLTEN SALTS

Stanley Cantor

In support of requirements for physical property information for molten-salt reactors, the viscosity of five salts has been determined by the oscillating-cup method.[1] The measurements of oscillation amplitudes and periods, and initial treatment of the data were performed at Mound Laboratory, Miamisburg, Ohio, by L. J. Wittenberg and R. Dewitt. Preparation of samples, fabrication of capsules, and supplementary interpretation of data were done at ORNL.

A summary of the data, including some interpretative comments, is given in the following table:

Composition (mole %)	Equation and Temp. Measd. (η, centipoise)	Comments
$72.7LiF,15.7BeF_2,11.6ThF_4$	$\eta = 0.109 \exp(4090/T)$ 826-946°K	Eq.[2] for $LiF-BeF_2-UF_4$ (70-18-12 m%) is $\eta = 0.09 \exp(4280/T)$
$70.1LiF,23.9BeF_2,6.0ThF_4$	$\eta = 0.0660 \exp(4380/T)$ 799-906°K	Eq.[2] for $LiF-BeF_2-UF_4$ (70-24-6 m%) is $\eta = 0.08 \exp(4350/T)$
$92.0NaBF_4,8.0NaF$	$\eta = 0.0877 \exp(2240/T)$ 681-810°K	Viscosities are about 10% less than those of pure $NaBF_4$
$NaBF_4$	$\eta = 0.0832 \exp(2360/T)$ 692-786°K	Viscosities slightly more than those of NaI at corresponding temperatures
KBF_4	$\eta = 0.0946 \exp(2280/T)$ 857-954°K	Viscosities slightly less than those of KI at corresponding temperatures

[1] L. J. Wittenberg, D. Ofte, and C. F. Curtiss, J. Chem. Phys. 48, 3253 (1968)

[2] B. C. Blanke et al, Density and Viscosity of Fused Mixtures of Lithium, Beryllium, and Uranium Fluorides, MLM-1086, pp. 56, 83 (Dec. 1956).

ELECTROCHEMICAL STUDIES

COULOMB INTERACTIONS AND NONIDEALITY IN CHARGE UNSYMMETRIC MOLTEN SALT MIXTURES**

J. Braunstein, K. A. Romberger, and R. Ezell*

Nonideality of many simple binary molten salt mixtures can be correlated with differences of ionic radii in the pure components by means of the conformal ionic solution theory (CIS), enabling estimation of thermodynamic properties of mixtures for which data are unavailable.[1,2] CIS predicts that the excess thermodynamic functions of solute in dilute solution are proportional to the square of a parameter, δ, whose principal variation is given by the difference between cation-anion distances (d_1-d_2) of the pure salts composing a charge-symmetric mixture (e.g., (Na,K)Cl). For mixtures of univalent and divalent salts (e.g., NaCl-$MgCl_2$), CIS predicts linear variation of the excess functions of the divalent salt with (δ). We have shown that CIS also predicts linear variation with (δ) for the limiting value of the univalent solvent's chemical potential interaction parameter ($\lim_{x \to o} (\mu_1^E/X^2)$); μ_1^E is the excess chemical potential of solvent and X is the mole fraction of divalent solute. We also have derived a similar relation from a simple linear model of Coulomb interactions in a mixture of hard-sphere ions.[3] Excess chemical potentials of alkali fluoride in mixtures of NaF with BaF_2, SrF_2, CaF_2 or MgF_2, and in mixtures of BeF_2 with LiF, NaF, KF, RbF or CsF confirmed the predicted relation for the fluorides (the only appreciable deviations occurring for NaF-MgF_2 and for KF-BeF_2). The relation appeared also to fit data for the mixtures of NaCl with $BaCl_2$, $SrCl_2$ or $CaCl_2$ and mixtures of KCl with $BaCl_2$, $SrCl_2$ or $CaCl_2$, only NaCl-$CaCl_2$ showing an appreciable deviation. The fit lends confidence to the usefulness of CIS and the simple ionic model of molten salt mixtures.

* ORAU Summer Student Trainee from University of Arkansas, 1969.

**Paper submitted to Journal of Physical Chemistry.

[1] H. Reiss, J. L. Katz and O. J. Kleppa, J. Chem. Phys. 36, 144 (1962).

[2] H. T. Davis, J. Chem. Phys. 41, 2761 (1964).

[3] J. Braunstein, "Statistical Thermodynamics of Molten Salts and Concentrated Aqueous Electrolytes," in Ionic Interactions: Dilute Solutions to Molten Salts, S. Petrucci, ed., Academic Press, in press.

EMF OF BINARY MOLTEN SALT CONCENTRATION CELLS

K. A. Romberger and J. Braunstein

In previous communications we have reported emf measurements of concentration cells with transference in molten $LiF-BeF_2$ with Be electrodes. We were able to (1) establish a nearly unique unicationic conduction mechanism (by lithium relative to fluoride) which is characteristic of silicates rather than simple molten salt mixtures, and (2) calculate ionic mobilities.[1] Since the accessible range of temperature and composition was seriously limited by containment in silica, an all-metal cell was designed and constructed, consisting of a molybdenum crucible, molybdenum stirrer and nickel electrode compartments fitted with nickel frits to provide communication between electrode compartments. The new cell, including stirrer, electrode compartments, thermocouple wells and a port for addition of material, is provided with an inert gas atmosphere, and is contained in a silica envelope which provides visibility. EMF measurements were found to be stable and reproducible within about 50 microvolts, with no evidence of internal short circuiting and virtually no dissolution or mass transport of beryllium metal, permitting experiments covering long periods of time with minimum contamination. Measurements with the new cell confirmed previous results with the silica cell, and have been extended to 775°C and to basic compositions in the $LiF-BeF_2$ system which could not be contained in silica. The new measurements also: (1) made it possible to determine the liquidus in BeF_2-alkali fluoride systems with unprecedented precision by equilibrium measurements; (2) permitted precise evaluation of excess chemical potentials of the alkali fluoride component.

[1] K. A. Romberger and J. Braunstein, Inorg. Chem. 9, 0000 (1970).

POTENTIOMETRIC MEASUREMENTS OF THE U^{4+}/U^{3+}, Ni^{2+}/Ni^{o}, AND Nb^{+z}/Nb^{o} COUPLES IN MOLTEN $2LiF-BeF_2$

B. F. Hitch and C. F. Baes, Jr.

Potentials were measured for the cells

$$\begin{array}{lll} \text{I} & \text{Pt(c)} & \left| \begin{array}{c} UF_3,\ UF_4 \\ 2LiF-BeF_2 \end{array} \right| \\ \text{II} & \text{Ni(c)} & \left| \begin{array}{c} NiF_2 \\ 2LiF-BeF_2 \end{array} \right| \\ \text{III} & \text{Nb(c)} & \left| \begin{array}{c} NbF_z \\ 2LiF-BeF_2 \end{array} \right| \end{array} \quad \left| \begin{array}{l} NiF_2\ (10^{-4}) \\ LiF\ (0.67) \\ BeF_2\ (0.33) \end{array} \right| \begin{array}{c} BeO(c) \\ \\ NiO(c) \end{array} \left| \right. \ Ni(c)$$

in which the reference electrode is nickel immersed in molten $2LiF-BeF_2$ saturated with BeO and NiO.

In each case the concentration of the solutes were varied by oxidation with NiF_2 or reduction with Be or Li metal. The assumed cell reactions, and the potentials derived from the measurements are as follows:

$$\text{I} \quad UF_3(d) + \tfrac{1}{2}BeF_2(d) + \tfrac{1}{2}NiO(c) \rightarrow UF_4(d) + \tfrac{1}{2}BeO(c) + \tfrac{1}{2}Ni(c)$$

$$E_I = 1.110 - 0.175 \log (X_{UF_4}/X_{UF_3}) \quad (610°C)$$

$$\text{II} \quad NiF_2(d) + BeO(c) \rightarrow BeF_2(d) + NiO(c)$$

$$E_{II} = 0.343 + 0.087 \log (X_{NiF_2}) \quad (605°C)$$

$$\text{III} \quad Nb(c) + 2BeF_2(d) + 2NiO(c) \rightarrow NbF_4(d) + 2BeO(c) + 2Ni(c)$$

$$E_{III} = 0.372 - 0.0386 \log (X_{NbF_4}) \quad (506°C)$$

The uncertainties in E_I and E_{II} are $\pm$ 15 mv and $\pm$ 10 mv, respectively. The expression for E_{III} is even more tentative since the oxidation state of the niobium in solution, while evidently at least +4, is still uncertain.

SINTERED BeO AS A CONTAINER MATERIAL FOR THE BeO, NiO/Ni^{o} REFERENCE ELECTRODE

B. F. Hitch and C. F. Baes, Jr.

Fritted silica tubes have been used previously to contain and insulate the BeO, NiO/Ni^{o} reference electrode, which consists of nickel im-

mersed in molten $2LiF-BeF_2$ saturated with BeO and NiO. This electrode has proven to be relatively reliable and especially convenient for potentiometric studies in molten fluorides; however, gradual attack of the silica by the fluoride melts caused some difficulties. Recently sintered BeO has been found to be a more suitable container material. The BeO compartments used, which were obtained from Brush Beryllium Corporation, consisted of tubes closed at one end by plugs of the same sintered BeO. Tests revealed that the seals between the tubes and the plugs were not complete, but in fact contained holes or cracks as large as 2μ. The electrical resistance measured with molten salt on the inside and outside of these compartments was quite low, typically 50-75 ohms. These compartments have been exposed to $2LiF-BeF_2$ melts for periods up to three weeks with no detectable weight loss or visible signs of attack.

The reliability of the BeO compartments was checked by measuring the potential of the cell

$$\mathrm{Be(c)}\left|\begin{matrix}\mathrm{LiF} & (0.67)\\ \mathrm{BeF_2} & (0.33)\end{matrix}\right|\left|\begin{matrix}\mathrm{NiF_2} & (10^{-4})\\ \mathrm{LiF} & (0.67)\\ \mathrm{BeF_2} & (0.33)\end{matrix}\right|\begin{matrix}\mathrm{BeO(c)}\\ \mathrm{NiO(c)}\end{matrix}\left|\mathrm{Ni(c)}\right.$$

over a temperature range of 500-700°C. The results differ by about 5 mv from those obtained previously[1] with the silica compartments. The present results, which are probably more accurate since the BeO seems much more inert, give

$$E^{o} = 1.892 - 0.044\ (T/1000) \quad \text{volts}$$

where T is the temperature in °K.

[1]B. F. Hitch and C. F. Baes, Jr., MSR Program Semiann. Prog. Rept. Feb. 28, 1969, ORNL-4396, p. 178.

ELECTRICAL CONDUCTIVITY AND IONIC MOBILITY IN MOLTEN MIXTURES OF BERYLLIUM FLUORIDE WITH LITHIUM FLUORIDE

G. D. Robbins and J. Braunstein

Previous communications have reported ionic transport properties of molten $LiF-BeF_2$ mixtures at temperatures near 500°C and compositions near

500°C and compositions near 50 mole percent BeF_2, and have pointed out analogies in electrical transport between fluoroberyllate and silicate systems.[1,2] In order to obtain a more extensive comparison of ionic mobilities in molten $LiF-BeF_2$ with those in other molten salt mixtures and in molten silicates, we have determined specific conductances, κ, in the range 34 - 70 mole percent BeF_2 at temperatures from near the liquidus to 550°C. Over this range of compositions and temperatures the data may be represented (σ = 0.007 by least squares computer fit) by the expression

$$\kappa = (a_1 + a_2X) \exp \left[\frac{-b_1 \exp(b_2X)}{T(°K) - (c_1 - c_2X)}\right]$$

where X is mole fraction BeF_2 and the six parameter values are:

a_1 = 7.1845; a_2 = 7.7458; b_1 = 252.57; b_2 = 3.2965;
c_1 = 467.24; c_2 = 333.96.

The activation energies vary with temperature, are lower than those for viscous flow, and vary from 5.0 to 10.0 kcal/mole between 34 and 70 mole percent BeF_2 at 550°C. In molten $MgO-SiO_2$ mixtures, with similar ionic radii but twice the charge (hence four times the electrostatic energy), activation energies are about 3.5 times those in the $LiF-BeF_2$ mixtures.

[1] K. A. Romberger and J. Braunstein, Inorg. Chem. 9, 0000 (1970).

[2] G. D. Robbins and J. Braunstein in Molten Salts: Characterization and Analysis, G. Mamantov, ed., Marcel Dekker, New York, 1969, p. 443.

ELECTRICAL CONDUCTIVITIES OF PROPOSED MSBR FUEL MIXTURES IN THE SYSTEM $LiF-BeF_2-ThF_4$

G. D. Robbins and A. S. Gallanter*

The specific conductances of four proposed MSBR fuel compositions[1] (melts A, B, D, and E below) have been determined from near the liquidus to 650°C. Two additional compositions (melts C and F) have been investigated to judge the effect of single-component additions at constant molar ratio of the other two components. In each mixture specific conductance, κ, appeared to vary linearily with temperature:

Melt	Composition (mole % $LiF-BeF_2-ThF_4$)	κ vs t(°C)
A	72-21-7	$\kappa = 1.562 + 7.386 \times 10^{-3}(t-500)$
B	73-16-11	$\kappa = 1.422 + 7.077 \times 10^{-3}(t-500)$
C	71-18.1-10.9	$\kappa = 1.278 + 7.481 \times 10^{-3}(t-500)$
D	68-20-12	$\kappa = 1.160 + 6.740 \times 10^{-3}(t-500)$
E	63-25-12	$\kappa = 1.056 + 6.111 \times 10^{-3}(t-500)$
F	60.5-28-11.5	$\kappa = 0.926 + 6.317 \times 10^{-3}(t-500)$

Attempts to obtain smoothly varying correlations of conductance as a function of composition for use in interpolation in this region of the composition diagram produced two useful relations; (1) Isothermal specific conductances, κ, and equivalent conductances (calculated on the basis of equivalents of fluoride and using Cantor's[1] densities), Λ_F vs equivalent fraction LiF; and (2) κ and Λ_F vs the difference in mole fractions of LiF and ThF_4.

*ORAU Summer Student Trainee, Brooklyn College, Brooklyn, New York.

[1]S. Cantor in "Physical Properties of Molten-Salt Reactor Fuel, Coolant, and Flush Salts," S. Cantor, ed., ORNL-TM-2316, August 1968, pp. 28-29.

NOBLE METAL FLUORIDES

SYNTHESIS OF NOBLE METAL FISSION PRODUCT FLUORIDES

C. F. Weaver, H. A. Friedman, and J. S. Gill

Procedures for the synthesis of the molybdenum fluorides were established. Excess molybdenum hexafluoride was refluxed over molybdenum metal in the temperature range 25 to 75°C until the metal was entirely consumed. The result was a yellow solution of MoF_5 dissolved in the excess MoF_6. The excess MoF_6 was pumped off at 75°C reaching pressures in the low micron range and leaving pure liquid MoF_5. The temperature of the system was slowly increased to 200°C while maintaining pressures in the micron range. During this step the reaction $2MoF_5 \rightarrow MoF_4\downarrow + MoF_6\uparrow$ occurred. The temperature was again slowly increased to 250°C with the pressure maintained in the micron range. During this step the reaction $3MoF_4 \rightarrow 2MoF_3 + MoF_6\uparrow$ occurred. The MoF_3 was a stable solid to approximately 400°C above which it decomposed forming the metal and higher fluorides. The disproportionation reactions were as simple as written above only if refluxing was maintained with the removal of the most volatile species, that is MoF_6. Analogous studies with the lower fluorides of Nb and Ru are in progress. Detailed reports of this work may be found in references 1-4.

[1]MSR Program Semiann. Prog. Rept. Feb. 28, 1969, ORNL-4396, pp. 157-162.

[2]MSR Program Semiann. Prog. Rept. Aug. 31, 1969, ORNL-4449, pp. 113-121.

[3]MSR Program Semiann. Prog. Rept. Feb. 28, 1970, ORNL-4548, (in press).

[4]Reactor Chem. Div. Ann. Prog. Rept. Dec. 31, 1968, ORNL-4400, pp. 33-39.

NIOBIUM AND MOLYBDENUM FLUORIDE SOLUTIONS IN MOLTEN Li_2BeF_4

C. F. Weaver and H. A. Friedman

Studies of the rate of disproportionation of Mo^{3+} in molten Li_2BeF_4 were conducted by dissolving about 1000 ppm of previously synthesized MoF_3 in the solvent at 500°C in a copper container. Molybdenum

left the system by a half-order process with a rate constant, defined as

$$K = t^{-1} (C_o^{1/2} - C^{1/2}), \text{ of } 7 \times 10^{-3} \text{ ppm}^{-1/2} \text{ hr}^{-1}.$$

This behavior was not affected by the He flow rate, surface area of the copper container, presence of UF_4, or the quantity of molybdenum metal produced by the disproportionation. These observations lead to the conclusion the disproportionation of MoF_3 in molten $LiF-BeF_2$ or $LiF-BeF_2-UF_4$ at 500°C was a homogeneous reaction.

Dilute solutions of niobium fluoride (< 3000 ppm) were prepared by passing HF through molten Li_2BeF_4 at 500°C in a copper unit containing excess Nb metal. In contrast to the Mo^{3+} behavior the niobium solutions were very stable. A solution containing 1500 ppm was held for 32 days with no loss of niobium. In addition reduction with one atmosphere of H_2 produced approximately 1.5×10^{-4} atmospheres of HF indicating that the Nb was only slightly more noble than Cr. A stronger reductant, Li metal, was then used to reduce the Nb and, hence determine its valence. The result was 3.7 ± 0.1 which has shown no concentration dependence. A detailed description of the molybdenum studies may be found in references 1-4 and those with the niobium solutions are described in reference 3.

[1]MSR Program Semiann. Prog. Rept. Feb. 28, 1969, ORNL-4396, pp. 157-162.

[2]MSR Program Semiann. Prog. Rept. Aug. 31, 1969, ORNL-4449, pp. 113-121.

[3]MSR Program Semiann. Prog. Rept. Feb. 28, 1970, ORNL-4548, (in press).

[4]Reactor Chem. Div. Ann. Prog. Rept. Dec. 31, 1968, ORNL-4400, pp. 33-39.

MASS SPECTROSCOPY OF MOLYBDENUM, NIOBIUM, AND RUTHENIUM

C. F. Weaver and J. D. Redman

The disproportionation of MoF_3 both pure and dissolved in molten Li_2BeF_4 was described in a previous report of this series.[1] Observation of the MoF_4 heated in a copper Knudsen effusion cell showed that below 220°C the MoF_4 neither evaporated or decomposed. Between 220 and 550°C

disproportionation occurred producing both MoF_5 and MoF_6. Above 550°C MoF_4 was also observed in the vapor. The residue after heating to 750°C was Mo metal. RuF_3 was shown to disproportionate in the temperature range 600 to 700°C as follows: $4RuF_3 \rightarrow Ru + 3RuF_4\uparrow$. Direct fluorination of Ru metal in a nickel cell produced RuF_4 over the range 450 to 629°C without reaction with the cell.

The reaction of MoF_6 gas with solid MoO_3 was studied to observe the production of oxyfluorides. At 140° pure $MoOF_4$ was produced. At lower temperatures the $MoOF_4$ contained MoF_6. At higher temperatures a mixture containing both $MoOF_4$ and MoO_2F_2 was produced. Above 250°C pure MoO_2F_2 was observed.

Evaporation of both NbF_5 and MoF_5 produced analogous results. The dimer and trimer of both were observed. Also the vapor pressure of both was lower and had a higher temperature dependence than reported in the literature indicating that activated rather than equilibrium evaporation occurred. Additional information is described in references 1-4.

[1]Reactor Chem. Div. Ann. Prog. Rept. Dec. 31, 1968, ORNL-4400, pp. 33-39.

[2]MSR Program Semiann. Prog. Rept. Feb. 28, 1969, ORNL-4396, pp. 157-162.

[3]MSR Program Semiann. Prog. Rept. Aug. 31, 1969, ORNL-4449, pp. 113-121.

[4]MSR Program Semiann. Prog. Rept. Feb. 28, 1970, ORNL-4548, (in press).

STRUCTURAL STUDIES

ABSORPTION SPECTROSCOPY OF MOLYBDENUM PENTAFLUORIDE

C. F. Weaver and F. A. Grimm[1]

Investigation of the infrared absorption of gaseous MoF_5 was initiated. Even though a pure spectrum has not been obtained, it has been possible to attribute some of the observed bands to MoF_5. The major impurity is believed to be $MoOF_4$. After subtracting the oxyfluoride absorption the bands attributed to MoF_5 at this point are located at 510, 770, and approximately 700 cm^{-1}. A trace of the absorption spectra at several temperatures may be found in reference 2.

[1]F. A. Grimm, Professor of Chemistry, University of Tennessee.

[2]MSR Program Semiann. Prog. Rept. Feb. 28, 1970, ORNL-4548, (in press).

COORDINATION EFFECTS ON THE SPECTRUM OF URANIUM(IV) IN MOLTEN FLUORIDES

L. M. Toth

The spectrum of U(IV) in molten fluoride solutions (primarily $LiF-BeF_2$ mixtures) exhibits a variation with melt composition which has been attributed to a change in the U(IV) coordination number. An equilibrium between 2 species:

$$UF_8^{-4} \rightleftarrows UF_7^{-3} + F^-$$

adequately explains the data. The identity of the species in fluoride rich solvents has been established as UF_8^{-4} by comparison of the melt spectra with crystal spectra of known coordination. Although crystal spectra of 7-coordinated U(IV) are more complicated, such a comparison suggests that the species present in fluoride-deficient melts is predominantly UF_7^{-3}.

Coordination equilibria have not been demonstrated in molten fluorides prior to this work. These studies have promise of evaluating crystal-field effects on actinide spectra in greater detail than has previously been possible. Furthermore it is apparent that similar co-

ordination equilibria affect the redox chemistry of multi-valent cations in the Molten Salt Reactor Experiment - e.g., U(III)-U(IV) and Nb(V) - Nb (valences less than V). Detailed understanding of these systems will be obtained only when the role of coordination effects are understood.

[1]L. M. Toth, J. Phys. Chem., submitted May 1970.

REFINEMENT OF THE UF_3 SPECTRUM

L. M. Toth

In connection with coordination studies on uranium systems, the spectrum of UF_3 (approx. 0.3 mole %) in $LiF-BeF_2$ (66-34 mole %) was found to agree with the previously reported spectrum[1] from 650-2500 mμ. However, from 250-650 mμ, it was found that the intensities of the reported peaks were approximately two times stronger than previously reported. For example the absorption coefficient at 360 mμ, ε_{360}, was found to be 860 ℓ $mole^{-1}cm^{-1}$, a value which is consistent with what is expected by comparing U(III) in non-fluoride systems (c.f., ε_{360} = 440, previously[1]).

The significance of this correction rests with the effect it has on U(III)/U(IV) ratios measured spectrophotometrically for the MSRE. Applying the correction to U(III) concentration determinations made using the 360 mμ peak caused much better agreement of the spectrophotometric values with those of other methods.

[1]J. P. Young, Inorg. Chem. 6, 1486 (1967).

THE CRYSTAL STRUCTURE OF $\gamma-Na_2ZrF_6$

G. D. Brunton

The crystal structure of $\gamma-Na_2ZrF_6$ is a new structure type with space group $P2_1/c$. The lattice parameters are a_o = 5.5562(7), b_o = 5.4069(6), c_o = 16.073(2)A and β = 95.886(6)^o. There are four formula weights per unit cell and the calculated density is 3.4728 g/cc.

The Zr ions are coordinated by $7F^-$ at distances of 2.012 and 2.167A. One of the Na ions is surrounded by $7F^-$ and the other by $8F^-$ at distances of 2.211 to 2.922 A.

THE CRYSTAL STRUCTURES OF KBF_4 AND $CsBF_4$

G. D. Brunton

The low temperature polymorphs of KBF_4 and $CsBF_4$ crystallize with the orthorhombic space group Pnma and are isomorphous with $KClO_4$. The lattice parameters for KBF_4 are: a_o = 8.6588(5), b_o = 5.4800(4) and c_o = 7.0299(8)A. The calculated density is 2.5067 g/cc. The lattice parameters for $CsBF_4$ are: a_o = 9.669(5), b_o = 5.888(3) and c_o = 7643(3) A. The calculated density is 3.353 g/cc. The B-F coordination in both structures is tetrahedral and the B-F distances are 1.378 to 1.391 A. There are no significant differences in the B-F distances between the two structures.

THE CRYSTAL STRUCTURE OF KU_2F_9

G. D. Brunton

The compound KU_2F_9 crystallizes with space group Pnma and with lattice constants a_o = 8.7021(9), b_o = 11.4769(4) and c_o = 7.0350(3) A. The U^{4+} ions are coordinated by $9F^-$ at distances of 2.292(1) to 2.39(3) A and the K^+ ions are coordinated by 10 F^- at distances 2.62(2) to 3.21(2) A. There are 4 formula weights per unit cell and the calculated density is 6.4851 g/cc.

OXIDE-FLUORIDE SYSTEMS

U^{4+}-Th^{4+} EXCHANGE BETWEEN MOLTEN FLUORIDE AND OXIDE SOLID SOLUTIONS[1]

C. E. Bamberger and C. F. Baes, Jr.

A study of the distribution of uranium between fluoride melts and $(U\text{-}Th)O_2$ solid solutions, now completed, was undertaken because of its obvious relevance to the oxide chemistry of MSBR fuel, and because of the potential value of such a two-phase solvent extraction system in reprocessing MSBR, and possibly other reactor fuels. The equilibrium quotient, Q, was determined for the following reaction at various compositions of the oxide and fluoride phases and at temperatures in the range 580 to 780°C.

$$U^{4+}(F) + Th^{4+}(O) \rightleftarrows U^{4+}(O) + Th^{4+}(F), \quad Q = \frac{X_{UO_2}\, X_{ThF_4}}{X_{UF_4}\, X_{ThO_2}}$$

(where X denotes mole fraction). Additions of reagents (UO_2, ThO_2, and UF_4 were made in such a way that equilibrium was approached from both directions; based on the UF_4 content of the fluoride phase, equilibrium was reached in 40 to 120 hours. Samples of the oxide phase were analyzed by x-ray diffraction, the cell parameter being directly and accurately proportional to the composition. The results obtained for the 72-16-12 mole % composition were fitted by least squares to an equation containing only two parameters.

$$\log Q = (2101 + 550X_{UO_2})/T \ .$$

The form of this expression results from the assumption that the oxide phase is a regular solution (i.e., one in which the entropy of mixing is ideal) and the assumption that the entropy of the exchange reaction is zero. Results obtained for different melt compositions at constant temperature and constant oxide composition indicated that Q did not depend on the composition of the fluoride phase. The parameters of the expression for Q give for the oxide solid solution $\log \gamma_{UO_2} = (275/T)X^2_{ThO_2}$ and $\log \gamma_{ThO_2} = (275/T)\, X^2_{UO_2}$, and for the molar heat of mixing of the equimolar mixture, $(\Delta H_m)_{0.5} = 315$ cal/mol.

[1] J. Nucl. Mat., 35, 177 (1970).

THE OXIDE CHEMISTRY OF PLUTONIUM IN MOLTEN SALTS - THE FREE ENERGY OF FORMATION OF PuF_3 AND PuF_4

C. E. Bamberger, R. G. Ross, and C. F. Baes, Jr.

The behavior of plutonium in molten fluorides in the presence of oxide ion has been studied in order to establish, in a reactor fuel salt, the conditions of redox potential and oxide concentration necessary to avoid the precipitation of plutonium oxides. Three salt mixtures, $LiF-BeF_2$ (66.7-33.3 mole %), $LiF-BeF_2-ZrF_4$ (65.7-29.3-5.0) and $LiF-BeF_2-ThF_4$ (72-16-12), containing PuF_3 have each been equilibrated with the oxide that is stable in that media (BeO, ZrO_2, and ThO_2, respectively) under various redox conditions and different temperatures. Only in the ThF_4-containing melt, equilibrated with ThO_2 and NiO, did the PuF_3 concentration decrease. This was confirmed to be the result of the following reaction

$$PuF_3(d) + \frac{3}{4}ThO_2(ss) + \frac{1}{2}NiO(c) \rightleftarrows PuO_2(ss) + \frac{3}{4}ThF_4(d) + \frac{1}{2}Ni^{o}(c) \qquad (1)$$

The solubility of PuF_3 in 72-16-12 salt was found to be the same in the absence and in the presence of ThO_2 at temperatures in the range 540-700°C, suggesting that a reported oxyfluoride, PuOF, is not stable. These results also confirmed that, as expected, the solubility of PuF_3 is nearly equal to that of CeF_3, measured by Barton.[1] The free energy of formation of PuF_3 was determined from the measured equilibria quotients of reaction (1) and the formation free energies available for $ThO_2(c)$, NiO(c), $PuO_2(c)$, and $ThF_4(d)$:[2,3]

$$\Delta G^{f}_{PuF_3(c)} = -336.1 \pm 2.6 \text{ and } -334.5 \pm 2.6 \text{ kcal/mole at } 615° \text{ and } 715°C.$$

These values are ∿18 kcal more negative than current literature values.[3] The latter are due to Buyers and Marbach[4] who derived them from (1) the distribution of plutonium between molten uranium metal and molten uranium fluoride at 1573°K, and (2) older formation free energies for UF_3 and UF_4 which indicated that the molten uranium fluoride was a mixture of both valences. However, using more recent estimates of the free energies of formation of UF_4 and UF_3 (-86.5 and -93.0 kcal/fluoride at 1573°K)[2] we conclude that UF_3 was the salt present under the experimental condi-

tions of reference 4. This information yields from reference 4 values of ΔG_{PuF_3} which are consistent with the present results. By combining our values of $\Delta G^f_{PuF_3}$ with data on the reaction of O_2 with PuF_3,[5] we have obtained:

$$\Delta G^f_{PuF_4} = -387.92 + 9.95\ (T/1000) \pm 2.8 \text{ kcal/mole}$$

From the results obtained we may conclude that no plutonium oxide would precipitate from a 72-16-12 mole percent $LiF-BeF_2-ThF_4-PuF_3$ mixture, even when saturated with ThO_2, provided the X_{UF_3}/X_{UF_4} ratio was $> 10^{-5}$, this limit is at approximately 3 orders of magnitude lower than the X_{UF_3}/X_{UF_4} ratios normally maintained in a Molten Salt Reactor fuel.

[1] C. J. Barton et al., Inorg. Chem. 9, 307 (1970).

[2] C. F. Baes, Jr., in Nuclear Metallurgy 15, Symposium in the Reprocessing of Nuclear Fuels, ed. by P. Chiotti, USAEC-DTI, p. 617 (1969).

[3] F. L. Oetting, Chem. Rev. 67, 261 (1967).

[4] A. G. Buyers and E. W. Marbach, Nucl. Sci. Eng. 2, 679 (1957).

[5] J. K. Dawson, R. M. Elliot, R. Hurst, and A. E. Truswell, J. Chem. Soc. 1954, 558.

FLUOROBORATES

THE SYSTEM $RbBF_4$-RbF

L. O. Gilpatrick, H. Insley, and C. J. Barton

Investigation of this binary system is nearly complete. Marked similarities exist between this system and the $NaBF_4$-NaF and KBF_4-KF systems. All are simple eutectic systems and each exhibits the polymorphic crystal transition of the pure fluoroborate compound at a temperature that is independent of composition. This demonstrates absence of solid solution of the alkali fluoride in the fluoroborate compound in all three systems.

Measured values for the system $RbBF_4$-RbF as determined by the differential thermal analysis technique are as follows:

Melting Point RbBF - 582°C
Melting Point RbF - 795°C (literature value)
Polymorphic Crystal Transition - 247°C
Melting Point Eutectic - 442°C
Eutectic Composition (mole %) RbF - 31.5%
$RbBF_4$ - 68.5%

Efforts to confirm liquidus and solidus temperatures in this system by quenching yielded unsatisfactory results in general because of difficulty in distinguishing between quench growth and phases that were crystalline at high temperatures. This difficulty had been observed previously during microscopic examination of quenched fluoroborate compositions but appeared to be a more severe problem in this system than in other binary and ternary systems of this type thus far examined.

PHASE RELATIONS IN THE SYSTEM NaF-KF-BF_3

L. O. Gilpatrick, C. J. Barton, H. Insley

The most recent work on this system was directed toward improving the accuracy of the measurement of the minimum liquidus temperature. The lowest temperature found for the liquidus was 377°C; however, the solidus temperature at this composition of 50-3-47 mole % NaF-KF-BF_3,

respectively, was found to be 373°C. The reduction of the two phase region to 4°C represents the closest experimental approach to the coincidence of liquidus and solidus temperatures, predicted by theory to exist at the minimum temperature, yet found for the system. This lack of coincidence is probably due to the presence of a small amount of a third phase, presumably an oxygen bearing species. We believe that further study of this system is not likely to reveal a composition melting at a temperature significantly lower than that of the $NaF-NaBF_4$ eutectic composition (384°C). A revised ternary phase diagram has been published[1] which incorporates our latest data.

[1]MSR Program Semiann. Prog. Rept. Aug. 31, 1969, ORNL-4449, p. 129.

VOLUMETRIC PROPERTIES OF MOLTEN AND CRYSTALLINE ALKALI FLUOROBORATES[1]

Stanley Cantor, Dana P. McDermott,[2] and L. O. Gilpatrick

Densities of the five molten alkali fluoroborates were each measured over a temperature interval of approximately 150°C using the metal dilatometer (described elsewhere in this Report). The molar volumes and expansivities derived from these data exhibit the order predicted from the periodic table. At equal corresponding temperatures (defined as $T/T_{melting}$, in °K) molar volumes of molten alkali fluoroborates were found to be slightly larger than the molar volumes of molten alkali iodides. Melting points and solid-state transition temperature were determined for three fluoroborates:

	$LiBF_4$	$RbBF_4$	CsBF
Solid-state transition	none observed	245°	169.5°C
Melting point	304°	582°	555°C

At the transition temperature, volume changes were predicted on the basis of analogous behavior of MBF_4 and $MClO_4$. The indices of refraction of the crystalline compounds were measured and from these, electronic polarizabilities were calculated from the Lorentz equation. The electronic polarizability of $(BF_4)^-$ (which averages $2.8A^3$), decreases with increasing alkali cation size. This trend is correlated with the decreas-

ing order of covalency in cation-anion bonds, e.g., Li^+ distorts (polarizes) the electronic charge of $(BF_4)^-$ in the direction of the Li-F bond axis more than does Na^+ in the Na-F bond axis.

[1]S. Cantor et al., J. Chem. Phys. 52, 4600 (1970).

[2]ORAU Summer Student, 1969, from Centre College, Danville, Kentucky.

SOLUBILITY OF Na_3CrF_6 IN $NaBF_4$-NaF (95-5 MOLE %)

C. J. Barton

Green crystals believed to be primarily Na_3CrF_6, although they contained significant quantities of iron, have been observed in corrosion test loops loaded with $NaBF_4$-NaF (92-8 mole %). No data on the solubility of this species in fluoroborate solvents exist but extensive studies of the solubility and stability of chromous and chromic fluorides in several other fluoride mixtures are available.

The compound Na_3CrF_6 was mixed with sufficient NaF and $NaBF_4$ to give a 10 mole % mixture and solvent composition of 92 mole % $NaBF_4$. The Na_3CrF_6 (prepared earlier by B. J. Sturm) was added in preference to CrF_3 because the combination of CrF_3 with solvent NaF would change the solvent composition significantly if CrF_3 were very soluble.

The procedure followed in CeF_3 solubility studies, described elsewhere in this document, was employed in the present investigation except that no tracer was used so sole reliance for the solubility measurements was placed on wet chemical analysis of samples removed with copper filter sticks. Two sets of samples were taken because of scatter of data in the low concentration range in the first set of samples. The solubility varied from 0.46 mole % Na_3CrF_6 at 700°C to 0.046 at 500°C and extrapolation to the eutectic melting point (384°C) shows that the solubility would be less than 0.01 mole % at the freezing point of the mixture. The calculated apparent heat of solution of Na_3CrF_6 in this solvent was 17.0 kcal/mole.

The average of six Na and B analyses, corrected for the Na in Na_3CrF_6, indicated a solvent composition of 95 mole % $NaBF_4$ instead of the intended 92 mole % eutectic mixture. Additional studies will be required to establish the effect of solvent composition on chromium solubility but the writer does not believe that it will be markedly different from the observed values in a 92 mole % $NaBF_4$ solvent. Nickel analysis results were low (20 to 30 ppm) in most samples but two samples taken at temperatures close to 700°C gave values of 300 and 390 ppm possibly indicating attack on the nickel container.

$LiBF_4$: DECOMPOSITION PRESSURES AND DERIVED THERMODYNAMIC INFORMATION

S. Cantor and D. P. McDermott[1]

For the decomposition reaction, $LiBF_4(c) \rightleftarrows LiF(c) + BF_3(g)$, we measured BF_3 vapor pressures in the range, 223-302°C. Pressures were determined by a manometer connected to a nickel vessel containing the salt. Two samples were studied: one being pure $LiBF_4$, the other, a 1:1 mixture of $LiBF_4$ and LiF which had been previously fused. The data from both samples fit on the same plot of log P vs 1/T. Therefore, there is no perceptible solid solubility of LiF in $LiBF_4$.

A computer-fitted least-squares equation for the data is

$$-R \ln P(atm) = 19{,}340/T(°K) - 30.77 .$$

A second-law analysis of the data yielded $\Delta H^0_{298} = 21.1$ kcal in excellent agreement with the value of 21.4 kcal obtained from reaction calorimetry.[2] The third-law analysis yielded an average $\Delta H^0_{298} = 20.3$ kcal.

By using $\Delta H^0_{298} = 21.4$, in combination with other thermodynamic data, the value of S^0_{298} for $LiBF_4(c)$ was calculated to be 34.0 ± .4 cal deg^{-1} $mole^{-1}$.

[1]ORAU Summer Student, 1969, from Centre College, Danville, Ky.

[2]P. Gross, C. Hayman, and H. A. Joel, Trans. Faraday Soc. 64, 317 (1968).

SOLUBILITY OF BF_3 GAS IN FLUORIDE MELTS

S. Cantor and W. T. Ward

The purposes of these measurements are to monitor changes in fluoride ion activity and, also, to provide data on how BF_3 might be used as a burnable neutron poison for purposes of reactor control. In this program we determine the solubility of BF_3 in molten fluoride mixtures as a function of temperature, pressure, and salt composition. The method, previously described by Shaffer et al,[1] consists of saturating the melt by bubbling BF_3 through it at constant temperature and pressure, then transferring a measured volume of the melt to a second vessel where the melt is stripped of BF_3 by sparging with helium. The BF_3 is then absorbed in an aqueous NaF solution and analyzed by mannitol titration.

The initial melt under investigation is $LiF-BeF_2$ (66-34 mole %). The preliminary data indicate a 35-45% higher BF_3 solubility than that reported by Shaffer et al[1] for $LiF-BeF_2-ZrF_4-ThF_4-UF_4$ (65-28-5-1-1 mole %). The latter melt, with 7 mole % $M^{IV}F_4$ (interacting with fluoride ions more strongly than BeF_2), probably has a lesser fluoride ion activity, and therefore a lower BF_3 solubility. A useful qualitative model of BF_3 solubility in fluoride melts is given by the reaction, $F^-(\ell) + BF_3(g) \rightleftarrows BF_4^-(\ell)$; BF_3 would only interact with fluoride ions which have not strongly interacted with polyvalent cations such as Be^{2+} and Th^{4+}.

A comparison of the thermodynamic quantities of BF_3 solubility, as defined by the relation, $\ln K = \Delta S/R = \Delta H/RT$, (where K is the Henry's law constant), is given below:

	ΔH	ΔS
$LiF-BeF_2-ZrF_4-ThF_4-UF_4$ (65-28-5-1-1 mole %)[1]	-15.1 kcal/mole	-22.2 cal/(mole-°K)
$LiF-BeF_2$ (66-34 mole %)	-18.5 kcal/mole	-24.0 cal/(mole-°K)

[1] J. H. Shaffer, W. R. Grimes, and G. M. Watson, Nucl. Sci. Eng. 12, 337 (1962).

MIXING REACTIONS OF MSBR FUEL AND COOLANT SALTS

D. M. Moulton, W. Jennings, Jr., and J. H. Shaffer

In an MSBR the fuel ($LiF-BeF_2-ThF_4-UF_4$) and coolant ($NaBF_4-NaF$) salts could unintentionally be mixed together. It is known that such mixtures give two immiscible salt layers;[1] but no information had been available on the degree of miscibility, except for thorium-free systems, or on any changes in BF_3 pressure. About 1 kg of $LiF-BeF_2-ThF_4$ (68-20-12 mole %) containing a little UF_4 and EuF_3 was mixed with 1.6 kg of $NaBF_4-NaF$ (92-8 mole %) at 538°C and treated with metallic thorium. The pressure over the system rose as high as 600 mm, compared with a BF_3 pressure for the pure coolant of 53 mm at this temperature, and had to be bled off several times. Analysis of the salts showed considerable mixing; a typical set of analyses is given below. The equality $N_{LiF} + N_{NaF} = N_{BF_3} + 2N_{BeF_2} + 4.5\ (N_{ThF_4} + N_{UF_4})$ held reasonably well in both phases. From this it seems that the beryllium and actinide cations coming into the upper phase established rather strongly bound coordination shells of 4 and 8-1/2 fluoride ions, destroying the BF_4^- complex and liberating BF_3 in the process. Since all of the fluoride phase cations have much higher charge densities than sodium, it is to be expected that they would destabilize the fluoroborate ion in this way.

Mixing of Fluoride and Fluoroborate Salt

	N_{LiF}	N_{BeF_2}	N_{NaF}	N_{ThF_4}	N_{UF_4}	N_{BF_3}	D_{Eu}
Lower	.498	.117	.257	.110	.0013	.0185	(upper/lower)
Upper	.094	.045	.430	.003	.00008	.428	.0044

[1] C. E. Bamberger *et al*, RCD Ann. Prog. Rept. Dec. 31, 1967, ORNL-4229, p. 20.

BORON TRIFLUORIDE PRESSURE OVER FLUOROBORATE COOLANT SALT ADMIXED WITH MSBR FUEL SALT

D. M. Richardson, W. K. R. Finnell, and J. H. Shaffer

Several experiments have been reported in which the pressure of BF_3 over mixtures of $NaBF_4$-NaF was higher than normal due to the presence of fuel fluoride salt.[1,2] Greater pressure elevations occurred when the proportion of fuel fluoride was increased. For the extreme case of a double-ended tube failure in a MSBR primary heat exchanger, it was estimated that the fluoroborate salt would be injected into the fuel salt in the volume ratio of 1 to 3 at 700°C. This condition was simulated in a static autoclave experiment.[3] The stainless steel vessel was approved for operation at 115 psia, 700°C and was hydrostatically tested at 1300 psig. The fuel salt, LiF-BeF_2-ThF_4 (72-16-12 mole %) + UF_4 (to produce 0.5 mole %), was added first as a liquid. After cooling, the fluoroborate, $NaBF_4$-NaF (92-8 mole %), was added under argon as a crushed salt. The system was sealed after baking and evacuation at 150°C. Initially, over a period of six days, all data lay on a log P versus 1/T°K line with an apparent heat of reaction of 15 kcal per mole, reaching 95 psia at 647°C. The pressure then rose quickly to 148.5 psia and the system was vented down to 100 psia. Concurrent temperature changes indicated that sudden mixing or stirring of the two liquids had occurred. Subsequent data lay on a line with slope of 20 kcal per mole that extrapolated to 148.5 psia at 647°C. It was not possible in this experiment to determine either that two immiscible liquid phases were always present or that a solid phase had not appeared. The definite result was that the pressure of BF_3 was more than an order of magnitude greater than that over $NaBF_4$-NaF (92-8 mole %). The effect of the large gas volume would be to reduce the mole fraction of $NaBF_4$ and to shift the mixture closer to the liquid-liquid immiscibility boundary.

[1] A. N. Smith and P. G. Smith, MSR Program Semiann. Prog. Rept. Aug. 31, 1968, ORNL-4344, p. 75.

[2] D. M. Moulton and J. H. Shaffer, MSR Program Semiann. Prog. Rept. Aug. 31, 1969, ORNL-4449, pp. 127-128.

[3] D. M. Richardson and J. H. Shaffer, MSRP Semiann. Prog. Rept. Feb. 28, 1970, ORNL-4568, pp.

PART II. DIRECT SUPPORT FOR THE MOLTEN SALT REACTOR EXPERIMENT

FUEL AND COOLANT CHEMISTRY

CORROSION OF THE MSRE SALT CIRCUITS

R. E. Thoma

As deduced from chemical analysis of samples removed from the circulating salt systems in the MSRE throughout the four year period of reactor operations, the chemical behavior of the fuel and coolant have provided a convincing demonstration of the feasibility of molten salt reactors. During this period, the concentration of constituents, corrosion products, oxide contaminants, and fission product species in the fuel, flush salt and coolant, were monitored on a continuing basis. From observed changes in the chromium concentration of the fuel salt, the average cumulative corrosion sustained by the MSRE fuel circuit since nuclear operations were initiated in 1965 appears to be even less than estimated previously, and extends to a maximum depth of 1.2×10^{-3} cm. This value derives from revised rates based on analyses of the chromium content of Hastelloy-N heats which were used in the fabrication of the fuel circuit components, for which the average is 7.25 wt. % rather than the nominal value of 6 wt. % used in previous estimated. From observed changes in the concentration of ^{95}Nb, $[U^{3+}]/[\Sigma U]$, and in the concentrations of structural metal cations in samples of the fuel removed from the fuel circuit during operations with ^{235}U and ^{233}U fuels, the slight attack which has occurred seems to be attributable to airborne contaminants introduced into the reactor during periods when the reactor core was opened for maintenance. Analyses of the circulating coolant salt indicated that during the four year period of its use the coolant circuit was not corroded to any measurable degree.

The chemical evidence regarding the extent of corrosion of the fuel circuit was confirmed from measurements of the chromium gradient in specimens of Hastelloy-N that were removed from the core after the Run 18 shutdown of the MSRE. The preponderant depletion of chromium in these samples, which had experienced the maximum average temperatures in the fuel circuit, occurred within 1 mil of the surface, and approximated the 2×10^{-14} cm^2/sec diffusion limited rates expected for the alloy.

POWER OUTPUT OF THE MSRE

R. E. Thoma

In the MSRE, fluid fuel was circulated at rates which were sufficiently rapid with respect to changes in the isotopic composition of the fissile species that the salt samples removed from the pump bowl were representative of the circulating stream. This characteristic of molten salt reactors makes it possible to use isotopic analyses for a variety of purposes. One potential application, that of appraising the cumulative power generated by the MSRE at various periods, became apparent with the initiation of ^{233}U operations, for with ^{233}U fuel the isotopic composition of the plutonium inventory (partly produced by that generated in ^{235}U operations as well as that added later) would change significantly during power production and would possibly serve as an accurate indicator of the power produced. About 600 grams of plutonium was produced during power operations with ^{235}U fuel (67% ^{238}U). Thereafter, additional plutonium was introduced into the fuel salt as a contaminant of ^{7}LiF-$^{233}UF_4$ enriching salt, and later to replenish the fissile inventory. Comparisons of the observed changes in ^{239}Pu and ^{240}Pu were compared with those estimated from absorption and capture cross section data for operations at various power levels between $\sim$ 7 and 8 megawatts. Within this range, best agreement between calculated and experimental values was obtained for a maximum power output of 7.4 Mw(th). The standard deviation within the analytical data corresponds to $\pm$ 0.05 Mw. Calculated values of the $^{239}Pu/^{240}Pu$ ratio lie within a one sigma deviation throughout ^{233}U operation of the MSRE.

Estimates of the power output of the MSRE from measured changes in isotopic composition is achieved with considerably greater precision from analyses of plutonium than from uranium because the rate of change in relative fraction of the most abundant isotopes for plutonium, ^{239}Pu and ^{240}Pu, is some four times that for the uranium pair, ^{233}U and ^{234}U. Comparisons were made of the observed and calculated isotopic changes of these uranium isotopes in the MSRE fuel circuit which should have accompanied operation of the reactor at a maximum power output of 7.4 Mw(th). The results indicate that the changes observed in the isotopic composition of the uranium were in excellent agreement with those for plutonium.

EXAMINATION OF SIMULATED FUEL SALT UNDER ASSUMED CHEMICAL CONDITIONS IN THE MSRE PUMP BOWL

J. H. Shaffer, W. P. Teichert, and W. R. Grimes

Beginning early in the operation of the MSRE on ^{233}U, the amount of gas entrained in the circulating fuel was much higher than that experienced during operation with the original ^{235}U fuel mixture.[1] This condition was associated with the initial insertions of beryllium metal rods into the fuel mixture in the pump bowl. As a result apparent densities of the salt in the pump bowl were lowered, salt overflow rates increased, and minor instabilities in reactor power level were encountered. During subsequent additions of beryllium and zirconium metals in the pump bowl, similar but inconsistent effects were observed. In some instances, void fractions in the pump bowl and fuel system were reduced during the metal insertion period.

An experiment was conducted with 12.5 kg of simulated MSRE fuel mixture, $LiF-BeF_2-ZrF_4-UF_4$ (64.8-30.0-5.0-0.25 mole % respectively), in a 10-in. diam. vessel to duplicate chemical conditions in the pump bowl. The objective of this experiment was to measure stable changes in the salt level (apparent changes in salt density) during insertions of beryllium and zirconium metal into the salt phase and during vigorous agitation of the salt by an argon sparge stream. Presumably, the partial reduction of tetravalent uranium to its trivalent state and or the reduction of structural metals from the salt by beryllium or zirconium might affect the surface tension of the salt in a manner that would promote the suspension of gas bubbles in the molten salt. However, this test failed to detect any change in salt volume under widely varied redox conditions.[2]

Subsequent investigations related the apparent density gradient in the salt and the appearance of voids in the circulating fuel of the MSRE to pump speed.[3] On the basis of these results void formation characteristics in the fuel and their anomalous relation to the insertion of beryllium or zirconium into the pump bowl reservoir were described according to gas solubility behavior.[4] These calculations showed that steady state void fractions in the reactor core could be established rapidly at low gas entrainment rates. Differences in conditions necessary to form voids in

the reactor core when argon was substituted for helium as the pump bowl cover gas also reflected differences in their solubility in the fuel salt. The effects of beryllium and zirconium on the surface tension of the salt were not evaluated. However, gas solubilities have been shown to vary widely as a function of salt surface tension.[5]

[1] MSR Program Semiann. Progr. Rept. Feb. 28, 1969, ORNL-4396, p. 1.

[2] Ibid., p. 135.

[3] Ibid., p. 11.

[4] MSR Program Semiann. Progr. Rept. Aug. 31, 1969, ORNL-4449, p. 102.

[5] M. Blander et al, J. Phys. Chem. 63, 1164 (1959).

FISSION PRODUCTS

FISSION PRODUCT DISTRIBUTION IN SALT SAMPLES FROM THE MSRE PUMP BOWL

E. G. Bohlmann and E. L. Compere

During the operation of MSRE on ^{233}U fuel, 35 salt samples were taken using evacuated capsules with fusible seals. The type most used had double wall construction to eliminate contamination of the outside of the inner sample capsule during exposure in the pump bowl. This sample capsule could be separated from the outer, protective capsule by abrading a weld and opening the outer capsule with a tubing cutter, necessitating minimal hot cell manipulation.

Analyses for constituent elements and fission products were compared with inventory values calculated from the operating history of the reactor; all fission products were assumed retained in the salt. Averages for salt seeking isotopes (^{95}Zr, $^{141-144}Ce$, ^{147}Nd) and constituent elements (Li, Be, Zr, U, ^{233}U) generally agreed acceptably with such inventory values.

The daughters of Xe and Kr (^{89}Sr, ^{91}Y, ^{137}Cs, ^{140}Ba) were similarly found in quantities agreeing with inventory; two of these, ^{89}Sr, and ^{137}Cs, whose gaseous precursors exist long enough to be partially stripped into off-gas and to diffuse into graphite, were found in suitably lower proportions (0.8-0.9) in the salt.

Concentrations of noble metal isotopes (^{99}Mo, $^{103-106}Ru$, ^{111}Ag, ^{125}Sb, $^{129m-132}Te$) found range from fractions to tens of percent of inventory with only a few values appreciably greater than 100%. Also, the proportionate composition of the noble metal isotopes remains relatively constant from sample to sample in spite of the widely varying amounts found. These observations suggest a labile, particulate material essentially in equilibrium with newly produced material. The latter statement is buttressed by the fact that ratios of isotopes of the same element, e.g., 39.6d ^{103}Ru and 367d ^{106}Ru, are intermediate between the ratio in which they are produced and calculated inventories.

Iodine (^{131}I), a daughter of Te, appeared in much larger quantities (∿50% of inventory) than Te indicating a return to the salt of this element.

Concentrations of ^{95}Nb in the salt at appreciable levels (>20% of inventory) were consistently observed during periods when increasing Cr^{+2}

concentration indicated the fuel salt to be sufficiently oxidizing to be corrosive. Increasing the U(III)/U(IV) ratio by reductant (Be, etc.) additions inhibited the corrosion and concurrently caused the ^{95}Nb to deposit out of the salt. This behavior suggests that Cr and Nb redox occur at similar potentials and that the absence of ^{95}Nb dissolved in the salt indicates conditions non-oxidizing to Cr. However, on two occasions when the other noble metals were appreciably present in the salt as described above (not generally correlatable with Nb behavior), ^{95}Nb was among them although the salt was probably adequately reducing. Thus the presence of ^{95}Nb in appreciable concentration in a salt sample is not a positive indication that its oxidation state is approaching a corrosive condition.

FISSION PRODUCT BEHAVIOR IN GAS SAMPLES FROM THE MSRE PUMP BOWL

E. L. Compere and E. G. Bohlmann

Gas samples taken during MSRE operation with ^{233}U fuel for the most part also used the double-wall evacuated capsule with fusible seal, to minimize contamination. Thirty-one samples and three intentionally plugged controls were taken.

The amount of isotope per cc of gas sample was compared with the amount produced by the reactor in unit time divided by the volume of purge gas flowing in unit time. Thirteen samples taken during power operation were considered most significant because the amounts of ^{89}Sr and ^{137}Cs found were consistent with what was expected based on a calculation of the amounts of their ^{89}Kr and ^{137}Xe precursors stripped into the pump purge gas.

Definite quantities of salt-seeking isotopes and constituent elements were found in the gas samples in ratios corresponding to salt inventory values; this generally amounted to a few tens of micrograms of salt, doubtless entrained as fine mist. Even metal fiber filters ($\sim 1\mu$) used to cover the entry of some capsules did not materially change this salt content of the gas.

Amounts of noble metal and tellurium-related isotopes corresponding to the presence of 1 to 2% of the production rate were also found in the gas samples. However, appreciable amounts of these isotopes found in the

intake nozzle section of the capsule (frequently analyzed separately) along with salt-seeking isotopes and constituent elements and diminished proportions of ^{89}Sr and ^{137}Cs indicate that noble metal and tellurium-related isotopes travel with the salt mist. Proportionate correction of capsule analyses for material found associated with the mist showed that quantities of noble metal isotopes amounting to less than 1 percent of production possibly were independently gasborne.

EXAMINATION OF MATERIALS IN MSRE OFF-GAS LINES

E. L. Compere, E. G. Bohlmann, J. L. Rutherford, and H. C. Savage

The 3-4 (std) liter/min purge flow of helium through the MSRE fuel pump bowl may transport gaseous or finely divided particulate materials into the off-gas system. Some characterization of these was afforded by the examination of deposits in parts of the system, before and after the period of operations with ^{233}U fuel.

The major part of a thin dusty film deposited in a line section 3-6 feet from the pump bowl appeared to be salt and carbonaceous soot, with enhanced proportions of noble metal, tellurium-related (Sb, Te, I) and rare gas daughter isotopes. In particular no transport of uranium by means other than as a constituent of salt mist was indicated.

A later study of deposited material in a straight tube section about 6 feet from the pump bowl revealed similar deposits. Observed amounts of ^{89}Sr and ^{137}Cs were accounted for by the decay of Xe and Kr precursors in the adjacent off-gas. However molecular transport of noble metal and tellurium-related isotopes as fluorides to produce the quantities observed in the deposits appears ruled out because these are relatively unstable thermodynamically, would not condense from the gas under system conditions, and if present should have attacked the tubing walls. Particulate matter bearing the noble metal and tellurium-related isotopes could account for the observed deposits provided suitable fractions of the isotope produced in MSRE entered the pump bowl gas and the off-gas system, provided particle sizes were such as to permit diffusion to tube walls at the proper rate, and the fraction sticking was high. The fraction of transported

material depositing at a given point was related to particle size using equations well established in aerosol diffusion theory. Using about 1% as the gas-borne fraction of these isotopes, as determined by pump bowl gas samples, either particle sizes of about 10Å or about 1000-5000Å are indicated by data from the single location; smaller particles deposit earlier, larger particles carry past, and intermediate sizes should deposit more than observed.

An on-line off-gas analysis apparatus using thermal conductivity measurement, with copper oxide oxidation and molecular sieve adsorption received gas about one hours flow from the pump bowl. Analyses of MSRE off-gas using this apparatus confirmed the presence of hydrogen and hydrocarbons in the stream in quantities consistent with the cracking of a few cc/day of lubricating oil leaking into the pump bowl gas space.

DEPOSITION OF SALT SOLUBLE FISSION PRODUCTS ON THE FOURTH SET OF SAMPLES FROM THE MSRE CORE

F. F. Blankenship and S. S. Kirslis

If samples removed from the core in June 1969, after 76,900 and 20,000 Mw hrs exposure, were representative of the whole reactor, the distribution of salt soluble fission products was as shown in the table below:

Distribution of Salt Soluble Fission Products in the MSRE on June 1, 1969

Isotope	Percent of Inventory		
	in salt[a]	on graphite	on metal
^{89}Sr	80	16	.08
^{91}Y	130	2	.07
^{95}Zr	100	0.2	.05
^{131}I	60	0.3	0.1
^{137}Ca	80	0.7	.03
^{140}Ba	110	1.0	0.1
^{144}Ce	120	0.1	0.03

(a) Typical data of Compere and Bohlmann for period just before the reactor was drained.

Since the fuel does not wet graphite, salt soluble fission products not having inert gas precursors (e.g., ^{95}Zr and ^{144}Ce) were almost absent from the graphite. Time effects were obscured by the operating history, but probably were not great.

Since flush salt was not used after the drain, increased amounts of the salt soluble fission products were expected, compared to earlier samples; generally this expectation was born out but not always.

In any case, the amounts are trivial, both on graphite and metal. The deposition on the metal was probably largely from fission recoil because the pattern followed that of the flux.

DEPOSITION OF METALLIC FISSION PRODUCTS ON THE FOURTH SET OF SAMPLES FROM THE CORE OF THE MSRE

F. F. Blankenship and S. S. Kirslis

If metallic fission products deposited to the same extent throughout the reactor as on samples removed from the core after exposures of 76,900 and 20,000 Mw hrs, the results are as shown in the accompanying table.

Distribution of Metallic Fission Products in the MSRE on June 1, 1969

Isotope	Percent of Inventory		
	in salt[(a)]	on graphite	on metal
^{95}Nb	<.1	7	3
^{99}Mo	12	4	26
^{103}Ru	1	2	4
^{106}Ru	1	3	8
^{111}Ag	4	5	16
^{125}Sb	<1	3	12
^{129}Te	1	3	18
^{132}Te	4	5	16

(a) Data of Compere and Bohlmann for sample taken ∿1 hr before the reactor was drained.

Also a few percent were carried out in the off-gas. However, there still remains a considerable unaccounted fraction. Possibly the figures

for deposition on metal are low. Time effects, again were obscured by the operating history.

The fact that flush salt had not been used after the drain did not change the values significantly from earlier samples for which flush salt was used.

Excessive deposition on reactor surfaces is of importance because it can lead to over heating when the fuel is drained. Most of the metal products are found on metal doubtlessly because there is where nucleation and growth are found.

EFFECT OF SURFACE ROUGHNESS ON THE DEPOSITION OF FISSION PRODUCTS ON GRAPHITE AND HASTELLOY N IN THE MSRE

S. S. Kirslis, F. F. Blankenship and L. Fairchild

A fifth set of long-term surveillance specimens of graphite (POCO Grade AXF-5Q) and Hastelloy N was exposed to fissioning molten fuel salt for 12,943 Mw hrs during the final runs 19 and 20 of the MSRE. These tubular specimens were specially designed to test the effects of surface roughness and different flow conditions on the deposition of fission products from the fuel salt on or into the solids.

There was no variation of deposition of any fission product with surface roughness for either graphite or Hastelloy N. For graphite, the adjacent samples were machined to surface roughnesses of 5, 25 and 125 microinches R.M.S. Most of the metal samples were machined to the same range of roughnesses, but they also included 1/16 in. diameter Hastelloy N wire samples with surfaces as drawn and one tube with surface as machined (of undetermined roughness).

Two different explanations are invoked for the lack of dependence of deposition on surface roughness, which clearly eliminates a simple adsorption theory. For the deposition of ^{95}Sr, ^{141}Ce and ^{144}Ce on graphite and of ^{89}Sr, ^{95}Zr, ^{137}Cs, ^{140}Ba, ^{141}Ce and ^{144}Ce on Hastelloy N, the quantity deposited amounted only to the equivalent of contamination by 1 to 4 mg of fuel salt per cm^2 of surface. Fission recoil is thought to be the mechanism by which these species are injected into the graphite and metal surfaces. The much heavier (by two or three orders of magnitude) depositions

of noble metal fission products (^{99}Mo, ^{95}Nb, ^{103}Ru, ^{129}Te, ^{132}Te) on metal and graphite are thought to be controlled by mass transfer through a stagnant film of salt adjacent to the surface. However, large differences in diffusion coefficients or accommodation coefficients for the different elements must be invoked to make the simple mass transfer model fit the data.

A similar model for the mass transfer of the rare gas precursors of ^{89}Sr and ^{140}Ba through a salt film is thought to account for the observed heavy deposition of these species in graphite. In the case of ^{137}Cs, a mobility of Cs in the graphite must be also postulated to account for the low concentration remaining in the graphite.

CONCENTRATION PROFILES OF FISSION PRODUCTS IN GRAPHITE, FIFTH SET OF SURVEILLANCE SPECIMENS

S. S. Kirslis, F. F. Blankenship and L. Fairchild

The interior surfaces of the two graphite tubes from the fifth set of surveillance specimens (see preceding section, this document) were sampled in a hot cell with a special adjustable boring tool making successive cuts 1, 2, 3, 10, and 10 and 20 mils thick. The graphite powder samples were dissolved and analyzed radiochemically for ^{89}Sr, ^{95}Zr, ^{140}Ba, ^{137}Cs, ^{141}Ce, ^{144}Ce, ^{99}Mo, ^{129}Te, ^{132}Te, ^{131}I, ^{95}Nb, ^{103}Ru and ^{106}Ru. A sample of each graphite piece which remained after boring was analyzed to provide information on fission product deposition on the exterior surfaces of the graphite tubes.

The concentration profiles and total depositions per cm^2 obtained were generally similar to those from previous sets of surveillance specimens. As usual, except for ^{89}Sr, ^{137}Cs and ^{140}Ba, the concentrations of fission products fell by two or more orders of magnitude in a few mils. For the three exceptions with rare gas precursors of appreciable half-life, the interior profiles were level, as previously observed for POCO graphite. The interior level averaged 3.7×10^{11} dpm/g for ^{89}Sr, about twice the average for POCO graphite in the fourth set of surveillance specimens and four times the average for POCO graphite in the third set. The interior concentrations for ^{140}Ba (and most other isotopes) were similar in the three sets of specimens.

The ^{89}Sr profiles were unusual also in that all five of them showed higher interior than surface concentrations. The first surface sample, about 1 mil thick, usually contained a concentration of about 2×10^{11} dpm/g of ^{89}Sr, which rose to about 4×10^{11} dpm/g at a depth of 5 mils. Hints of similar behavior were noted for ^{140}Ba and ^{137}Cs. A re-examination of profiles for ^{89}Sr, ^{140}Ba and ^{137}Cs from previous surveillance specimens also frequently showed low concentrations in the first few mils from the salt-exposed surface. Typically, the concentrations would fall from a high initial value at the surface to a low value at a depth of 3 to 5 mils, then rise to a level intermediate value.

This mobility was anticipated for ^{137}Cs which is known to exhibit a volatility as the element or carbide. Some information on a high mobility of ^{89}Sr and ^{140}Ba diffusing through pyrolytic carbon coatings on UO_2 and UC_2 fuel particles is in accord with the observed profiles. Since the fuel salt or flush salt should be an effective sink for elemental ^{89}Sr, ^{140}Ba and ^{137}Cs, thin diffusion from the interior of the graphite toward the salt could conceivably result in the observed concentration gradients, particularly during low power or zero power operation.

HYDRODYNAMIC EFFECTS ON THE DEPOSITION OF FISSION PRODUCTS ON GRAPHITE AND HASTELLOY N IN THE MSRE

S. S. Kirslis, F. F. Blankenship and L. Fairchild

The several tubular test specimens of graphite and Hastelloy N in the fifth set of surveillance specimens were intentionally arranged to provide some variety of flow conditions under which the fuel contacted the graphite and metal surfaces. The low pressure drops available made it impossible to extend the flow conditions into the turbulent range. The flow conditions varied only from stagnant fuel salt to linear velocities of about a foot per second or Reynolds numbers of about 700. Turbulence promoter wires were wrapped around one graphite and one metal tube, although sizable effects on turbulence were not expected at these low velocities.

On the Hastelloy N specimens, deposition of fission products varied significantly from the average only for the tube containing stagnant fuel salt with a 1 1/2 in. long gas phase region above the salt. Deposition on

Hastelloy N from stagnant salt was about the same as from flowing fuel for ^{89}Sr, ^{95}Zr, ^{137}Cs, ^{140}Ba, ^{141}Ce and ^{144}Ce. As expected, heavy deposition of ^{89}Sr and five-fold greater deposition of ^{140}Ba than from salt took place from the gas phase on Hastelloy N. For ^{99}Mo, deposition from stagnant fuel was even heavier than the heavy deposition from flowing fuel. There was equally heavy deposition of ^{99}Mo on the metal surfaces contacting the gas phase. But the deposition from stagnant salt of ^{95}Nb, ^{103}Ru, ^{132}Te and ^{131}I was lower by a factor of 10 than from flowing salt. The quantities of ^{95}Nb, ^{103}Ru, ^{106}Ru and ^{131}I on gas-exposed Hastelloy N were another factor of 10 lower. The amounts of ^{132}Te on Hastelloy N exposed to stagnant salt and to the gas phase were similar. The different behaviors of ^{99}Mo, ^{132}Te, and the remaining noble metal fission products are difficult to explain.

There was no graphite specimen exposed to stagnant fuel; thus no significant variations of deposition on the graphite specimens were observed.

It was rather disappointing that the above results did not confirm the film controlled diffusion model more definitely. The decreased deposition of ^{95}Nb, ^{103}Ru, ^{106}Ru, ^{132}Te and ^{131}I from the stagnant fuel is in accord with the model. The behavior of ^{99}Mo is anomalous.

ELECTRON MICROSCOPE EXAMINATION OF PARTICLES IN THE GAS PHASE ABOVE FUEL SALT IN THE MSRE

S. S. Kirslis, F. F. Blankenship and L. Fairchild

The topmost test assembly in the fifth set of surveillance specimens was a Hastelloy N tube closed at the top end, open to flowing salt at the bottom end, and containing a central rod with 11 electron microscope screens attached every 1/2 in. vertically. Post-irradiation examination of the rod and screens showed that during MSRE power operation the salt level in the tube rose so that only the top two screens were in the helium gas phase at the top of the tube. Because of adhesion from the long heating, it was not possible to remove the copper screens from the Hastelloy N rod without damaging the delicate carbon film on the screens.

With the electron microscope it was possible to see irregularly shaped

particles with a sintered appearance on a few remaining scraps of carbon film. The particles were about 0.1 to 10 microns in size, occasionally strung together in chains, and gave electron diffraction patterns suggestive of Li_2BeF_4 crystals. No other kinds of particles could be identified on the screens from the gas phase above the molten fissioning salt. Radiochemical analyses had shown that deposits on the gas phase tube walls contained 6 to 9 x 10^{15} atoms of ^{99}Mo per cm^2 at reactor shutdown. Apparently this material did not collect into particles big enough to see with the electron microscope.

COMPARISON OF DEPOSITION OF NOBLE METAL FISSION PRODUCTS ON GRAPHITE AND HASTELLOY N, FIFTH SET OF SURVEILLANCE SPECIMENS

S. S. Kirslis, F. F. Blankenship, and L. Fairchild

One of the assemblies in the fifth set of surveillance specimens was designed expressly to compare fission product deposition on metal and graphite surfaces exposed to fissioning fuel under identical conditions. The fuel was made to flow in a 1/16 in. wide annulus between a Hastelloy N core 1/2 in. in diameter and a 5/8 in. I.D. POCO graphite tube.

The deposition of noble metal fission products on these graphite and metal surfaces is compared in the following table. The unit of activity used in the table is grams of theoretical salt per cm^2 of surface. The theoretical salt contains all of each nuclide which would be found in the fuel salt if decay were the only loss mechanism.

The last two columns of the table give the average depositions on the 12 graphite and the 13 metal surveillance specimens exposed to flowing fuel salt during the same period.

Each value can be multiplied by the total area of graphite ($\sim 2 \times 10^6$ cm^2) or metal ($\sim 1 \times 10^6$ cm^2) and divided by the total grams of fuel ($\sim 5 \times 10^6$) in the reactor yield the fraction of total nuclide present to be found on the graphite or metal.

Comparison of Fission Product Deposition on Graphite and Hastelloy N

	Adjacent Graphite	Adjacent Hastelloy N	Average Graphite	Average Hastelloy N
^{95}Nb	0.36	0.45	0.30	0.54
^{99}Mo	0.31	1.93	0.31	3.02
^{103}Ru	0.12	0.18	0.09	0.23
^{106}Ru	0.09	0.22	0.07	0.23
^{129}Te	0.04	--	0.06	--
^{132}Te	--	1.37	--	3.16
^{131}I	0.007	0.24	0.005	0.30

These results show that the deposition behavior on adjacent specimens is generally similar to that on geometrically separated samples and confirm the previously noted preference of most noble metal nuclides to deposit on metal rather than graphite. However, in previous tests more ^{95}Nb usually deposited on graphite than on metal.

GAS TRANSPORT IN MSRE MODERATOR GRAPHITE

R. B. Evans, III, J. L. Rutherford and A. P. Malinauskas

A detailed investigation of the gas transport characteristics of MSRE moderator graphite has been conducted.[1,2] These studies demonstrate that the impregnation treatments which had been applied for purposes of permeability reduction yield a material which is nonhomogeneous with respect to gas transport. For the specimen on which the most extensive measurements had been made, the inhomogeneity imparted to the sample as a result of impregnation was such that the characteristic transport coefficients were found to increase approximately exponentially from the surface to the core of the graphite.

All of the moderator graphite which was surveyed was sufficiently impermeable that gas transport at conditions of reactor operation could be approximated reasonably well by considering only the free-molecule or Knudsen mechanism, although the overall variation of the Knudsen transport coefficient was observed to be of the order of 10^3.

A simple mathematical model was developed to predict the transport

characteristics of fission-product gases in the MSRE graphite. Comparison with in-pile experimental data yielded amazingly good agreement for the short-lived isotopes. On the basis of this comparison, it appears feasible to eliminate expensive sectioning and counting techniques employed to determine concentration profiles of the fission products in the MSRE moderator graphite in favor of gas transport measurements for those species which have noble-gas precursors. We hasten to note, however, that in-pile experiments have special merit in other respects; for example, they yield information about nuclides that do not have gaseous precursors.

[1] A. P. Malinauskas, J. L. Rutherford, and R. B. Evans III, Gas Transport in MSRE Moderator Graphite. I. Review of Theory and Counterdiffusion Experiments, ORNL-4148 (Sept. 1967).

[2] R. B. Evans III, J. L. Rutherford, and A. P. Malinauskas, Gas Transport in MSRE Moderator Graphite. II. Effects of Impregnation. III. Variation of Flow Properties, ORNL-4389 (May 1969).

PART III. MOLTEN SALT BREEDER STUDIES

REDUCTIVE EXTRACTION STUDIES

REDUCTIVE EXTRACTION OF PROTACTINIUM AT HIGH CONCENTRATIONS FROM MSBR FUEL SOLVENT SALT INTO LIQUID BISMUTH[1]

R. G. Ross, C. E. Bamberger, and C. F. Baes, Jr.

In continued studies of the reductive extraction of protactinium, we have investigated the effect of the protactinium concentrations up to 2000 ppm on its extraction from $LiF-BeF_2-ThF_4$ (72-16-12 mole %) by thorium metal in liquid bismuth. Measurements were made at 625°C both (1) by adding Pa^{4+} to a system containing $LiF-BeF_2-ThF_4$, and bismuth with thorium metal reductant, and (2) by adding thorium metal reductant to a system containing $LiF-BeF_2-ThF_4-PaF_4$ and bismuth. The resulting equilibrium quotient of mole fractions calculated for the reaction

$$Pa^{4+}(F) + Th^{\circ}(Bi) \rightleftarrows Pa^{\circ}(Bi) + Th^{4+}(F)$$

was 1480. This agrees well with the value of 1450 obtained previously with protactinium concentrations below 100 ppm, thus indicating that the protactinium distribution is independent of its concentration in the range investigated.

[1]A fuller description of this work has been published in MSR Program Semiann. Progr. Rept. August 31, 1969, ORNL-4449.

EXTRACTION OF CERIUM AND THORIUM FROM $LiF-BeF_2$ (66-34 mole %) INTO BISMUTH AT 600°C

J. H. Shaffer, W. P. Teichert, D. M. Moulton, and D. M. Richardson

Previous experiments have examined the extraction of rare earths into bismuth from $LiF-BeF_2-ThF_4$ mixtures having constant thorium concentrations of 3, 6, 9, and 12 mole %.[1] As a continuation of this program, the extraction of cerium at low and varying thorium concentrations in the salt phase has been studied. The purpose of this experiment was to simulate the salt-bismuth conditions in the proposed electrolytic cell, to provide further data relating to the thermodynamic activity of ThF_4 in the salt phase, and to examine cerium behavior in an extraction system containing reduced thorium in excess of its solubility in bismuth.

The starting salt mixture was 2.2 kg of LiF (65.75 mole %), BeF_2 (33.87 mole %), and ThF_4 (0.38 mole %) with a cerium content of about 2.35 x 10^{-5} mole fraction. Essentially all of the cerium and thorium were

extracted into 3 kg of bismuth by the stepwise addition of 10 grams of lithium to the metal phase.

Values of pertinent equilibrium quotients calculated from these data are

$$D^3_{Ce}/D^4_{Th} = 6.4$$

$$D_{Ce}/D^3_{Li} = 3.3 \times 10^9$$

$$D_{Th}/D^4_{Li} = 2.6 \times 10^{12}$$

where

$$D_i = (N_i)_{metal}/(N_i)_{salt}.$$

Calculations of material balances for thorium and cerium showed a substantial loss of cerium from the bismuth solution when solid thorium was present. At the conclusion of the experiment about 86% of Th and 38% of Ce were calculated to be in solid phase. This possible finding of solid solution formation of Ce and Th probably precludes further interest in separating cerium from thorium in bismuth by cold-zone deposition of thorium.[2]

[1]MSR Program Semiann. Progr. Rept. Aug. 31, 1968, ORNL-4344, p. 176.

[2]Reactor Chemistry Div. Ann. Progr. Rept. Dec. 31, 1968, ORNL-4400, p. 53.

REDUCTIVE EXTRACTION OF SODIUM AND STRONTIUM FROM SIMULATED MSBR FUEL SOLVENT INTO BISMUTH

D. M. Richardson, W. P. Teichert, and J. H. Shaffer

The behavior in the reductive extraction process of the alkaline earth strontium, a fission product, and of the alkali metal sodium, a possible contaminant, were measured at 650°C under equilibrium conditions in extraction vessels intended to simulate the first rare earth extractor. Each 4-in. IPS vessel contained a mild steel liner, 3 kg of hydrogen-fired bismuth, and approximately 3 kg of $LiF-BeF_2-ThF_4$ (72-16-12 mole %). In addition, one salt contained 1.44×10^{-4} mole fraction SrF_2 (200 ppm Sr) with radiotracer ^{85}Sr (0.515 MeV gamma). The other salt contained 1×10^{-2} mole fraction NaF (3600 ppm Na) with radiotracer ^{22}Na (0.511 MeV annihilation radiation). Stepwise additions of approximately 0.5 g lithium metal were

made directly into the bismuth phases. Equilibrium was tested by temporary insertion of a beryllium electrode into the salt. At equilibrium the salts were sampled with hydrogen-fired, copper filter sticks and the bismuth phases were directly sampled through dip tubes with graphite ladles. Lithium metal additions were continued until the metal phases were approximately 0.002 mole fraction Li. Distributions were determined by gamma spectrometer counting of salt and metal samples; six days were allowed for decay of thorium daughter activity in the bismuth. Thorium activities in the salt were corrected by using a salt blank without radiotracer. The distribution of lithium was based on spectrographic assay of bismuth samples and on inventory balance for the two phases. The distribution coefficients obtained for strontium were: $\log D_{Sr} = 2 \log X_{Li} + 2.093$, where X_{Li} is the mole fraction lithium in the bismuth phase. The equilibrium quotient was $K_Q = D_{Sr}/(D_{Li})^2 = 65$. The separation factor at X_{Li} of 0.002 was 0.179. For sodium the distribution coefficients were: $\log D_{Na} = \log X_{Li} + 1.186$. The equilibrium quotient was $K_Q = D_{Na}/D_{Li} = 10.9$.

REDUCTIVE EXTRACTION OF SODIUM AND CESIUM FROM MOLTEN LiCl INTO BISMUTH

D. M. Richardson, W. K. R. Finnell, W. P. Teichert, and J. H. Shaffer

The extraction of sodium and cesium from LiCl into bismuth containing dissolved lithium has been measured at 650°C. These distributions are of interest since the behavior of fuel impurities and of the more abundant fission products could affect the design and operation of the LiCl-bismuth back-extraction system. In both experiments 4-in. IPS vessels were used, each containing a mild steel liner and 3 kg of hydrogen-fired bismuth. Added to one vessel was 1.9 kg of LiCl containing 1 mole % NaCl (5400 ppm Na) labeled with ^{22}Na (0.511 MeV annihilation radiation). Added to the other vessel was 1 kg of LiCl containing 1 mole % CsCl (30,400 ppm Cs) labeled with ^{137}Cs (0.661 MeV gamma). Reduction was produced by stepwise additions of 0.5 g to 1.0g of lithium metal directly into the bismuth phase. At least six hours of argon sparging was allowed for equilibration. The salt was sampled with hydrogen-fired filter sticks and the bismuth was sampled directly with graphite ladles. The highest lithium concentrations examined were 4 mole % in bismuth for sodium, and 7 mole % in bismuth for

cesium. Distributions were determined by gamma spectrometer counting of salt and metal samples. The distribution of lithium was based on spectrographic assay of bismuth samples and on inventory balance for the two phases. The distribution coefficients obtained for sodium were: log $D_{Na} = \log X_{Li} - 0.195$, where X_{Li} is the mole fraction lithium in the bismuth phase. The equilibrium quotient was: $K_Q = D_{Na}/D_{Li} = 0.63$. For cesium the distribution coefficients were: $\log D_{Cs} = \log X_{Li} - 1.503$. The equilibrium quotient was $K_Q = D_{Cs}/D_{Li} = 0.031$.

DISTRIBUTION OF CERIUM, EUROPIUM, AND STRONTIUM BETWEEN MOLTEN LiCl AND BISMUTH

D. M. Moulton, W. P. Teichert, and J. H. Shaffer

These distributions were studied using lithium chloride that had been purified by slowly heating in argon and HCl, and melted and treated with H_2-HCl for several hours to remove water and oxides. A bismuth slug that was left over from an earlier experiment which contained Li, Th, and Ce was placed in a vessel with salt and oxidized gently with an H_2-HCl mixture. It was possible to control the oxidation so that several samples could be taken during the process. In a second experiment the LiCl was prepared with europium and strontium chlorides and reduced into bismuth with thorium and lithium as usual. In both cases the samples were analyzed radiochemically for the rare earth and spectrographically for the rest. Writing the equilibrium constants $K_Q(M) = D_M/D_{Li}^{(n)}$, we found $\log K_Q(Ce) = 8.312 \pm 0.384$, $\log K_Q(Eu) = 2.284 \pm 0.025$ and $\log K_Q(Sr) = 1.024 \pm 0.141$ where the theoretical values of n (3,2,2) were used. No meaningful thorium data could be gotten since it distributed too strongly to the bismuth for good salt values. All of these elements will move into lithium chloride from the primary bismuth stream, leaving the thorium behind. Removing the divalent elements by extraction into a second bismuth stream will require highly reducing conditions.

CALCULATED BEHAVIOR OF ALKALI METALS IN EXTRACTION FROM FLUORIDES AND CHLORIDES INTO BISMUTH

D. M. Moulton

Calculations have been made, using published data from several sources, to predict the extraction of sodium, rubidium, and cesium from $LiF-BeF_2-ThF_4$ and LiCl into bismuth. The standard free energy for the process $MX_{(l)} + Li_{(l)} = LiX_{(l)} + M_{(l)}$ at 650° was calculated by adding the appropriate heats of transition and heat capacity integrals to the room temperature data.[1] Where supercooled liquids were involved the heat capacity of the liquid was extrapolated back into the low temperature region. A few numbers were missing and had to be estimated by analogy with known quantities. The activity coefficients of Li and Na in Bi were taken from some Argonne work[2] while for Rb and Cs in Bi, which have not been measured, the activity coefficient of K was taken as a good approximation.[3] Salt-phase activity coefficients were derived from the heat of mixing data of Kleppa and co-workers[4] using the fairly well justified assumptions that the heat of mixing does not vary with temperature and the entropy of mixing is ideal. Because Kleppa's data refer to mixtures of the heavier salts with pure LiF it was finally necessary to assume that the ratio γ_{LiF}/γ_{MF} did not change much on going to the fuel solvent mixtures.[5] The results of these calculations are presented in the table.

D_M/D_{Li}	Na	Rb	Cs
Fluoride	27	650	20,000
Chloride	0.2	0.042	0.019

The difference between fluorides and chlorides is a result of the greater stability of salts where both ions have either a high or a low charge density. The calculations are, of course, no better than the data that went into them, but experiments which have recently been done tend to confirm the general pattern.[6] In practical terms the heavy alkalis should move very strongly out of the fluoride and into the chloride, from which they cannot be extracted at all.

[1] O. Kubaschewski et al., Metallurgical Thermochemistry, Fourth Ed., Pergamon, Oxford, 1967, Tables A, B, C.

[2] M. S. Foster et al., Inorg. Chem. 3, 1428 (1964); A. K. Fischer et al., J. Phys. Chem. 71, 1465 (1967).

[3]R. R. Hultgren et al., Selected Values of Thermodynamic Properties of Metals and Alloys, Wiley, New York, 1963, p. 530.

[4]L. S. Hersh and O. J. Kleppa, J. Chem. PHys. 42, 1309 (1965); J. L. Holm and O. J. Kleppa, J. Chem. Phys. 49, 2425 (1968).

[5]J. Braunstein, private communication.

[6]D. M. Richardson et al., this report.

BISMUTH ALLOYS AS SOLVENTS FOR REPROCESSING MSBR FUELS BY REDUCTIVE EXTRACTION

D. M. Moulton, W. Jennings, Jr., and J. H. Shaffer

Several combinations of bismuth with other metals have been tried in an attempt to improve the performance of pure bismuth as a reductive extraction solvent. One major problem is the low solubility of the thorium-bismuth intermetallic which prevents further rare earth removal. Magnesium and also gold form fairly low melting eutectics with thorium at thorium contents of several mole percent. These were added to bismuth to see whether they would increase thorium solubility. Both experiments were run as conventional extractions of cerium from a salt phase. Magnesium was such a strong reductant that it removed all the thorium from the salt (67-30-3 mole % $LiF-BeF_2-ThF_4$) while its metal-phase concentration did not get high enough (< 0.02 mole fraction) to affect the solubility appreciably. An earlier experiment had indicated that gold might help a little, but in this work the rare earth distribution at saturation was about the same at 0, 5, 10, and 20 mole % Au in Bi, and the higher scatter in the unfiltered metal samples when gold was present suggested some precipitate formation.

A second problem in the extraction process is the need to maintain salt invariance. This means that if chemical reductants or oxidants are used, they must be removed before the salt is returned to the reactor. An electrochemical cell has been proposed as a way of avoiding this problem, but there are several practical difficulties associated with it. Titanium metal was tried as a reductant for U and Pa, the plan being that salt invariance could be maintained by volatilizing the product TiF_4; but Ti was not a strong enough reductant to remove even a measurable amount of the Pa ($D_{Pa} < 0.003$).

TIN AND TIN ALLOYS AS SOLVENTS FOR REDUCTIVE EXTRACTION OF RARE EARTHS FROM MSBR FUEL SOLVENTS

J. H. Shaffer, W. P. Teichert, and D. M. Moulton

An experimental program was conducted to examine the application of tin and binary mixtures with tin as the metal phase solvent for the reductive extraction of rare earths from the MSBR fuel solvent. The equipment and procedures used for these experiments were very similar to those used for studies of the salt-bismuth system except that graphite was used as the containment material. Each experiment utilized 2.6 kg of tin or tin mixture and 255 to 3 kg of $LiF-BeF_2-ThF_4$ (72-16-12 mole %) containing approximately 4.8×10^{-5} mole fraction of cerium.

The reported solubility of thorium in tin at 600°C is < 0.025 atom % (< 489 ppm);[1] however, the results of these experiments indicated solubilities of 2700 to 2900 ppm by weight. The value for the equilibrium quotient at 600°C,

$$K_Q = D^4_{Ce}/D^3_{Th},$$

from these data was 0.054. Separation factors calculated from the equation,

$$\ln D_{Ce}/D_{Th} = 1/4 \ln (K_Q N_{ThF_4}) - 1/4 \ln N_{Th^\circ},$$

were significantly lower than those obtained in the salt-bismuth system at comparable thorium concentrations in the metal phase.

The results of similar experiments using binary mixtures of tin with zinc, copper, and titanium could not be distinguished from those obtained with pure tin. Aluminum was found too reducing toward thorium for application in the reductive extraction process even at low concentrations in tin.

[1] E. E. Hayes and P. Gordon, BMI-1300 (1958), p. 131.

EXTRACTION OF THORIUM FROM MSBR FUEL SOLVENT SALT INTO LEAD

D. M. Richardson, W. K. R. Finnell, and J. H. Shaffer

Evidence was found in early equilibrium experiments that thorium, but not rare earths, was reductively extracted into lead. A consequent process to remove high cross section fission products would be: thorium reduction into lead (1), complete reduction of rare earths into bismuth (2), and recovery of thorium by hydrofluorination (3). Steps (1) and (3) and transport

of thorium by electromagnetically pumped lead were tested in a 304 SS loop at 625°C. Lead was recirculated between two 4-in. IPS graphite-lined vessels, each with a 3-in. deep lead pool. One contained $LiF-BeF_2-ThF_4$ (65-23-12 mole %) with CeF_3 labeled with ^{144}Ce and was electrolyzed between a Be rod anode in the salt and the lead-graphite walls as cathode. The other contained $LiF-BeF_2$ (66-34 mole %) and was sparged with H_2-HF to reoxidize thorium. After 79 ampere hours of electrolysis and 233 hours of lead pmmping, 25 grams of thorium were transferred to the recovery salt. If only thorium was reduced, the coulomb consumption would have produced 171 grams of thorium for transport through the lead. However, the same fraction of cerium was transferred to the recovery salt and it would appear that the nonequilibrium conditions of electrolytic reduction caused transfer of all metals soluble in lead in proportion to their concentration in the salt. Lithium transfer was not measured. An additional factor that contributed to the apparent inefficiency was that the graphite cathode supplied 85% of the total cathode area and was found to be covered with adherent materials containing thorium metal. The extraction of reduced metal from the electrolyzer was monitored by the potential of a beryllium electrode in the salt and was observed to be very slow. Total time with the lead molten exceeded 1000 hours without plugging or other indication of serious corrosion.

OTHER SEPARATIONS

PLATINIDE PRECIPITATION FROM BISMUTH SOLUTIONS

D. M. Moulton, W. Jennings, Jr., W. K. R. Finnell, J. H. Shaffer, and W. R. Grimes

In the MSBR reductive extraction process uranium and fission product zirconium will be removed at the same stage and will not be separated from each other. A possible separation step makes use of the fact that zirconium forms the very stable intermetallic compound $ZrPt_3$. If this is stabler than any uranium platinide, then, when salt containing U and Zr is placed in contact with bismuth containing U and Pt, the U in the metal will pass into the salt, reducing the Zr which will precipitate as $ZrPt_3$. The salt will then be free of Zr and ready for further processing. From time to time the Zr-Pt-Bi phases will have to be cleaned up, probably by hydrofluorination of the Zr into a waste salt. The object of this study was to establish that $ZrPt_3$ would precipitate from bismuth solution while a uranium platinide would not.

An extraction experiment was carried out, using 12 g of metallic uranium to extract 1.9 g of Zr from 3.5 kg of $LiF-BeF_2-ThF_4$ (72-16-12 mole %) into 3 kg of Bi at 600°. When about one-third of the Zr had been transferred, 11.3 g of Pt was added. The zirconium in the salt dropped from 65% of the total to 21% while the uranium rose from 71 to 88%. A further addition of uranium dropped the Zr to 10% in the salt while the uranium percentage remained constant. The zirconium balance (salt plus metal), which had been essentially 100% before the platinum addition, dropped to about 12% but the uranium balance was unaffected. Since the added amount of platinum was slightly less than stoichiometric for $ZrPt_3$ it is possible that an even better separation could have been made.

It was hoped that such a process might also work for the rare earth-thorium separation by forming an insoluble rare earth platinide but no corresponding thorium compound. When 2.8 kg of $LiF-BeF_2$ (66-34 mole %) with a little cerium was reduced into 3 kg of bismuth with 6.0 g of Th and 0.16 g of Li, the Ce and Th distributions were both about 3. Now 8.2 and then 7.3 g of Pt were added. Some 90% of the Ce went back into the salt while most of the thorium just disappeared from the metal and did not appear in the salt. The lithium also disappeared from the metal. When 2.24 g more

lithium was added, the cerium all extracted, but appeared in the melt, not as a solid phase. The thorium disappeared from the salt, about half appearing in the metal and half presumably forming a solid. Despite the loss at the time of the platinum additions, there was no evidence of a lithium platinide during the latter part of the experiment. Thus platinide formation does not show any promise for rare earth removal. Since thorium does seem to form an insoluble platinide, the conditions of its formation need to be studied further so that it can be kept from interferring with the zirconium.

PURIFICATION OF SODIUM FLUOROBORATE

H. W. Kohn and C. R. Benson

We have attempted to measure equilibrium quotients for the reactions

$$O^{=} + HF \rightleftarrows OH^{-} + F^{-} \qquad (1)$$

and

$$OH^{-} + HF \rightleftarrows H_2O + F^{-} \qquad (2)$$

in $NaBF_4$-9% NaF eutectic by sparging with HF and measuring H_2O by Karl Fisher reagent, HF by alkalimetry and $O^{=}$ plus any OH^{-} by $KBrF_4$ oxidation. The data have not been accurate enough to allow us to assess the credibility of OH^{-} in these melts. In particular the water determinations have errors due to large blanks, and the oxide analyses disagree with oxide inventory (added B_2O_3 minus measured water). If we assume all O present as OH^{-},

$$K_{2\ 450°C} = \frac{[H_2O]}{[OH^{-}][HF]} = 1.31, \text{ and } K_{2\ 425°C} = 1.64.$$

If we assume all O present as $O^{=}$, K_1K_2 = 145 at 450°C and 240 at 425°. Auxiliary experiments designed to test the stability of OH^{-} in fluoroborate have given conflicting results. If B_2O_3 be added to the melt it will adsorb HF without giving off much water for about an hour, arguing that K_1 is large compared with K_2, yet, at constant (large) oxide values the ratio $H_2O/(HF)^2$ is more nearly constant than the ratio H_2O/HF.

THE REMOVAL OF CHLORIDE FROM SIMULATED MSBR FUEL SOLVENT BY REACTION WITH ANHYDROUS HYDROGEN FLUORIDE

F. A. Doss, C. R. Benson, W. R. Grimes, and J. H. Shaffer

According to current MSBR fuel reprocessing technology, molten lithium chloride will be employed for the back-extraction of rare earths from bismuth. This close-coupled process could result in the contamination of the fluoride fuel mixture with chloride ion which would penalize the neutron economy of the reactor even at 20 ppm levels. Therefore, an experimental program was conducted to examine the chemical feasibility of an HF-H_2 sparge treatment for removing chloride from a molten MSBR fuel solvent mixture and to provide a basis for preliminary engineering design of a process system.

Equilibrium quotients and relative velocity constants for the reaction,

$$Cl^- + HF \rightleftarrows F^- + HCl,$$

were determined with 2.7 kg of LiF-BeF_2-ThF_4 (72-16-12 mole %) initially containing 1 wt % chloride ion as NaCl.[1] Seventeen reaction periods of 4 hours each were conducted at 650 and 750°C, at gas sparge rates of 0.5, 1, and 1.5 liters per minute of H_2 (NPT), and at nominal HF influent concentration of 3, 5, and 7 milliequivalents HF per liter of H_2.

Each experiment where reaction rate data could be obtained showed very good agreement with pseudo first-order kinetics. Calculated velocity constants at 650°C varied from 0.2 to 0.76 (mole fraction HF-hr)$^{-1}$ and were related to stripping efficiency and HF mass flow rates.

Calculations of equilibrium quotients for each experimental point showed that steady-state conditions prevailed between the gas and liquid phases. These values were based on the equation,

$$K_Q = \frac{P_{HCl}}{P_{HF}} \cdot \frac{N_{F^-}}{N_{Cl^-}} ,$$

and were derived from analyses of the gas effluent and on the chloride content of the melt, hypothetically calculated as the cation mole fraction of NaCl. Values at 650°C varied from 6 to 10 and did not show a satisfactory correlation with gas sparge rates. Values for K_Q at 750°C were essentially constant at about 4.4 $\pm$ 0.5.

[1]MSR Program Semiann. Progr. Rept. Feb. 28, 1970, ORNL-4568 (in press).

EQUILIBRATION OF RARE EARTH-CONTAINING MOLTEN FLUORIDES WITH VARIOUS SOLIDS

C. E. Bamberger and C. F. Baes, Jr.

In search of an alternative method for removal of rare-earth fission products from MSBR fuels we have begun a series of experiments to synthesize sparingly soluble compounds containing rare earths which could act as selective ion exchangers for such fission products. The tests have involved as starting materials, various oxides and other compounds which our experience and/or available thermochemical data suggest might be stable or nearly stable in molten fluorides at temperatures of 500-700°C. The solids tested (ThO_2, $ThSiO_4$, UO_2-ThO_2 solid solutions, Cr_2O_3, Fe_3O_4, NiO, V_2O_5, Al_2O_3, TiO_2, Nb_2O_5, WO_3, Na_3PO_4 and $CaF_2 \cdot YF_3$ solid solutions) were equilibrated with the rare earth-containing melt (72-16-12 mole % LiF-BeF_2-ThF_4) by mechanical stirring. In some instances these materials were formed "in situ" by metathetical reactions of double fluorides with ThO_2 in order to provide oxide ion and, when necessary, NiO was added as an oxidant. While, thus far, the compounds tested have not led to the formation of a sparingly soluble rare earth containing compound, the results obtained confirmed thermochemical calculations that Cr_2O_3, TiO_2, Nb_2O_5, and Fe_3O_4 are relatively insoluble in the molten fluorides used; Cr_2O_3 and TiO_2 are so insoluble that they hold considerable promise as container or insulator materials for molten fluorides.

Efforts will be continued to synthesize a compound of suitable properties for the removal of rare earths from molten fluorides.

REMOVAL OF CERIUM FROM MOLTEN LiCl WITH ZEOLITE

D. M. Moulton, W. Jennings, Jr., and J. H. Shaffer

The lithium chloride which is to be used as the back extractant to oxidize rare earth fission products from bismuth will itself need to be cleaned up periodically. As an alternative to a second bismuth extraction with high lithium concentrations, we have examined the absorption of fission products with zeolite ion exchanger. It has been shown that zeolite will remove cesium and rubidium from lithium chloride at 600°.[1] In our experiment Linde zeolite 4A ($NaAlO_2 \cdot SiO_2$) was ground to below 200 mesh and soaked in 13M LiCl to exchange the sodium. About 25 g of the dried material was used to treat 157 mg of $CeCl_3$ in 1.5 kg of LiCl at 650°. The procedure was

to add the purified salt to a vessel containing the zeolite in a slightly reducing atmosphere. Filtered samples showed 60% of the cerium activity gone, referred to the salt before transfer. Several unfiltered dipper samples were taken in such a way as to collect some of the solid. These showed cerium concentrations from 1.3 to 9.7 times that of the original salt. Presumably this was due to zeolite particles containing absorbed cerium, though the possibility of an oxide or oxychloride precipitate cannot be completely excluded. The selectivity coefficient for cerium is defined as D_{Ce}/D_{Li}. The zeolite phase was not analyzed, but assuming that all of the lost cerium was in it and that the zeolite formula was $LiAlO_2 \cdot SiO_2$, the selectivity coefficient is 278. This is of the same order as the 246 and 63 for cesium and rubidium by Platek and Marinsky and indicates that this would be an effective way of removing rare earths from the lithium chloride.

[1] W. A. Platek and J. A. Marinsky, J. Phys. Chem. 65, 2118 (1961).

TRITIUM BEHAVIOR

HYDROGEN CHEMISTRY IN MOLTEN SALT REACTORS

R. A. Strehlow

Since tritium produced in a molten salt reactor must be contained or processed, a survey was made of the relevant hydrogen chemistry.

The chemical form of the hydrogen will be influenced by the equilibrium with the U^{+3}/U^{+4} couple primarily. The reaction,

$$UF_4 + 1/2\ H_2 = UF_3 + HF,$$

which has been studied by Long and Blankenship[1], shows that a significant fraction of the tritium in a reactor can be present as HF. The solubilities of these hydrogeneous species and their diffusivities will determine the rates at which they can be removed from the fuel salt.

Additionally there is the possibility that under the conditions prevailing in the core some fraction of the hydrogen can be associated with carbon in the form of hydrocarbon species. At low pressures of hydrogen and in the presence of radiation an unknown quantity of tritium could be stored in the graphite moderator or released as methane or acetylene. Initial thermodynamic calculations have been made, which indicate that at reactor temperatures and expected hydrogen pressures the hydrocarbons should not form to an appreciable equilibrium extent.

Hydrogen (tritium) which is not released to the fuel sparging gas can permeate to the coolant mixture and conceivably and undesirably through the secondary heat exchanger to the atmosphere. To calculate the rate at which such losses might occur it is necessary to know the extent to which Sievert's Law [$(\text{Permeability}) \propto (\text{Pressure})^{1/2}$] applied and what functional form the pressure dependence is expected to follow at the anticipated low pressures of tritium. This has been examined in detail. It was concluded that at pressures and temperatures appropriate to the reactor a Sievert's relation is anticipated. Finally, the applicability of mass law procedures to minimize tritium permeation has been briefly studied. Under the conditions of higher hydrogen pressures, some methane formation as well as decrease in tritium permeation is expected.

[1] G. Long and F. F. Blankenship, "Stability of Uranium Trifluoride. Part II. Stability in Molten Fluoride Solution," ORNL-TM-2065, Part II, Nov. 1969.

HYDROGEN SOLUBILITY IN MOLTEN SALTS

J. E. Savolainen and A. P. Malinauskas

Tritium is produced in nuclear reactors by a number of mechanisms, including fission. The principal sources are ternary fission and neutron irradiation of deuterium, lithium, and boron. Unlike most fission products however, the tritium so produced can potentially penetrate metals quite easily, and thus be transported ultimately into the steam cycle of the nuclear power plant, where removal of the radioactive species is difficult.

In a molten salt reactor this problem is particularly acute since LiF is a major molten salt component. Hence, to provide for the adequate removal of the tritium which is produced, it is necessary to establish the relative importance of the several mechanisms responsible for the tritium transport. One of these is the solubility of the gas in the molten salt, In view of its suspected low solubility, and the difficulty in containing hydrogen and hydrogen isotopes at elevated temperatures, the experimental aspects of the problem are complex. Nonetheless, an apparatus for solubility determinations has been designed and is currently under construction. The apparatus design and the underlying operational principles are similar to the two-bulb technique developed by Grimes, Smith, and Watson.[1]

[1] W. R. Grimes, N. V. Smith, and G. M. Watson, J. Phys. Chem. 62, 862 (1958).

GRAPHITE

PYROLYSIS OF POLYACENAPHTHYLENE

R. A. Strehlow

Thermal analysis and a temperature gradient furnace have been used to prepare samples of pyrolyzed polyacenaphthylene with well characterized thermal histories. The resulting tars are of practical use in the preparation of specialty graphite bodies and in the study of the relations between chemical composition and graphite microstructure. Synthetic tars have been prepared with effective softening points as low as 180°C from this starting material. (Applicability as a binder in graphite technology broadens with decreases in softening point). Characterization methods for the product were developed using thin layer chromatography in combination with gas chromatography and mass spectroscopy. In typical tars of low softening point, twelve compounds were found to be present in readily detectable amounts. The compound decacyclene was found to be dominant in the tars (more than 75% by weight). This compound is an oxidized cyclic trimer of acenaphthylene and possesses several unique properties which make it useful in graphite fabrication technology. Principal among these are a good carbon yield (in excess of 85% with an associated volumetric yield near 65%) and the ability to form of a highly graphitic structure.

Carbonization studies of decacyclene have been analyzed using gel permeation chromatography and the temperature dependence examined. The oxidative polymerization of this material was found to proceed over a narrow temperature range and yield a carbon with significant structural variation. Early stages of carbonization were found to proceed with the development of a mesophase of unusual character. The mesophase (polymeric semi-carbon) developed with an apparent onion-skin texture instead of the more common lamellar structure.

PART IV. AQUEOUS SYSTEMS

REACTORS

ASSESSMENT OF WATER TECHNOLOGY IN UNATTENDED BOILING- AND PRESSURIZED-WATER REACTORS

G. H. Jenks

Reactor types which are of possible interest in Army work include PWR's and BWR's capable of operating reliably for long periods without operator attention. We completed a review and assessment of water technology in PWR's and BWR's with the objectives of (1) providing additional bases for judging the feasibility and merits of unattended reactors of either type; (2) recommending materials, coolant compositions, and operating procedures; and (3) recommending research and development work which would aid in the development of such reactors. Secondary steam systems as well as primary systems were included in this work.[1] Our previous work of similar nature has been published.[2,3]

We concluded that, from the standpoint of water technology, unattended reactors of either type would be possible using, for the most part, certain state-of-the-art materials, water compositions and purification methods, and operating procedures.

We believe that it would be necessary to develop methods for controlling gas distribution in the steam pressurizer of a sealed PWR and suggested that a pressurizer design proposed previously by Jenks and Samuels[3] be investigated for this application.

Means of minimizing the leakage of air into the steam system and loss of vapor from the system should be investigated and utilized. A method of minimizing loss of steam from gland-seal boxes on the turbine was suggested for investigation.

[1] G. H. Jenks, ORNL report to be published.

[2] G. H. Jenks and J. C. Griess, Water Chemistry in Pressurized and Boiling Water Power Reactors, ORNL-4173 (November 1967).

[3] Reference Design and Technology Assessment of a 1500 kw(e) State-of-the Art Pressurized Water Reactor, G. Samuels, Program Director, M. E. Lackey, report editor, ORNL-TM-2604.

CORROSION OF ELECTROLESS NICKEL PLATE ON ALUMINUM AT HIGH HEAT FLUXES

J. C. Griess, R. D. Cheverton,* and J. R. McGuffey**

To increase the life or power level of aluminum clad fuel elements in high performance reactors the corrosion of aluminum must be prevented or minimized. The first results with electroless nickel as a means of preventing such corrosion were presented last year.[1]

Additional testing in deionized water flowing at 50 fps showed that at a heat flux of 1.55×10^6 Btu/hr ft^2 with surface temperatures between 171 and 181°C a 0.5 mil nickel plate protected the aluminum during a 40-day test whereas a similarly exposed unplated specimen showed temperature increases up to 135°C ($Al_2O_3 \cdot H_2O$ formation) and penetrations as deep as 14 mils. Increasing the heat flux to 2.83×10^6 Btu/hr ft^2 and the velocity to 118 fps at the same surface temperatures caused most of the nickel to be eroded or corroded during a 14-day test, but no temperature increases were observed and the maximum penetration of the aluminum was only 0.5 mils.

After 13 weeks in the ORR, fuel plates lost their 0.5 mil nickel plate even though the heat flux was only 4×10^5 Btu/hr ft^2, the flow rate, 30 fps; and the surface temperature, < 100°C. Based on out-of-reactor tests, the corrosion of electroless nickel should have been so low that most of the nickel should have remained; therefore, it appears that radiation either caused the nickel to spall from the surface or accelerated the corrosion of electroless nickel appreciably.

*Reactor Division
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[1] J. C. Griess et al., "Reactor Chemistry Div. Ann. Progr. Rept. Dec. 31, 1968," ORNL-4400, pp. 61-64.

RDT STANDARDS FOR PRIMARY COOLANT SYSTEMS OF WATER REACTORS

P. D. Neumann and H. C. Savage

As part of the Standards Program established at ORNL by the AEC Division of Reactor Development and Technology (RDT), we have prepared three RDT standards which establish requirements for the coolant chemistry in

primary systems of pressurized-water (PWR), boiling water (BWR), and research or test reactors.[1]

Preparation of these standards involved the assembling of the necessary technical information and editing it into a suitable format. The preliminary drafts were reviewed by, and comments received from people at ORNL, representatives from reactor designers, builders and operators, and other AEC laboratories. These comments were used as the basis for extensive editing and rewriting after which an advanced draft was distributed for review. When all pertinent comments are incorporated into the advanced draft, a final draft is submitted to AEC-RDT for approval and issuance as a tentative standard.

The standards and their present status are:

1. RDT A1-1 - Control of Coolant Composition in Pressurized-Water Reactors has been submitted to AEC-RDT for approval as a tentative standard.
2. RDT A1-2 - Control of Coolant Composition in Boiling-Water Reactors has been distributed for review.
3. RDT A1-3 - Control of Coolant Composition in Water-Cooled Research and Test Reactors has been issued as a preliminary draft for comment.

These standards reflect existing technology and should provide a source of sound, proven information for use by designers, builders, and operators of reactor systems and components.

[1] H. C. Savage et al., Reactor Chem. Div. Ann. Progr. Rept. Dec. 31, 1968, ORNL-4400, p. 60.

RE-EVALUATION OF NEED FOR EXCESS OXIDANT IN HFIR COOLANT

G. H. Jenks

I have re-analyzed the radiation and thermal chemistry of the HFIR coolant as part of a re-evaluation of the need for addition of excess oxidant to stabilize the HNO_3 (10 μm) against radiation decomposition.[1,2] Experimental information on the composition of the HFIR coolant during irradiation and previously available experimental and theoretical information on radiation and thermal chemistry of dilute HNO_3 solutions were employed.

The results led to the conclusions that:

1. The excess oxidant concentration in the HFIR high pressure system is near 750 μm when O_2 is added to the head tank, and near 230 μm without this addition.
2. The nitric acid concentration within the core is reduced because of NO formation. The HNO_3 concentration at the core exit (with 10 μm hydrogen ion in sample) is 2 to 4 μm during the O_2 addition and 1 to 2 μm without the addition; the HNO_2 concentration at the core exit is negligible.
3. Increasing the excess oxidant to 2000 μm would increase the (HNO_3) at the core exit but would not provide assurance that the sum of (HNO_3) and (HNO_2) at this location would exceed 5 μm. An increase in the operating concentration of HNO_3 to 20 μm along with an increase in excess oxidant to 2000 μm would provide this assurance, but the acceptability of this acidity from the standpoint of corrosion of all HFIR components has not been demonstrated.
4. Hydrogen ions are generated within the core through the formation of HO_2. At 230 μm excess oxidant, and at temperatures at less than 110°C the hydrogen ion concentration produced by the HO_2 is probably about 10 μm or somewhat more. At higher temperatures, the acidity produced by HO_2 would be less than this but the amount cannot be estimated reliably.

[1]ORNL report to be published.

[2]G. H. Jenks, ORNL-3848, 1965.

DESALINATION STUDIES

THE CORROSION OF COPPER ALLOYS IN SODIUM CHLORIDE SOLUTIONS*

J. C. Griess, A. L. Bacarella, and E. G. Bohlmann

The corrosion of copper and copper alloys in salt water solutions is being investigated from 25 to 155°C using both weight loss and electrochemical measurements. This study is conducted for the Office of Saline Water.

Since the last report the following information based on weight loss data has been obtained. The corrosion rates of Admiralty brass, 70-30 and 90-10 cupronickel, and Monel 400 in 1M NaCl at 150°C (2-3, 0.1-0.4, 0.7-0.8, and 0.1-0.3 mpy, respectively) were only slightly higher than at 125°C. The presence of 6 ppm oxygen in the same solution increased the corrosion rate of Admiralty brass by more than an order of magnitude but had little effect on the cupronickels except the 70-30 alloy underwent crevice corrosion. The presence of 10 ppm sulfide significantly ($\sim$ 10X except for Admiralty brass) increased the corrosion rates, but within the range of 7 to 10 pH was without effect.

Electrochemical polarization curves have been obtained with the same alloys and copper from 25 to 155°C. Anodic polarization curves obtained with copper in deaerated 1M NaCl were consistent with published thermodynamic and kinetic data; the corrosion product was $CuCl_2^-$ with no evidence of Cu_2O formation even at pH values as high as 9. With the cupronickel alloys anomalous anodic behavior was frequently observed at the higher temperatures. Cathodic polarization in the absence of oxygen showed only an activatation process for the reduction of water. With oxygen in the solution corrosion was limited by diffusion of oxygen although the value of the limiting current varied from material to material.

*Research sponsored by the Office of Saline, Water, U. S. Department of The Interior.

ALKALINE SCALE SUPPRESSION USING CARBON DIOXIDE*

S. A. Reed, D. M. Eissenberg[1], and C. C. Littlefield[2]

Experiments were continued at the Office of Saline Water Test Station at Wrightsville Beach, North Carolina, to verify that CO_2 injected into cold sea water feed to sea water distillation plants would prevent formation of alkaline scale ($CaCO_3$ and $Mg(OH)_2$) in the brine heater at temperatures to 290°F. The experiments provided the necessary information for the design of a pilot plant to proof test the process in conjunction with an operating distillation plant. This work has been summarized in a recent publication.[3]

A 40,000 gpd pilot plant was designed and is now being constructed at Wrightsville Beach. Shakedown and preliminary operational tests are scheduled to begin in mid-April 1970 and to be completed in June 1970. The pilot plant will then be operated to furnish dealkalized seawater feed to a multi-effect-multi-stage (MEMS) flash evaporator for a period of about four months. During this period of operation parametric studies will be made to optimize the process. The effect of the following variables on the process will be determined: (1) stripping steam rate, (2) feed rate of brine, (3) brine temperature, (4) tower packing materials and size, (5) attrition rate of packing, and (6) packing regeneration recycle time.

Following successful operation with the MEMS plant the pilot plant is scheduled to be operated in conjunction with a vertical tubed evaporator plant.

*Research sponsored by the Office of Saline Water, U. S. Department of The Interior.

[1]ORNL Reactor Division.

[2]ORGDP.

[3]S. A. Reed, C. C. Littlefield, and D. M. Eissenberg, "Control of Alkaline Scale Using Carbon Dioxide," ORNL-TM-2817 (to be published as an Office of Saline Water Research and Development Report).

OSW MATERIALS INFORMATION CENTER*

J. L. English and S. A. Reed

The Materials Information Center, operated for the Office of Saline Water, U. S. Department of the Interior, by Oak Ridge National Laboratory, became fully operative during 1969. Purpose of the Center is collection,

indexing, abstracting, retrieval, evaluation, and dissemination of information on corrosion and performance of materials used in all processes concerned with desalination of seawater and brackish waters. Six indexed bibliographic reports, each containing approximately 50 abstracts, have been issued on a quarterly basis since December, 1968. Abstracts are accompanied by appropriate keywords for retrieval of specific information from the computerized system upon request. Efforts were concentrated on processing of research and development reports issued by the Office of Saline Water. Of 506 reports reviewed, 334 were abstracted for pertinent information contained therein. During the coming year, in addition to processing Office of Saline Water reports, attention will be directed to open literature publications dealing with materials performance in saline water conversion processes.

A computerized program for storage and retrieval of information on equipment behavior from Materials Performance Reporting Systems (MPRS) plant inspection forms developed by the Center was completed. Approximately 1150 forms freom Freeport (Texas) and Senator Clair Engle (California) plants have been processed and entered into the system. Typical search questions submitted have demonstrated both the flexibility and capability of the program. Entry of information from the two test beds will be continued as well as information from Roswell (New Mexico) and Webster (South Dakota) plants and from Wrightsville Beach pilot plant operations.

*Research sponsored by the Office of Saline WAter, U. S. Department of The Interior.

HIGH TEMPERATURE STUDIES

OPERATING TEST OF AN IMPROVED HIGH TEMPERATURE ISOPIESTIC APPARATUS

J. Braunstein, R. Ray, and H. Braunstein*

The operating characteristics of the modified high temperature isopiestic apparatus have been defined with solutions from 3 to 60 molal and from 60°C to 215°C. The precision and reproducibility of weighing is usually ± 0.15 mg and agreement between duplicate samples of a salt generally 0.1%. A new procedure, loading dry pulverized salts (rather than solutions) followed by evacuation, minimizes the danger of splatter and incomplete deaeration; dissolution following addition of deaerated water is complete in 1-2 days at 100°C. A rocking mechanism was designed and installed to assist the attainment of isopiestic equilibrium, which requires 3 to 24 hrs following addition or removal of water, as determined by periodic weighing *in situ*. The return to temperature equilibrium following addition or removal of water is usually the limiting factor, with the shorter times attainable at the higher temperatures and concentrations. The temperature in the air space surrounding the isopiestic vessel is controlled to ± 0.06°C by an 18 junction chromel-constantan thermopile activating a Leeds and Northrup P.I.D. Controller with a saturable reactor-type power supply. After equilibration the measured temperature of the massive copper block on which the solution pans rest fluctuates no more than 0.0015° during the course of a day. An isopiestic comparison of concentrated solutions whose absolute vapor pressures have been reported by other investigators revealed several inconsistencies, but agreement was found between LiCl and $LiNO_3$ at 100°C and between LiCl and $LiNO_3$-KNO_3 at higher temperatures. These results provide a basis for calculating some water activities from isopiestic ratios.

*Oak Ridge Graduate Fellow from the University of Maine under appointment from Oak Ridge Associated Universities.

A FLOWING EMF CELL FOR MEASUREMENTS AT ELEVATED TEMPERATURES

F. H. Sweeton, R. E. Mesmer, and C. F. Baes, Jr.

Studies of the dissociation of water have been started using the flowing EMF cell previously described.[1] The chemical composition of the

cell is

$$Pt|H_2(m_3),\ HCl(m_1),\ HCl(m_2)||KCl(m_2),\ KOH(m_1),\ H_2(m_3)|Pt.$$

The cell has no vapor phase and the hydrogen is all in solution, the concentration, $\underline{m}_3$, being that obtained by presaturation of the solutions at 25°C with 1 atmosphere of H_2 gas. The cell is constructed of Teflon parts mounted inside a metal pressure vessel. Teflon pressure seals for the incoming solution and electrical leads have operated satisfactorily up to 300°C and up to 1500 psi. We have obtained EMF readings that are essentially independent of flow rate down to quite low rates. Reasonably small volumes of solution have been sufficient to flush out the cell. Data taken at 50°C with solutions containing 0.15 m HCl have given values of log Q_w' (= log $\underline{m}$ $(H^+)\underline{m}(OH^-)$) that agree within 0.02 units with the accurate data of Harned and Hamer[2]. Values of log Q_w' at 50, 100, 150, 200, and 250°C determined with this solution as -13.0_1, -11.9_6, -11.2_6, -10.8_3, and -10.6_0. These measurements are continuing with varying concentrations of KCl.

[1]F. H. Sweeton and R. W. Ray, Reactor Chem. Div. Ann. Progr. Rept. Dec. 31, 1967, ORNL-4229, pp. 100-102; F. H. Sweeton, R. W. Ray, R. E. Mesmer, and C. F. Baes, Jr., Reactor Chem. Div. Ann. Progr. Rept. Dec. 31, 1968, ORNL-4400, pp. 88-89.

[2]H. S. Harned and W. J. Hamer, J. Am. Chem. Soc. 55, 2194 (1933).

HIGH TEMPERATURE ISOPIESTIC STUDIES OF CONCENTRATED AQUEOUS ELECTROLYTES

H. Braunstein* and J. Braunstein

Isopiestic ratios (relative to LiCl) were measured from which water activities were calculated for the single salts $LiNO_3$, LiBr, and $Ca(NO_3)_2$ as well as for the equimolar salt mixtures, $(Li,K)NO_3$, $(Li,Cs)NO_3$, and $(Ca,Cs)NO_3$ at 100°C, 120°C, and 150°C. At 100°C and 16 molal, the water activities ranged from 0.17 to 0.62 in the order LiBr, LiCl, $Ca(NO_3)_2$, $LiNO_3$, $(Ca,Cs)NO_3$, $(Li,K)NO_3$, $(Li,Cs)NO_3$ whereas at 3.7 molal the range of activity was only 0.80 to 0.89. The isopiestic behavior of $Ca(NO_3)_2$ and $LiNO_3$, along with equimolar mixtures of each of these with $NaNO_3$, KNO_3 and $CsNO_3$, was studied from 120° to 215° at 3 to 20 molal. Results indicate a limited range of composition and temperature where the effect of

adding a weakly hydrated salt (e.g., $CsNO_3$) to a strongly hydrated salt ($Ca(NO_3)_2$) has little effect on the water activity, but, in general, provide no evidence of extra stability of particular species with fixed hydration numbers in the liquid. The isopiestic ratios of $Ca(NO_3)_2$, $Cd(NO_3)_2$ and three mixtures of these two salts were examined at 60°C to 120°C from 4 to 16 molal to elucidate the competition for water molecules between two cations of equal charge and size but differing polarizability. The isopiestic molalities were found to be linear in the mole fraction, with Cd^{2+} apparently more strongly hydrated than Ca^{2+}; the preferential hydration of Cd^{2+} over Ca^{2+} increases with water content but decreases with temperature. Specific electrolyte-water interactions thus become most pronounced at high salt concentrations where molten salt models are most applicable, and theoretical work in this direction is in progress.

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THE HYDROLYSIS OF ALUMINUM ION AT ELEVATED TEMPERATURES

R. E. Mesmer and C. F. Baes, Jr.

The potentiometric cell, which was recently demonstrated in measurements of the apparent ionization product of water up to 292°C,[1] has now been applied to the study of aluminum ion hydrolysis behavior at temperatures up to 150°C in 1 m KCl. The slow kinetics of aluminum ion hydrolysis reactions at low temperatures have been known for some time, and probably account for the inconsistent explanations reported on the hydrolysis behavior. This difficulty has been overcome at temperatures between 100° and 150°C where data have been collected over wide ranges of hydroxyl numbers and solution composition. The data in acidic media are consistent with schemes involving three species: $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, and $Al_{14}(OH)_{34}^{8+}$. These results are also in essential agreement with the potentiometric and ultracentrifuge work of Aveston at 25°. In basic media data at 150°C indicate the hydroxide-to-aluminum ratio to be 4.00 ± 0.02. Combining this result with solubility studies at low temperatures we conclude that the species is $Al(OH)_4^-$ or more probably AlO_2^- based on Raman evidence at a lower

temperature.[2] The enthalpy change per hydroxide bond calculated from the temperature coefficients is -5.2 ± 0.7 kcal for the polymeric cationic aluminum species which is somewhat lower than the values previously found for Th^{4+}, UO_2^{2+}, Be^{2+} and several other metal ions.

[1]R. E. Mesmer, C. F. Baes, Jr., and F. H. Sweeton, J. Phys. Chem. 74, 1937 (1970).

[2]L. A. Carreira, V. A. Maroni, J. W. Swaine, Jr., and R. C. Plumb, J. Chem. Phys. 45, 2216 (1966).

COMPLETE EQUILIBRIUM CONSTANTS, ELECTROLYTE EQUILIBRIA, AND REACTION RATES[1]

W. L. Marshall

Application of the complete equilibrium constant ($\underline{K}°$),[2] which includes solvent as a reactant, has revealed recently several additional correlations of aqueous electrolyte behavior. Of particular importance, the conventionally derived standard state change in molar volumes ($\Delta\underline{V}$) between products and reactants (excluding solvent) has been shown experimentally to be proportional merely to the compressibility of the solvent; the significance of this relationship has been described. All other conventional thermodynamic properties can be calculated as a function of both pressure and temperature from the known pressure-volume-temperature behavior of the solvent. Analogous behavior for rate constants has been considered, with the product being the activated complex. There appeared to be no significant effect of viscosity on the complete constants within the precision of measurements. Several comparisons of the description of ionization behavior by means of $\underline{K}°$, fugacity, and activity coefficients were made. From these comparisons over wide ranges of pressure, temperature, and dioxane-water mixed solvent compositions, the overall utility of fugacity, with its defined relationship to chemical potential, was questioned in that the use of $\underline{K}°$ simplified the description of electrolyte-solvent equilibria. A knowledge of fugacities (and/or activity coefficients) was unnecessary, and therefore the complete constant would appear to have much potential usefulness.

[1]Modified Abstract of paper: W. L. Marshall, J. Phys. Chem. 74, 346 (1970).

[2](a) W. L. Marshall and A. S. Quist, Proc. Natl. Acad. Sci., U.S., 58, 901 (1967); (b) A. S. Quist and W. L. Marshall, J. Phys. Chem. 72, 1536 (1968).

ELECTRICAL CONDUCTANCES AND IONIZATION BEHAVIOR OF SODIUM CHLORIDE IN DIOXANE-WATER SOLUTIONS AT 100°C TO 4000 BARS OF PRESSURE[1]

L. B. Yeatts, L. A. Dunn[2], and W. L. Marshall

The ionization behavior of sodium chloride in dioxane-water at 100°C to pressures of 4000 bars was determined from electrical conductance measurements of dilute solutions (0.001-0.02 m). The conductance equation of Shedlovsky was used to calculate the limiting equivalent conductances (Λ_o) and conventional ionization constants (K) for sodium chloride in solvent mixtures whose compositions ranged from 30 to 70 wt. % dioxane. The complete ionization constant ($K°$) is represented by

$$NaCl(aq) + k\ H_2O \rightleftarrows Na(aq)^+ + Cl(aq)^- \text{ where } K° = K/C_{H_2O}^{k}$$

and where dioxane is considered to be an inert diluent.[3] A plot of log K vs log C_{H_2O} (mol/l) showed a linear relationship over the entire range of solvent composition and pressure, and provided a value of log $K°$ of -12.70. The value of k of 7.8, the net change in waters of solvation, correlated smoothly with previously published values of 6.4 at 25°C from studies in dioxane-water (1 bar)[3] and 10.2 from those in water at 400-800°C (to 4000 bars).[4] This common curve of k vs temperature supports a generalization for simple salts, over a wide range of temperature, that varying the concentration of water either by hydrostatic pressure or by dilution with dioxane does not change the isothermal value of $K°$. This constant depends only on temperature, and thus this study supports the general solvation relationship presented previously.[3]

[1]Combined Abstract of papers: (a) L. A. Dunn and W. L. Marshall, J. Phys. Chem. 73, 2619 (1969); (b) L. B. Yeatts, L. A. Dunn, and W. L. Marshall, to be submitted for publication (1970).

[2]Present address: Department of Chemistry, University of Tasmania, Hobarth, Tasmania.

[3](a) W. L. Marshall and A. S. Quist, Proc. Natl. Acad. Sci., U.S., 58, 901 (1967); (b) A. S. Quist and W. L. Marshall, J. Phys. Chem. 72, 1536 (1968).

[4] A. S. Quist and W. L. Marshall, J. Phys. Chem. 72, 684 (1968).

SURFACE CHEMISTRY

THE EFFECT OF SURFACE WATER ON THE ADSORPTIVE PROPERTIES OF UNIFORM, NONPOROUS, THORIUM OXIDE

R. B. Gammage, E. L. Fuller, Jr., and H. F. Holmes

Adsorption isotherms have been measured for water vapor, nitrogen, and argon on a nonporous sample of thorium oxide outgassed at temperatures between 25°C and 1000°C. Uniformity of the clean surface is evidenced by the multilayer stepwise adsorption of each adsorbate. Irreversibly bound water has the profound effect of masking the physisorption potential of the surface and causes the step structure of the isotherms of water, nitrogen, and argon to be lost. The amount of nitrogen or argon adsorbed on the water covered surface is reduced and the low apparent specific surface area susgests that there is a less than normal density of packing of these adsorbate molecules. In contrast the amount of physisorbed water increases as more water becomes irreversibly bound to the surface. Comparison with "standard" isotherms for water vapor shows that "normal adsorption behavior" occurs only after conducting several sorption cycles in water vapor. On the clean surface a layer of water is first chemisorbed and the following physical adsorption of water is apparently site-oriented to give a co-area which is larger than the normal 10.6 $A^{\circ 2}$/molecule. Although not decisive, localization effects are indicated for nitrogen adsorbed on the clean surface (1000°C outgassing), such effects extending even into the multilayer region, while a change in physical state is indicated for argon in passing from the monolayer to the multilayer region.

ADSORPTION OF WATER ON THORIUM OXIDE BETWEEN 25° AND 500°C

R. B. Gammage, E. L. Fuller, Jr., and H. F. Holmes

Reversible and irreversible adsorptions of water vapor on thorium oxide surfaces have been studied gravimetrically between 25° and 500°C. On an oxide with fine pores the water which became irreversibly bound between these two temperatures was equivalent in weight to 40 hydroxyls/100 $Å^2$ an amount far in excess of the 12.8 hydroxyls/100 $Å^2$ required to completely hydroxylate the 100 face. The excess is attributed to molecular water strongly associated with the surface hydroxyls. Between 300° and 500°

the irreversible adsorption involves only surface hydroxyls (mass equivalent) and poses no kinetic barrier to obtaining equilibrium isotherms. The irreversible binding of molecular water below 300° is so kinetically complicated and slow that there is considerable difficulty in establishing the equilibrium isotherms. Measurements were also made on a non-porous sample of thorium oxide. The irreversible adsorption of 36 hydroxyls/100A°^{2} (mass equivalent) is close to that observed with the porous sample. The capacity of the open surface for reversible adsorption is considerably lower than that of the finely porous oxide, so much so that above 350° it was not detectable. Reversible adsorption on the porous oxide could be measured at temperatures up to, and including, 500°.

HEATS OF IMMERSION IN THE ZIRCONIUM OXIDE-WATER SYSTEM

H. F. Holmes, E. L. Fuller, Jr., and R. B. Gammage

The heat of immersion of zirconium oxide in water at 25°C has been measured calorimetrically. For this study, a series of samples having a common chemical identity were prepared by calcining at 100° intervals from 600° to 1000°C. This treatment resulted in specific surface areas of 87 to 3.5 m^2/g. Prior to the immersion experiments the samples were outgassed at temperatures ranging from 25° to 500°C. The magnitude of the heat of immersion (values ranging up to -1100 $ergs/cm^2$)clearly indicates that the initial interaction of water with a zirconium oxide surface is chemical in nature. All of the samples exhibited two concurrent slow releases of heat having half-lives of about 4 and 30 minutes. With the exception noted below, the heat of immersion generally increased with increasing outgassing temperature. One of the samples (87 m^2/g) has a maximum in the heat of immersion as a function of the outgassing temperature. It is possible that the slow heat release and the maximum are related phenomena. Relating the results to the crystal modification present in the various samples strongly suggests that the metastable tetragonal form has a much lower surface energy than the stable monoclinic form. With the exception of the just mentioned phenomenon the heat of immersion (on a unit area basis) decreased with decreasing specific surface area.

INFRARED SPECTRA OF THORIUM OXIDE SURFACES

E. L. Fuller, Jr., R. B. Gammage, and H. F. Holmes

Spectra of thorium oxide of varying specific surface area, porosity, degree of heterogeneity, and mode of preparation have been obtained. In each case the surface hydroxyl and hydrating water species are characterized as a function of pressure and temperature in the presence of various gases. The general results of our findings are as follows. I. There are four types of OH bonds on the surface as noted in the characteristic vibrational frequencies: (a) the free OH band (3742 cm^{-1}), where the hydrogen is vibrating freely, and (b) three specific hydrogen-bonded species [3665, 3555 and 3380 cm^{-1}, reflecting increasing perturbation effects on (a)]. II. The relative population of these species is a function of the temperature and the H_2O pressure for a given material. Furthermore the distribution (but not the type) is a function of the surface parameters noted above. III. The tenacity of the binding is noted in the signal retention in vacuo at temperatures of 800°C. In addition the concentration is further enhanced by the presence of water vapor even at temperatures aoove 500°C. IV. The systematic assymetry induced by the field of the surface and the hydrogen-bonding is reflected in grossly skewed band shapes. Current analyses of these band shapes are informative in deducing the type of bonding involved. V. The replacement of the H_2O species with D_2O verifies the band assignments and proceeds via kientics that mechanistically provide confirmation of the strong, rigid hydrogen-bonding involved. At no time have we observed the slow diffusional kinetics normally associated with bulk or internal species.

OTHER STUDIES

THE HYDROLYSIS OF FERROUS ION IN DILUTE CHLORIDE AT 25°

R. E. Mesmer and S. A. Whitehead

The hydrolysis behavior of Fe^{2+} was recently examined between 50° and 300° in acidic and basic media by Sweeton and Baes from measurements on the solubility of Fe_3O_4.[1] The value of the log K for the Eq. (1)

$$Fe^{2+} + H_2O = Fe(OH)^+ + H^+ \qquad (1)$$

obtained by extrapolation to 25° was 9.3 ± 0.5. This result was consistent with earlier work of Hedstrom in 1 M $NaClO_4$ (9.5 ± 0.2); but, because of the wide range of the other reported values and the relatively large uncertainties, we have examined the equilibrium using the titration procedure on a solution of 0.003 M $FeCl_2$ prepared from very pure zone-refined iron. The cell employed a H_2 electrode for measurement of acidity. Measurements were made to hydroxyl numbers of 0.006 where precipitation commenced. The results of these data give 9.58 ± 0.08 for the log K. The strong charge and radius effect on hydrolysis behavior is exhibited by the $Fe(OH)^+$ and $Fe(OH)^{2+}$ complexes whose stabilities differ by seven orders of magnitude. The thermodynamic data available on these two equilibria indicates that this difference in stabilities originates from the ΔS for the hydrolysis reactions.

[1] F. H. Sweeton and C. F. Baes, Jr., J. Chem. Thermodynamics (in press).

ELECTROCHEMISTRY OF U AND OF U-ALLOYS IN AQUEOUS SOLUTIONS

G. H. Jenks

This investigation of the electrochemistry of U and of U-alloys in aqueous solutions at 25°C has the objective of obtaining information applicable to the understanding and controlling of corrosion and stress cracking of these materials at ambient temperatures.

The results of open circuit and polarization measurements on uranium in 0.1 M K_2SO_4, pH 5.3 to 6, and in 1 N H_2SO_4 with one or more of the gas atmospheres, $4H_2$:96Ar,Ar, 20 O_2:80Ar, led to tentative conclusions which include the following:

1. A passive film forms on uranium above potentials near those for the equilibrium,

$$UH_3 + H_2O \rightleftarrows UO + 5H^+ + 5e^- \quad (E_o = -0.422 - 0.0591\ pH). \qquad (A)$$

2. The passive film is removed, and increasing anodic rates occur, above potentials near those for the equilibrium between UO_2 and soluble UO_3,

$$UO_2(anh) + H_2O \rightleftarrows UO_3(anh) + 2H^+ + 2e^- \quad (E_o = 1.657 - 0.0591\ pH). \quad (B)$$

3. The cathodic rate on the passive metal increases sharply below potentials near those for the equilibrium,

$$UH_3 + 2H_2O \rightleftarrows UO_2 + 7H^+ + 7e^- \quad (E_o = -0.716 - 0.0591\ pH). \quad (C)$$

This indicates that UH_3 is formed from UO_2 and/or by reaction with H_2O below these potentials.

Passive films form on the alloy (U, 7.5 Nb, 2.5 Zr) in the above solutions. In the 0.1 M K_2SO_4, the film remains passive and, apparently, intact up to the highest voltage tested, 5 v. In 0.1 N and 1 N H_2SO_4, the passive films dissolve above potentials near those for reaction (B) above. The anodic film formed in 0.1 M K_2SO_4 also dissolves during subsequent anodization in 0.1 N H_2SO_4. Cathodic polarization of a specimen in 0.1 M K_2SO_4 with a 4% H_2 atmosphere, both before and after anodization, showed sharply increasing cathodic currents at potentials about 125 mv above (positive) those for reaction (C) above. Cathodic behavior in other solutions remains to be determined and/or clarified.

THE EFFECT OF SOLVENT ON THE ELECTROCHEMISTRY OF IRON

A. L. Bacarella and A. L. Sutton

Corrosion is an electrochemical process generally involving the oxidation of a metal to metal ion in solutions and in deaerated acid solutions reduction of hydrogen ions to hydrogen gas. The detailed mechanism of this corrosion process is the province of electrochemical kinetics. For iron, in H_2-saturated aqueous acidic sulfate solution, it has been shown[1] that the anodic process is

$$i_+ = k_+ \frac{[H_2O]^n}{[H^+]} \exp \frac{3FE_{Fe}}{2RT} \quad (1)$$

and the cathodic process is

$$i_- = k_- \, [H_2O]^m [H^+] \exp \frac{-FE_{Fe}}{2RT} \tag{2}$$

Since measurements have been performed only in aqueous solvent the kinetic order with respect to water could not be determined. We have made measurements in H_2-saturated ETOH-HOH solvent from pure water to 98.4 wt % ETOH at constant 0.5M H_2SO_4. Other workers[2] have postulated an "absolute acidity" scale for ETOH-HOH whereby pH measurements in ETOH-HOH can be referred to the same standard state as pH measurements in pure water, i.e., the infinitely dilute water solvent. Using the parameters provided by these workers we have shown that the anodic process is second order with respect to water:

$$i_+^s = k_+ \frac{[H_2O]^2}{[H^+]} \exp \frac{3FE_{Fe}}{2RT} \tag{3}$$

and the cathodic process is first order with respect to water

$$i_-^s = k_- \, [H_2O][H^+] \exp \frac{-FE_{Fe}}{2RT} \, . \tag{4}$$

[1]E. J. Kelly, J. Electrochem. Soc. 112, 124 (1965).

[2]Boris Cutbezahl and Ernest Grunwald, J. Am. Chem. Soc. 75, 505 (1953).

PART V. CHEMICAL SUPPORT FOR HIGH TEMPERATURE GAS-COOLED REACTORS

THE "AMOEBA EFFECT" IN COATED FUEL PARTICLES

S. Cantor, H. J. deNordwall, and G. D. Brunton

The fuel kernel of pyrolytic carbon-coated fuel particles has been observed to migrate, under the influence of a temperature gradient, through the carbon coatings. This phenomenon, known as the "amoeba effect", has been found to occur in both oxide and carbide fuels at temperatures greater than about 1500°C, and is readily characterized by the preferred direction of the kernel migration, viz., up the thermal gradient. The present study seeks to determine the chemical aspects associated with this effect.

Thus far, our study of the literature (mostly reported from Gulf General Atomic (GGA) and the Dragon Project) leads us to suspect that

1. The migration of oxide kernels is chiefly a consequence of the transport of graphite via the reaction $C(s) + CO_2(g) = 2CO(g)$,[1]
2. The migration of carbide kernels is caused by the temperature-dependent solubility of $(U,Th)C_2$ in graphite.[2] (Unfortunately, independent solubility data are not currently available to test this hypothesis.)

Other mechanisms for the amoeba effect are being considered as well. However, the sorting out of possible interactions is hampered by uncertainties concerning the chemical state of the species within the coated particles.

To increase our knowledge about the chemical aspects of carbide-coated particles, X-ray diffraction patterns were obtained on particles which had been heated by GGA at 1450°C under flowing helium for periods of 9000 and 18,300 hrs. The X-ray study detected $(Th,U)O_2$ crystals in the particles that had been heated; oxide crystals were not detected in unheated controls. The X-ray results thus suggest that oxygen-containing species are present in carbide fuel particles and, upon heating, some of the carbide reacts to form oxides.

[1] R. H. Flowers and G. W. Horsley, "The Influence of Oxide Kernels on the Manufacture and Performance of Coated Particle Fuel," AERE-R-5949 (Nov. 1968).

[2] T. D. Gulden, Gulf General Atomic, San Diego, California, personal communication.

DIFFUSION OF ACTINIDES IN PYROCARBONS: THIN-LAYER EXPERIMENTS

R. B. Evans III, J. O. Stiegler[1], and G. M. Watson

The diffusion of uranium and thorium in columnar pyrocarbons between temperatures of 1450 and 2065°C have been studied using the usual thin-layer depletion technique. Constant coefficients are obtained that are in good agreement with results reported elsewhere for uranium diffusion in the < a > direction at actinide concentrations less than about 0.15 mg actinide/cm^3. Diffusion coefficients increase at higher actinide concentration. The anisotropic pyrocarbons are well oriented with the basal planes aligned parallel to the deposition surface. Diffusion coefficients parallel to the deposition surfaces are about three orders of magnitude greater than those in the perpendicular direction; the difference is due primarily to the preexponential term in the usual Arrhenius equation. Autoradiographic studies of specimens in which diffusion occurred perpendicular to the deposition surface show segregation of actinides to growth cone centers or boundaries depending on whether diffusion occurs along or opposite the direction of growth of the pyrocarbon. The segregation is attributed to rapid diffusion parallel to the deposition surface coupled with the roughened nature of these surfaces.

[1]Metals and Ceramics Division.

FISSION-GAS RELEASE MEASUREMENTS AS A METHOD OF EVALUATING FUEL BEHAVIOR DURING IRRADIATION

R. M. Carroll and O. Sisman

Because of the difference in properties of the various Xe and Kr isotopes and their precursors, the physical condition of the fuel can be fairly accurately deduced by studying the magnitude and isotopic ratios of the fission gas released. This technique can be especially useful in showing changes in the physical condition of the fuel.[1]

For best results a sweep gas system is used to transport the fission gas from the fuel to a monitoring station, and the fuel temperature and fissioning rate are continuously monitored and controlled. However, it is often possible to infer the condition of the fuel from fission-gas release data and a guess at the temperature and power density.

One important use of fission-gas monitoring is to ensure that the physical condition of a fuel specimen has not changed. For example, changes in the surface of the fuel and closing of interconnected porosity by fission sintering can be detected and observed. Grain growth may be distinguished from cracking or chemical reaction of the fuel. Thermal stress cracking may be distinguished from swelling of the fuel caused when pressure of trapped fission gases exceeds the strength of the fuel matrix.

It should be noted that it is seldom possible to fully evaluate the condition of the fuel by a single observation. The irradiation conditions and the time-dependent behavior must be considered as well as the ratio of the isotopes of the fission gas and the emission rate as a function of temperature.

[1] R. M. Carroll and O. Sisman, "Evaluating Fuel Behavior During Irradiation by Fission-Gas Release," Submitted to Nucl. Appl. Tech., April 1970.

BEHAVIOR OF MIXED OXIDE FUELS DURING IRRADIATION

R. M. Carroll, O. Sisman, and T. W. Fulton

Fuel materials consisting of plutonium-uranium oxides in which uranium comprises the major fraction of heavy metal will apparently be used in the first generation of fast breeders. We have, accordingly, studied the release of fission gases from such fuels during irradiation in our special facility in the Oak Ridge Research Reactor where we can vary, independently, the specimen temperature and the fission rate.

Three specimens of $(Pu,U)O_2$ material manufactured in different ways have been irradiated. Two of these were of pressed and sintered (Pu 0.25, U 0.75)O_2 supplied by Battelle Northwest Laboratory; one of these BNWL specimens consisted of high (97%) density sintered pellets, while the other consisted of 21 spheres (903 micron average diameter) ground from a production batch of Fast Flux Test Facility candidate fuel. The third specimen was (Pu 0.2, U 0.8)O_2 prepared at ORNL by the sol-gel technique as spheres of 645 micron average diameter.

The high density BNWL pellets upon irradiation showed evidence of some initial porosity which decreased by irradiation sintering. When the specimen temperature was raised to 1450°C, in an attempt to speed up this sintering

process, the fission gases were released very rapidly. At this temperature the mixed oxide specimen (unlike many previous tests with UO_2) apparently became sufficiently plastic to permit release of nearly all the fission gas produced. Post-irradiation examination showed that the fuel specimen was broken into several large lumps with fission gas bubbles at the grain boundaries which were interconnecting and reaching the free surface.

The ground spheres of BNWL material also exhibited irradiation sintering and the onset of very rapid gas release at sufficiently high temperatures. By careful manipulation of the specimen temperature we were able to study the temperature at which breakaway gas release occurred as a function of burnup. This breakaway release temperature decreased steadily with burnup to the maximum (4.5% of the heavy metal) studied. At 4% burnup and 900°C, for example, ^{133}Xe was released at 15% of its formation rate.

The sol-gel specimen (51 spheres) proved difficult to evaluate quantitatively since irradiation sintering and thermal shock cracking of the spheres led to erratically changing rates of gas release. The temperature dependence of the gas release rates was largely obscured by this behavior; gas release rates (at temperatures below breakway) were approximately twice those of the BNWL spheres. After burnup to about 1.7% the sol-gel specimen emitted bursts of fission gas; this behavior is apparently due to bursting pockets of trapped gas. The effect of temperature on these gas bursts appeared to show no change as the burnup was subsequently increased to 2.9%. Some of this behavior is clearly a conseqeunce of the much larger fraction of closed pores in the sol-gel material.

FAILURE OF SiC COATINGS AT TEMPERATURES ABOVE 1800°C

M. T.Morgan, R. L. Towns, and C. D. Baumann

Postirradiation annealing experiments with coated fuel particles are being performed to study the fission-product retention of various coatings as a function of irradiation dose and temperature. Cesium release from TRISO coated UO_2 particles is currently under investigation. The TRISO coating consists of a buffer layer of porous carbon, a layer of high density isotropic pyrocarbon, a SiC barrier layer, and an outer layer of high density isotropic pyrocarbon.

High cesium release, together with the absence of Kr release, during the postirradiation anneals at temperatures of 1800°C and higher, indicated failure of the SiC layers of the TRISO coatings. There was some correlation between size of the coated particle and cesium release; in some samples the smaller coated particles retained cesium while the larger coated particles did not. This would seem to indicate that the SiC layer might be cracking under stresses induced by differential thermal expansion and gas pressure, which could be influenced by particle size. Recent investigations have shown that porosity in the SiC layer may also be the cause of the cesium release, however.

The SiC layers of TRISO coatings on coated particles which released cesium were exposed by burning off the outer PyC coating. Some of these coated particles disintegrated, but others remained intact; these were examined at 100X power with an optical microscope. No cracks were apparent. Scanning electron micrographs revealed porosity in fragments of the SiC layer from one of these coated particles which had been annealed for 11 hr at 2000°C and which released about 50% of the cesium. This evidence does not rule out the possibility that submicroscopic cracks may also be present. Additional studies are being made.

A METHOD FOR THE AQUEOUS OXIDATION OF RADIOACTIVE GRAPHITE CRUCIBLES PRIOR TO ANALYSIS

M. T. Morgan and R. L. Towns

Fission products are collected on graphite crucibles and other furnace components during postirradiation anneals of fuel materials. Some of the fission products in the graphite can be determined by gamma spectroscopy, but radiochemical procedures are necessary for others, such as strontium. To remove these fission products, it is necessary to oxidize the graphite. Since the fission products diffuse into the walls of the container materials at high temperatures, an aqueous method of oxidation is preferred.

The method finally adopted for the oxidation of the graphite crucibles was based on a procedure for the determination of sulphur in coal.[1] The procedure, which takes from three to four hours for each crucible, involves a mixture of nitric, perchloric, and chloracetic acids. The graphite is cooked in the nitric acid to remove organic material before the perchloric

acid is added. Chloracetic acid is added to prevent frothing and potassium dichromate is added as a catalyst for the oxidation.

[1]G. Frederic Smith and A. Garrett Deem, "Determination of Sulfur in Coal by Perchloric Acid Method," Analytical Edition, Industrial and Engineering Chemistry 4, 227 (April 15, 1932).

FEASIBILITY OF MEASURING THERMAL DIFFUSIVITY DURING IRRADIATION AT REALISTIC POWER LEVELS

R. M. Carroll, R. B. Perez, and J. G. Morgan

Our method of measuring thermal diffusivity during irradiation is to make a step change in the fission power generated by the fuel specimen and then measure the time dependence of the resulting temperature changes. One problem in measuring the thermal diffusivity of UO_2 during irradiation is that there is a large temperature gradient at any realistic power level. This makes it very difficult to measure the temperature at any point except at the center of symmetry of the specimen. By measuring only the time response of the temperature at the center of symmetry, we are able theoretically to determine the thermal diffusivity; however, this procedure is difficult to apply.

In attempting to develop the method we have solved many problems involving instrumentation, irradiation technique, computer processing of data, non-fission heating,[1] stored energy release,[2] and the mathematical formulations of the general theory into computer codes.[3] We have completed the computer program for obtaining the values of thermal diffusivity from the general theory. Data for UO_2 under different irradiation conditions are now being evaluated.

[1]R. M. Carroll, R. B. Perez, and O.Sisman, "Measurements of Non-Fission Heating in a High Neutron Flux Reactor," Nucl. Sci. Eng. 36, 232-237 (1969).

[2]R. M. Carroll, R. B. Perez, and O. Sisman, "The Effect of Stored Energy on Measurements of Thermal Diffusivity During Irradiation," Nucl. Sci. Eng. 39 (1), 123-126 (Jan. 1970).

[3]R. B. Perez, R. M. Carroll, and O. Sisman, The Theory of a Time-Dependent Heat Diffusion Determination of Thermal Diffusivities with a Single Temperature Measurement, ORNL-4478 (in press).

SOLID FISSION-PRODUCT RELEASE FROM COATED-PARTICLE FUELS DURING IRRADIATION

P. E. Reagan, J. G. Morgan, O. Sisman, and H. E. Robertson

Of the many sweep capsules irradiated to study fission-gas release and coated particle stability, five were examined for solid fission-product release as well. Fission products, to reach the cooler regions of the capsule, had to cross a two-millimeter gas gap. Irradiation temperatures of the fuel ranged from 1200°C to 1570°C and the maximum burnup was 6% FIMA. The data led to the following conclusions: (1) Ba and Sr are not retained by a pyrolytic carbon (PyC) coating but are retained by a SiC layer. (2) Iodine release from particles with cracked coatings agrees with post-irradiation heating data. (3) Most of the released fission products were trapped in the graphite surrounding the coated particles.

The fraction of fission products retained in the fuel is shown in the following table. The first two experiments were with uncoated fuel, the other two had coatings which remained intact throughout the irradiation.

Fuel	Coating	Fraction Found in Fuel					
		^{95}Zr	^{144}Ce	^{89}Sr	^{140}Ba	^{137}Cs	^{106}Ru
UO_2	Bare	0.96	0.96	na*	na	0.79	0.96
UC_2	Bare	0.95	na	0.067	0.21	0.56	0.98
UO_2	PyC	1.0	1.0	0.53	0.56	0.97	na
UO_2	PyC-SiC	1.0	1.0	na	1.0	1.0	na

*na - not analyzed.

FISSION-PRODUCT MONITORING IN HIGH-TEMPERATURE GAS-COOLED REACTORS

C. D. Baumann

As an aid in the development of an instrumentation system capable of identifying and measuring the accumulation of fission products in high-temperature gas-cooled reactor loop circuits and loop components, the applicability of the following systems as HTGR component plateout monitors was examined: ionization chambers, beta and gamma spectrometers, charged-wire precipitators, Cerenkov detectors, filters, diffusion tubes, thermal gradient tubes, deposition tubes, and impactors. On the basis of this study

it was concluded that the deposition tube and the gamma spectrometer systems showed the most promise for further development.

SLIP AND CREEP IN POLYATOMIC GAS MIXTURES[1]

B. K. Annis and E. A. Mason[2]

At pressures somewhat less than those for which a gas behaves entirely as a continuum, the finite mean free path manifests itself as corrections to the boundary conditions for the Navier-Stokes equations. These corrections take the form of various apparent discontinuities in macroscopic variables at the boundaries, and are known by such names as viscous slip, thermal creep, diffusive slip, and temperature jump.

In this work it was shown how the corrections for viscous slip, thermal creep, and diffusive slip can be readily obtained from the results of standard continuum kinetic theory by the conceptual trick of regarding the solid boundary as one component of a gas mixture. (This is sometimes called the dusty-gas model when applied to porous media.) The manipulations become particularly simple where the gas pressure may be considered "high" (that is, the mean free path is much smaller than any geometric dimension of the apparatus). In this manner it was possible to obtain for the first time explicit expressions for slip and creep in polyatomic gas mixtures. The most significant result thus obtained is that the thermal creep depends only on the translational parts of the thermal conductivity and thermal diffusion coefficients.

[1]Phys. Fluids 00, 0000 (1970).

[2]Division of Engineering, Brown University.

ROTATIONAL COLLISION NUMBERS OF N_2, O_2, CO AND CO_2 FROM THERMAL TRANSPIRATION MEASUREMENTS[1]

A. P. Malinauskas, J. W. Gooch, Jr., B. K. Annis, and R. E. Fuson[2]

The phenomenon of thermal transpiration has been shown to provide an accurate method for the determination of the contribution to thermal conductivity arising from the flux of translational energy. Since this quantity is sensitive to the rotational-translational energy exchange which often occurs in collisions involving polyatomic gas molecules, information

about the probability of this type of exchange, as expressed by the "rotational collision number," may be obtained. In the present work thermal transpiration data were obtained for N_2, O_2, CO, CO_2 and all the noble gases at a characteristic temperature of 504°K. In terms of the model adopted to describe the phenomenon, helium was found to be anomalous. It was likewise demonstrated that modifications in the model were also necessary in the treatment of the remaining gases. The necessary alterations, presumably resulting from accommodation effects, were taken into account by a curve fitting procedure. As a result, the significance of some of the parameters is open to question, and this in turn has led to alternate methods of data analysis. Several possible ways of treating the data were therefore considered, but the final results proved to be relatively insensitive to the method selected. Application of the model in the lowest approximation yields the following rotational collision numbers: N_2, 6.0; O_2, 2.2; CO, 1.3; CO_2, 1.9.

[1]J. Chem. Physics 00, 0000 (1970).

[2]Physics Department, Tennessee Technological University.

COMPOSITION DEPENDENCE OF THE THERMAL DIFFUSION FACTOR OF A DUSTY GAS[1]

B. K. Annis, A. P. Malinauskas, and K. S. Yun[2]

The separation of the components of a binary gas mixture in the presence of a temperature gradient is characterized by a parameter α_T, the thermal diffusion factor, which is a complicated function of mass, intermolecular force, and concentration. Until recently analytic expressions for this quantity were available only for dilute gases possessing no internal degrees of freedom, so that all collisions were elastic, and for this type of gas one important simplification was found to exist; to a very good approximation $(\alpha_T)^{-1}$ depends linearly on mole fraction. This approximation becomes progressively more accurate as the mass difference increases, and plays a crucial role in the "dusty-gas" model description of thermal transpiration in which the flow of a gas through a porous medium is regarded as a diffusion problem where one of the components is infinitely massive.

However, theoretical work in gas transport has now progressed to a point where polyatomic molecules, and subsequently inelastic collisions, may be accurately described. The thermal diffusion factor proves to be relatively sensitive to such collisions. The present study finds that as a consequence of inelastic collisions, the linear dependence of $(\alpha_T)^{-1}$ on composition is no longer valid even in the limit wherein one of the components is infinitely massive.

[1] J. Chem. Phys. 52, 1992 (1970).

[2] Department of Chemistry, University of Mississippi.

PART VI. NUCLEAR SAFETY

KINETICS OF THE STEAM-GRAPHITE REACTION

C. M. Blood and A. P. Malinauskas

Steam leakage into the coolant of a high-temperature gas-cooled nuclear reactor was recognized as an undesirable contingency at virtually the inception of this reactor concept, owing to the potential such inleakage has for the deterioration of the graphite core structure and the generation of hydrogen and carbon monoxide. Unfortunately, studies of the steam-graphite reaction, with an aim toward a practical definition of safety limits, necessarily involve a description of several phenomena which are coupled in a complex way.

As an example of this coupling, the rate of reaction is partially determined by the extent of graphite surface exposure, which is, in turn, altered by steam attack. Thus in this example two mechanisms must be specified: one that describes the reaction rate dependence upon exposed surface area, and another that specifies the changes in surface area as a result of steam attack.

Several attempts have been made to present a unified mathematical description of the overall process. The most promising of these to date concerns a quasi-steady-state argument for the special case in which all aspects involving diffusional transport of the steam may be neglected, a condition which we have been able to approximate quite well by using an EGCR moderator-type graphite. This argument, coupled with a semiempirical expression for the extent of surface area development with carbon removal, has been found to yield an adequate representation of the experimental data.

IN-PILE BEHAVIOR OF HTGR FUEL ELEMENTS IN MIXTURES OF STEAM AND HELIUM

S. H. Freid, W. H. Montgomery, H. J. de Nordwall, O. Sisman

The objective of these experiments is to demonstrate that rate constants measured out-of-pile can be used to describe the way carbon is removed from an operating HTGR fuel element.

An experiment to study the in-pile behavior of HTGR fuel elements in mixtures of steam and helium has been described previously.[1] It has been constructed and awaits safety review. In the first experiment we aim to demonstrate the superior resistance of SiC coated fuel particles to steam in the improbable situation where the exposure to steam is sufficiently prolonged to destroy a large part of the protective carbon matrix and its carbon envelope. Future experiments will be concerned with demonstrating the protection the fuel and matrix receive from the surrounding structural graphite when there is a steep radial temperature gradient.

[1]S. H. Freid, H. J. de Nordwall, B. F. Roberts, O. Sisman, and W. H. Montgomery, Reactor Chemistry Div. Ann. Prog. Rept. Dec. 31, 1968, ORNL-4400, 1970, pp. 120.

THE IMPORTANCE OF TRANSIENT EFFECTS IN HIGH-TEMPERATURE GAS-COOLED REACTOR FUEL ELEMENT OXIDATION

H. J. de Nordwall, M. N. Ozisik[1]

The need to use transient solutions to the equations describing the reaction of steam with graphite has been examined in detail after it had been observed[2] that the gas transport characteristics of a sample of EGCR moderator type graphite did not vary sufficiently rapidly early in the reaction to explain the observed increase in reaction rate with extent of reaction.

The rate, extent, and spatial variation of carbon loss from a graphite cylinder exposed to steam had been calculated as a function of time. The geometrical arrangement considered was a hollow cylinder with a helium-steam mixture on the inside. At the outer boundary either a zero concentration or a zero steam flux was maintained. The reaction was assumed to be first order. Changes in the rate of carbon removal with extent of reaction, other than those associated with establishing a steady-state steam concentration gradient, were not considered.

Calculations using constants derived from current experimental work[3] led us to conclude that the time needed to establish a concentration gradient is insignificant compared with the times for which the hot core of a high temperature gas-cooled reactor could be accidentally exposed to steam. This conclusion could change if very much tighter graphites, or more massive sections, equivalent to thicker cylinders in our analysis, were to be used in future gas-cooled reactors.

[1]North Carolina State University, Raleigh, N. C.

[2]A. P. Malinauskas, C. M. Blood, J. W. Gooch, Jr., and B. K. Annis, Nuclear Safety Program Ann. Prog. Rept. Dec. 31, 1968, ORNL-4374, p. 295, 1970.

[3]A. P. Malinauskas and C. M. Blood, Nuclear Safety Program Ann. Prog. Rept. Dec. 31, 1969, ORNL-4511, p. 85, 1970 and unpublished work.

AN ANALYSIS OF THE PROTECTION OF FUEL MATRICES BY A SURROUNDING CARBON ENVELOPE

H. J. de Nordwall and G. M. Watson

A two-zone reacting system representing a graphite outer envelope and a more reactive fuel matrix has been examined theoretically using a steady-state analysis in plane geometry, to investigate how well the outer graphite envelope (Zone 1) might protect the hotter and more reactive fuel matrix (Zone 2). The boundary conditions considered were a constant steam concentration at the steam-graphite interface and a zero steam flux at the inner fuel boundary (z = 0). If J_a is the steam flux at z = a where x_1, the mole fraction of steam, is x^o, and J_b is the steam flux at z = b, the graphite-fuel interface, then one can show[1] that

$$J_b/J_a = \frac{\left[\dfrac{D'_2\ \varepsilon_{t2}\ k_2}{D'_1\ \varepsilon_{t1}\ k_1}\right]^{1/2} \tanh b/L_2}{\sinh\ (a-b)/L_1 + \cosh\ (a-b)/L_1} ,$$

where

$$L_i \equiv \left[\frac{D'_i n}{k_i\ \varepsilon_{ti}}\right]^{1/2} ,$$

D_i' is the effective diffusion coefficient for the system He-H_2O in the relevant zone, k_i is the rate constant for the reaction of steam with carbon, assumed to be first order in this instance, ε_{ti} is the open porosity of the medium and n is the total molecular density in the steam-helium mixture. The number of CO and H_2 molecules present is assumed to be insignificant.

At constant temperature J_b/J_a decreases exponentially as $(a-b)/L_1$ increases, after $(a-b)/L_1 > 1$, for likely values of the numerator which is a measure of the relative reactivity of the carbon in the two zones. However as the temperature of both zones is allowed to rise, J_b/J_a falls rapidly because a second exponential variation, that of k with temperature, is introduced. Since one may assume that J_b represents the rate of removal of carbon from Zone 2, one is led to expect a sharply defined temperature above which the fuel matrix is well protected by the structural graphite, provided that the diffusional mechanisms considered here apply in real situations.

[1]H. J. de Nordwall and G. M. Watson, Nuclear Safety Program Ann. Prog. Rept. Dec. 31, 1969, ORNL-4511, p. 89, 1970.

CESIUM RELEASE FROM A BONDED BED OF BISO COATED UO_2 PARTICLES DURING A POSTIRRADIATION ANNEAL AT 1250°C

M. T. Morgan and R. L. Towns

Coated particle fuels, in which the coatings consist of a silicon carbide layer which is interspersed between two dense pyrocarbon layers, retain fission products quite well under normal reactor operational conditions. For some high-temperature gas-cooled reactor applications however, it is advantageous to eliminate the silicon carbide layer, so that the resulting "BISO" coating is comprised of a porous carbon layer over which is deposited a dense isotropic layer of pyrolytic carbon. Unlike the TRISO coatings which contain the silicon carbide, these BISO coatings can be penetrated more readily by some of the fission products, such as Ba, Sr, and Cs. Moreover, the cesium which is released could contaminate the heat exchangers and other auxiliary equipment, and thus

cause a maintenance problem. To evaluate this problem we are annealing a bonded bed of BISO coated particles, which had been irradiated to 20% burnup of ^{235}U, to determine the retention of cesium and strontium by the coated particles and the matrix of the bonded bed. The bonded-bed is enclosed in a graphite can and contains approximately 100 coated UO_2 particles.

The sample has now accumulated 1500 hours annealing time at 1250°C. We plan to terminate the anneal at 2000 hours, at which time the bonded bed will be analyzed to determine the distribution of cesium and strontium in the coated particles, the matrix, the can, and the furnace components. An analysis of the furnace tube and liner has indicated a Cs release of approximately 5% at 1000 hours and 9% at 1300 hours. Up to now, no coating failures have been detected; such failures would certainly be obvious through the appearance of ^{85}Kr in the continuously monitored helium sweep gas.

BEHAVIOR OF IODINE IN ZIRCALOY CAPSULES

Horst Feuerstein[1]

The behavior of iodine in Zircaloy capsules in the temperature range 400-800°C was investigated. The experimental conditions represented a simplified model of the inner cladding surface of a water-cooled reactor fuel rod. Elemental iodine containing either ^{130}I or ^{131}I was condensed in the Zircaloy capsules, which were then sealed by fusion welding at high vacuum. After heat treatment for a period sufficiently long to allow thermodynamic equilibrium at a particular temperature, each capsule was opened. The material in the gas phase diffused out of the capsule and was collected along a thermochromatographic tube and analyzed by gamma spectrometry.

The following reaction chain was assumed: (1) chemisorption of the iodine on the metal surface, (2) reaction of the chemisorbed iodine with the metal to form ZrI_4, (3) chemisorption of the ZrI_4 on the metal surface, and (4) reaction of the chemisorbed ZrI_4 with the metal to form lower iodides.

A series of thermodynamic calculations, based on reported values for the properties of ZrI_2, ZrI_3, and ZrI_4, were performed, and the results were compared with the experimental data. The iodine release behavior at 400°C could be explained reasonably well with this model; however, the iodine behavior at higher reaction temperatures appears to be more complex, and probably involves intermediate phases which decompose rapidly to other species.

[1]Research participant from Gesellschaft F. Kernforschung, Karlsruhe, Germany.

ADSORPTION AND DESORPTION OF IODINE AND IODIDES FROM METAL SURFACES

E. Hoinkis[1]

The goal of this investigation is a description of the chemistry of iodine in high temperature gas-cooled reactors, in particular in relation to its retention on steam generator and other metallic surfaces.

The partial pressures of the various iron iodides in equilibrium with gaseous iodine, solid iron and solid FeI_2 have been calculated as functions of temperature and pressure, and existing information on the kinetic and equilibrium properties of this system and the system $Fe(s)-FeI_2(s)-H_2O(g)$ have been reviewed. The conclusion reached was that the region of low iodine concentration likely to be found in a reactor had not been investigated well enough, since both the equilibrium and the kinetic data lacked precision and definition. Experiments have therefore been designed to study the adsorption of iodine and FeI_2 on iron and Fe_3O_4. Desorption rates in vacuo, helium and mixtures of helium and steam will also be measured.

[1]Research Participant from Hahn-Meitner Institut für Kernforschung, Berlin, Germany.

AEROSOL FILTRATION

R. E. Adams, R. J. Davis, and J. Truitt

A study[1] has been made of the filtration of radioactive agglomerate particles of oxide mixtures by commercial high efficiency fibrous filter media. The objective was to ascertain the effects of environmental conditions, which are possible in a nuclear reactor containment filter system after a severe accident, on the filtration efficiency of the filter media.

The aerosols which were used in this study were generated in electric arcs, using activated metal samples. The filtration efficiencies were measured in a system consisting of three filters in series; the efficiency of filtration was taken to be the ratio of activity found on the first filter to the total activity found on all three filters.

Filtration efficiencies of several commercial media were measured as a function of temperature (25-100°C), aerosol velocity (3.5-10 ft/min), relative humidity (0-100%), and particle substance (UO_2-stainless steel oxide mixture, ZrO_2-UO_2 mixture, and dioctyl phthalate). Small decreases in efficiency were observed on increasing the temperature, velocity and humidity. Particle substance had no discernible effect; nor were significant differences observed between the samples of commercial media which were employed.

The oxide aerosols were experimentally characterized as to particle size distribution and samples of filter media were characterized as to fiber size distribution. These data, along with existing theory, allowed approximate estimates to be made concerning the effects of environmental parameters (temperature, humidity and air velocity) on filtration efficiency.

[1] R. J. Davis, J. Truitt, J. S. Gill, and R. E. Adams, "Removal of Radioactive Aerosols on High Efficiency Fibrous Filter Media," ORNL-4524, April 1970.

AEROSOL BEHAVIOR IN CONTAINMENT STRUCTURES

R. E. Adams, R. J. Davis, and J. S. Gill

Part of the radiological dose to personnel near a reactor accident might be due to radioactive smoke. The objective of this work is to enable a prediction of such a dose; specifically, it is to provide a means of estimating the concentration of radioactive aerosol in a containment vessel as a function of time after an accident.

There are two aspects of the program; one conceptual, the other experimental. The conceptual effort has led to a computer calculation of aerosol mass concentration vs time as a consequence of smoke generation, coagulation, and settling. The calculation code is based on a postulated, steady-state particle size distribution function.[1,2] This makes possible a macroscopic description of the aerosol (in contrast to the more usual microscopic, particle by particle, description). The resulting calculation is straightforward; values of concentration vs time which have been calculated in this manner have been shown[3,4] to fit available experimental data very well.

There are several aspects of the code which require further development. The more important of these are: (1) a demonstration that the assumed size distribution function is adequate, and (2) a determination of the dependence of the maximum and minimum particle sizes on time and environmental conditions. The experimental program has therefore been oriented to satisfy these requirements. The apparatus which is employed essentially consists of a four-inch diameter pipe. Metal oxide particles are generated at one end of the pipe in an electric spark and are blown down its length. The aerosol is then sampled at the other end of the tube and the particle size distribution determined. Varying the tube length, tube diameter, and the flow rate enable us to vary the initial concentration, age and Reynolds number of the aerosol, whereas the humidity is varied by adding water to the inlet air.

The data obtained thus far suggest that: (1) the postulated size distribution function between sharply defined maximum and minimum particle sizes is an adequate representation of the aerosols, and (2) that

the minimum size increases and the maximum size decreases with time.

[1]S. K. Freidlander and C. S. Wang, J. Coll. Int. Sci. 22, 126-132 (1966); 24, 170-179 (1967).

[2]B. Y. H. Liu and K. T. Whitby, J. Coll. Int. Sci. 26, 161-165 (1968).

[3]R. J. Davis, "Estimation of Aerosol Concentration in a Nuclear Reactor Containment After an Accident," The Proceedings of the International Congress on the Diffusion of Fission Products, Saclay, France, Nov. 4-6, 1969, Societe Francaise de Radioprotection, 26 Rue d'Ulm, 75-Paris, France.

[4]R. J. Davis, "A Simple Model for the Estimation of Aerosol Concentration in a Closed Vessel," to be published in Am. Ind. Hyg. Assoc. J.

THE FUNCTION OF CONDENSING STEAM IN WET AEROSOL SCRUBBERS

R. J. Davis and J. Truitt

The worst part of particulate air pollution consists of small particles, approximately in the size range 0.2-2 microns. These are the particles that are most apt to evade the trapping devices in the human breathing system, that are almost wholly responsible for reduced visibility, and that coagulate and settle slowly, and hence have long airborne lifetimes. These are also the particles that are most difficult to filter or scrub out of polluted air. The objective of this program has been to observe the influence of condensing steam on the growth of particles within this size range in the hope that the effect might enhance the efficiency of wet aerosol scrubbers.[1]

Five particle substances have been studied: (1) iron oxide, (2) chromium oxide, (3) stainless steel oxide, (4) dioctyl phthalate (DOP), and (5) latex. The oxide aerosols contained particles of wide size distribution; the DOP and latex particles were of narrow size distribution.

The results suggest that: (1) the steam condenses on the particles rather than on the walls in the case of both hydrophobic as well as hydrophilic substances; (2) the particles are swept toward the walls by thermophoresis; and (3) particle growth due to steam condensation

increases the removal efficiency. In terms of practical implications: (1) condensing steam does tend to remove particles in the size range 0.2 to 2 microns diameter, (2) a device based on thermophoresis sweep alone would probably not be economically feasible, and (3) a device which takes advantage of particle growth in condensing steam as well as thermophoresis appears to be quite feasible.

[1] J. Truitt and R. J. Davis, "The Function of Condensing Steam in Wet Aerosol Scrubbers," to be published in Am. Ind. Hyg. Assoc. J.

RADIOIODINE TRAPPING IN OFF-GAS SYSTEMS OF FUEL REPROCESSING PLANTS

R. E. Adams, R. D. Ackley, and Zell Combs

Radioiodine trapping by solid sorbents is being investigated as a part of a Chemical Technology Division program concerned with the prevention of iodine release from Liquid Metal Fast Breeder Reactor (LMFBR) fuel reprocessing plants. In this phase of the program, considerable emphasis has been given to determining the applicability of silver zeolite for removing volatile forms of radioiodine from air streams. The silver zeolite, as employed here, is prepared by treating Linde Molecular Sieves Type 13X (sodium zeolite), 1/16 in. pellets, with silver nitrate solution, and represents a development of Maeck, Pence, and Keller at Idaho Nuclear Corporation.[1]

A group of experiments was performed to establish approximately the effective capacity of silver zeolite for trapping iodine in the forms of methyl iodide and butyl iodide (1-iodobutane) at 100 and 200°C. This sorbent ($AgNO_3$-treated 13X) was observed to be highly effective ($\geq$ 99.9%) for trapping airborne iodine as either methyl iodide or butyl iodide at 100 and 200°C for iodine loadings at least as high as 20 mg per cm^3 of sorbent. The corresponding air face velocities were 50 fpm at 100°C and 63 fpm at 200°C. Certain other sorbents were also investigated in these experiments but they exhibited poorer performance, especially at high loadings.

Tests are being made of the susceptibility of the silver zeolite to poisoning by airborne impurities and to damage by abnormal operating conditions. These studies are far from complete, but present indications are that this trapping agent will withstand such deleterious effects as well if not better than most sorbents that might be considered.

The principal known drawback as regards the use of silver zeolite is its high cost. Accordingly, the efficacy of zeolites with cations other than silver has been investigated using preparations with 13X type of zeolite as the base. Of the materials obtained by treatment with some 17 solutions of different metal salts, only those corresponding to cadmium or potassium showed some promise. Cadmium and potassium zeolite (13X-based) were found highly effective for trapping iodine, as methyl iodide, at 200°C at low iodine loading (around 0.4 mg/cm^3); unfortunately they were not as effective as may be required at high loadings. Further work on the development of less expensive sorbents as well as on the applicability of silver zeolite is planned.

[1] W. J. Maeck, D. T. Pence, and J. H. Keller, A Highly Efficient Inorganic Adsorber for Airborne Iodine Species (Silver Zeolite Development Studies), IN-1224 (October 1968).

TRAPPING OF RADIOACTIVE METHYL IODIDE FROM FLOWING STEAM-AIR BY IODIZED CHARCOAL

R. E. Adams, R. D. Ackley, and Zell Combs

The use of iodized charcoal for decontaminating radioactive methyl iodide ($CH_3{}^{131}I$) transported in flowing steam-air has been investigated in two series of tests sponsored by the Nuclear Energy Systems Division of Westinghouse Electric Corporation. In the first series[1] of tests the effects of a reactor accident environment on charcoal efficiency were studied; in the second series of tests the additional effect of containment spray solution applied to the charcoal was considered. Approximate conditions for each decontamination test included 130°C (266°F), 55 psia, steam-air face velocity of 40 fpm, 6 mg CH_3I/m^3 (except for two tests with 80 mg/m^3), 1.5 hr CH_3I injection time, and a calculated average relative humidity (R.H.) of 94% or higher. All of the tests were on one type of iodized charcoal, MSA 85851. The test bed dimensions were 3.5 in. in diameter and 2 in. deep. Two modes of flow, downward and upward, were employed. The aqueous spray solution contained 2000 ppm boron, on a weight basis, added as $Na_2B_4O_7$.

First Test Series

In tests with ^{131}I-labeled CH_3I at 6 mg/m^3, and with perforated metal used to retain the charcoal, $CH_3{}^{131}I$ decontamination efficiencies (D.E.'s) ranging from 30.7 to 98.6% were observed, depending to a considerable extent on the degree to which the charcoal was wetted with condensed steam. The effect of gross wetting or flooding of the charcoal and then purging with (approximately) 100% R.H. air on the subsequent D.E., also at 100% R.H., was investigated. With downward flow, D.E.'s of 10 to 19% were obtained; with upward flow, the D.E.'s were 3 to 5%. In tests with CH_3I at 80 mg/m^3, only a slight lowering in $CH_3{}^{131}I$ D.E., relative to tests at 6 mg/m^3, was observed. (These results were similar in this respect to those obtained previously for MSA 85851 iodized charcoal at room temperature.)

Second Test Series

Applying 2000 ppm boron spray solution into the charcoal to the extent of 20 or 40 wt % resulted in a small to moderate loss in $CH_3{}^{131}I$ decontamination capability. In a test where charcoal flooding plus 147 wt % spray injection pertained, the overall loss in decontamination capability was large, but

was not much larger than that observed when flooding (to a similar degree) alone was induced.

[1]R. D. Ackley and R. E. Adams, Trapping of Radioactive Methyl Iodide from Flowing Steam-Air: Westinghouse Test Series, ORNL-TM-2728 (December 1969).

[2]R. D. Ackley and R. E. Adams, Effect of Containment Spray Solution on Trapping of Radioactive Methyl Iodide from Flowing Steam-Air by Iodized Charcoal: Westinghouse Test Series, ORNL-TM-2805 (January 1970).

AGING, WEATHERING, AND POISONING OF IMPREGNATED CHARCOALS USED FOR TRAPPING RADIOIODINE

R. E. Adams, R. D. Ackley, and Zell Combs

Aging, weathering (exposure to flowing air), and poisoning are processes which might adversely affect charcoal performance, especially with regard to trapping radioiodine in the form of methyl iodide (CH_3I). Accordingly, some effort has been applied toward investigating the effects of the above processes. The bulk of the data obtained, and which have been reported[1], is representative of four different types of charcoal. Three types are iodized, thus providing ^{131}I trapping capability via isotopic exchange, and the other is triethylenediamine-impregnated. The influences of the processes were examined by observing the variation in ^{131}I of $CH_3{}^{131}I$ removal capability for the iodized charcoals or in CH_3I removal capability for the amine-impregnated charcoal. The results, which were generally in accord with expectation, indicated the following: (1) aging, per se, has little or no effect on impregnated charcoal performance; (2) weathering with air at around 50% relative humidity has an appreciable detrimental effect; and (3) poisoning of iodized charcoal can have a large detrimental effect on the methyl iodide efficiency.

[1]R. D. Ackley, Zell Combs, and R. E. Adams, Aging, Weathering, and Poisoning of Impregnated Charcoals Used for Trapping Radioiodine, ORNL-TM-2860 (March 1970).

IGNITION OF CHARCOAL ADSORBERS BY FISSION PRODUCT DECAY HEAT

R. E. Adams and R. P. Shields

Charcoal adsorbers are used in reactor safety systems to assist in the removal of the large quantities of iodine which could be released into the containment atmosphere following an improbable reactor accident. The heat generated by decay of radioiodine trapped in the adsorbers is expected to be dissipated under normal air flow conditions but a potential fire hazard could be created if the air flow is reduced or interrupted. This hazard is being evaluated.

To aid in the assessment of the effects of decay heat in a charcoal adsorber a basic differential equation was developed to specify the temperature profile which would develop from a specified loading of radioiodine on a charcoal adsorber. The differential equation accounts for the multiple, position-dependent, time dependent heat source resulting from decay of radioiodine with the attendant beta and gamma emission into the charcoal mass, and the loss of heat as a result of gas flow through the charcoal mass.

The original computer program was developed to allow the computation of temperature profiles through the depth of the charcoal mass and accounted for heat loss only to the flowing air. However, the original program has been replaced recently with an adaptation of a more general heat transfer computer program which will compute temperature profiles in the three dimensions of a charcoal adsorber. This program incorporates a subroutine so that any analytical function dependent on position, time and temperature can be used in the heat generation term; it also has the flexibility of accommodating changes in physical properties of the adsorber system as functions of temperature.

In the laboratory, measurements have been made of those physical properties of charcoal which are required for inclusion in the computer program. These measurements include heat capacity and thermal conductivity as functions of temperature, the volumetric heat transfer coefficient for various air flow rates through the bed, bed porosity, and pressure drop through the charcoal as a function of flow rate.

COMPARATIVE NATURAL DEPOSITION BEHAVIOR OF RADIOIODINE IN TWO DIFFERENT CONTAINMENT ENVIRONMENTS

G. W. Parker, G. E. Creek, and W. J. Martin

The deposition behavior of radioiodine released into a steam and air filled test containment tank (CRI), presenting in one case surfaces of polished stainless steel and in another case a painted metal surface consisting of a typical epoxy type material known as Amercoat-66, has been studied in a joint ORNL-LOFT Fission Product Behavior Program. Four types of tracer radioiodine were employed: elemental iodine, methyl iodide, a mixture of the two, and a mixture containing I_2 and CH_3I in which a small fraction was also adsorbed on vaporized particles, such as SnO_2.

We found that in the presence of exposed stainless steel, initially extremely rapid chemisorption takes place involving only the reactive species (I_2 or HI); while in the painted containment, the chemisorption process which affects both reactive and organic iodine is slowed by an order of magnitude. In contrast to the stainless steel surface the Amercoat paint adsorbs methyl iodide in a relatively rapid process although slower than the rapid chemisorption of free iodine onto the stainless steel surfaces.

Approximate half-times which were observed for deposition in each containment environment are tabulated below:

$T_{1/2}$ (Half-Time for Deposition)

	SS Containment	Amercoat-66
I_2	2-5 minutes	20 minutes
CH_3I	No deposition	20-360 minutes
Particulate	90 minutes (settling)	90 minutes (settling)

FUEL ROD FAILURE IN SIMULATED LOSS-OF-COOLANT ACCIDENTS

R. A. Lorenz and G. W. Parker

Large water-cooled power reactors provide emergency cooling systems to prevent excessive fuel rod temperatures even though many fuel rods have failed. We are examining modes of fuel rod failure under loss-of-coolant accident conditions for water-cooled reactors using seven-rod clusters of Zircaloy-clad UO_2 fuel rods exposed in the Transient Reactor Test Facility (TREAT). In such tests, where fissioning in the UO_2 fuel pellets provides realistic simulation of such an accident, we hope to assess the extent to which swelling and rupture of the fuel rods will reduce the effectiveness of the emergency cooling measures.

The first experiment in this series used rods which were filled with helium (to simulate accumulated fission gases) at pressures between 115 and 215 psia (at 25°C). The reactor transient was sized to yield a maximum cladding temperature of about 1000°C in the simulated accident. All the rods swelled and ruptured; the swelling was sufficient to block 50% of the cooling channel area over several inches of rod length. Release of ^{133}Xe and ^{131}I from the center rod (previously irradiated separately to 650 megawatt days per metric ton) was 0.1 to 0.2% of the inventory, 0.05% of the ^{137}Cs was released and 0.0008% of the low volatility fission products (Ru, Ba, Sr, Ce, and Zr) were released. A relatively large fraction (6.7%) of the released ^{131}I was in a chemically unreactive form and was probably present as CH_3I.

The second experiment was performed using Zircaloy-4 clad rods which were pressurized with 65 to 75 psia helium (25°C) and surrounded by a heat-reflective sleeve; a maximum cladding temperature of approximately 1300°C was attained. Average diametral increase at the rod rupture location was 60% (compared with 36% in the first experiment) and in both experiments the ruptures occurred within 2-1/4 in. of axial length. Approximately 1.1% of the zirconium cladding reacted with steam compared with 0.2% in the first experiment. The hole formed when the center irradiated rod (previously irradiated to 2500 Mwd/MT) ruptured was very small so that fission product release was generally less than in the first experiment.

RUPTURE TESTS OF IRRADIATED FUEL RODS

M. F. Osborne and G. W. Parker

Irradiation effects may influence the rupture properties of the Zircaloy cladding on the fuel rods used in water-cooled, power reactors. Consequently, experimental work comparing the rupture characteristics of unirradiated Zircaloy tubing and both unirradiated and irradiated Zircaloy-clad UO_2 power reactor fuel rods is being conducted. The experimental parameters are based on the conditions predicted for a hypothetical Loss-of-Coolant Accident.[1,2]

The experimental equipment[3] is located in a hot cell, and is operated remotely. The 0.565 in. diameter fuel rods,mounted vertically in concentric quartz tubes in a flowing atmosphere of steam and argon, are heated by high frequency induction. Cladding temperature is monitored by thermocouples, and the internal gas pressure of the fuel rod is monitored by a pressure cell. The rods are pressurized with argon from 50 to 400 psig and heated to rupture at heating rates of between 10 and 50°F/sec.

The fuel rods were found to rupture at temperatures in the range 1600 to 2000°F, varying inversely with internal pressure. In general, the rods swelled 25 to 50% of circumference in the rupture area. Such swelling, which is significant since it may limit emergency core cooling in an accident, was maximized at low pressure and moderate heating rate. No significant differences in tests of unirradiated and irradiated rods up to a burnup of 7000 Mwd/T, have been observed. The data compare well with the results of in-reactor transient tests.[4]

[1] P. L. Rittenhouse, Failure Modes of Zircaloy-Clad Fuel Rods, USAEC Report ORNL-TM-2347, Oak Ridge National Laboratory, 1968.

[2] P. L. Rittenhouse, Failure Modes of Zircaloy-Clad Fuel Rods, Part 2: Program Revisions, USAEC Report ORNL-TM-2548, Oak Ridge National Laboratory, 1969.

[3] M. F. Osborne and G. W. Parker, Design, Equipment, and Program for Fuel Rod Burst Experiments, USAEC Report ORNL-TM-2850, Oak Ridge National Laboratory, 1970.

[4] R. A. Lorenz and G. W. Parker, TREAT Fuel Rod Failure Loss-of-Coolant Experiment, this report.

THE EFFECT OF THIRD COMPONENT ADDITIVES ON THE REACTION RATE OF CH_3I WITH $Na_2S_2O_3$

B. A. Soldano and W. T. Ward

One problem of concern in the design of light-water reactors is the rapid removal of methyl iodide from the atmosphere of the containment building in the event of a loss-of-coolant accident. The most desirable solution, however, is one which can be readily adapted without major modification to the methods currently employed to mitigate the more serious consequences of loss-of-coolant accidents. In spray systems, for example, an effective catalyst-additive combination, in low concentration, would be welcome. Such a combination is presently being sought.

Those ions which enhance the electronic transitions between short-lived singlet states and long-lived triplet states of organic molecules appear to be likely catalysts,[1] and it is on this basis that investigations of the catalytic activity of $Ni(NH_3)_4SO_4$ on the reaction between $Na_2S_2O_3$ and CH_3I had been performed. The effectiveness of this catalyst is demonstrated in the table below, wherein we have tabulated reciprocal pseudo first order rate constants for the reaction between dilute ($\sim 10^{-8}$ molar) amounts of CH_3I and 0.13 normal $Na_2S_2O_3$ in a pH 9.3 borated solution.

Temperature (°C)	1/k, Reciprocal of Pseudo First-Order Reaction Rate Constant	
	With Trace Catalyst	Without Trace Catalyst
25	6.3	12.3
30	4.7	6.1
35	2.7	3.9
40	1.8	2.8
50	0.7	1.3
60	0.3	0.6

Note also that the approximate two-fold increase in reaction rate appears to be unaffected by temperature, over the range investigated.

[1] P. J. Wagner and G. S. Hammond, in Advances in Photochemistry, Vol. 5, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, editors, Interscience Publishers, New York, 1968, pp. 21-153.

[2] Ruth Slusher, R. L. Bennett, and R. E. Adams, Nuclear Safety Program Ann. Progr. Rept. for Period Ending Dec. 31, 1969, pp. 60-62, March 1970.

COMPARISON OF MATERIALS IN IODINE-ABSORBING SPRAY SOLUTIONS

J. C. Griess and A. L. Bacarella

During the past year a program to determine the corrosion resistance of many materials in iodine-absorbing spray solutions (0.15M NaOH-0.28M H_3BO_3 either with or without 0.064M $Na_2S_2O_3$) from 35 to 140°C was completed and the results have been published.[1] The principal conclusions are summarized below.

At all temperatures iron- and nickel-base alloys and Zircaloy-2 have adequate corrosion resistance in both solutions. Even with 100 ppm chloride,cracking of the austenitic stainless steels was not observed. Aluminum alloys undergo very severe attack at all temperatures producing H_2. Copper corrodes appreciably in the presence of thiosulfate but not in its absence; alloying with nickel reduces its corrosion rate. Zinc on galvanized surfaces corrodes but the actual rates were not determined. Concrete was not deleteriously affected on exposure to either solution during simulated reactor accident conditions, and several proprietary organic coatings were stable under the same conditions. The latter results were published separately.[2]

[1] J. C. Griess and A. L. Bacarella, "Design Considerations of Reactor Containment Spray Systems, Part III. The Corrosion of Materials in Spray Solutions," ORNL-TM-2412 (December 1969).

[2] J. C. Griess, T. H. Row, C. D. Watson and G. A. West, "Design Considerations of Reactor Containment Spray Systems, Part V. Protective Coating Tests," ORNL-TM-2412 (to be issued).

PART VII. SPECIAL RESEARCHES

THE EFFECTS OF NEUTRON IRRADIATION ON CARBIDES OF REFRACTORY METALS

G. W. Keilholtz, R. E. Moore, and H. E. Robertson

Polycrystalline specimens of the monocarbides of Ti, Zr, Ta, Nb, and W were irradiated in the Engineering Test Reactor (ETR) over three temperature ranges: 60 to 130°C; 130 to 415°C; and 1000 to 1100°C.[1-3] Metallographic examinations revealed no separation at grain boundaries even in specimens irradiated to fast fluences greater than 4×10^{21} neutrons/cm^2 (> 1 MeV). At the lower temperatures, however, fluences greater than 2×10^{21} neutrons/cm^2 caused gross fracturing of specimens of the carbides of Zr, Ta, and Nb. The external dimensions of all five carbides increased rapidly at the beginning of irradiation, but then leveled off at what may be regarded as saturation levels. There were shrinkages below these levels after exposure to very high fluences. The saturation levels were about the same for the two lower temperature ranges, but in-reactor thermal annealing at 1000-1100°C substantially reduced the saturation levels and also virtually eliminated gross fracturing of specimens, at least up to the highest fluences attained (4 to 5×10^{21} neutrons/cm^2). Lattice parameter measurements and out-of-reactor thermal annealing of specimens irradiated over the intermediate temperature range (130 to 415°C) indicated that defect clusters as well as vacancies and interstitials were present.[4] The initial dimensional changes of the refractory metal carbides appear to be similar to those of cubic silicon carbide.[5] A damage model[4] based on competing rate processes for the production and annealing-out of both clusters and point defects has been developed which can adequately account for the behavior described above.

[1] G. W. Keilholtz, R. E. Moore, and H. E. Robertson, Reactor Chem. Div. Ann. Prog. Rept. Dec. 31, 1968, ORNL-4400, pp. 147-148.

[2] G. W. Keilholtz, R. E. Moore, and M. F. Osborne, Nucl. Appl. 4 (5), 330-336 (1968).

[3] G. W. Keilholtz and R. E. Moore, Trans. Am. Nucl. Soc. 12 (1), 101 (1969).

[4] D. A. Dyslin, R. E. Moore, and H. E. Robertson, Fuels and Materials Development Program Quar. Progr. Rept. Sept. 30, 1969, ORNL-4480, pp. 245-254.

[5] R. P. Thorne, V. C. Howard, and B. Hope, Proc. Brit. Cer. Soc. 7, 449-459 (1967).

IRRADIATION OF COMMERCIAL ALUMINA CERAMICS CONSIDERED FOR USE AS THERMOINIC ELECTRICAL INSULATORS

G. W. Keilholtz, R. E. Moore, and H. E. Robertson

Specimens of four commercial alumina ceramics were irradiated at high temperatures in the Engineering Test Reactor (ETR) to evaluate their usefulness as electrical insulators in nuclear-powered thermionic converters.[1-3] The four types were: I, Coors AD-995; II, Wesgo AL-995; III, GE Opaque Lucalox; IV, GE Transparent Lucalox. Grain sizes were 13, 23, 6, and 25 μm, respectively. Over the temperature range 580 to 1070°C, specimens in which grain-boundary separation was absent increased linearly in volume from 1.8% to 3.1% over the fluence range 1.0 to 3.0 x 10^{21} neutrons/cm^2 (> 1 MeV). Type III alumina, which has a very small grain size, was the only type in which grain-boundary separation was always absent in the specimens examined metallographically. Gross fracturing, however, was related to purity rather than grain size, at least up to a fluence of 3.0 x 10^{21} neutrons/cm^2. None of the specimens of Types III and IV, the two purest types, fractured, but Type I, the least pure type, fractured most severely. Exposure of specimens of the same four types to fluences ranging from 3 to 6 x 10^{21} neutrons/cm^2 in another irradiation assembly produced more gross fracturing and also much greater expansion in volume. These results were probably due not only to an increase in the grain volume as the fluence was increased but also to additional grain-boundary separation caused by the increase in grain volume, which is anisotropic at high temperatures.[1,3] Based on the observed behavior, alumina for nuclear thermionic applications must be of high purity to minimize fracturing and of small grain size to minimize separation at grain boundaries.

[1] G. W. Keilholtz, R. E. Moore, H. E. Robertson, and D. A. Dyslin, Reactor Chem. Div. Ann. Progr. Rept. Dec. 31, 1968, ORNL-4400, pp. 148-150.

[2] G. W. Keilholtz and R. E. Moore, Nucl. Appl. 3 (11), 686-91 (1967).

[3] R. E. Moore, D. A. Dyslin, and H. E. Robertson, Fuels and Materials Development Program Quar. Progr. Rept. Dec. 31, 1969, ORNL-4520, pp. 245-252.

A NEUTRON DAMAGE MODEL TO DESCRIBE CHANGES IN PROPERTIES OF CARBIDES AS A FUNCTION OF FAST FLUENCE

R. E. Moore

A damage model is proposed to explain the saturation of dimensional changes and certain other properties of refractory carbides such as β-SiC, TiC, and ZrC during irradiation by fast neutrons.[1,2] It is assumed that defects resulting from atoms displaced in a collision cascade can be annealed out in a subsequent cascade that overlaps the region of a crystal that had been affected by the first cascade. The production and the annealing out of defects are treated as competing rate processes in which the values of the rate constants reflect the parameters of the system. Two types of displaced atoms - single displacements and displaced atoms residing in clusters (amorphous regions) - are recognized in the mathematical treatment.

The solution of the appropriate rate equations for the processes involved results in the expressions:

$$n_A/n_T = C_1 e^{-m_1(\emptyset t)} + C_2 e^{-m_2(\emptyset t)} + C_3$$

$$n_B/n_T = C_4 e^{-m_1(\emptyset t)} + C_5 e^{-m_2(\emptyset t)} + C_6$$

where n_A is the number of single displacements, n_B the number of displaced atoms residing in clusters, n_T the total number of atoms in the crystal, the C_i and m_i are complicated expressions in terms of the rate constants, and $(\emptyset t)$ is the fast-neutron fluence.

The atom fractions, n_A/n_T and n_B/n_T, approach constant values, C_3 and C_6, as $(\emptyset t) \rightarrow \infty$, similarly, any property that is a simple function only of these atom fractions will likewise approach a limiting value as $(\emptyset t) \rightarrow \infty$. Thus, saturation of property changes can be explained by this displacement model. Effects of transmutations, gas generation, and other effects are ignored in the model, but their importance may be evaluated by comparing actual changes in properties of a material with those predicted from the model.

[1] R. P. Thorne, V. C. Howard, and B. Hope, Proc. Brit. Cer. Soc. 7, 449-459 (1967).

[2] G. W. Keilholtz, R. E. Moore, and M. F. Osborne, Nucl. Appl. 4, 330 (1968).

TRAPPED ELECTRONS IN GAMMA-IRRADIATED POLYMERS

R. M. Keyser, W. W. Parkinson, and F. Williams[1]

The characteristics and identification of electrons trapped in gamma-irradiated hydrocarbon polymers were described in the previous report.[2] The electron spin resonance (ESR) linewidth (ΔH_{ms}) of the trapped electron singlet was found to be significantly less in these polymers than that reported in alkane glasses, ranging from 3.4 gauss in polyethylene down to 2.6 in poly(4-methylpentene-1). In addition, the spin-lattice relaxation time of trapped electrons in polyethylene has been found to be equal to or greater than 2×10^{-2} sec. This value is an order of magnitude greater than that for alkane glasses. Both the linewidths and the relaxation times indicate that trapped electrons interact less strongly with their surroundings in semi-crystalline polymers than in alkane glasses.

Optical absorption between 700 and 2000 nm, attributable to trapped electrons, has been measured in irradiated poly(4-methylpentene-1). The band maximum lies beyond 2000 nm, the limit of the available spectrometers but the band is strongly red-shifted compared to that in alkane glasses. This longer wavelength for the optical absorption, the greater spin-lattice relaxation time, and the decreased resonance linewidth imply that the trapping site is a void, which is larger in the polymers than in the alkane glasses.

Measurements of electron-trapping in crystalline n-hexatriacontane (C_{36}), both pure and containing C_{24} to C_{32} linear hydrocarbons, indicated that the trapping sites were row vacancies or chain-end defects. An analysis of the thermal decay of trapped electrons in polyethylene proved complex but indicated that there were populations of differing thermal stabilities. Bleaching and radical-annealing experiments showed that the trapped electron yield decreases with increasing free radical concentration.

[1]Department of Chemistry, University of Tennessee, Knoxville.

[2]R. M. Keyser, W. W. Parkinson, and F. Williams, Reactor Chem. Div. Ann. Prog. Rept. Dec. 31, 1968, ORNL-4400, p. 151.

RADIATION-INDUCED REACTIONS OF HYDROCARBONS

W. W.Parkinson, Ruth Slusher, and W. K. Kirkland

The reactions produced by gamma radiation in solutions of naphthalene in n-hexane are being investigated to explore the possibility of hydrogenating and alkylating aromatics such as those in coal, utilizing radiation. Earlier work[1] had shown that about 80% of the radiation products were of such high molecular weight and low volatility that gas chromatography was unsuitable as an analytical method.

Application of thermogravimetric analysis and differential thermal analysis to the radiation products showed that they comprised such a broad range of compounds of similar boiling and melting points that fractionation by thermal methods was impractical.

Gel permeation and thin-layer chromatography methods showed promise when coupled with mass spectrometry for identification. The treatment of thin-layer chromatography spots with fluorescein and bromine confirmed that a substantial part of the radiation products contained olefin rather than aromatic unsaturation, supporting earlier mass spectrometric evidence. These results indicate that radiation has produced additional reactions to the aromatic nucleus as well as substitution reactions.

[1] W. W. Parkinson, W. K. Kirkland, and R. M. Keyser, Reactor Chem. Div. Ann. Progr. Rept. Dec. 31, 1968, ORNL-4400, p. 152.

THE DEVELOPMENT OF RADIATION-RESISTANT INSULATORS

M. J. Kelly, W. W. Parkinson, W. K. Kirkland, and C. W. Lindsey

The apparent electrical conductivity of high-resistance plastics has been examined. The observed, time-dependent conductivity of high-purity polystyrenes, commercial plastics of lower purity, and of the copolymer in use for dosimeters can be accounted for on the basis of dielectric charging and low values of conductivity; both varying with the polar nature of the base polymer and the impurities. During irradiation the conductivity increases greatly. Decay after irradiation has a time dependence related to the composition of the specimen.

To be suitable for dosimeter use, the radiation-induced conductivity must decay rapidly. The material currently used, a copolymer of styrene and α-methyl styrene (Cerex 250B) was found to have unusually rapid decay of conductivity following irradiation. By polymer fractionation and by varying the synthesis ingredients, the chemical species active in reducing conductivity was identified as sulfate chain ends arising from persulfate initiator in the polymerization recipe.

Styrene homopolymers have been synthesized with sulfate end groups and shown to have as low conductivity as the copolymer. Polymers with sulfate end groups and (NH_4) cations have shown low but erratic conductivity, and polystyrenes having end groups of moderate polarity have lower dielectric charging prior to irradiation and some reduction in post-irradiation conductivity.

PARTICIPATION IN PLOWSHARE ACTIVITIES

C. J. Barton and M. J. Kelly

Two experiments, Gasbuggy and Rulison, are presently in progress to evaluate the effectiveness of nuclear explosive stimulation of natural gas production from reservoirs uneconomic to exploit using present technology. Radioactivity released and induced by the nuclear explosion in the gas-bearing rock formation represents a potential public hazard if gas from such wells enters normal commercial channels. It has been demonstrated that the only radioactive isotopes of consequence in the product gas after decay of noble gases of short half-life are ^{85}Kr and tritium.

Members of the Reactor Chemistry Division have been working with the Health Physics Division on a theoretical evaluation of consumer products from natural gas containing ^{85}Kr and tritium to determine the radiation exposure to the consumer using such products over a wide variety of conditions and concentrations.

Reactor Chemistry personnel have been primarily involved with studying exposure pathways, the most significant of which appear to be open flame cooking and heating in household use. All other modes of exposure seem to be of secondary importance.

It would be imprudent to draw firm conclusions on the radiation exposure levels to the public until the studies have been completed, but at this point in the study the technique of nuclear stimulation remains viable. The controlling factor appears to be one of economics rather than one of unacceptable levels of public exposure to radiation.

PUBLICATIONS AND PAPERS

Compiled by Dorothy Caldwell

JOURNAL ARTICLES:

Adams, R. E. and R. D. Ackley
"International Atomic Energy Agency Symposium on Operating and Developmental Experience in the Treatment of Airborne Radioactive Wastes," Nuclear Safety 10(4), 316 (1969)

Adams, R. E. and R. D. Ackley
"The Tenth USAEC Air Cleaning Conference," Nuclear Safety 10(4), 324 (1969)

Annis, B. K., A. P. Malinauskas, and K. S. Yun
"Composition Dependence of the Thermal Diffusion Factor of a Dusty Gas," J. Chem. Phys. 52, 1992 (1970)

Baes, C. F., Jr.
"A Polymer Model for BeF_2 and SiO_2 Melts," J. Solid State Chem. 1, 159 (1970)

Bamberger, C. E. and C. F. Baes, Jr.
"U^{4+}-Th^{4+} Exchange Between Molten Fluoride and Oxide Solid Solutions," Trans. Am. Nucl. Soc. 12(2), 446 (1969)

Barton, C. J., M. A. Bredig, L. O. Gilpatrick, and J. A. Fredricksen
"Solubility of CeF_3 in Molten Mixtures of Lithium, Beryllium, and Thorium Fluorides," Inorg. Chem. 9, 307 (1970)

Baumann, C. D. and P. E. Reagan
"Models for Fission-Gas Release from Pyrocarbon Coated Particles," Nucl. Appl. Tech. 7, 537 (1969)

Braunstein, J. and H. Braunstein
"Association and Hydration Equilibria in $NH_4NO_3 + 2H_2O$ + AgCl or AgBr," Inorg. Chem. 8, 1558 (1969)

Braunstein, J. and H. Braunstein
"Association of Cd^{2+} Ion and Br^- in the Solvent $KNO_3 + Ca(NO_3)_2 + H_2O$," Inorg. Chem. 8, 1528 (1969)

Braunstein, J.
"Comment on Complex Ion Equilibria in Molten Salt Mixtures," J. Phys. Chem. 73, 754 (1969)

Braunstein, J.
"States, Indistinguishability, and the Formula S = k ln W in Thermodynamics," J. Chem. Educ. 46, 719 (1969)

Brunton, G.
"Refinement of the Structure of $NaBF_4$, Acta Cryst. B24, 1703 (1968)

Brunton, G. D.
"The Crystal Structure of β-$KCeF_4$," Acta Cryst. B25(3), 600 (1969)

Brunton, G. D. and D. R. Sears
"The Neutron and X-ray Crystal Structure of $(Na,Li)_7Th_6F_{31}$ With More Than One Least Squares Minimum," Acta Cryst. B25(12), 2519 (1969)

Brunton, G. D.
"The Crystal Structure of Na_3CrF_6," Materials Research Bulletin 4, 621 (1969)

Brunton, G. D.
"The Crystal Structure of KU_2F_9," Acta Cryst. B25(9), 1919 (1969)

Brunton, G. D.
"The Crystal Structure of KBF_4," Acta Cryst. B25, 2161 (1969)

Brunton, G. D.
"Refinement of the Crystal Structure of $\beta_1K_2UF_6$," Acta Cryst. B25, 2163 (1969)

Brunton, G. D.
"The Crystal Structure of γ-Na_2ZrF_6," Acta Cryst. B25, 2164 (1969)

Cantor, S., W. T. Ward, and C. T. Moynihan
"Viscosity and Density in Molten BeF_2-LiF Solutions," J. Chem. Phys. 50(7), 2874 (1969)

Cantor, S.
"Book Review of 'Molten Salts Vol. I, Electrical Conductance, Density, and Viscosity Data,' by G. J. Janz, Natl. Std. Ref. Data Ser.," J. Am. Ceram. Soc. 52, 365 (1969)

Cantor, S., D. P. McDermott, and L. O. Gilpatrick
"Volumetric Properties of Molten and Crystalline Alkali Fluoroborates," J. Chem. Phys. 52, 4600 (1970)

Cantor, S.
"Metal Dilatometer for Determining Density and Expansivity of Volatile Liquids at Elevated Temperature," Rev. Sci. Instrum. 40, 967 (1969)

Carroll, R. M. and H. E. Robertson
"Handling PuO_2 Outside Glove Boxes," Nucl. Appl. 6, 7 (1969)

Carroll, R. M., R. B. Perez, and O. Sisman
"The Effect of Stored Energy on Measurements of Thermal Diffusivity During Irradiation," Nucl. Sci. Eng. 39, 123 (1970)

Carroll, R. M., R. B. Perez, and O. Sisman
"Measurements of Non-Fission Heating in a High Neutron Flux Reactor," Nucl. Sci. Eng. 36, 232 (1969)

Carroll, R. M., J. G. Morgan, R. B. Perez, and O. Sisman
"Fission Density, Burnup, and Temperature Effects on Fission Gas Release from UO_2," Nucl. Sci. Eng. 38, 143 (1969)

Carroll, R. M.
"Fission-Gas Behavior in Fuels," Nuclear Safety 10(3), 210 (1969)

Carroll, R. M., J. G. Morgan, R. B. Perez, and O. Sisman
"Fission-Gas Release from UO_2 During Irradiation Under Extreme Conditions," Trans. Am. Nucl. Soc. 12(1), 76 (1969)

Compere, E. L., H. C. Savage, and J. M. Baker
"High Intensity Gamma Irradiation of Molten Sodium Fluoroborate-Sodium Fluoride Eutectic Salt," J. Nucl. Mater. 34, 97 (1970)

Cuneo, D. R. and H. E. Robertson
"Fission-Product Profiles in Graphite Exposed to Fissioning ^7LiF-BeF_2-ZrF_4-UF_4," Trans. Am. Nucl. Soc. 12, 80 (1969)

Cuneo, D. R., E. L. Long, Jr. and J. H. Coobs
"Performance of Pyrolytic Carbon Coated UO_2 and UC_2 Microspheres at High Burnup," Trans. Am. Nucl. Soc. 12, 548 (1969)

Dunn, L. A. and W. L. Marshall
"Electrical Conductances and Ionization Behavior of Sodium Chloride in Dioxane-Water Mixtures at 100°," J. Phys. Chem. 73, 2619 (1969)

Dunn, L. A. and W. L. Marshall
"Electrical Conductances of Aqueous Sodium Iodide and the Comparative Thermodynamic Behavior of Aqueous Sodium Halide Solutions to 800° and 4000 Bars," J. Phys. Chem. 73, 723 (1969)

Evans, R. B. III, L. D. Love, and E. A. Mason
"Grahams Laws: Simple Demonstrations of Gases in Motion. Part II. Experiments," J. Chem. Educ. 46, 423 (1969)

Evans, R. B. III, L. D. Love, and E. H. Kobisk,
"Preliminary Self-Diffusion Measurements with Pyrocarbons," J. Appl. Phys. 40, 3058 (1969)

Feuerstein, H.
"Behavior of Iodine in Zircaloy Capsules," Trans. Amer. Nucl. Soc. 12(1), 541 (1969)

Grimes, W. R.
"Molten Salt Reactor Chemistry," Nucl. Appl. Tech. 8, 137 (1970)

Hitch, B. F. and C. F. Baes, Jr.
"An EMF Study of Molten Lithium Fluoride-Beryllium Fluoride Solutions," Inorg. Chem. 8, 201 (1969)

Keilholtz, G. W. and G. C. Battle, Jr.
"Air Cleaning as an Engineered Safety Feature in Light Water Cooled Power Reactors," Nuclear Safety 10(1), 46 (1969)

Keilholtz, G. W. and R. E. Moore
"Fast-Neutron Stability of Refractory Metal Carbides at High Temperatures, Trans. Am. Nucl. Soc. 12(1), 101 (1969)

Keyser, R. M. and F. Williams
"Characterization of Trapped Electrons in Gamma Irradiated Hydrocarbon Polymers by Electron Spin Resonance and Optical Absorption Spectroscopy," J. Phys. Chem. 73, 1623 (1969)

Kohn, H. W. and T. E. Willmarth
"Metallic Colloids in Molten Salts," Science 163, 924 (1969)

Malinauskas, A. P. and M. D. Silverman
"Gaseous Diffusion in Neon-Noble Gas Systems," J. Chem. Phys. 50, 3263 (1969)

Malinauskas, A. P., Whisenhunt, S. J., Jr. and J. Q. Searcy
"Determination of the Viscosity Coefficients of Gases," J. Chem. Educ. 46, 781 (1969)

Malinauskas, A. P., J. W. Gooch, Jr. and J. D. Redman, "The Interaction of Tellurium Dioxide and Water Vapor," Nucl. Appl. Tech. 8, 52 (1970)

Marshall, W. L.
"Correlations in Aqueous Electrolyte Behavior to High Temperatures and Pressures, Record of Chem. Prog. 30(2), 61 (1969)

Marshall, W. L.
"Complete Equilibrium Constants, Electrolyte Equilibria, and Reaction Rates," J. Phys. Chem. 74, 346 (1970)

Mason, E. A. and R. B. Evans III
"Graham's Laws: Simple Demonstrations of Gases in Motion. Part I. Theory," J. Chem. Educ. 46, 358 (1969)

Mesmer, R. E. and C. F. Baes, Jr.
"Fluoride Complexes of Beryllium(II) in Aqueous Media," Inorg. Chem. 8, 618 (1969)

Moulton, D. M.
"Comments on the Paper, Activity Coefficients for Ionic Melts," J. Phys. Chem. 73, 4022 (1969)

Parker, G. W., R. A. Lorenz, and G. E. Creek
"The Calculation of Fission Product Release From Core-Coolant Safeguarded Reactors," Trans. Am. Nucl. Soc. 12(1), 902 (1969)

Quist, A. S. and W. L. Marshall
"The Electrical Conductances of Some Alkali Metal Halides in Aqueous Solutions from 0 to 800° and to 4000 Bars," J. Phys. Chem. 73, 978 (1969)

Reagan, P. E., E. L. Long, Jr., J. G. Morgan, and J. H. Coobs
"Irradiation Performance of Pyrolytic Carbon and Silicon Carbide Coated Fuel Particles," Nucl. Appl. Tech. 8, 417 (1970)

Robbins, G. D.
"Measurement of Electrical Conductivity in Molten Fluorides, A Survey," J. Electrochem. Soc. 116, 813 (1969)

Robbins, G. D. and J. Braunstein
"Specific Conductance of Molten Potassium Nitrate," J. Electrochem. Soc. 116, 1218 (1969)

Roberts, B. F., S. H. Freid, G. W. Parker, L. F. Parsley, and T. H. Row
"Evaluation of Various Methods of Fission-Product Aerosol Simulation," Trans. Amer. Nucl. Soc. 12, 326 (1969)

Savage, H. C., N. E. Bolton, H. O. Phillips, K. A. Kraus and J. S. Johnson
"Hyperfiltration of Plant Effluents," Water and Sewage Works 116, 102 (1969)

Sears, D. R. and J. L. Hoard
"Crystal Structure of Ammonium Manganese Fluoride," J. Chem. Phys. 50, 1066 (1969)

Steinfink, H. and G. Brunton
"The Crystal Structure of $Cs_4Mg_3F_{10}$," Inorg. Chem. 8, 1665 (1969)

Sweeton, F. H., C. F. Baes, Jr. and G. H. Jenks
"Solubility of Ferrosoferric Oxide in Dilute Acid and Base Solutions to 300°C," Trans. Am. Nucl. Soc. 12, 82-83 (1969)

Thoma, R. E.
"Book Review of 'Atlas of Miscibility Gaps in Molten Salt Systems' by C. Sinistri, P. Franzonsini and M. Rolla," J. Am. Ceram. Soc. 52, 301 (1969)

Thoma, R. E.
"Book Review of 'Halides of the Lanthanides and Actinides' by D. Brown," J. Amer. Ceram. Soc. 52, 389 (1969)

Thoma, R. E.
"Book Review of 'Thorium Fuel Cycle--Proceedings of 2nd International Thorium Fuel Cycle Symposium," J. Am. Ceram. Soc. 52, 242 (1969)

Toth, L. M., J. P. Young, and G. P. Smith
"Diamond-Windowed Cell for Spectrophotometry of Molten Fluoride Salts," Anal. Chem. 41, 683 (1969)

Toth, L. M., G. D. Brunton, and G. P. Smith
"The Structure and Spectrum of Potassium Hexafluoromolybdate(III)," Inorg. Chem. 8, 2694 (1969)

Truitt, J., R. J. Davis, and J. S. Gill
"Filter Efficiencies of Commercial Media to Reactor Accident Aerosols," Trans. Am. Nucl. Soc. 12, 330 (1969)

Yeatts, L. B. and W. L. Marshall
"Aqueous Systems at High Temperature. Apparent Invariance of Activity Coefficients of Calcium Sulfate at Constant Ionic Strength and Temperature in the System $CaSO_4$-Na_2SO_4-$NaNO_3$-H_2O to the Critical Temperature of Water. Association Equilibria," J. Phys. Chem. 73, 81 (1969)

CONTRIBUTIONS TO BOOKS AND PROCEEDINGS:

Ackley, R. D. and R. E. Adams
"Aging and Weathering of Impregnated Charcoals Used for Trapping Radioiodine," pp 170-184, 10th AEC Air Cleaning Conference, August 1968, CONF-680821

Adams, R. E., R. D. Ackley, and R. P. Shields
"Application of Impregnated Charcoals for Removing Radioiodine from Flowing Air at High Relative Humidity," pp 387-402 in Proceedings of the IAEA Symposium on Treatment of Airborne Radioactive Wastes, New York, August 1968

Baes, C. F., Jr.
"The Chemistry and Thermodynamics of Molten Salt Reactor Fuels," p. 617 in Proceedings of Reprocessing of Nuclear Fuels Symposium, Aug. 1969, CONF-690801

Bennett, R. L. and R. E. Adams
"Development of a Sampling Device for Distinguishing the Forms of Iodine in a Humid Atmosphere," pp 235-262 in 10th AEC Air Cleaning Conference, August 1968, CONF-680821

Davis, R. J., J. Truitt, J. S. Gill, and W. D. Yuille
"The Effects of Moisture on the Character and Filtration of UO_2-Stainless Steel Aerosols," pp 345-364 in Proceedings of the IAEA Symposium on Treatment of Airborne Radioactive Wastes, New York, Aug. 26-30, 1968.

Gilpatrick, L. O., S. Cantor, and C. J. Barton
"Differential Thermal Analysis Apparatus with Agitation and Sealed Specimens for Molten Salt Phase Studies," pp 85-96 in Thermal Analysis Vol. I, Instrumentation, Organic Materials and Polymers, Academic Press, New York, 1969.

Holmes, H. F., E. L. Fuller, R. B. Gammage, and C. H. Secoy
"The Effect of Irreversibly Adsorbed Water on the Character of Thorium Oxide Surfaces," p. 70 in Hydrophobic Surfaces, Academic Press, N. Y., 1969

Long, E. L., Jr., F. R. McQuilkin, D. R. Cuneo, J. R. Lindgren, J. N. Siltanen
"Irradiation Tests of Fuel Rods Containing UO_2 and $(U,Pu)O_2$ for GCFR," Proceedings of International Symposium on Ceramic Nuclear Fuels, Washington, D. C., May 3-8, 1969

Morgan, M. T. and R. L. Towns
"Technique and Apparatus for Inspection, Handling, and Annealing Highly Radioactive Fuel Microspheres," National Symposium on Developments in Irradiation Testing Technology, Sept. 1969, Sandusky, Ohio, CONF-690910

Moulton, D. M., W. R. Grimes, and J. H. Shaffer
"The Distribution of Metals Between Molten Fluorides and Liquid Metals," p. 479 in Molten Salts - Characterization and Analysis, Marcel Dekker, N. Y., 1969

Parker, G. W., H. Buchholz, and W. J. Martin
"Radioactive Aerosol Size Classification Experience with a Low Pressure Cascade Impactor," pp 263-311, 10th AEC Air Cleaning Conference, Aug. 1968, CONF-680821

Parkinson, W. W.
"Radiation-Resistant Polymers," p. 783 in Encyclopedia of Polymer Science and Technology - Vol II, John Wiley and Sons, 1969

Robbins, G. D. and J. Braunstein
"Electrical Conductivity Measurements in Molten Fluoride Mixtures, and Some General Considerations on Frequency Dispersion," p 443 in Molten Salts - Characterization and Analysis, Marcel Dekker, N. Y., 1969

Ross, R. G., W. R. Grimes, C. J. Barton, C. E. Bamberger, and C. F. Baes
"The Reductive Extraction of Protactinium and Uranium from Molten Lithium Fluoride-Beryllium Fluoride-Thorium Fluoride Mixtures into Bismuth," pp 363-374 in Proceedings of Reprocessing of Nuclear Fuels Symposium, Aug. 1969, CONF-690801

Shaffer, J. H., D. M. Moulton, and W. R. Grimes
"The Reductive Extraction of Rare Earths from Molten Lithium Fluoride-Beryllium Fluoride-Thorium Fluoride Mixtures into Bismuth," pp 375-84 in Proceedings of Reprocessing of Nuclear Fuels Symposium, Aug. 1969, CONF-690801

Thoma, R. E.
"The Role of Phase Equilibria in Molten Salt Research," pp 81-119 in Molten Salts - Characterization and Analysis, Marcel Dekker, N. Y., 1969

REPORTS ISSUED:

Ackley, R. D. and R. E. Adams
"Trapping of Radioactive Methyl Iodide from Flowing Steam-Air: Westinghouse Test Series," ORNL-TM-2728, Dec. 1969

Ackley, R. D. and R. E. Adams
"Effect of Containment Spray Solution on Trapping of Radioactive Methyl Iodide from Flowing Steam-Air by Iodized Charcoal: Westinghouse Test Series," ORNL-TM-2805, Jan. 1970

Ackley, R. D., Zell Combs, and R. E. Adams
"Aging, Weathering, and Poisoning of Impregnated Charcoals Used for Trapping Radioiodine," ORNL-TM-2860, March 1970

Baumann, C. D.
"Fission-Product Monitoring in High-Temperature Gas-Cooled Reactors," ORNL-TM-2791, Dec. 1969

Bennett, R. L., Ruth Slusher, and R. E. Adams
"Reactions of Iodine Vapor with Organic Paint Coatings," ORNL-TM-2760, April 1970

Bopp, C. D. and J. J. J. Myron
"Radiolysis of Tetra Hydro Furan-Cyclohexene Mixtures. Part A, Liquid Products. Part B, Gas Yields," ORNL-4320, Feb. 1969

Bowman, C. R., M. J. Kelly, and P. S. Rohwer
"Theoretical Evaluation of Consumer Products from Project Gasbuggy. 2nd Quarterly Progress Report," ORNL-TM-2513, March 1969

Cantor, S.
"Evaluation of the Chemical Thermodynamics in the Report 'Applicability of Metal Oxides to the Development of New Processes for Removing SO_2 from Flue Gases (by TRACOR Corp.),'" ORNL-TM-2744, Oct. 1969

Cheverton, R. D., J. C. Griess, and J. R. McGuffey
"Development of Electroless Nickel Coating for High Performance Aluminum Fuel Plates," ORNL-TM-2642, Aug. 1969

Davis, R. J.
"A Nuclear Safety Particle Primer," ORNL-4337, Jan. 1969

Davis, R. J., J. Truitt, J. S. Gill, and R. E. Adams
"Removal of Radioactive Aerosols on High Efficiency Fibrous Filter Media," ORNL-4524, April 1970

Evans, R. B. III, J. L. Rutherford, and A. P. Malinauskas
"Gas Transport in MSRE Moderator Graphite. II. Effects of Impregnation. III. Variation of Flow Properties," ORNL-4389, May 1969

Fredricksen, Judy A., L. O. Gilpatrick, and C. J. Barton
"Solubility of Cerium Trifluoride in Molten Mixtures of LiF, BeF_2, and ThF_4," ORNL-TM-2335, Jan. 1969

Freid, S. H., H. J. de Nordwall, D. R. Cuneo, J. A. Conlin, C. L. Segaser, and E. L. Long
"Fission Product Release from an Overheated HTGR Fuel-ORR Poolside Capsule-06-11," ORNL-TM-2388, Feb. 1969

Fuller, E. L. Jr., H. F. Holmes, and R. B. Gammage
"Infrared Studies of Thorium Oxide Surfaces," ORNL-4378, March 1969

Griess, J. C. and A. L. Bacarella
"Design Considerations of Reactor Containment Spray Systems - Part III The Corrosion of Materials in Spray Solutions," ORNL-TM-2412, Part III, Dec. 1969

Hammond, R. P., C. C. Burwell, R. S. Carlsmith, J. G. Delene, L. C. Fuller, A. E. Goldman, D. B. Lloyd, J. T. Roberts, J. E. Savolainen, and R. P. Wichner
"The Unclad Metal Breeder Reactor for Desalting OR Power," ORNL-4202, Jan. 1969

Jacobs, D. G., E. G. Struxness, and M. J. Kelly
"1st Quarterly Progress Report on the Theoretical Safety Evaluation of Consumer Products from Project Gasbuggy," ORNL-TM-2427, Feb. 1969

Jacobs, D. G. and M. J. Kelly
"Theoretical Evaluation of Consumer Products from Project Gasbuggy, 4th Quarterly Progress Report," ORNL-TM-2721, Oct. 1969

Jacobs, D. G. and M. J. Kelly
"Theoretical Evaluation of Consumer Products from Project Gasbuggy, 5th Quarterly Progress Report," ORNL-TM-2862, Feb. 1970

Kasten, P. R., E. S. Bettis, W. H. Cook, W. P. Eatherly, D. K. Holmes, R. J. Kedl, C. R. Kennedy, S. S. Kirslis, H. E. McCoy, A. M. Perry, R. C. Robertson, D. Scott and R. A. Strehlow
"Graphite Behavior and its Effects on MSBR," ORNL-TM-2136, Feb. 1969

Keilholtz, G. W. and G. C. Battle, Jr.
"Fission Product Release and Transport in LMFBR," NSIC-37, March 1969

Kelly, M. J., P. S. Rohwer, and D. G. Jacobs
"Theoretical Evaluation of Consumer Products from Project Gasbuggy, 2nd Quarterly Progress Report, ORNL-TM-2513, March 1969

Kraus, K. A., R. J. Raridon, J. S. Johnson, E. G. Bohlmann, and F. A. Posey
"Desalination Research at Oak Ridge," OSW-R&D-468, Aug. 1969

Littlefield, C. C., D. M. Eissenberg, and S. A. Reed
"Control of Alkaline Scale Using Carbon Dioxide Suppression, ORNL-TM-2415, March 1969

Long, G. and F. F. Blankenship
"The Stability of Uranium Trifluoride. Part I. Stability in the Solid Phase. Part II. Stability in Molten Fluoride Solution, ORNL-TM-2065, Nov. 1969

Lorenz, R. A., G. W. Parker, and D. O. Hobson
"Preliminary Evaluation of the First Fuel Rod Failure Transient Test of a Zircaloy-Clad Fuel Rod Cluster in TREAT," ORNL-TM-2774, Nov. 1969

Matheney, G. B., G. W. Parker, and D. H. Walker
"ORNL-LOFT Fission Product Support Program, Part J in Engineered Safety Systems Investigation," IDO-17258, May 1969

McDuffie, H. F., H. E. McCoy, and R. C. Robertson
"Assessment of Molten Salts as Intermediate Coolants for LMFBR's," ORNL-TM-2696, Sept. 1969

Morgan, M. T. and R. L. Towns
"Techniques and Apparatus for Inspection, Handling, and Annealing Highly Radioactive Fuel Microspheres," ORNL-TM-2495, March 1969

Morgan, M. T.
"Wrist Action Manipulators for Shielded Glove Boxes," ORNL-TM-2512, April 1969

Morgan, M. T., D. M. Hewett, and E. L. Long, Jr.
"Fuel Migration in Pyrocarbon Coated Particles, ORNL-TM-2717, Nov. 1969

Myron, J. J. J. and W. W. Parkinson
"Radiation Induced Reactions of Some Furan Chemicals," ORNL-4373, Aug. 1969

Osborne, M. F. and G. W. Parker
"Fission Product Release from Naval Reactor Fuel," ORNL-2762, Dec. 1969

Osborne, M. F. and G. W. Parker
"Design, Equipment, and Program for Fuel Rod Burst Experiments," ORNL-TM-2850, Feb. 2, 1970

Robbins, G. D. and J. Braunstein
"Specific Conductance of Molten Potassium Nitrate," ORNL-4375, Mar. 1969

Roberts, B. F., S. H. Freid, G. W. Parker, L. F. Parsly, and T. H. Row
"Evaluation of Various Methods of Fission Product Aerosol Simulation," ORNL-TM-2628, Sept. 1969

Sears, D. R. and C. D. Bopp
"Radiation Chemical Study of Plastics for Charged Particle Track Registration. Pt. A. Radiation Chemistry of Cellulosic Charged Particle Track Detectors. Pt. B. Possible Methods of Alpha Particle Track Registration with PTFE," ORNL-4351, July 1969

Sweeton, F. H., C. F. Baes, Jr. and G. H. Jenks
"The Solubility of Ferrosoferric Oxide in Dilute Acid and Base Solutions to 300°C," ORNL-TM-2667, July 1969

Thoma, R. E. and J. E. Ricci
"Fractional Crystallization Reactions in the System $LiF-BeF_2-ThF_4$," ORNL-TM-2596, July 1969

THESIS:

Keyser, R. M.
"An Electron Spin Resonance Study of Trapped Electrons in Gamma Irradiated Hydrocarbon Polymers," Thesis submitted in partial fulfillment of the requirements for the Ph.D. degree, University of Tennessee, Knoxville, Tennessee, April 1970

PATENTS:

Grimes, W. R., D. M. Moulton, and J. H. Shaffer
"Extraction of Protactinium from Molten Salt Mixtures into Bismuth-Tin Solution, U.S. Pat. 3,495,975, Feb. 17, 1970

Shaffer, J. H., D. M. Moulton, and W. R. Grimes
"Method for Separating Uranium and Protactinium from Spent Molten Fluoride Salt Mixtures Containing Rare Earth Fission Products," U.S. Pat. 3,473,897, Oct. 21, 1969

Thoma, R. E. and G. M. Hebert
"Coolant Salt for a Molten Salt Breeder Reactor," U.S. Pat. 3,448,054, June 3, 1969

Ward, W. T. and R. E. Adams
"Method of Removing Radioiodine Values from a Gaseous Medium," U.S. Pat. 3,466,137, Sept. 9, 1969

PAPERS PRESENTED AT TECHNICAL MEETINGS:

Baes, C. F., Jr.
"The Chemistry and Thermodynamics of Molten Salt Reactor Fuels," presented at Nuclear Fuel Reprocessing Symposium, Ames, Iowa, Aug. 25, 1969

Baes, C. F., Jr.
"A Polymer Model for Beryllium Fluoride and Silicon Dioxide Melts," presented at American Chemical Society Meeting, Minneapolis, Minn., April 13-18, 1969

Bamberger, C. E. and C. F. Baes, Jr.
"U^{4+}-Th^{4+} Exchange Between Molten Fluoride and Oxide Solid Solutions," presented at American Nuclear Society Meeting, San Francisco, Calif., Nov. 30-Dec. 4, 1969

Barton, C. J., L. O. Gilpatrick, and J. A. Fredricksen
"Solubility of Cerium(III) Fluoride in Molten Mixtures of Lithium Fluoride, Beryllium Fluoride, and Thorium Tetrafluoride," presented at American Chemical Society Meeting, Minneapolis, Minn., Apr. 13-18, 1969

Barton, C. J., G. D. Brunton, D. Hsu, L. O. Gilpatrick, and H. Insley
"Phase Relations in the System Potassium Fluoride-Cerium(III) Fluoride," presented at American Chemical Society Meeting, New York, N. Y., Sept. 8-12, 1969

Barton, C. J.
"Applications of Radioactive Tracers in Molten Salt Research," presented at American Chemical Society Meeting, Richmond, Va., Nov. 5-8, 1969

Blankenship, F. F. and S. S. Kirslis
"Disposition of Fission Products in a Molten Salt Reactor," presented at American Chemical Society Meeting, Houston, Texas, Feb. 22-27, 1970

Braunstein, H. and J. Braunstein
"Isopiestic Equilibria of Calcium Nitrate-Water, Cadmium Nitrate-Water and Mixed Nitrate-Water Systems," presented at American Chemical Society Meeting, Richmond, Va., Nov. 5-8, 1969

Braunstein, J.
"Quasi-Lattice Models and Association Equilibria in Ionic Liquids," presented at Physical Chemistry Seminar, Purdue University, Lafayette, Ind., March 19, 1969

Braunstein, J.
"Ionic Transport Properties in Molten Fluorides," presented at Chemistry Seminar, Purdue University, Lafayette, Ind., March 20, 1969

Braunstein, J.
"Some Aspects of Solution Chemistry in Liquid Mixtures of Inorganic Salts with Water, University of Miami, Miami, Fla., Chemistry Dept., Feb. 16, 1969

Braunstein, J.
"Thermodynamics of Concentrated Aqueous Electrolytes," presented at Gordon Research Conference on Molten Salts, Meriden, N. H., Aug. 25-29, 1969

Braunstein, J.
"Electrical Conductivity and Transference in Molten Mixtures of Beryllium Fluoride and Alkali Fluorides," presented at Gordon Research Conference on Molten Salts, Meriden, N. H., Aug. 25-29, 1969

Braunstein, J.
"Electrical Conductivity and Transference in Molten Mixtures of Beryllium Fluoride and Alkali Fluorides," presented at Chemistry Seminar, University of Maine, Orono, Maine, Sept. 2, 1969

Braunstein, J., K. A. Romberger, and R. Ezell
"Interaction Parameters for Excess Chemical Potential in Molten Mixtures of Alkali and Alkaline Earth Halides with a Common Anion," presented at American Chemical Society Meeting, Richmond, Va., Nov. 5-8, 1969

Braunstein, J. and G. D. Robbins
"Electrolytic Conductance Measurements and Capacitive Balance," presented at American Chemical Society Meeting, Richmond, Va., Nov. 5-8, 1969

Cantor, S., L. O. Gilpatrick, and D. P. McDermott
"Volumetric Properties of Molten and Crystalline Alkali Fluoroborates," presented at American Chemical Society Meeting, Richmond, Va., Nov. 5-8, 1969

Carroll, R. M., J. G. Morgan, R. B. Perez, and O. Sisman
"Fission-Gas Release from UO_2 During Irradiation Under Extreme Conditions," presented at American Nuclear Society Meeting, Seattle, Wash., June 16-19, 1969

Coobs, J. H. and O. Sisman
"Coated Particle Fuels Development at Oak Ridge National Laboratory," presented at 15th AEC Coated Particle Fuels Working Group Meeting, Los Alamos Scientific Laboratory, New Mexico, Dec. 10-11, 1969

Cuneo, D. R. and H. E. Robertson
"Fission-Product Profiles in Graphite Exposed to Fissioning Lithium-7 Fluoride Beryllium Fluoride-Zirconium Fluoride-Uranium(IV) Fluoride," presented at American Nuclear Society Meeting, Seattle, Wash., June 15-19, 1969

Davis, R. J.
"Estimation of Aerosol Concentration in a Nuclear Reactor Containment After an Accident," presented at International Congress on the Diffusion of Fission Products, Saclay, France, Nov. 4-5, 1969

Davis, R. J.
"The Science and Technology of Aerosols," ORNL Laboratory Chemistry Colloquium, Oak Ridge, Tenn., May 19, 1969

Davis, R. J.
"Some Aspects of Nucleation and Growth," presented at Specialist Meeting on the Behavior of Nuclear Aerosols in Closed Systems," Karlsruhe, Germany, Nov. 12, 1969.

Davis, R. J.
"A Nuclear Safety Aerosol Program at ORNL," presented at Second AEC Aerosol Technology Meeting, Albuquerque, N. M., Jan. 8-9, 1970

Feuerstein, H.
"Behavior of Iodine in Zircaloy Capsules," presented at American Nuclear Society Meeting, San Francisco, Calif., Nov. 30-Dec. 4, 1969

Fuller, E. L., Jr., H. F. Holmes, and R. B. Gammage
"Infrared Studies of Thorium Oxide Surfaces. I. Characterization of Adsorbed Water," presented at 43rd National Colloid Symposium, Cleveland, Ohio, June 23-24, 1969

Gammage, R. B., E. L. Fuller, Jr., and H. F. Holmes
"Effect of Surface Hydration on the Adsorption of Nitrogen and Argon by Thorium Oxide," presented at Symposium on Surface Area Determination, Bristol, England, July 17-19, 1969

Grimes, W. R.
"Chemistry and Chemical Processing of Molten Salts," presented at Fourth Annual Conference on Engineering at ORNL, sponsored by ORAU and ORNL, Oak Ridge, Tennessee, April 28-29, 1969.

Keilholtz, G. W.
"The Storage and Retrieval of Technical Information," presented at Knoxville Torch Club, University of Tennessee, May 11-15, 1970

Keilholtz, G. W.
"Fast-Neutron Stability of Refractory Metal Carbides at High Temperatures," presented at American Nuclear Society Meeting, Seattle, Washington, June 15-19, 1969

Keyser, R. M., W. W. Parkinson, and F. Williams
"Electron Spin Resonance and Optical Characterization of Trapped Electrons in Gamma Irradiated Hydrocarbon Polymers," presented at Conference on ESR in Radiation Chemistry, Chalk River, Ontario, Canada, May 6-9, 1969

Kohn, H. W. and S. S. Kirslis
"Radioaerosol Formation Over Molten Salts," presented at American Chemical Society Meeting, Minneapolis, Minn., April 13-18, 1969.

Malinauskas, A. P.
"Kinetics of the Steam-Graphite Reaction," presented at American Institute of Chemical Engineers, Cleveland, Ohio, May 4-7, 1969

Marshall, W. L.
"Conductances and Equilibria of Aqueous Electrolytes over Extreme Ranges of Temperature and Pressure," presented at Department of Chemistry, Indiana State University, Terre Haute, Indiana, April 28, 1969

Marshall, W. L.
"Conductances and Equilibria of Aqueous Electrolytes Over Extreme Ranges of Temperature and Pressure," presented at Department of Chemistry, Southern Illinois University, Carbondale, Illinois, Apr. 29, 1969

Marshall, W. L.
"Complete Equilibrium Constants and Electrolyte Equilibria," presented at American Chemical Society Meeting, New York, N. Y., Sept. 12-19, 1969

Marshall, W. L.
"Chemistry and the Environment," presented at Tennessee Junior Science and Humanities Symposium, University of Tennessee, Knoxville, Tennessee, March 5-7, 1970

Mesmer, R. E., C. F. Baes, Jr., and F. H. Sweeton
"Acidity Measurements at Elevated Temperatures. IV. Apparent Ion Product of Water in 1 Molal Potassium Chloride up to 292°C," presented at American Chemical Society Meeting, Houston, Texas, Feb. 22-26, 1970

Morgan, M. T. and R. L. Towns
"Techniques and Apparatus for Inspection, Handling, and Annealing Highly Radioactive Fuel Microspheres," presented at National Symposium on Developments in Irradiation Testing Technology, Lewis Research Center, Sandusky, Ohio, Sept. 9-11, 1969

Parker, G. W., R. A. Lorenz, and G. E. Creek
"The Calculation of Fission Product Release from Core-Coolant Safeguarded Reactors," presented at American Nuclear Society Meeting, San Francisco, Calif., Nov. 30-Dec. 4, 1969

Quist, A. S.
"The Ionization Constant of Water to 800°C and 4000 Bars," presented at American Chemical Society Meeting, New York, N. Y., Sept. 12-19, 1969

Robbins, G. D. and J. Braunstein
"Specific Conductance of Molten Potassium Nitrate," presented at Electrochemical Society Meeting, New York, N. Y., May 4-9, 1969

Roberts, B. F., S. H. Freid, G. W. Parker, L. F. Parsley, and T. H. Row
"Evaluation of Various Methods of Fission-Product Aerosol Simulation," presented at American Nuclear Society Meeting, Seattle, Wash., June 15-19, 1969

Romberger, K. A. and J. Braunstein
"Ion Transport in Molten Beryllium Fluoride-Lithium Fluoride Mixtures," presented at American Chemical Society Meeting, New York, N. Y., Sept. 7-12, 1969

Ross, R. G., W. R. Grimes, C. J. Barton, C. E. Bamberger, and C. F. Baes, Jr.
"The Reductive Extraction of Protactinium and Uranium from Molten Lithium Fluoride-Beryllium Fluoride-Thorium Fluoride Mixtures into Bismuth," presented at Nuclear Fuel Reprocessing Symposium, Ames, Iowa, Aug. 25, 1969

Shaffer, J. H., D. M. Moulton, and W. R. Grimes
"The Reductive Extraction of Rare Earths from Molten Lithium Fluoride-Beryllium Fluoride-Thorium Fluoride Mixtures into Bismuth," presented at Nuclear Fuel Reprocessing Symposium, Ames, Iowa, Aug. 25, 1969

Soldano, B. A.
"Osmotic Properties of Electrolyte Solutions at High Temperatures," presented at Chemistry Department, Furman University, Greenville, S. C., March 24, 1969

Soldano, B. A. and W. T. Ward
"Uptake of Methyl Iodide by Water Solutions and Drops," presented at American Nuclear Society Meeting, Seattle, Wash., June 15-19, 1969

Steinfink, H. and G. D. Brunton
"The Crystal Structure of $Cs_4Mg_3F_{10}$," presented at American Crystallographic Association Meeting, Seattle, Wash., Mar. 23-29, 1969

Sweeton, F. H., C. F. Baes, Jr., and G. H. Jenks
"Solubility of Ferrosoferric Oxide in Dilute Acid and Base Solutions to 300°C," presented at American Nuclear Society Meeting, Seattle, Wash., June 15-19, 1969

Truitt, J., R. J. Davis, and J. S. Gill
"Filter Efficiencies of Commercial Media to Reactor Accident Aerosols," presented at American Nuclear Society Meeting, Seattle, Wash., June 15-19, 1969

Weaver, C. F. and J. D. Redman
"A Knudsen Effusion Study of the Fluorides of Molybdenum, Niobium, and Ruthenium from 25-900°C," presented at Eleventh Annual Time-of-Flight Mass Spectrometer Symposium, Rochester, New York, October 7-9, 1969

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