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ANNUAL REPORT

Period Ending May 31, 1972

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REACTOR CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

For Period Ending May 31, 1972

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JULY 1972

OAK RIDGE NATIONAL LABORATORY
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PART I. MOLTEN SALT CHEMISTRY



FLUORIDE SYSTEMSTHERMODYNAMICS OF LiF-BeF₂ MIXTURES FROM EMF MEASUREMENTS WITH Be AND Li-Bi ELECTRODESD. D. Sood¹ and J. Braunstein

The electromotive force of the electrochemical cell Be|LiF,BeF₂|Li,Bi measures the free energy of the process



if the electrodes are reversible. We have now demonstrated applicability of the Nernst equation to the Li,Bi alloy electrode at concentrations between 1.2×10^{-4} and 2.4×10^{-3} atom fraction lithium in bismuth with fixed salt composition. Previous difficulties with an exact test of the Nernst equation in this system, attributed to analytical difficulties at very low lithium concentrations, were circumvented by adding lithium to the molten bismuth coulometrically. The observed long term stability of the emf of this cell indicates that the solubility of reduced species in the salt as Li⁰, Be⁰ or Be⁺, although perhaps not demonstrably absent,³ is extremely low, since such solubility would provide a direct short circuit of the electrodes in the cell. The EMF has been measured at concentrations between 15 and 33 mole percent BeF₂, and at temperatures between 830°C and the liquidus, thus providing data needed to calculate not only the isothermal chemical potentials in this region but also the partial molar entropy and enthalpy.

¹On assignment to ORNL from the Bhabha Atomic Research Center, Bombay, India.

²D. D. Sood and J. Braunstein, Reactor Chem. Div. Ann. Progr. Rept., May 31, 1971, ORNL-4717, p. 13.

³H. R. Bronstein and D. L. Manning, J. Electrochem. Soc. 119, 125 (1972).

INTERACTION PARAMETERS OF ALKALI FLUORIDE-ALKALINE EARTH FLUORIDE MIXTURES AND THE COMPLEX-ION MODEL

D. D. Sood¹ and J. Braunstein

The limiting excess chemical potential interaction parameter of LiF in molten LiF-BeF₂ mixtures ($\lim_{X \rightarrow 0} (\mu_{\text{LiF}}^{\text{E}}/X^2)$, where $\mu_{\text{LiF}}^{\text{E}}$ is the excess chemical potential of LiF and X is the mole fraction of beryllium fluoride), correlates satisfactorily with the interaction parameters and ion sizes in other alkali-alkaline earth fluoride mixtures, using the conformal ionic solution theory (CIS).^{2,3} On the other hand, the liquidus data are reproduced well, at compositions up to 0.25 mole fraction BeF₂, when calculated under the assumption of ideal mixing of the pseudocomponents LiF and Li₂BeF₄.⁴ The agreement of the ionic and complex-ion models here may be the (accidental) result of the relative ion sizes.

In a mixture containing mole fraction X of BeF₂, the mole fraction of M₂BeF₄ (where M is an alkali metal) is $y = X/(1 + 2X)$ and the excess chemical potential of MF, based on mixing with M₂BeF₄ rather than with BeF₂, becomes $\mu_{\text{MF}}^{\text{E}'} = \mu_{\text{MF}}^{\text{E}} + RT \ln \frac{1-X}{1-y}$. Since the transformed interaction parameter, $\lim_{y \rightarrow 0} (\mu_{\text{MF}}^{\text{E}'}/y^2)$, must be zero if MF and M₂BeF₄ mix ideally, it follows that the untransformed interaction parameter, $\lim_{X \rightarrow 0} (\mu_{\text{MF}}^{\text{E}}/X^2)$, must have the value -2RT (or -nRT if the compound is M_nBeF_{2+n}). Hence if the alkali fluoride - beryllium fluoride mixtures are ideal dilute solutions of M₂BeF₄ in MF, the untransformed limiting interaction parameters must all be about -4 kcal/mol near the melting point of MF. For LiF-BeF₂, the interaction parameter is close to this, -5 kcal/mole. The untransformed interaction parameters for several other alkali-alkaline earth fluorides, however, vary with the ion sizes in general accord with ICS, from -1 kcal/mol in NaF-BaF₂ to -12 kcal/mole in CsF-BeF₂.³

¹On assignment to ORNL from Bhabha Atomic Research Center, Bombay, India.

²K. A. Romberger and J. Braunstein, MSR Program Semiann. Progr. Rept., Feb. 28, 1970, ORNL-4548, Aug. 1970, p. 161.

³J. Braunstein, K. A. Romberger, and R. Ezell, J. Phys. Chem. 72, 4383 (1970).

⁴K. A. Romberger, J. Braunstein and R. E. Thoma, J. Phys. Chem. 76, 1154 (1972); M. A. Bredig, Chemistry Div. Ann. Progr. Rept., May 20, 1971, ORNL-4706, p. 156.

ELECTROCHEMICAL MASS TRANSPORT IN MOLTEN BERYLLIUM FLUORIDE - ALKALI FLUORIDE MIXTURES

H. R. Bronstein,¹ J. Truitt, and J. Braunstein

The uncommon unicationic conduction process in molten LiF-BeF₂ mixtures,² whereby electrical current is carried only by lithium ions (relative to fluoride as the reference constituent), suggests a number of interesting consequences,³ of possible theoretical and practical importance, that can best be investigated by electrochemical scanning methods such as voltammetry and chronopotentiometry. For example, an electrochemical cell with a small beryllium electrode and a large inert electrode dipping in an alkali fluoride - beryllium fluoride melt should show appreciable difference in electrical conductivity for anodic or cathodic current flow. I.e., a film of virtually pure highly resistive BeF₂ should be formed at a Be anode since the mobile alkali cations migrate away; on reversal of polarity BeF₂ is reduced, with alkali ions carrying current to the Be cathode. The system should thus be partially rectifying. Furthermore, the relaxation of the high resistance film of BeF₂ on current reversal should depend on the beryllium-alkali ion ratio in the melt and on the ionic diffusivities, providing information on these properties.

Preliminary chronopotentiometric measurements have been made⁴ at a Be electrode in an NaF-BeF₂ melt containing approximately 75 mole percent BeF₂. Qualitatively, the results appear consistent with the expected behavior, and extremely well defined transitions are observed in the chronopotentiograms. On passage of constant anodic current at the Be electrode, the measured potential first rises rapidly to a very nearly constant value as, presumably, Be(II) is formed in the melt. A rather abrupt rise in electrode

potential towards the instrumental limit then occurs, to sustain the imposed constant current. This is presumed due to the formation of a resistive BeF_2 film. On reversal of polarity, the potential drops very rapidly to a nearly constant value suggesting rapid reduction of the BeF_2 film and the absence of diffusion control of cathodic current. The above tentative interpretation is under further investigation.

¹On loan to RCD from ORNL Chemistry Division.

²K. A. Romberger and J. Braunstein, *Inorg. Chem.* **9**, 1273 (1970).

³J. Braunstein and K. A. Romberger, "High Temperature Ionic Switching Device," CNID 2739.

⁴We wish to acknowledge Dr. T. A. Mueller's valuable suggestions and aid in initiating the chronopotentiometric measurements.

ELECTRICAL CONDUCTANCE AND GLASS TRANSITION TEMPERATURES IN ALKALI FLUORIDE - BERYLLIUM FLUORIDE MELTS

G. D. Robbins and J. Braunstein

The temperature dependence of the Arrhenius energy for electrical conductance of glass-forming molten fluorides has been under investigation along with measurements of the glass transition temperature.¹ Conductance measurements in $\text{NaF}-\text{BeF}_2$ have been extended to the compositions 75, 80, 85, and 90 mole percent BeF_2 at temperatures between 485 and 600°C, from previous measurements at 43 to 70% BeF_2 . The Arrhenius energies for the new compositions increase from 10.7 to 15.4 kcal/mole with increasing BeF_2 content. Previously measured glass transition temperatures in this region showed little composition dependence, and this was verified. The absence of composition dependence stimulated optical² and electron microscopic³ examination of the quenched glasses for possible phase separation, with inconclusive results.

Glass transition temperatures were measured also for $\text{LiF}-\text{BeF}_2$ mixtures containing 52 to 75 mole percent BeF_2 and found to be 117-120°C, about 60° higher than estimates based on the temperature dependence of the Arrhenius energy.

¹G. D. Robbins and J. Braunstein, Reactor Chem. Div. Ann. Progr. Rept., May 31, 1971, ORNL-4717, p. 10-11.

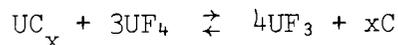
²G. D. Brunton, Reactor Chemistry Division, private communication.

³L. D. Hulett, Analytical Chemistry Division, private communication.

EQUILIBRATION OF URANIUM CARBIDES WITH DILUTE SOLUTIONS OF UF₄ IN LiF-BeF₂ (66-34 MOLE %) AT 550°C¹

L. M. Toth and L. O. Gilpatrick

The equilibration of dilute molten fluoride solutions of UF₄ with UC, U₂C₃, and UC₂ at 823°K:



has been investigated to establish that UC₂ is the stable carbide phase in contact with dilute UF₃-UF₄ solutions contained in graphite. When UC was used as the reagent to reduce UF₄ via the above equilibrium, UC₂ was identified as the product of the metastable reaction giving further evidence that UC₂ is the stable carbide phase in contact with graphite at these temperatures. These observations are contrary to previous thermodynamic data which predict that UC₂ is unstable at temperatures less than 1500°C and that U₂C₃ should be the stable carbide phase for the above equilibrium.²

The carbides were identified by x-ray powder patterns. UF₃ and UF₄ concentrations in solution were measured by near IR-visible absorption spectrophotometry and equilibrium quotients, $Q = (UF_3)^4 / (UF_4)^3$ were calculated for each of the carbides in contact with the molten fluoride solution.

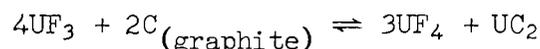
¹Paper submitted to J. Inorg. Nucl. Chem. March 1972.

²E. K. Storms, The Refractory Carbides, vol. 2, pp. 171-213, Academic Press, Inc., New York (1967).

DISPROPORTIONATION OF UF₃ IN MOLTEN LiF-BeF₂ IN GRAPHITE CONTAINERS

L. M. Toth and L. O. Gilpatrick

In a previous document¹ in this series we reported a study, by absorption spectroscopy, of the reaction



and the values for the ratio

$$R = \text{UF}_3 / (\text{UF}_3 + \text{UF}_4)$$

obtained in these experiments. Since the values for R were substantially lower than those predicted from thermodynamic data of Long and Blankenship,² and since the presence of UC₂ was never positively identified in these early studies, we have performed additional experiments with this system. In these experiments (see preceding section of this report) the reactions of pure uranium carbides with dissolved UF₄ were used to establish that UC₂ is indeed the stable carbide. In these studies (with UC₂ equilibrated with dissolved UF₄ in graphite containers) we obtained the following values for R and for the equilibrium quotient $Q = \text{UF}_3^4 / \text{UF}_4^3$.

Equilibrium Quotients (Q) in Mole Fractions and Equilibrium Ratios (R) for the Reaction $3\text{UF}_4 + \text{UC}_2 \rightleftharpoons 4\text{UF}_3 + 2\text{C}$ at Various Temperatures in LiF-BeF₂ (66-34 mole %)

Temperature (°C)	500	550	600	650	700
Q(x10 ⁺⁶)	0.118	3.37	39	269	1340
R	0.101	0.187	0.334	0.450	0.546

These new data agree quite well with those predicted from the work of Long and Blankenship and show UF₃ to be considerably more stable than did our previous study. It now seems likely that the previous study achieved equilibrium with some oxy-carbide phase rather than with UC₂.

¹L. M. Toth, "Disproportionation of UF₃ Solutions in Graphite Containers," Reactor Chem. Div. Annu. Progr. Rep. May 31, 1971, ORNL-4717, p. 9.

²G. Long and F. F. Blankenship, The Stability of UF₃, Part II. The Stability in Molten Fluoride Solution, ORNL-TM-2065, Part II, Nov. 1969.

PHASE EQUILIBRIA IN THE SYSTEM $\text{LiF}-\text{BeF}_2-\text{CeF}_3$ AND RELATED BINARY SYSTEMS

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

No new experimental data have been obtained on this system, but a critical examination of the available information has resulted in a complete phase diagram. Compositions of the three ternary points in the system were determined from knowledge of phase relations in the binary system $\text{LiF}-\text{BeF}_2$ ¹ and by extrapolation of published data on the solubility of CeF_3 in $\text{LiF}-\text{BeF}_2$ mixtures.² These are listed in the table below along with data on the three binary systems.

Invariant Points in the System $\text{LiF}-\text{BeF}_2-\text{CeF}_3$ and
Related Binaries

Composition (mole %)			Temperature (°C)	Phase Transition
LiF	BeF ₂	CeF ₃		
67.16	32.72	0.12	458.4	Ternary eutectic
46.86	53.05	0.09	363.0	Ternary eutectic
67.24	32.76	0.00	458.9	Binary eutectic ¹
66.67	33.33	0.00	459.1	Melting point of $2\text{LiF}\cdot\text{BeF}_2$ ¹
46.9	53.1	0.00	363.5	Binary eutectic ¹
0.0	96.0	4.	540	Binary eutectic
81.5	0.0	17.5	755	Binary eutectic
66.59	33.29	0.12	458.6	Saddle point, $\text{CeF}_3 - 2\text{LiF}\cdot\text{BeF}_2$ join

¹K. A. Romberger, J. Braunstein, and R. E. Thoma, J. Phys. Chem. (in press).

²W. 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, October 1959.

SOLUBILITY OF BF_3 GAS IN FLUORIDE MELTS

S. Cantor and R. M. Waller

These measurements serve to determine activity of fluoride ion in molten mixtures of LiF-BeF_2 , $\text{LiF-BeF}_2\text{-ThF}_4$, and LiF-ThF_4 . Since the scope of this study involves measurements in a relatively large number of melts, we have changed our method of measurement from the sparge-and-strip technique¹ to a vapor-pressure method which generates data faster and with greater accuracy. The reliability of the new method was established by the good agreement with older data obtained in solvents of LiF-BeF_2 (66-34, 80-20 mole %).

The systematic study of the solubility of BF_3 in LiF-BeF_2 melts of varying composition is continuing. The results in the composition range, 50-90 mole % LiF showed that the Henry's law constant (solubility per unit pressure) varies nearly linearly with the activity of LiF . The enthalpies of solution of BF_3 in this solvent composition range are about the same-- 15 kcal/mole.

Solubilities of BF_3 were also measured in MSBR solvent, 72-16-12 mole % $\text{LiF-BeF}_2\text{-ThF}_4$. The activities of LiF , as obtained from the Henry's law constants in the solvent, are nearly one-half those observed in 72-28 mole % LiF-BeF_2 . This trend is consistent with the hypothesis that LiF-ThF_4 interactions are considerably stronger than LiF-BeF_2 interactions.

The results described above indicate that equilibrium solubility of BF_3 in MSBR fuel salt under low partial pressures (~ 0.2 atm) is sufficient to assure positive shut-down of the reactor. We conducted an experiment on the rate of BF_3 dissolution in quiescent fuel solvent; the results suggest that BF_3 gas at moderate pressures (~ 3 atm) can be effective in a shut-down system for the MSBR.

¹Reactor Chem. Div. Annu. Progr. Rep. May 31, 1971, ORNL-4717, p. 23.

STRUCTURAL STUDIESTHE CRYSTAL STRUCTURE OF α -KTh₆F₂₅¹

G. D. Brunton

Crystals of α -KTh₆F₂₅ are hexagonal-rhombohedral, $R\bar{3}m$, with hexagonal $a_0 = 8.313(2)$, $c_0 = 25.262(4)\text{\AA}$, $Z = 3$ and $\rho(\text{cal}) = 6.281 \text{ g.cm}^{-3}$. Structural units of α -KTh₆F₂₅ are identical to those of CsU₆F₂₅² and comprise two adjacent rings of Th⁴⁺-F polyhedra, 6 polyhedra per ring, with an alkali metal ion centered between the rings. The structural units are stacked ABCABC along c_0 in α -KTh₆F₂₅ and ABAB in CsU₆F₂₅. K-F distances are 3.19(2) and 3.20(3) \AA . Th-F distances range from 2.308(1) to 2.541(9) \AA .

¹G. D. Brunton, Acta Cryst. B28, 144 (1972).²G. D. Brunton, Acta Cryst. B-27, 245 (1971).THE CRYSTAL STRUCTURE OF K₇Th₆F₃₁¹

G. D. Brunton

The complex fluoride K₇Th₆F₃₁ is isostructural with Na₇Zr₆F₃₁.² It is trigonal, $R\bar{3}$, with hexagonal axes $a_0 = 15.293(2)$ and $c_0 = 10.449(2)\text{\AA}$, $Z = 3$ and $\rho_{\text{cal}} = 5.307 \text{ g.cm}^{-3}$. The eight Th-F distances range from 2.24(1) to 2.41(1) \AA . The K-F distances range from 2.63(2) to 3.36(2) \AA .

¹G. D. Brunton, Acta Cryst. B27, 2290 (1971).²J. H. Burns, R. D. Ellison, and H. A. Levy, Acta Cryst. B24, 230 (1968).THE CRYSTAL STRUCTURE OF RbTh₃F₁₃¹

G. D. Brunton

The complex fluoride RbTh₃F₁₃ crystallizes with space group P2₁ma; $a_0 = 8.6490(5)$, $b_0 = 8.176(2)$, and $c_0 = 7.4453(4)\text{\AA}$. There are two formula weights per unit cell and the calculated density is 6.488 g.cm⁻³.

There are two thorium ions in the asymmetrical unit and each of these ions has nine nearest neighbor fluorine ions at the corners of capped trigonal prisms. The Th-F distances range from 2.32(3) to 2.48(2)Å. The Rb ion has eleven nearest neighbor fluorine ions in the range 2.79(3) to 3.37(2)Å. The final discrepancy index is 0.0710 for 2134 Ag K α reflections $> \sigma$.

¹G. D. Brunton, Acta Cryst. B27, 1823 (1971).

THE CRYSTAL STRUCTURE OF Rb₅Zr₄F₂₁¹

G. D. Brunton

The complex fluoride Rb₅Zr₄F₂₁ crystallizes with space group P2₁; a₀ = 11.520(5), b₀ = 11.222(5), c₀ = 7.868(2)Å and cos β = -0.1445(3). Calculated density = 3.930 g.cm⁻³ and Z = 2. The structure was solved by a tangent-formula procedure and was refined by Fourier and least squares methods to a final discrepancy index (R) of 0.0508 for 1376 observed Cu K α reflections. The F⁻ coordination polyhedra are different for each of the four crystallographically independent Zr ions. Seven F⁻ ions are nearest neighbors to Zr(1) at the corners of a pentagonal bipyramid, and the interatomic distances are 1.99(2) to 2.20(2)Å. The second Zr ion has eight nearest neighbor F⁻ ions [1.98(2) to 2.24(2)Å] at the corners of an irregular antiprism. Zr(3) is octahedrally coordinated by 5F⁻ at distances of 1.90(2) to 2.10(2)Å. The fourth Zr ion has seven nearest neighbor F⁻ ions at the corners of an irregular antiprism with one corner missing. Interatomic distances Zr(4)-F are 1.95(2) to 2.19(2)Å. The Rb-F distances range from 2.68(2) to 3.21(3)Å. The structure is composed of cross-linked chains of Zr-F polyhedra. Chains are connected by Zr(2)-Zr(4) edge-sharing polyhedra and the space between the polyhedra is filled with Rb ions. Integrated intensities were measured by the θ -2 θ scan technique using unfiltered Cu K α radiation.

¹G. D. Brunton, Acta Cryst. B27, 1944 (1971).

THE CRYSTAL STRUCTURE OF β -YTTERBIUM TRIANTIMONIDE¹

G. D. Brunton and H. Steinfink

A previously reported phase Yb_5Sb_2 ² is shown to be a low-temperature polymorph of Yb_5Sb_3 . β - Yb_5Sb_3 crystallizes in the orthorhombic system, space group Pnma, $a_0 = 12.398(2)\text{\AA}$, $b_0 = 9.562(2)\text{\AA}$, and $c_0 = 8.246(2)\text{\AA}$, $Z = 4$, $\rho_{\text{calcd}} = 8.343 \text{ g/cm}^3$. Molybdenum radiation was used to measure the integrated intensities of 1555 independent reflections with a scintillation counter and a four-circle diffractometer. The parameters were refined by least squares to $R = 0.0797$ for 1252 reflections greater than σ using anisotropic temperature factors. The structure consists of trigonal prisms formed by Yb whose centers are occupied by Sb. The prisms articulate by edge sharing into hexagons, and by face sharing they form hexagonal columns parallel to $[010]$. Within the columns are rhombs formed by two Yb and two Sb, and the Sb atoms are shared with the next rhombs to produce an infinite chain. The structure is very closely related to Rh_5Ge_3 .³ The shortest Yb-Yb bond length is 3.543\AA and the shortest Yb-Sb distance is 3.044\AA . There is only a tenuous relationship between the structures of the high-temperature α form and the low-temperature β form.

¹G. D. Brunton and H. Steinfink, *Inorg. Chem.* 10, 2301 (1971).²R. E. Bodnar and H. Steinfink, *Inorg. Chem.* 6, 327 (1967).³S. Geller, *Acta Cryst.* 8, 15 (1955).THE CRYSTAL STRUCTURE OF Li_2MoF_6 ¹

G. D. Brunton

Crystals of Li_2MoF_6 are tetragonal $P4_22_12$ with $a_0 = 4.6863(7)$ and $c_0 = 9.191(2)\text{\AA}$, $Z = 2$ and the calculated density is 3.687 g/cc . The Li^+ and Mo^{4+} ions are octahedrally coordinated. The Li-F distances range from $2.017(2)$ to $2.102(7)\text{\AA}$ and the Mo-F distances range from $1.927(2)$ to $1.945(2)\text{\AA}$. The MoF_6^{--} ion is coordinated by 10 Li^+ .

¹G. D. Brunton, *Mat. Res. Bull.* 6, 555 (1971).

THE CRYSTAL STRUCTURE OF A RUBIDIUM IRON FELDSPAR¹G. D. Brunton, L. A. Harris,² and O. C. Kopp³

RbFeSi₃O₈ is a synthetic hydrothermal intermediate microcline with Fe³⁺ substituting 38.9, 48.7, 10.2, and 11.0 atomic percent respectively for Si at tetrahedral positions. Lattice parameters for the triclinic cell ($\bar{C}1$) are $a_0 = 8.952(4)$, $b_0 = 13.127(5)$, $c_0 = 7.359(2)\text{\AA}$, $\alpha = 90.05^\circ$, $\beta = 116.47^\circ$, and $\gamma = 89.35^\circ$ at 24°C. The calculated density is 3.032 gm/cm³ and $Z = 4$. The Rb-O interatomic distances range 3.033(6) - 3.348(5)\text{\AA}. The average T-O distances are 1.702, 1.734, 1.620, and 1.622\text{\AA} respectively for the four independent tetrahedral positions. An asymmetrical ($C1$) structure was also refined and the discrepancy factors $R(F_0^2)$ and $wR(F_0^2)$ for the two structures are not significantly different at the 0.01 level. The $\bar{C}1$ model is probably the correct structure because several of the T-O distances in the $C1$ model are abnormally short, e.g. $T_2(O_i) - O_B(O_i)$, 1.50(3)\text{\AA}.

¹G. D. Brunton, L. A. Harris, and O. C. Kopp, "Crystal Structure of Rubidium Iron Feldspar," Amer. Min. (in press).

²Metals and Ceramics Division.

³Department of Geology, University of Tennessee (Consultant to the Metals and Ceramics Division).

OXIDE-FLUORIDE SYSTEMS

THE OXIDE CHEMISTRY OF PROTACTINIUM IN MSBR FUEL SALT

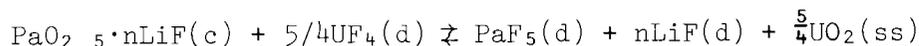
R. G. Ross, C. E. Bamberger and C. F. Baes, Jr.

We have completed studies of the effect of temperature and redox potential on the solubility of protactinium oxide in MSBR fuel salt (LiF-BeF₂-ThF₄-UF₄, 72-16-12-0.3 mole %). The details have been reported elsewhere.¹⁻³ These studies show that when the protactinium is in the 4+ state the equilibrium solid oxide, if it were present, would be ThO₂-UO₂-PaO₂ solid solution containing very little PaO₂.⁴ Thus, under the mildly reducing conditions normally maintained in an MSBR, inadvertent oxide precipitation would not be markedly different than in the absence of protactinium. However, when the system is sufficiently oxidizing for protactinium to be in the 5+ state, a very insoluble Pa(V) oxide phase can be precipitated.

$$\log (X_{\text{Pa}^{5+}})(X_{\text{O}^{2-}})^{2.5} = 0.91 - 12.76 (10^3/T).$$

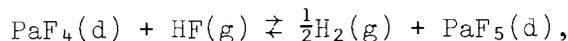
The stoichiometry of the Pa⁵⁺ precipitation indicated the O/Pa ratio to be 2.5 in the oxide phase; however, it could not be identified as Pa₂O₅. Moreover, the apparent entropy of solution is higher by ~23 e.u./mole than expected for Pa₂O₅. We are thus led to believe that the oxide phase is an addition compound, Pa₂O₅·nLiF.

In order to demonstrate that oxide precipitation is a feasible protactinium separation method, we have measured the equilibrium,



$$\log (X_{\text{UO}_2} \gamma_{\text{UO}_2})^{\frac{5}{4}} (X_{\text{PaF}_5}) / (X_{\text{UF}_4})^{\frac{5}{4}} = 4.49 - 5.69(10^3/T).$$

At 550°C the PaF₅ concentration could be lowered to ~10 ppm before a UO₂-rich solid solution with ThO₂ is precipitated. In order to fully develop a separation process, a measure of the equilibrium,



is desired. While we have been able to estimate that

$$\log (X_{\text{PaF}_5})(f_{\text{H}_2})^{\frac{1}{2}} / (X_{\text{PaF}_4})(P_{\text{HF}}) = -3.9 + 5.2 (10^3/T) \pm 0.5$$

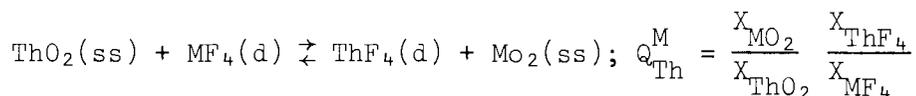
we expect to continue efforts to obtain a more precise value.

- ¹R. G. Ross, C. E. Bamberger and C. F. Baes, Jr., MSR Program Semiann. Progr. Rept. Feb. 29, 1972, ORNL-4872.
- ²MSR Program Semiann. Progr. Rept. Aug. 31, 1971, ORNL-4728, pp. 62-66.
- ³Reactor Chem. Div. Ann. Progr. Rept. May 31, 1971, ORNL-4717, pp. 17-18.
- ⁴C. F. Baes, Jr., "Ternary Solid Solutions of ThO₂, PaO₂ and UO₂," MSRP Semiann. Progr. Rept. Feb. 29, 1972, ORNL-4872.

BINARY SOLID SOLUTIONS OF PaO₂ AND OTHER ACTINIDE DIOXIDES AND THEIR EXCHANGE EQUILIBRIA WITH MOLTEN SALT REACTOR FLUORIDES

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

The dioxides of thorium, protactinium, uranium and plutonium, all of which are relatively insoluble in molten fluoride mixtures, can form substitutional solid solutions by exchange reactions of the type



involving the solid solution (ss) and the molten fluoride phase (d). It is of interest to study such exchange equilibria not only because the inadvertent precipitation of fissile oxide solids from an MSR fuel should be avoided, but also because such reactions might provide a means of separating and recycling fissile and fertile elements of reactor fuels.

A study of the exchange reaction involving Pa⁴⁺ and Th⁴⁺ has been carried out in which PaO₂-ThO₂ solid solutions ($X_{\text{PaO}_2} \leq 0.33$) were formed by equilibration of ThO₂ with molten LiF-BeF₂-ThF₄-PaF₄ (72-16-12-0.05 mole %) in the temperature range 570-730°C.¹ The resulting values of the distribution quotient $Q_{\text{Th}}^{\text{Pa}}$, along with previously measured values² of Q_{Th}^{U} and a value of $Q_{\text{Th}}^{\text{Pu}}$ derived indirectly from other previous measurements,³ are consistent with the following expressions

$$\ln \gamma_{\text{MO}_2} = \left(\frac{1.228 \pm .15}{T} \right) 10^6 \left(\frac{\Delta a}{a_{\text{ThO}_2}} \right)^2 X_{\text{ThO}_2}^2; \quad \ln \gamma_{\text{ThO}_2} = \left(\frac{1.228 \pm .15}{T} \right) 10^6 \left(\frac{\Delta a}{a_{\text{ThO}_2}} \right)^2 X_{\text{MO}_2}^2$$

$$\ln Q_{\text{Th}}^{\text{M}} = \left(\frac{1.318 \pm .027}{T} \right) 10^6 \left(\frac{\Delta a}{a_{\text{MO}_2} a_{\text{ThO}_2}} \right) + \left(\frac{1.228 \pm .15}{T} \right) 10^6 \left(\frac{\Delta a}{a_{\text{ThO}_2}} \right)^2 (2X_{\text{MO}_2} - 1)$$

wherein the activity coefficients in the solid solution are related to the difference in the lattice parameters ($\Delta a = a_{\text{ThO}_2} - a_{\text{MO}_2}$) as suggested by Hietala's model⁴ for heats of mixing of alkali metal halides solid solutions.

¹C. E. Bamberger, R. G. Ross, C. F. Baes, Jr. and D. D. Sood, MSR Program Semiann. Progr. Rept. Aug. 31, 1971, ORNL-4728, p. 62.

²C. E. Bamberger and C. F. Baes, Jr., *J. Nucl. Mat.* 35, 177 (1970).

³C. E. Bamberger, R. G. Ross and C. F. Baes, Jr., *J. Inorg. Nucl. Chem.* 33, 767 (1971).

⁴J. Hietala, *Ann. Acad. Scient. Fennicae, Series A VI Physica* 121-123 (1963).

TERNARY SOLID SOLUTIONS OF ThO₂, PaO₂, and UO₂

C. F. Baes, Jr.

In an MSBR fuel, thorium, protactinium, and uranium will all be present as tetravalent ions under normal operating conditions. The oxide phase which could be precipitated by oxide--inadvertently by contamination or intentionally for the purpose of fuel reprocessing--will be a ternary ThO₂-PaO₂-UO₂ solid solution. In order to predict the composition of this oxide phase as a function of fuel composition and temperature it is necessary to estimate the activity coefficients of the component oxides in the solid solution.

The activity coefficients in such a ternary solid solution were estimated by imagining a two-step mixing process: First one component is separated into two portions such that when each is mixed with one of the two remaining components, binary solutions of equal lattice parameters (assuming Vegard's law) are produced. The heat of mixing of each of these binary solutions may be approximated (as in the previous section) from their compo-

sition and the difference in lattice parameters of the component oxides. The heat of mixing of these binary solutions to produce the final ternary solution should be zero. Assuming the entropy of mixing is ideal, the expression for the activity coefficient of one of the component oxides in terms of the mole fractions (X_i) and its lattice parameters (a_i) is

$$\gamma_1 = \exp \frac{A}{RTa_1^2} [(X_2 + X_3)[(a_1-a_2)^2X_2 + (a_1-a_3)^2X_3] - (a_2-a_3)^2X_2X_3]$$

Analogous expressions are obtained for the other components. The constant $A = 2,440$ kcal/mole (see previous section).

From these expressions and the binary exchange equilibrium constants (see previous section) we may calculate that for an MSBR fuel of the composition LiF-BeF₂-ThF₄-UF₄-PaF₄ (72-16-12-0.1-0.03 mole %) the oxide phase in equilibrium with it (at 600°C) will have the composition ThO₂-UO₂-PaO₂ (3.6-95-1.3 mole %). In general, the ratio Pa/U in the oxide phase should be about 1/7 that in the fluoride phase.

THE OXIDE CHEMISTRY OF NIOBIUM(V) IN MOLTEN Li₂BeF₄

Gann Ting,¹ C. F. Baes, Jr., G. Mamantov²

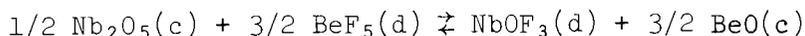
Niobium is a fission product of special interest in the MSBR since its appearance as a dissolved species in the fuel apparently can be used as an indicator of the redox potential;³ moreover, Nb₂O₅, like Pa₂O₅, is expected to be sparingly soluble in MSBR fuels and it has been suggested that Nb(V) might serve as a stand-in for Pa(V) in studies of MSBR fuel reprocessing. The purpose of the present continuing study is to explore the chemistry of niobium in molten fluorides by means of equilibria involving oxide phases of Nb(V).

Molten Li₂BeF₄ was equilibrated with BeO and Nb₂O₅ in a graphite-lined vessel under circulating mixtures of CO₂ and CO. The niobium content found in filtered salt samples can be represented by the expression

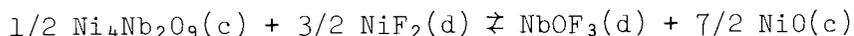
$$\log (X_{\text{Nb(V)}}) = 1.70 - 5.27 (1000/T)$$

There was no effect of the CO₂/CO ratio (i.e., the redox potential) on the niobium concentration, indicating that only Nb(V) was formed in solution;

however; the observed solubilities were much too high to be explained by the formation of the relatively unstable ⁴NbF₅. Rather the stability of Nb(V) in our experiments is most plausibly explained by the formation of an oxyfluoride, probably NbOF₃



In another series of measurements carried out in a nickel container, Nb₂O₅, BeO, and NiO were equilibrated with Li₂BeF₄ under circulating argon. The niobium and nickel oxides reacted to form NiNb₂O₆ and, later, Ni₄Nb₂O₉. As a result, the concentration of niobium in solution was lowered by a factor of about ten. We plan next to equilibrate Ni₄Nb₂O₉ and NiO in molten Li₂BeF₄. The expected equilibrium reaction



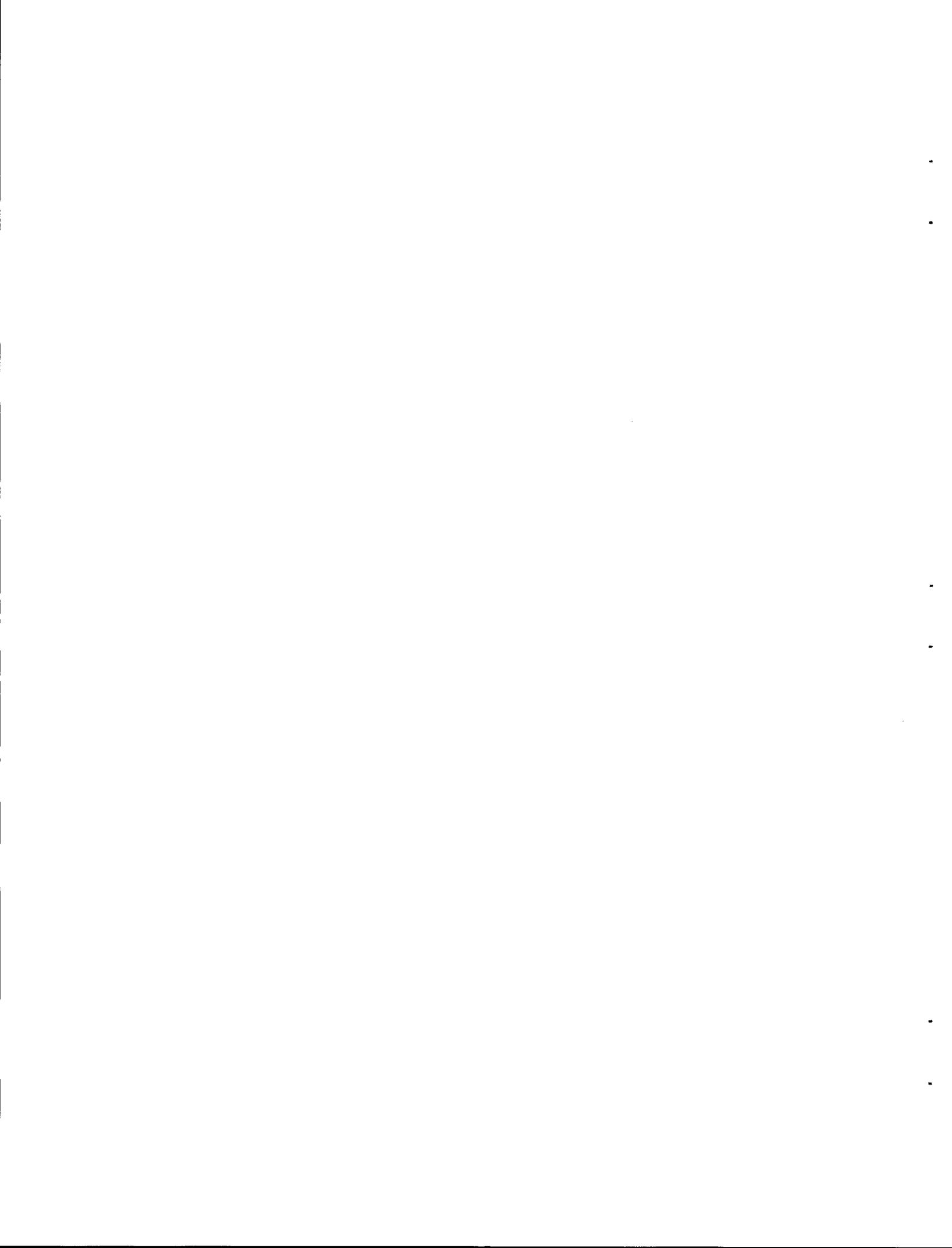
should indicate the dependence of the niobium solubility on the NiF₂ concentration and thus verify the presumption that the Nb(V) component in solution is NbOF.

¹Alien Guest from Institute of Nuclear Energy Research, Republic of China.

²Consultant from the University of Tennessee.

³R. E. Thoma, Chemical Aspects of MSRE Operation, ORNL-4658, pp. 94-99 (Dec. 1971).

⁴C. F. Weaver and H. A. Friedman, MSR Program Semiann. Progr. Rept. Feb. 28, 1970, ORNL-4548, pp. 124-125; C. F. Weaver, H. A. Friedman, and J. S. Gill, MSR Program Semiann. Progr. Rept. Aug. 31, 1970, ORNL-4622, p. 71; C. F. Weaver and J. S. Gill, MSR Program Semiann. Progr. Rept. Feb. 28, 1971, ORNL-4676, pp. 85-86.

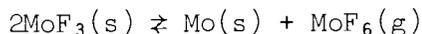


NOBLE METAL FLUORIDES

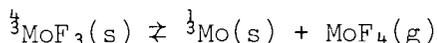
MOLYBDENUM FLUORIDES

C. F. Weaver and J. D. Redman

Mass spectrometric studies of the thermal decomposition of solid MoF and the reaction of Mo with gaseous MoF₆ have been described previously.¹ One of the reactions observed



is of especial interest; careful measurement of the pressure of gaseous MoF at equilibrium yields the standard free energy change for this reaction, and in combination with the standard free energy of formation of gaseous MoF₆,² yields the standard free energy of formation of solid MoF₃. The pressure of MoF₆ at 700°C (973°K) was 0.79×10^{-6} atm, yielding 27 kcal for the standard free energy of the reaction written above. From this information, the standard formation free energy per bond for solid MoF₃ is -55 ± 0.3 kcal compared with -50.5 kcal per bond² for MoF₆(g) at the same temperature. In addition the reaction



at 700°C yielded a MoF₄ pressure of 4.6×10^{-6} atm and hence a ΔG° of 24 kcal. This number combined with the ΔG_f° of MoF₃(s) yields ΔG_f° of MoF₄(g) of -49 ± 1 kcal per bond. The errors were estimated from pressure calibration measurements.

¹R. A. Strehlow and J. D. Redman, MSR Program Semiann. Progr. Rept. Feb 29, 1968, ORNL-4254, pp. 134-6.

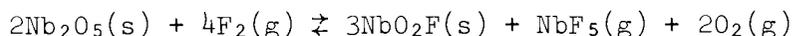
²C. F. Baes, Jr., Reactor Chem. Div. Ann. Progr. Rept Dec. 31, 1966, ORNL-4076, p. 49.

NIOBIUM FLUORIDES AND OXYFLUORIDES

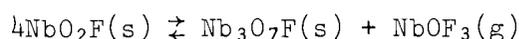
C. F. Weaver and J. D. Redman

A study of the vapor products from the reaction of Nb₂O₅ and F₂ was made over the temperature range 375 to 550°C. Fluorine was introduced into a nickel reaction-effusion cell containing pure, outgassed Nb₂O₅. The

residue remaining after several hours of fluorination was a mixture of $\text{Nb}_3\text{O}_7\text{F}$ and $\text{Nb}_{31}\text{O}_{77}\text{F}$, as identified by x-ray diffraction analysis. The vapor species consisted of NbF_5 , NbOF_3 , and O_2 . The current results, together with those from earlier studies of the thermal decomposition of NbO_2F , indicate that the dominant reactions were:



and



The standard enthalpy, ΔH° , of the second reaction above was calculated from the mass spectrometric data of both experiments to be 30 ± 1.5 kcal/mole of NbOF_3 .

In addition, a study of the vapor products of the reaction of $\text{Nb}_2\text{O}_5(\text{s})$ and $\text{NbF}_5(\text{g})$ was made over the temperature range 350 to 750°C. Below 550°C the vapor was a complex mixture of NbF_5 (monomer and dimer), NbF_3 , niobium oxyfluorides, and an oxyfluoride polymer. The oxyfluoride polymer fragment Nb_2OF_3^+ has not been observed before. Analogy with other fluoride polymers suggests that the precursor lost one fluorine atom during ionization and that its formula was Nb_2OF_4 . Above 550°C the vapor was simpler as shown below.

Species	Pressure (torr x 10 ³)				
	600°	625°	650°	700°	750°
NbF_5	2.4	3.6	1.8	2.6	4.3
NbOF_3	20		130	130	66
Nb_2OF_3^+ precursor	0.72	0.6	0.36	0.24	1.4

THE FLUORINATION OF NIOBIUM WITH MOLYBDENUM HEXAFLUORIDE

C. F. Weaver and J. D. Redman

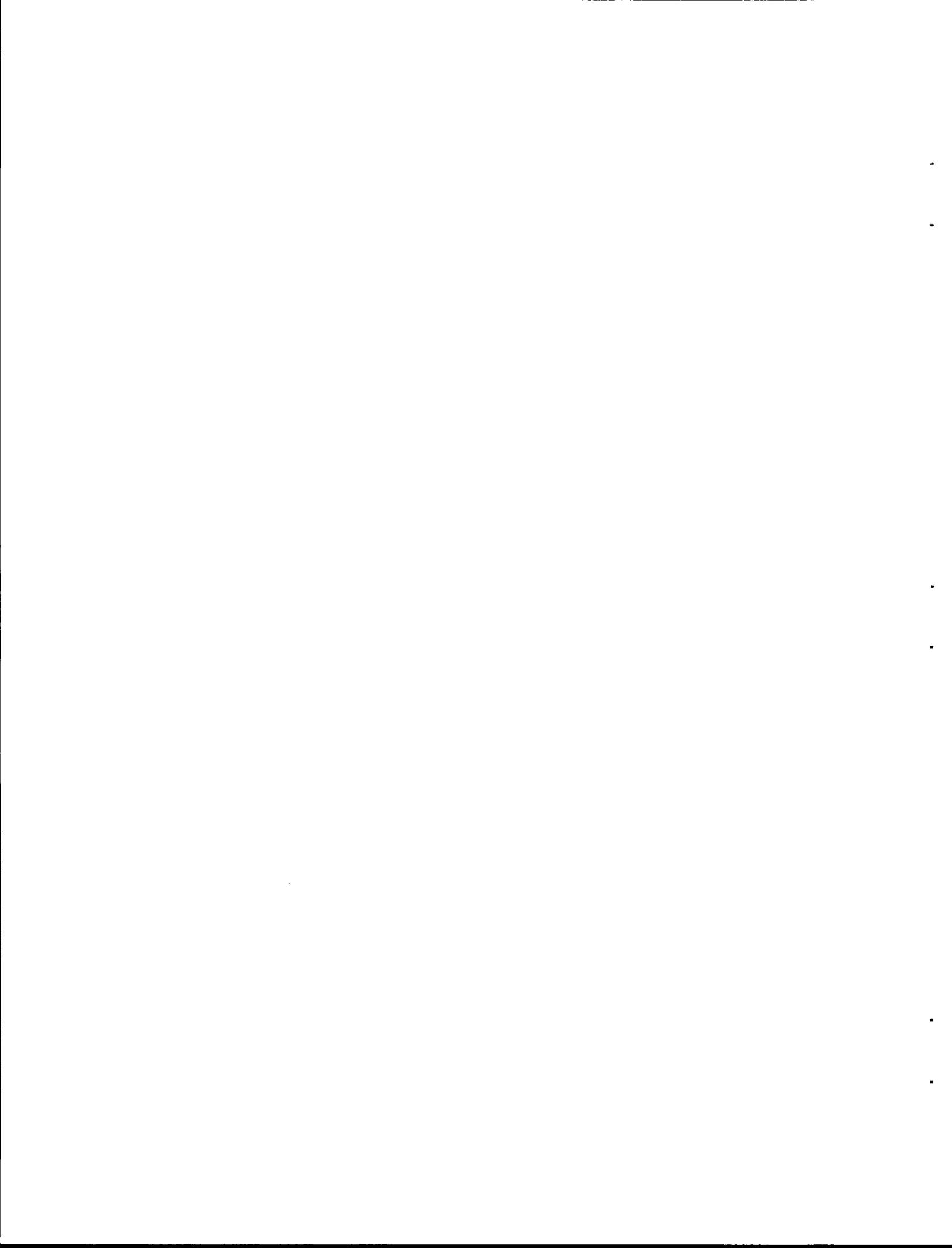
In earlier work the chemistry of Nb and Mo have been studied separately; the fact that these elements appear together during MSR operations and fuel processing make the interactions of their fluorides of interest. The reaction of MoF_6 vapor with Nb metal was observed for this reason.

The reaction was carried out in a copper Knudsen effusion cell and monitored over a temperature range of 25 to 750°C. A similar study of the reaction of MoF₆ with Mo was reported earlier.^{1,2} In general the two reactions were similar. The same molybdenum fluoride vapor products appeared at nearly the same temperature whether the reducing metal was Mo or Nb. The oxygen impurity was observed as oxyfluorides. In the temperature range 200 to 450° the MoOF₄ was dominant while Nb₂OF₄ was favored in the range 500 to 750°C. No mixed Nb-Mo species were observed although other mixed metal species are known. The effusing fluorides reacted with structural Ta in the apparatus producing both the previously reported MoTaF₁₀¹⁰ and a new compound NbTaF₁₀.

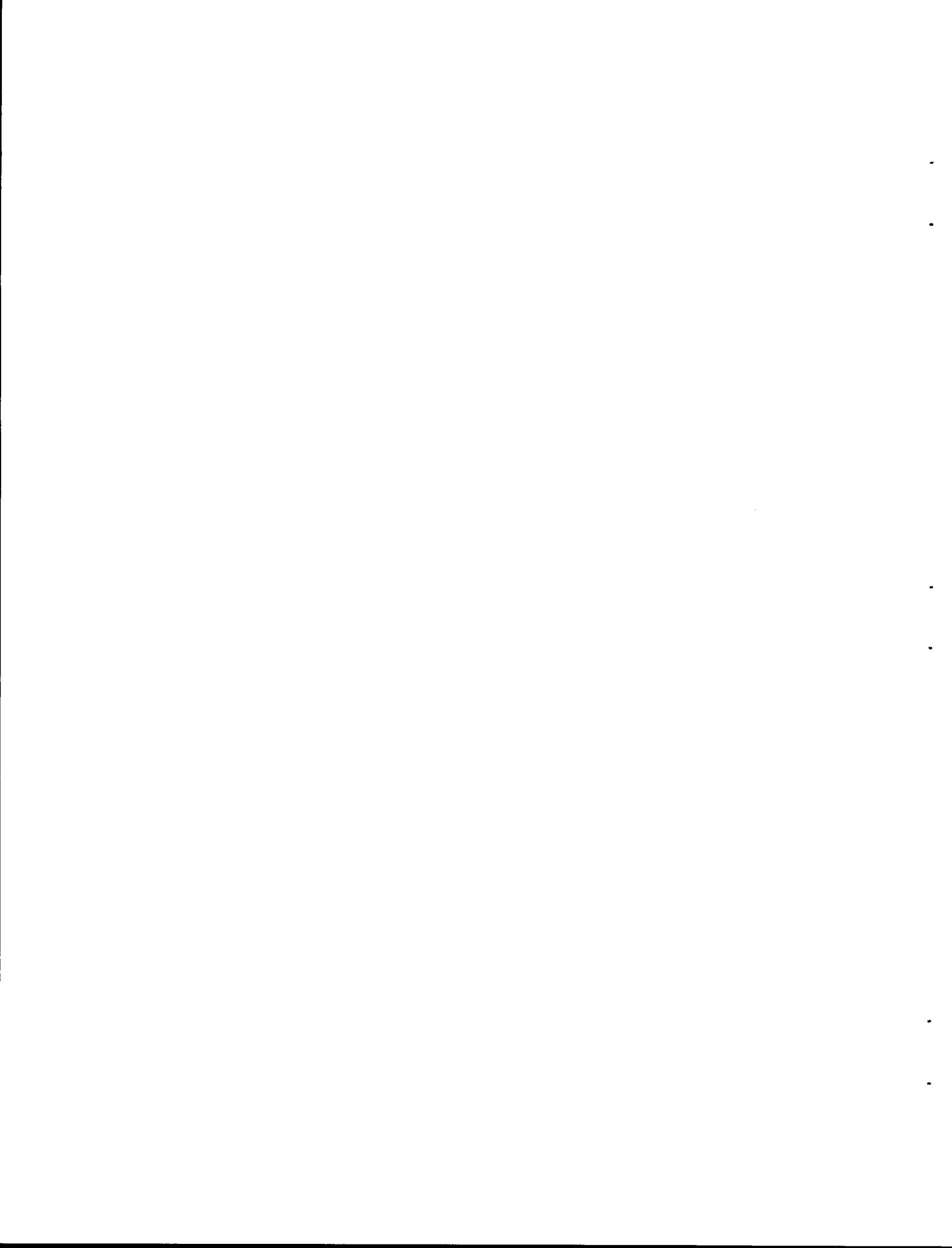
In this study the ratio of MoF₄ to MoF₅ was greater than found in the reduction of MoF₆ with Mo, possibly a reflection of the greater reducing power of Nb compared to Mo. X-ray diffraction analysis identified the residue in the cell at the conclusion of the study as being MoF₃ and Mo. The Nb was completely consumed.

¹J. D. Redman and R. A. Strehlow, Reactor Chem. Div. Ann. Progr. Rept. Dec. 31, 1967, ORNL-4229, pp. 37-39.

²J. D. Redman and R. A. Strehlow, MSR Program Semiann. Progr. Rept. Feb. 29, 1968, ORNL-4254, pp. 134-136.



PART II. MOLTEN SALT REACTOR STUDIES



FISSION PRODUCT BEHAVIOR IN MSRE

FISSION PRODUCT CONCENTRATIONS ON MSRE SURFACES

E. L. Compere and E. G. Bohlmann

The recovery of segments of surfaces from the fuel circulating system of the Molten-Salt Reactor Experiment in January 1971 permitted the direct comparison of the intensity of deposition of several fission product isotopes at a number of points around the circuit. Activity determinations were available^{1,2} on segments of a central graphite bar and a control rod thimble from the core center, on segments of heat exchanger tube and shell, and on specimens cut from the pump bowl mist shield.

Table II.1 shows the number of atoms of several nuclides per unit area of these specimens on December 12, 1969 (the shutdown date for MSRE), and the total reactor inventory/total reactor surface area as of this time. It may be seen that ⁹⁹Tc, which may well have been deposited as its precursor ⁹⁹Mo, was deposited considerably more strongly on metal surfaces in all regions than on core graphite.

Both ⁹⁵Nb and ¹⁰⁶Ru appear to have been deposited more strongly in the core than in the heat exchanger, and ruthenium was particularly strongly deposited on metal at the gas liquid interface in the pump bowl. Precision of the 35 day-⁹⁵Nb data was low because over a dozen half-lives had elapsed between reactor shutdown and specimen counting.

For ¹²⁵Sb strong depositions occurred in almost all locations, particularly on metal. Tellurium, an antimony daughter was similarly deposited.

Generally these data show somewhat higher intensities of deposition than those reported³ for standard surveillance specimens; there is nothing in the data presented here to show directly whether deposition occurred by an atomic or particulate mechanism. The relative scatter of the data do not permit us to relate them to mass transfer coefficients of the region.

¹S. S. Kirslis and F. F. Blankenship, "Examination of Moderator Graphite from MSRE," MSR Program Semiann. Progr. Rept. Aug. 31, 1971, ORNL-4728.

²H. E. McCoy, "Examination of MSRE Components," MSR Program Semiann. Progr. Rept. Aug. 31, 1971, ORNL-4728, pp. 89-110.

³F. F. Blankenship et al., MSR Program Semiann. Progr. Rept. Feb. 28, 1970, ORNL-4548, pp. 104-111.

Table II.1 Fission Product Concentration on Graphite and Metal Surfaces in MSRE

Inventory/total flow area (dpm/cm ²)	⁹⁹ Tc	⁹⁵ Nb	¹⁰⁶ Ru	¹²⁵ Sb	¹²⁷ Te				
	Graphite Metal	Graphite Metal	Graphite Metal	Graphite Metal	Graphite Metal				
	3050	127	52	16	9				
Observed Activity, dpm/cm ²									
Core center									
Top	150	17,26	6,13	6,9	2,4				
Middle	1500	100	90	40	15	22	15	6	3
Bottom	2500	50	120	11	18	9	36	4	10
Heat Exchanger									
Tube	1200	23	7	15	5				
Shell	2200	29	7	29	8				
Pump Bowl									
Subsurface	1500	22	14	31	5				
Interface			385,41	86,54					

SOME FACTORS AFFECTING THE DEPOSITION INTENSITY OF NOBLE METAL FISSION PRODUCTS

E. L. Compere, E. G. Bohlmann, and S. S. Kirslis

Paired metal and graphite tubular surfaces under both turbulent and laminar flow conditions in the final surveillance specimen array^{1,2} of the MSRE have permitted some discrimination to be made between surface effects ("sticking factor") and flow dependent mass transport effects in the deposition of noble metal fission product nuclides from fuel salt.

The activity (on December 12, 1969) of any given fission product isotope on unit surface area can be compared with total MSRE inventory divided by total MSRE surface. The thus normalized "relative deposition intensities" can be compared from region to region or nuclide to nuclide. The relative deposition intensities for salt seeking nuclides (⁹⁵Zr, ¹⁴¹Ce, ¹⁴⁴Ce) on either graphite or metal surfaces were of the order of (or less than) calculated relative impingement intensities (~0.003) for recoil from fissions in adjacent salt. This was also the case on metal surfaces for salt seeking daughters (⁸⁹Sr, ⁹¹Y, ¹³⁷Cs, ¹⁴⁰Ba) of noble gas fission products. However, porous graphite permits entry and decay of the noble gas fission products, and for these the observed relative deposition intensities were sharply higher. Such deposition intensities varied with the half-life of the entering gas, and in the case of ¹³⁷Cs,³ also indicated some subsequent return of Cs to the salt by diffusion.

In regions of flow more turbulent than most of the reactor core, the relative deposition intensity of ⁸⁹Sr on graphite specimen surfaces was ~2; comparable values in the region of laminar flow were about 0.2. Mass transport of precursor ⁸⁹Kr was undoubtedly atomic.⁴ Penetration was considerable because of negligible sticking of the noble gas, and retention of the decay product ⁸⁹Sr was high ("sticking factor" ~ 1).

In the case of noble metal nuclides, the amounts on metal surfaces were always higher than on the comparable graphite surface, though considerable variation between elements is shown in Table II.2. Tellurium and molybdenum were most strongly deposited. The differences between ¹⁰³Ru and ¹⁰⁶Ru have been interpreted⁵ as being due to a time lag before deposition, possibly in particulate form. Iodine values were about an order of magnitude

below tellurium, but were otherwise similar and indicate that the amounts found were probably residual from deposition of tellurium precursors. Deposition of niobium was similar to ruthenium, though two or threefold higher.

As in the case of ^{89}Sr on graphite, the high deposition intensities of Te (and possibly Mo) on metal surfaces implies a fairly high "sticking factor" for these elements.

The selectivity of metal surfaces, relative to graphite surface with similar flow, for the various noble metal fission product nuclides demonstrates that sticking factors must differ appreciably between the surface types.

Table II.2. Relative Deposition Intensities (Median) of Noble Metal Nuclide on Graphite and Metal

	Turbulent		Laminar	
	Graphite	Metal	Graphite	Metal
^{99}Mo	-	0.5 ⁺	0.2	1.3
^{95}Nb	0.2	0.3	0.2	0.3
^{103}Ru	0.04	0.1	0.06	0.1
$^{106}\text{Ru}^*$	0.1	0.3	0.16	0.3
$^{129\text{m}}\text{Te}^{**}$	0.07		0.15	
^{132}Te		2		0.9
^{131}I	0.005	0.4	0.003	0.1

*Based on inventory formed during exposure period only.

**Assuming 16% of ^{129}Sb decays to $^{129\text{m}}\text{Te}$.

¹E. L. Compere, E. G. Bohlmann, and S. S. Kirslis, "Some Factors Affecting the Deposition Intensity of Noble Metal Fission Product," MSR Program Semiannu. Progr. Rept. Feb. 29, 1972, ORNL-4872.

²C. H. Gabbard, Design and Construction of Core Irradiation-Specimen Array for MSRE Runs 19 and 20, ORNL-TM-2743 (December 22, 1969).

³E. L. Compere and S. S. Kirslis, "Cesium Isotope Migration in MSRE Graphite," Part II, this report.

⁴R. J. Kedl, A Model for Computing the Migration of Very Short-Lived Noble Gases into MSRE Graphite, ORNL-TM-1810 (June 1967).

⁵E. L. Compere and E. G. Bohlmann, "Noble Metal Fission Product Behavior," MSR Program Semiannu. Progr. Rept. Aug. 31, 1970, ORNL-4622, pp. 111-118.

LABORATORY STUDIES OF FISSION PRODUCT BEHAVIOR

CORROSION OF METALS BY SIMULATED FISSION PRODUCTS

J. H. Shaffer, H. E. McCoy,¹ W. P. Teichert, and W. R. Grimes

Postoperational examination^{2,3} of Hastelloy-N specimens from components of the Molten Salt Reactor Experiment has shown grain boundary cracks on most, if not all, metal surfaces that were exposed to the fuel salt mixture during operation. Since such cracks are absent from other metal surfaces (cracks occur on the fuel side of heat exchanger tubes but not on the coolant side), it seems likely that one or more fission products are responsible for this special corrosion process. This investigation, as a joint effort with the Metals and Ceramics Division, seeks identification of those fission products which are capable of producing grain boundary cracks in Hastelloy N alloy, assessment of potential damage by this cause in an MSBR, and the evaluation of remedial measures, both chemical and metallurgical, as they are proposed during this program.

Primary attention has been focussed on these fission products whose fluorides are less stable in the molten salt environment than those of the components of Hastelloy N. Tests have been conducted with tellurium, selenium, iodine, cadmium, arsenic, and antimony of this fission product group and with sulfur which was known to be an initial minor contaminant of the fuel (and coolant). All these elements have relatively low boiling points. The experimental procedures, accordingly, consisted in sealing weighed quantities of each element, along with clean metallurgical specimens machined for subsequent tensile testing, in evacuated ampoules of quartz, heating the sealed ampoules at 300°C for 24 hours to volatilize the material into the specimens, and then soaking the sealed system at 650°C for the desired interval.

Preliminary tests used quantities of these elements sufficient to yield concentrations of 100 ppm by weight of the material if it were uniformly distributed in outer 5 mils of Hastelloy N specimens. After 1000 hours of exposure to these quantities of material (which were generally slightly larger than the dosage in MSRE) the specimens were examined metallographically before and after tensile testing. These specimens treated with tellurium showed superficial grain boundary cracks not unlike those observed in specimens from MSRE;⁴ none of the other elements produced significant effects under the test conditions.⁴

Subsequent tests with tellurium using the same experimental conditions reproduced these cracks in Hastelloy N, produced cracks to a lesser extent in pure Ni, but produced no appreciable attack on 304L stainless steel.

The effects of temperature and tellurium concentrations on these metals were further examined by additional tests during 1000 hour thermal soaking periods. Samples exposed to Te concentrations of 300, 1000, and 10,000 ppm and temperatures of 550, 650, and 700°C were evaluated. The samples were exposed to Te for 1000 hours, deformed to failure at 25°C, and sectioned for metallographic examination. The examination showed that:

(a) Hastelloy N cracked under all test conditions; the severity of cracking increased with temperature and with concentration of Te.

(b) Ni-200 cracked under most conditions with the depth of cracking increasing with temperature and concentration of Te. The severity of cracking is generally less in the Ni-200 than in Hastelloy N,

(c) Type 304L stainless steel showed good resistance to cracking. Some shallow cracks were present in the samples exposed to the highest concentration of Te at 550 and 650°C.

Experiments now in progress will evaluate corrosive effects of the selected fission products (i.e., tellurium, selenium, sulfur, iodine, arsenic, antimony, and cadmium) at a concentration of 300 ppm on Hastelloy N alloy, stainless steel type 304L, and pure nickel for extended time periods of 3000, 5000, and 10,000 hours at a temperature of 650°C. Other experiments, also in progress, will investigate the effect of tellurium on metal tensile specimens immersed in a molten mixture of lithium and beryllium fluorides. In these experiments, tellurium, introduced as its volatile hexafluoride in a gas stream, should deposit on the metal surfaces by

spontaneous reduction.

¹ORNL Metals and Ceramics Division.

²B. McNabb and H. E. McCoy, MSR Program Semiannu. Progr. Rept. Feb. 28, 1971, ORNL-4676, pp. 147-166.

³B. McNabb and H. E. McCoy, MSR Program Semiannu. Progr. Rept. Aug. 31, 1971, ORNL-4728, pp. 89-106.

⁴H. E. McCoy et al, MSR Program Semiann. Progr. Rept. Feb. 29, 1972, ORNL-4872, Chapter 11.

THE FLUORINATION OF TELLURIUM WITH COBALT TRIFLUORIDE

C. F. Weaver and J. D. Redman

Recent studies, of which the preceding section of this report form a part, have suggested that tellurium may play an important part in the special grain boundary corrosion of Hastelloy N. Consequently, the reactions, stability and volatility of tellurium fluorides are being investigated. This work was initiated with a mass spectrometric study of the reaction of cobalt trifluoride with tellurium metal in a nickel cell.

The first experiment was made with CoF_3 and Te in a compartmented cell where mixing could occur only by volatilization of the Te. It was found that observable reaction started at 225°C evolving TeF_6 at a pressure of 5×10^{-5} torr. The pressure of this species was 3×10^{-3} and 3×10^{-2} torr at 250°C and 275°C , respectively. At 300°C a mixture of TeF_6 and TeF_4 was evolved at pressures of 6×10^{-2} and 5×10^{-3} torr respectively. No other species was produced until the temperature reached 400°C . Tellurium vapor was observed at 400°C , cobalt trifluoride at 600°C , and nickel fluoride at 700°C . In addition a deposit of grayish white material formed on the lid of the effusion cell; this compound was not identified but seems very likely to be a lower fluoride of tellurium.¹ A pink residue of cobaltous fluoride and a black residue of nickel telluride, both of which were identified by x-ray diffraction, remained within the cell. A second experiment duplicated the first except that the solid CoF_3 and Te were mixed. This mixture, which did not react at ambient temperature,

started to evolve volatile tellurium fluorides at slightly less than 200°C, and was difficult to control.

It appears that reaction of Te with CoF_3 offers a convenient means of preparing volatile tellurium fluorides for study of effects of these compounds upon salt-metal systems.

¹D. R. Vissers and M. J. Steindler, Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part X. A Literature Survey on the Properties of Tellurium, Its Oxygen and Fluorine Compounds, ANL-7142, p. 22 (February 1966).

THERMAL STABILITY OF SOME PERTINENT METAL TELLURIDES

C. F. Weaver and J. D. Redman

The likelihood that tellurium was at least partly responsible for grain boundary corrosion of Hastelloy N in MSRE has prompted a study of the stability of the pertinent metal tellurides. Initial studies have been performed by heating, over the temperature range from ambient to 800°C, pure commercial tellurides in nickel effusion cells under high vacuum while monitoring the evolved material with a time-of-flight mass spectrometer.

These initial studies have shown that nickel telluride (Ni_3Te_2) and chromium telluride (CrTe) are stable and nonvolatile below 800°C. No vaporized compound nor elemental Te were observed in either case though they should have been detectable at pressures as small as 10^{-4} torr.

Molybdenum telluride (MoTe_2), on the other hand, showed no measurable vaporization, but it evolved tellurium vapor at temperatures above 750°C. Complete decomposition, yielding metallic Mo as the product, of a 0.1 gram sample occurred in 6.5 days at 800°C and yielded Te pressures near 10^{-3} torr.

Bismuth telluride (Bi_2Te_3) produced no volatile species below 450°C. Between 450 and 800°C, however, the material proved both volatile and unstable; vapor species of Bi_2Te_3 , Bi, and Te were observed.

Other tellurides, including those of iron, and products obtained by treatment of Hastelloy N and other alloys with Te are under study.

TRITIUM BEHAVIOR

SOLUBILITY OF HYDROGEN IN MOLTEN FLUORIDES

A. P. Malinauskas and D. M. Richardson

One of several phenomena associated with the behavior of tritium in a Molten Salt Breeder Reactor concerns its solubility in the molten fluoride. However, whereas it had been possible to estimate the solubility of tritium as TF from existing data for HF and DF, until the present work had been initiated, no solubility data were available with which estimates could be made assuming the dissolved species to be either T₂ or TH. An apparatus had therefore been designed and constructed to provide the desired results.

Measurements of the solubilities of both He and H₂ have been made at 600°C in molten Li₂BeF₄ as a function of saturation pressure. The resulting data indicate a linear relationship between solubility and saturation pressure, that is, Henry's law was found to apply to both the He-Li₂BeF₄ and the H₂-Li₂BeF₄ systems.

The present results for helium appear to be significantly less than those reported by Watson et al.¹ for essentially the same composition of LiF-BeF₂ molten salt however, whereas the hydrogen data obtained thus far indicate a remarkable insensitivity to temperature when viewed in terms of the surface tension model of Blander et al.² for gas solubility. Both observations are readily apparent from the values of the Ostwald coefficient K_C which are presented below. (This coefficient is defined as the ratio of the concentration of the gas in solution to its concentration in the gas phase.)

Ostwald Coefficients (10³K_C) of Hydrogen and Helium in Li₂BeF₄

Temperature (°C)	Hydrogen		Helium	
	This Work	Theoretical ²	This Work	Watson <u>et al.</u> ¹
500		1.46	3.86	4.75
600	3.11	2.71	6.02	8.27
700	3.53	4.51	9.16	11.92
800		6.93		17.15

¹G. M. Watson, R. B. Evans III, W. R. Grimes, and N. V. Smith, J. Chem. Eng. Data 7, 285 (1962).

²M. Blander, W. R. Grimes, N. V. Smith, and G. M. Watson, J. Phys. Chem. 63, 1664 (1959).

PERMEATION OF METALS BY HYDROGEN AS A FUNCTION OF PRESSURE FROM 4×10^{-3} TORR TO 30 TORR

H. C. Savage and R. A. Strehlow

The permeation of tritium produced in nuclear reactors through steam generators to the environment presents several chemical problems. One of these is the question of the proper extrapolation procedure to use in assessing the permeation flow as a function of pressure. The literature offers ample evidence that the permeation flow departs from the square root dependence expected (due to the dissociative solution of hydrogen in metals) as the driving pressure is decreased below some tens of torrs.

Experiments have been performed in which permeation flow rates can be measured under steady state flow conditions at driving pressures of deuterium down to nearly 10^{-3} torr. The apparatus used a measured argon flow past the "downstream" side of a metal permeation tube specimen at a conveniently measurable pressure level. The argon flow was then sampled and analyzed for deuterium using a mass spectrometer. Deuterium was used for enhanced sensitivity due to protium levels in the mass analyzer. The nickel-based alloy, Hastelloy-N, was studied at temperatures of reactor interest, 600-700°C. The results of this series of determinations showed no departure from the square-root relation over the entire pressure range from 4×10^{-3} to 31 torr.

Values for the permeation constant determined in this work agreed within 10-20% of the earlier work on this alloy even though the low pressure behavior was profoundly different. The difference between the work described here and that in the literature is attributed to the fact that a steady-state method was used here. In the older work, because of experimental difficulties at the low pressures, a transient method was used which we believe led to artifactual behavior.

HYDROGEN PERMEATION OF OXIDE COVERED METALS

H. C. Savage and R. A. Strehlow

It is well known that oxide coatings yield a marked reduction in the permeability of many metals to hydrogen. No oxide films are possible on the metal surfaces exposed in MSBR to molten fluorides at high temperatures; however, an oxide film will be present, and perhaps one with low permeability can be produced and maintained, on the steam side of the MSBR steam generator. Studies have, accordingly, been initiated to study hydrogen permeability of such films.¹

One model leading to a decrease of permeation rate upon oxidation of a metal would be to view the oxide as offering a resistance to flow in series with that of the metal. If this were so, the pressure dependence of permeation rate would be expected to vary from a one-half power dependence at high pressures to a first power dependence at low pressures. An 18-8 stainless steel was studied as a metal which was expected to form a protective oxide coating. Hydrogen permeation data for the clean metal showed a one-half power pressure dependence. After a light coating of oxide was permitted to form, the permeation rate was found to have decreased by a factor of eight. The pressure dependence, however, was not changed from the half power. This indicated that the oxide coating was not continuous and that defects in the oxide permitted ready access of the hydrogen to the metal.

A model was derived for the observed behavior based upon the notion that the oxide defects (holes or cracks) which permit permeation flow to occur with a constriction resistance additional to the bulk resistance of the metal. The relations obtained in terms of defect geometry are based on the derivations from potential theory as applied to the analogous phenomenon of electrical contact resistance. An example of a relation obtained from this model is as follows for holes at average separation, 2ℓ , and average radius, a :

$$I_T = D_T A K_s \left(\frac{1}{\Delta X + \frac{\ell^2}{a}} \right) \cdot \Delta(P_T^2)$$

where I_T is the permeation flow rate through a specimen; D_T is the diffusivity of tritium in the metal; A , the area; K_s , the solubility constant

(Sievert's constant) of tritium in the metal; ΔX the specimen thickness; and P_{T_2} , the pressure of tritium. Although the model has not yet been tested, it appears to fit the salient features of the phenomena associated with oxide structure and with the permeation process.

¹R. A. Strehlow, Reactor Chem. Div. Annu. Progr. Rept. May 31, 1971, ORNL-4717, p. 54.

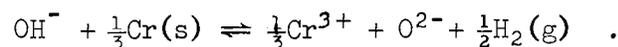
HYDROGEN BEHAVIOR IN FLUOROBORATE COOLANT SALT

S. Cantor and R. M. Waller

A potentially valuable mechanism for isolation and control of tritium would be available if the NaF-NaBF₄ coolant salt could contain an appreciable concentration of hydroxyl ion (presumably as NaBF₃OH) and if rapid isotopic exchange of this species with entering tritium could be achieved. This continuing study^{1,2} attempts to define the extent and the conditions under which the fluoroborate mixture can retain hydroxide species.

In these experiments, sealed and evacuated capsules of nickel containing the salt under study with coupons of metal capable of reacting with the contained OH⁻ are heated within a silica vessel connected to apparatus for pressure measurement and recovery of the gas diffusing from the nickel capsule.

An important series of such experiments used samples of fluoroborate coolant drawn from a long-term thermal convection loop, operated by the ORNL Metals and Ceramics Division, for testing corrosion of Hastelloy-N. Careful material balance data on the H₂ diffusing from the sealed capsule over a nearly six-week reaction period showed, in confirmation of chemical analyses, the salt sample to contain substantial concentrations (26-40 ppm) of hydrogen. Such concentrations would be more than adequate for exchange and control of the tritium. The reaction producing gaseous hydrogen in these experiments can be represented by the equation



At 535°C, the equilibrium quotient (Q) for the reaction was estimated from pressure measurements and mass balance and is given by the expression

$$Q = 5.9 \times 10^{-4} P_{H_2}^{\frac{1}{2}} / (OH^-)$$

where P_{H_2} is the partial pressure of hydrogen in atmospheres; (OH^-) is the concentration of hydroxide ion in ppm; the constant 5.9×10^{-4} was obtained from the analytical concentrations of chromium and oxide in the salt sample and from the activity of chromium (~ 0.1) in Hastelloy N.

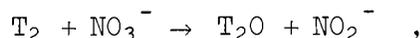
¹S. Cantor and R. M. Waller, MSR Program Semiannu. Progr. Rept. Feb. 28, 1971, ORNL-4676, p. 88.

²S. Cantor and R. M. Waller, Reactor Chem. Div. Annu. Progr. Rept. May 31, 1971, ORNL-4717, p. 52.

THERMAL STABILITY OF NITRATE-NITRITE MIXTURES

C. F. Weaver and J. D. Redman

The diffusive path of tritium from the reactor fuel through the heat exchangers and fluids to the steam system could certainly be blocked by a coolant salt capable of oxidizing the tritium to T_2O or HTO and allowing its controlled recovery in that form. Salt mixtures such as HITEC [$(NaNO_2 - NaNO_3 - KNO_3$ (40-7-53 wt %)] have been used commercially as heat transfer fluids at high temperatures. Such mixtures should, by the reaction



which has a large negative standard free energy change, provide such oxidation and control. Consequently, HITEC has been given some consideration as an additional (third loop) coolant for an MSBR. Such mixtures are known to undergo some thermal decomposition. Accordingly, a small study, by mass spectrometric techniques, was constructed to determine the amount and the identity of the vapor species evolved upon heating the individual components and the commercial mixture.

The three individual component salts all evolved NO. In addition, the nitrates produced O_2 and the nitrite produced N_2 . These permanent gases do not allow accurate pressure measurements because of background interference, but the total pressures were in the range of 0.1 to 1 torr at the upper temperature limit ($450^\circ C$) of these experiments. In addition to the NO, O_2 , and N_2 , Na and K were carried into the gas phase by some

unidentified species.

These results are in agreement with the conclusion of Kust and Burke¹ (who did not determine composition of the evolved gases) that nitrate melts decompose at lower temperatures than previously suggested.^{2,3} The earlier higher temperature studies² (600-780°C) produced mixtures of O₂, N₂, and NO₂ while at the lower temperatures (up to 450°C) of these experiments we saw NO and N₂ or NO and O₂ for nitrite and nitrate respectively.

The gases NO, O₂, N₂ (and possibly N₂O) were observed over HITEC along with unidentified species carrying Na and K in a non-metallic form. Total pressures were about an order of magnitude lower for the ternary mixture when compared with the components at the same temperatures.

¹R. N. Kust and J. O. Burke, "Thermal Decomposition in Alkali Metal Nitrate Melts," Inorg. Nucl. Chem. Letters 6, 333-5 (1970).

²Eli S. Freeman, "The Kinetics of the Thermal Decomposition of Sodium Nitrate and of the Reaction Between Sodium Nitrite and Oxygen," J. Phys. Chem. 60, 1487-93 (1956).

³B. D. Bond and P. W. M. Jacobs, "The Thermal Decomposition of Sodium Nitrate," J. Chem. Soc. A, 1265-8 (1966).

DISSOCIATING GAS HEAT TRANSFER SCHEME AND TRITIUM CONTROL IN MOLTEN SALT POWER SYSTEM

E. L. Compere

The paths of tritium produced in Molten Salt Reactors must be controlled if it is to be retained or recovered rather than passing into the environment. An important and easy loss route is by diffusion through heat transfer surfaces separating primary, secondary and steam systems, with ensuing passage in diluted form in water leaked or otherwise returned to the environment. Means which serve to block this passage and permit tritium recovery are thus of great importance.

The recent Russian development¹ of power systems employing a dissociating gas (e.g., nitrogen tetroxide) as the working fluid, and U. S. examination^{2,3} of the transport properties of such materials, led to a speculative consideration of their application to molten salt reactor systems.

On heating, liquid nitrogen tetroxide becomes gaseous (critical

temperature, 151°C) and dissociates rapidly and reversibly into nitrogen dioxide (~ 50 to $\sim 200^{\circ}\text{C}$) absorbing ~ 7 kcal/mole NO_2 . At temperatures of ~ 300 - 700°C , nitrogen dioxide dissociates reversibly and fairly rapidly into nitric oxide and oxygen, absorbing 14 kcal/mole NO_2 . These dissociations strongly increase both the effective heat capacity and thermal conductivity. These properties should permit a reduction in required heat transfer and in required pumping power in power system applications.

Chemical stability of the nitrogen oxide system is tolerable. The irreversible decomposition of nitric oxide to the elements can occur both homogeneously and on surfaces, but literature data extrapolated down to 600°C indicate reaction rates are slow enough to permit makeup intervals of at least several months.

In the Russian work, nitrogen tetroxide was the primary power system working fluid, passing over stainless steel-clad reactor fuel elements and driving a gas turbine. Unusually high thermodynamic efficiencies were claimed. Application in molten salt systems⁴, however, would have to be less direct because leakage into the circulating salt fuel might result in appreciable reaction with the graphite moderator in the core. For a Molten Salt Breeder Reactor, the dissociating gas system would drive a gas turbine, replacing the steam turbine system; but a secondary coolant, such as molten lithium beryllium fluoride, would transport heat between the primary and power systems.

The materials of construction should be stainless steels, or chromium containing alloys such as Inconel or Hastelloy-N, which can be heated in pressurized air. Oxide film buildup on the surface would inhibit corrosion processes. Tritium entry into the power system would be inhibited by these films, which would be moderately heavier than oxide films in steam systems.

The necessity of good containment of the relatively toxic nitrogen oxides should permit such tritium as enters (also any H_2 from additions to the salt system) to accumulate for an extended time in this system in the form of very dilute nitric acid or water without further dilution by environmental hydrogen; the full production rate of T_2 is ~ 0.04 g mole/day. In this form, except for necessarily controlled leaks, tritium should be retained in the system. At suitable intervals, tritium could, presumably, be recovered without appreciable further hydrogen dilution. Processes

involving adsorption, chemical reaction, or freezing are possible.

The advantages of using dissociating nitrogen tetroxide as the working fluid in the power system of a molten salt breeder reactor include blockage of a major tritium loss path from the system, considerable capacity of the power system fluid to retain tritium without hydrogen dilution probable increased resistance to tritium passage into the power system, and also the possibility of increased thermal efficiency of the system due to enhanced thermal conductivity and heat capacity.

¹A. K. Krasin and V. B. Nesterenko, "Dissociating Gases: A New Class of Coolants and Working Substances for Large Power Plants," Atomic Energy Review 9(1), 177-194 (1971), IAEA, Vienna.

²Roger A. Svela and Richard S. Brokaw, "Thermodynamic and Transport Properties for the $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ System," NASA TN D-3327 (N66-18171), 1966.

³M. Blander, L. G. Epel, A. P. Fraas, and R. F. Newton, Aluminum Chloride as a Thermodynamic Working Fluid and Heat Transfer Medium, ORNL-2677 (1959).

⁴E. L. Compere, "Dissociating Gas Heat Transfer Scheme and Tritium Control in Molten-Salt Power Systems," MSR Program Semiannu. Progr. Rept. Aug. 31, 1971, ORNL-4728, pp. 60-61.

SEPARATIONS PROCESSES

REMOVAL OF FISSION PRODUCTS FROM LITHIUM CHLORIDE

J. H. Shaffer, D. M. Richardson, W. Jennings, and W. R. Grimes

The metal transfer process^{1,2} removes fission products, especially the rare earths and alkaline earths, from MSBR fuel by transferring them, through a molten alloy of bismuth containing lithium and thorium, to essentially pure lithium chloride. As a second step in this process the fission products are removed from the LiCl by extraction into a bismuth-lithium alloy of considerably higher lithium concentration. The fission products are ultimately removed from this bismuth alloy by hydrofluorination into a fluoride mixture for discard; the bismuth is, accordingly, available for return to the system, but the excess of ⁷Li must be discarded with the fission products. A small program has been conducted as time permits to attempt a more simple and economic method of removing these fission products

from molten LiCl.

Preliminary experiments showed that Ce^{3+} , added as $CeCl_3$ traced with ^{144}Ce , was selectively removed from molten LiCl on powdered Zeolite 4A ion exchange material.³ A subsequent experiment,⁴ using dried, commercial spheres (No. 8 mesh) of sodium-form Zeolite 4A, confirmed this selective removal of Ce^{3+} , and showed that zeolite containing as much as 0.13 g Ce^{3+} per gram of exchanger resulted from equilibration with LiCl containing ca 5000 ppm of Ce^{3+} . Essentially complete exchange of Li^+ for Na^+ was also observed; conversion of the Zeolite to the lithium form appears easy. The distribution observed followed the empirical relationship:

$$\ln (\text{ppm Ce in salt}) = 12.163 + 1.35 \ln (\text{g Ce/g Zeolite})$$

This relationship suggests that zeolite in equilibrium with the process LiCl (which would contain about 100 ppm of trivalent rare earths) would contain about 3.7 mg of rare earth per gram. This corresponds to a discard of zeolite, assuming excellent separation from the molten LiCl, containing 15 grams of 7Li per gram of trivalent rare earth. Similar experiments showed essentially no removal of Ba^{2+} (added as $BaCl_2$ and traced with ^{133}Ba) from the molten LiCl. It seems clear that application of such ion exchangers will be ineffective with alkaline earths; they will probably prove ineffective for divalent rare earths as well, though this point may be worth checking.

Selective precipitation of rare earth species as oxides from MSBR fuels is impossible because prior precipitation of UO_2-ThO_2 and of ThO_2 occurs. Precipitation of these oxides from essentially pure LiCl, however, has seemed worth study. The total rare earth content of the loaded LiCl stream is expected to be about 100 ppm; precipitation and precipitate recovery from such dilute solutions is expected to prove difficult. Most attention has, therefore, been paid to precipitation of rare earths (present in the LiCl as chlorides and containing radiotracer isotopes) by addition of Li_2O or other oxides in the presence of carriers or sparingly soluble oxides with which the precipitated oxide may form compounds or solid solutions.

Boric oxide (B_2O_3) proved to be sparingly soluble (about 30 ppm B) in molten LiCl containing 100 ppm of Ce^{3+} , added as $CeCl_3$ with ^{144}Ce tracer, but was ineffective as a precipitant for the cerium. Addition of Li_2O to

the LiCl-B₂O₃ system precipitated a substantial fraction of the Ce³⁺, but as excess Li₂O was added the B₂O₃ dissolved in the melt. Material balance considerations suggest that conversion to and dissolution of LiBO₂ occurred. Subsequent sparging with BCl₃, which presumably reacted with the Li₂O and LiBO₂ to form LiCl and B₂O₃, returned to precipitated Ce³⁺ to solution and dropped the soluble boron to its original value. While it is possible that BCl₃ may be a useful reagent for removal of excess Li₂O in other similar processes, it does not seem likely that precipitation in the presence of B₂O₃ will be useful.

Similar experiments which added Li₂O to LiCl containing divalent europium chloride and solid Y₂O₃ precipitated as much as 70% of the europium but the data were difficult to reproduce and probably do not represent a useful equilibrium process. Preliminary studies in which Li₂O was added to LiCl containing EuCl₂ and added YCl₃ have shown considerably more reproducible behavior and seem considerably more encouraging.

Continuing experiments will further evaluate these systems and will examine solutions containing both di- and tri-valent rare earths with added carriers such as AlCl₃, ThCl₄, ZrCl₄ and, perhaps, other readily precipitable ions.

¹L. E. McNeese, MSR Program Semiann. Progr. Rept. Feb. 28, 1970, ORNL-4548, pp 282-288.

²M. J. Bell and L. E. McNeese, MSR Program Semiann. Progr. Rept. Aug. 31, 1970, ORNL-4622, pp. 199-202.

³D. M. Moulton and J. H. Shaffer, MSR Program Semiann. Progr. Rept. Aug. 31, 1970, ORNL-4622, p. 109.

⁴D. M. Richardson and J. H. Shaffer, MSR Program Semiann. Progr. Rept. Aug. 31, 1971, ORNL-4728, p. 67.

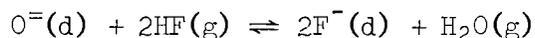
DEVELOPMENT OF PROCESSES FOR OXIDE REMOVAL FROM MOLTEN FLUOROBORATE

J. H. Shaffer and W. P. Teichert

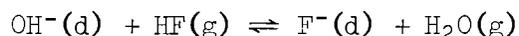
Purity of sodium fluoroborate and sodium fluoride from commercial sources is such as to require only the minimal processing measured of mixing and moisture removal before their use as a molten-salt fluid in high

temperature engineering systems. As a secondary coolant in an MSBR, however, appreciable oxide contamination will probably occur through occasional leaks from the steam generator. Thus, a process for removing oxide ion from molten fluoroborates is needed to permit sustained reactor operation at small steam inleakage rates. The continuous operation of this process could also provide effective recovery of tritium from the reactor system if hydroxyl ion stability and tritium exchange rates with hydrogen in the molten fluoroborate coolant are found sufficient. These objectives are the basis of an experimental program to develop processes for the removal of oxide and hydroxyl ions from the proposed MSBR fluoroborate coolant mixture.

Previous efforts to apply direct hydrofluorination for this process have indicated that the equilibria,

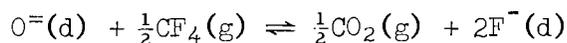


and

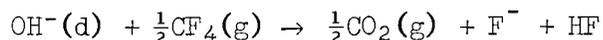


do not permit a genuinely effective process. Treatment with elemental F_2 would certainly suffer to remove O^{2-} and OH^- , but the corrosion rates inherent in such processing would probably lead to considerable engineering complexity. Accordingly, this program is currently investigating possible reactions of CF_4 and other fluorocarbons for this application.

Thermodynamic information on some of the boron compounds of interest in this process is not available and the complex behavior of oxide ion in molten fluoroborates lacks adequate description. However, free energy considerations indicate that reactions of the type



should be much more favorable than corresponding reactions with HF. In addition, hydroxyl ion removal by the reaction,



should be further enhanced by the free energy of HF as a reaction product.

Though CF_4 , from thermodynamic considerations, should be reactive at elevated temperatures its reactions are frequently sluggish kinetically; catalysts may be required to achieve sufficient reaction efficiencies for the process. The results of preliminary experiments conducted thus far have, indeed, failed to yield identification of CO_2 as a reaction product, and the HF found in the gas effluent could not be adequately correlated with the very low hydroxyl ion content of the melt. Difficulties in

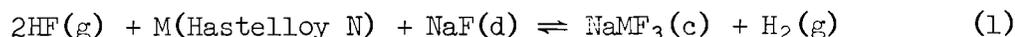
analysis of the complicated effluent gas stream (HF, H₂O, BF₃, and CO₂ and perhaps others in argon) have also been encountered.

SPECIAL STUDIES

THE FREE ENERGIES OF FORMATION OF NaNiF₃ and NaFeF₃

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

The compounds NaNiF₃ and NaFeF₃ have been shown to be stable and relatively insoluble in NaBF₄-NaF mixtures.¹ A knowledge of their formation free energies would permit an estimate of the equilibrium position of such corrosion reactions as



where M is either Ni or Fe. The free energies of formation of NaNMF₃ were estimated from measurements of the equilibria



where a_{NaF} is the activity of NaF. The experimental procedure consisted of equilibrating MF₂ and NaNMF₃ with molten NaBF₄, while measuring the BF₃ pressures which are proportional to a_{NaF} . The latter were calculated using the equilibrium constant for the reaction of thermal decomposition of NaBF₄ measured by Cantor.^{2,3} The values of K₂ measured were combined with ΔG^f values for NiF₂(c),⁴ FeF₂(c),⁴ and NaF(l)⁵ to yield

$$\Delta G^f(\text{NaNiF}_3(c)) = [-296.38 + 59.72 (T/10^3)] \pm 1.4$$

$$\Delta G^f(\text{NaFeF}_3(c)) = [-307.82 + 55.05 (T/10^3)] \pm 1.4$$

Furthermore, combining the values of K₂ with the equilibrium constants for the reduction of NiF₂(c) and of FeF₂(c) by hydrogen⁴ we obtained the equilibrium constants for reaction (1)

$$\log [P_{\text{H}_2}/P_{\text{HF}}^2 a_{\text{Ni}} a_{\text{NaF}}] = [-9.25 + 7.78 (10^3/T)] \pm 0.05$$

$$\log [P_{\text{H}_2}/P_{\text{HF}}^2 a_{\text{Fe}} a_{\text{NaF}}] = [-8.23 + 10.28 (10^3/T)] \pm 0.05$$

From these it appears that for molten NaBF₄-NaF mixtures contained in Hastelloy-N relatively large HF partial pressures may be tolerated in the presence of hydrogen ($P_{\text{HF}}/P_{\text{H}_2} \sim 40$ at 600°C) without oxidation of the nickel to NaNiF₃.

- ¹F. A. Doss and J. H. Shaffer, private communication.
- ²S. Cantor (editor), Physical Properties of Molten Salt Reactor Fuel, Coolant, and Flush Salts, ORNL-TM-2316, p. 34 (Aug. 1968).
- ³S. Cantor, R. E. Roberts, and H. F. McDuffie, Reactor Chem. Div. Annu. Progr. Rep. Dec. 31, 1967, ORNL-4229, p. 55.
- ⁴C. M. Blood, Solubility and Stability of Structural Metal Difluorides in Molten Fluoride Mixtures, ORNL-CF-61-5-4 (Sept. 1961).
- ⁵JANAF Thermochemical Tables, 2nd ed., U.S. Dept. of Commerce, NSRDS-NBS-37 (June 1971).

A STIRRED VESSEL FOR MOLTEN SALT RESEARCHES AT REDUCED GAS PRESSURES

J. H. Shaffer, F. A. Doss, and L. V. Wilson¹

Studies of various chemical equilibria in molten salts have generally lacked efficient melt agitation on systems requiring an absolute control of impurities in the gas phase. Owing to the operational requirements for shaft seals and bearings on small mechanical stirrers at elevated temperatures, laboratory practices have largely used inert gas sparging and, in some instances, rocking furnaces to achieve conditions of equilibrium in the melt. However, the limitations imposed by these methods becomes more acute in molten fluoroborate systems because of the relatively high vapor pressure of BF_3 and its necessary inclusion in the sparge gas stream. Recent studies of the ionic solubility of nickel and iron in molten NaBF_4 - NaF (92-8 mole %) did yield identification of NaNiF_3 and NaFeF_3 as the solid saturating phase (by x-ray diffraction examinations) but the solubility data over the temperature range of 475 to 600°C was widely scattered and gave abnormal values for the heats of solution. Since adequate material balance of BF_3 in the system could not be guaranteed, correlation of nickel and iron solubility values with melt composition was attempted. However, the precision of chemical analyses of the major salt constituents was not sufficient for accurate determination of salt composition dependency in either case. Thus, the development of a stirrer assembly which would permit determination of melt composition from measurements of the BF_3 vapor pressure was begun.

An engineering design study has been completed and fabrication details provided for a stirred vessel which can be operated at reduced gas pressures. The stirrer utilizes a magnetic coupling between the motor and propeller shafts across a steel membrane seal. This feature effectively encloses the bearing assembly within the gas-tight salt vessel. Ports for connecting the vessel to valved gas lines and for withdrawing salt samples under controlled atmospheres are also provided. The salt vessel was sized to fit in a 5-inch diameter tube furnace and to contain about 2 liters of molten salt. Fabrication costs for the complete experimental apparatus are estimated at about \$4,000.

¹ORNL Reactor Division.

PREPARATION OF NaBF_4 - NaF (92-8 MOLE %) FOR ENGINEERING LOOP TEST AND RELATED PRODUCTION ACTIVITIES

F. A. Doss, W. P. Teichert, W. Jennings, Jr., and J. H. Shaffer

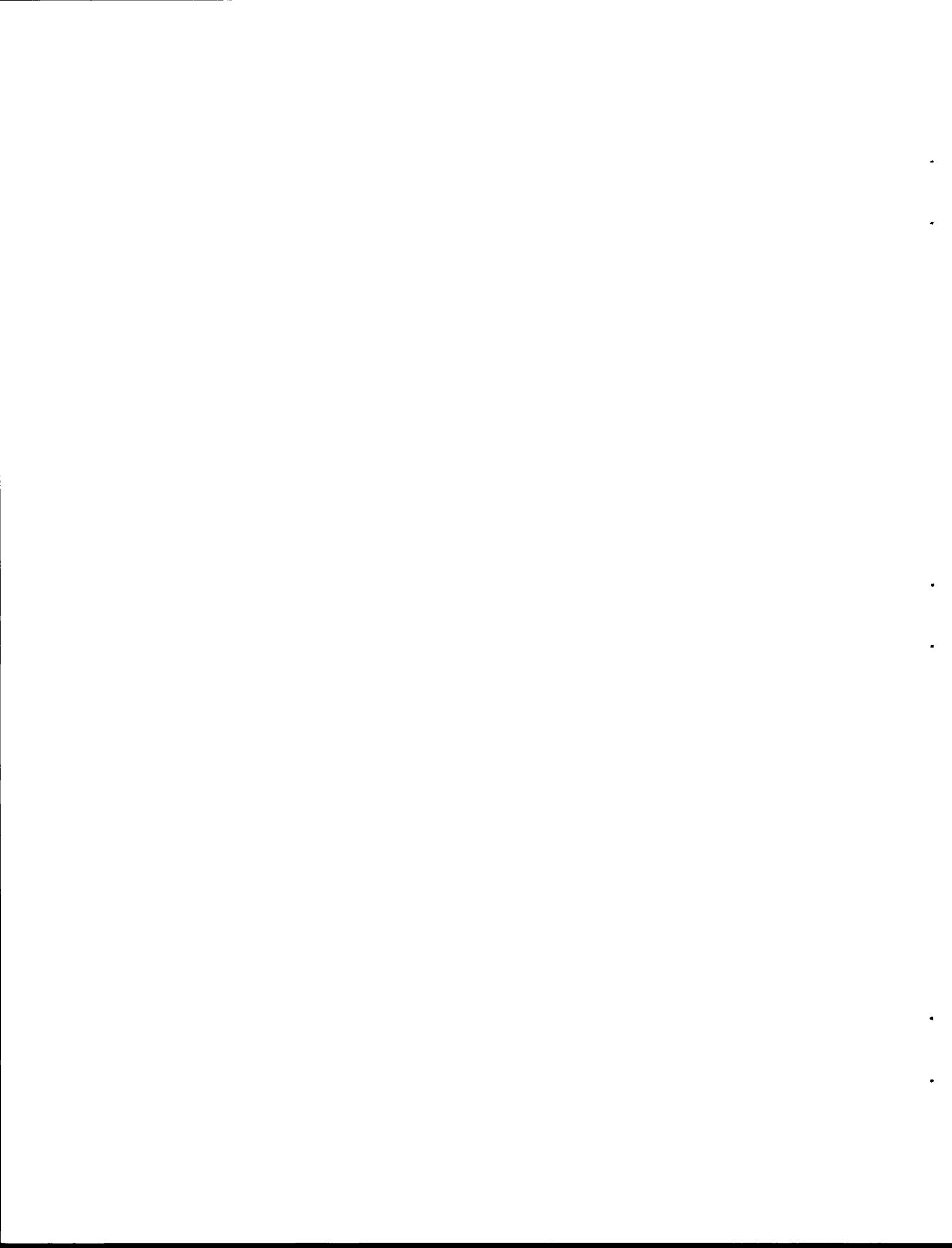
The preparation of approximately 1,550 lbs of the fused mixture, NaBF_4 - NaF (92-8 mole %), for use in operating the Coolant Salt Technology Facility (CSTF) was begun on January 3, 1972, and completed on March 7. This production operation was conducted in the Fluoride Production Facility in six batch operations of about 258 lbs each. Finished materials were piped as liquid directly into the detached CSTF drain tank from the batch processing unit.

Sodium fluoroborate used in this production effort was purchased from the Harshaw Chemical Company as a custom preparation to sufficiently restrict impurity concentrations for this high temperature application. Sodium fluoride which was added to make the fused fluoroborate mixture was RACS grade and did not significantly affect the total impurity content of the mixture. With these starting materials the salt purification procedure was reduced effectively to the removal of water vapor by evacuation of gases while heating the powdered salts at controlled rates up to 300°C. Although materials specifications allowed 1000 ppm by weight of water in the starting materials, only negligible quantities were collected in the gas effluent cold trap during each run. The salt mixture was then heated

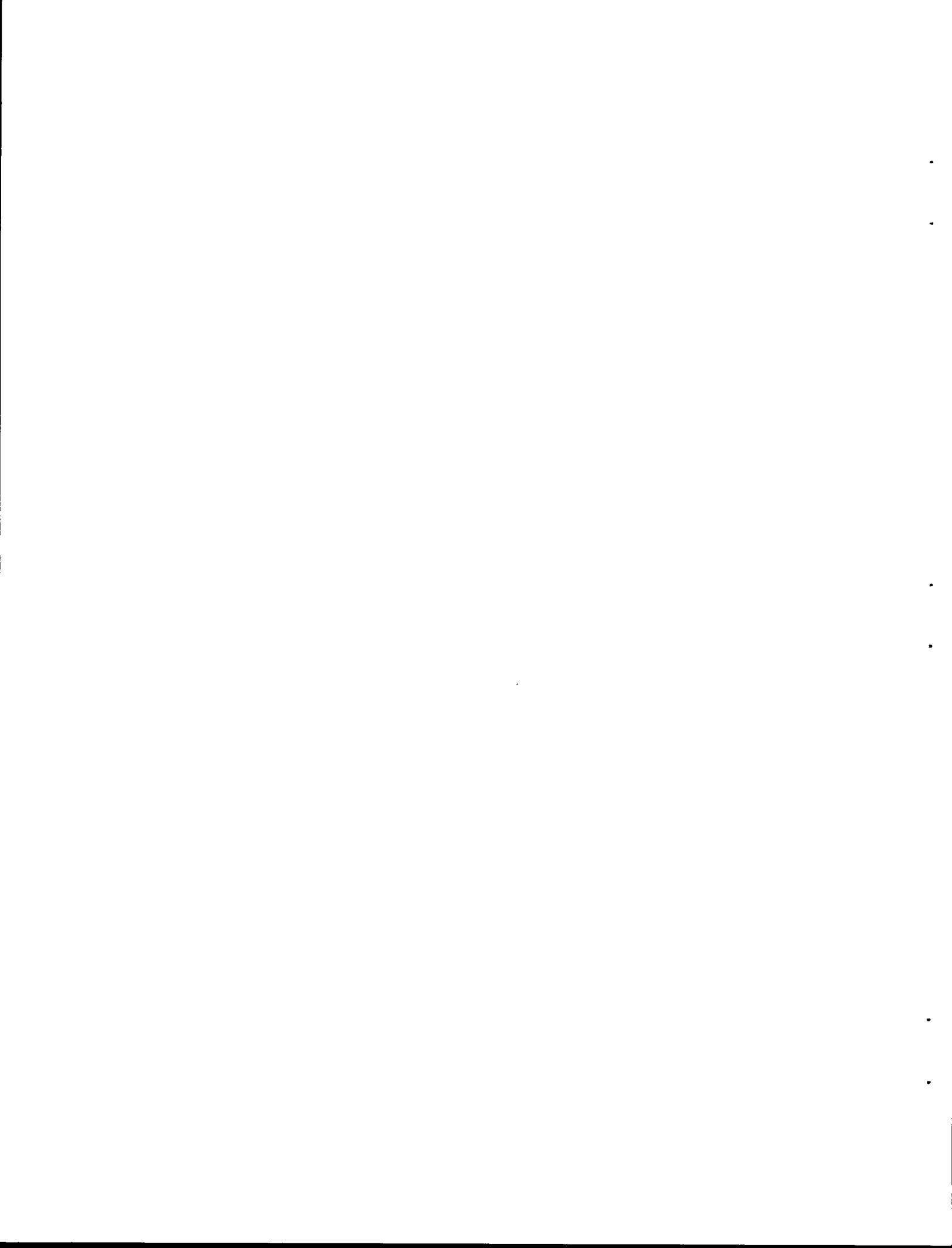
beyond its melting point to 500°C under a static atmosphere of argon and then sparged with BF_3 at 10 liters per minute for about 10 minutes to insure mixing. Residual BF_3 was purged from the system, and a filtered sample of the molten salt was withdrawn before transferring the salt batch to the drain tank by displacement with argon.

The results of chemical analyses from the six batch preparations yielded average values for nickel, chromium, iron, and oxide impurity contents of 16, 13, 141, and 319 ppm by weight, respectively. The results proton analyses on five of the six batches corresponded to 15 ppm by weight and, if present as the hydroxyl ion, would imply its association with 240 ppm of the total oxide found. The average values reported for the major constituents (i.e., sodium, boron, and fluorine) differed from those calculated for the mixture by quantities no greater than the error limits of the analytical determinations.

The Reactor Chemistry Division is also responsible for the preparation of all fused salts required for the operation of the various chemical, metallurgical, and engineering tests of the Molten Salt Reactor Program. This commitment was satisfied by the production of about 600 lbs of $\text{LiF}-\text{BeF}_2-\text{ThF}_4$ (72-16-12 mole %), for engineering development studies of MSBR fuel reprocessing technology and an additional 420 lbs of NaBF_4-NaF (92-8 mole %), 80 lbs of $\text{LiF}-\text{BeF}_2$ (66-34 mole %), and about 25 lbs of assorted fused salt mixtures for smaller research and development studies of the MSRP.



PART III. AQUEOUS STUDIES

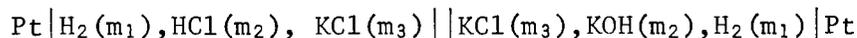


EQUILIBRIA AT ELEVATED TEMPERATURE

POTENTIOMETRIC DETERMINATION OF THE ION PRODUCT OF WATER TO 300°C AND ITS VARIATION WITH IONIC STRENGTH, PRESSURE AND DENSITY

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

The study of the dissociation of water to 300°C by means of the flowing EMF cell¹



has been completed. The resulting ion product values ($Q_w = [\text{H}^+][\text{OH}^-]$), which have been measured as a function of temperature, ionic strength, and pressure, have been fitted by means of an empirical expression involving these independent variables and 15 adjustable parameters. Included in the fit were data of Harned and Hamer² on a similar cell in the temperature range 0 to 60°C, and calorimetric data on the heat of neutralization near room temperature. The smoothed values of Q_w agree quite well with existing values in the same temperature range, derived mostly from conductance measurements at high temperatures, and it appears that K_w is now known to .004 to .02 log units over the range from 0° to 300°C at the saturation pressure of water.

The Q_w can alternatively be expressed as a relatively simpler function of temperature, ionic strength and solution density. The pressure coefficient of K_w is nearly proportional to the compressibility of water and inversely to the absolute temperature.

The thermodynamic quantities derived for the ionization process undergo great changes as salt is added to the solvent at high temperatures. The extent to which this effect can be attributed to the association of either HCl or KOH is yet unknown.

¹F. H. Sweeton, R. E. Mesmer, and C. F. Baes, Jr., Reactor Chem. Div. Ann. Progr. Rept., May 31, 1971, ORNL-4717, p. 60

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

PHOSPHORIC ACID EQUILIBRIA IN KCl MEDIA TO 300°C

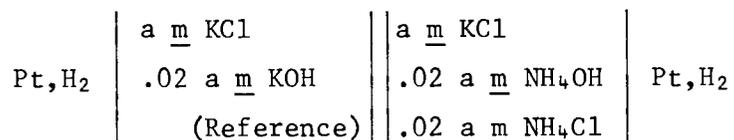
R. E. Mesmer

The phosphoric acid dissociation equilibria are being investigated up to 300°C in KCl media. Phosphates are commonly added to boilers to precipitate alkaline earth salts and also to control pH. Knowledge of their dissociation equilibria is of concern in this application as well as others in which the buffering capacity of the phosphates is utilized. Presently results have been obtained in 1.0 m, 0.5 m, and 0.25 m KCl on the first and second dissociation steps. No attempt will be made to determine the ionic strength effect on the third dissociation step since it is too slight to be accurately determined above 150°C even in 1 m KCl. Experiments in 1 m KCl have established that polyphosphates do not form at total phosphate concentrations up to 0.04 m. Also, tests for the presence of phosphite in the solutions after making measurements at high temperatures shows no significant reductions under the conditions of our experiments. By the end of this year we expect to have completed the measurements on the first and second dissociation reactions of phosphoric acid at 0.1 m and possibly 0.05 m KCl concentrations. This will permit an extrapolation to infinite dilution and contribute new data on another valuable buffer system for high temperature work.

AMMONIUM HYDROXIDE DISSOCIATION IN KCl MEDIA TO 300°C

B. F. Hitch and R. E. Mesmer

Studies of the dissociation of ammonium hydroxide have been started utilizing the flowing EMF cell designed by F. H. Sweeton¹. The volatility of ammonia makes this cell ideally suited since no gas phase exists. The cell, which may be represented as



is being used to study the NH₃ equilibria as a function of pressure, temperature (up to 300°C), and KCl concentration (up to 3 m).

Previously, values for this equilibrium have been determined by EMF^{2,3} up to 50°C, and by conductance measurements⁴ in dilute solutions up to 343°C. We hope to verify the latter data by the more accurate potentiometric method and extend the data to salt concentrations up to 3 m. Measurements have been completed on solutions containing 0.1, 0.2, and 0.4 m KCl over the temperature range specified above. Values of log Q at 50°C determined from our measurements agree within 0.025 units with the previous EMF data.² Values obtained from our measurements for $\Delta \log Q / \Delta P$ are consistently higher than those obtained for water dissociation. In 0.1 m KCl solutions, values for H₂O range from $2.21 \times 10^{-5} \text{ psi}^{-1}$ at 50°C to $4.25 \times 10^{-5} \text{ psi}^{-1}$ at 250°C. Corresponding values for the NH₄OH equilibrium are $3.07 \times 10^{-5} \text{ psi}^{-1}$ and $5.69 \times 10^{-5} \text{ psi}^{-1}$, respectively. Measurements are being continued at higher salt concentrations.

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²D. H. Everett and D. A. Landsman, Trans. Faraday Soc. 50, 1221 (1954).

³R. G. Bates and G. D. Pinching, J. Research Nat'l Bur. Standards 42, 648 (1959).

⁴A. S. Quist and W. L. Marshall, J. Phys. Chem. 72, 3122 (1968).

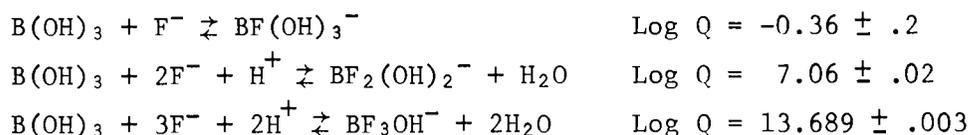
FLUOROBORATE EQUILIBRIA IN AQUEOUS SOLUTIONS

R. E. Mesmer, K. M. Palen,¹ C. F. Baes, Jr.

Previous studies of fluoroborate species in aqueous solutions^{2,3} have shown that BF₄⁻ ion is a stable species whose formation from and decomposition to BF₃OH⁻ occurs slowly by an acid catalyzed reaction. The stability of BF₃OH⁻ and especially of the other fluoroborate species BF₂(OH)₂⁻ and BF(OH)₃⁻ which are expected to form had not been determined however.

We have investigated the formation of these fluoroborate species in 1 m NaCl solution at 25° by means of potentiometric titrations in which the free fluoride ion concentration was measured with the LaF₃ electrode and the pH was measured with the hydrogen electrode. The procedure consisted of the addition of acid to 0.01 and 0.03 m boric acid containing

0.02-0.08 m NaF, with variation of the pH from 7 to 2. Under these conditions negligible amounts of the slowly forming BF_4^- ion, were produced. The results are explained by the following reactions and equilibrium quotients:



Under the conditions of measurement, BF_3OH^- was the major species formed and the species BF(OH)_3^- was barely detectable. Combined with other equilibrium quotients, known previously, these results give the following log Q values for the stepwise replacement of OH^- by F^- in the conversion of B(OH)_4^- to BF_4^- : $-5.3 \pm .2$; $-6.3 \pm .2$; $-7.10 \pm .02$; $-8.40 \pm .1$. Those quotients decrease by about one log unit per fluoride added. This is similar to the decrease found previously⁴ in the stepwise addition of fluoride to the complexes of a number of metal ions. There was no evidence for the formation of the undissociated acids HBF_3OH or $\text{HBF}_2(\text{OH})_2$ or for the formation of polyborate species.

¹Summer Trainee in 1971.

²C. A. Wamser, J. Am. Chem. Soc. 70, 1209 (1948); *ibid.*, 73, 409 (1951).

³M. Anbar and S. Guttmann, J. Phys. Chem. 64, 1896 (1960).

⁴R. E. Mesmer and C. F. Baes, Jr., Inorg. Chem. 8, 618 (1969).

¹⁹F NMR STUDIES ON FLUOROBORATES IN AQUEOUS SOLUTION

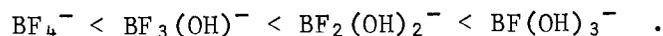
R. E. Mesmer and A. C. Rutenberg¹

¹⁹F NMR spectrometry is a valuable technique for the study of species occurring in solution, particularly when the lifetimes are greater than a few milliseconds so that multiplet structure and the characteristic chemical shifts (peak positions) can be observed. We have recently observed the spectra of BF_4^- , $\text{BF}_3(\text{OH})^-$ and $\text{BF}_2(\text{OH})_2^-$ in solutions of 1.0 m and 2.0 m

$\text{NaBF}_x(\text{OH})_{4-x}$ where x was varied from 1.0 to 3.0. At 0°C the $\text{BF}_2(\text{OH})_2^-$ ion gives a ^{19}F signal without multiplet structure well resolved from the other fluoroborates and the free fluoride. At 27° there is partial merge of the signal of the $\text{BF}_2(\text{OH})_2^-$ with that of the F^- and the lifetime was estimated at 0.4 milliseconds. At 65° the two signals coalesce at a median position as expected for approximately equally populated states.

Semiquantitative estimates of the equilibrium quotients for the formation of the fluoroborates from $\text{B}(\text{OH})_3$ and fluoride were obtained from the NMR data and potentiometric measurements of the H^+ and F^- ion concentrations. These results are quite consistent with the much more precise data reported in the previous summary.²

From these NMR results and previous observations^{2,3} the rates of exchange of fluoride with the fluoroborates increase in the order



Interestingly the chemical shifts for the fluoroborates are regularly spaced as are those for the fluoroberylates⁴ which were recently reported. However, the sequential addition of fluorides to the B and Be species cause shifts in the opposite directions.

¹Y-12 NMR Laboratory.

²See page 55, This Report.

³C. A. Wamser, J. Am. Chem. Soc. 70, 1209 (1948); *ibid.*, 73, 409 (1951).

⁴M. G. Hogben, K. Radley, and L. W. Reeves, Can. J. Chem. 48, 2959 (1970).

SOLUBILITY AND COMPARATIVE THERMODYNAMIC RELATIONSHIPS FOR CALCIUM SULFATE IN AQUEOUS SODIUM PERCHLORATE SOLUTIONS AT 25-250°C, 0-6 MOLAL NaClO_4 ¹

R. Kalyanaraman,² L. B. Yeatts, W. L. Marshall

In a continuing program, the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 0 and 25°C and of CaSO_4 at higher temperatures was determined in aqueous NaClO_4 solutions at temperatures from 0 to 350°C and at molalities of NaClO_4 from 0 to 6 molal. The purpose of this study was to compare the solubility behavior of CaSO_4 in these NaClO_4 solutions with the previously determined

solubilities of CaSO_4 in separate aqueous solutions of NaCl , NaNO_3 , and LiNO_3 . It was initially expected that the present study would yield solubilities of similar magnitude in NaClO_4 solutions. Surprisingly, the solubilities of CaSO_4 were sharply lower in NaClO_4 solutions at low temperatures and at high ionic strengths than values in the other 1-1 salts under the same experimental conditions. At higher temperatures (150-340°C), however, these solubilities in NaClO_4 solutions rose to approach those obtained in the other salt solutions.

The solubilities of CaSO_4 in $\text{NaClO}_4\text{-H}_2\text{O}$ solutions are described by an extended Debye-Hückel equation,

$$\ln s = \ln s_0 + 4S\sqrt{I}/(1+A\sqrt{I}) + BI + CI^2$$

where I is the ionic strength, S is the Debye-Hückel limiting slope, s and s_0 are the molal solubilities of CaSO_4 at I and at zero ionic strength, respectively, and A , B , and C are adjustable parameters. Although at temperatures above 100° a value of $A = 1.6$ provides the best fit for the solubilities in NaCl , NaNO_3 , and LiNO_3 solutions, a value of $A = 1.7\text{-}1.8$ provides a better fit for the present solubilities in aqueous NaClO_4 solutions. Related studies are in progress in an attempt to present a unified interpretation of the solubility behavior in concentrated electrolyte solutions.

¹To be submitted for publication.

²International Atomic Energy Fellow (1971) from Trombay, India.

SOLUBILITY AND ASSOCIATION EQUILIBRIA OF CALCIUM SULFATE FROM 0 to 350°C IN THE MIXED ELECTROLYTE SYSTEM, SODIUM SULFATE - SODIUM PERCHLORATE - WATER¹

R. Kalyanaraman,² L. B. Yeatts, and W. L. Marshall

Measurements have been made of the solubility at 0 and 25°C of calcium sulfate dihydrate and at 150, 250, and 350°C of anhydrous calcium sulfate in the mixed-electrolyte system, $\text{Na}_2\text{SO}_4\text{-NaClO}_4\text{-H}_2\text{O}$. By assuming a model

involving some association of Ca^{2+} and SO_4^{2-} ions to form CaSO_4° , association quotients (Q_a) and ion solubility product quotients (Q_{isp}) were obtained for calcium sulfate at ionic strengths to six molal and at temperatures to 350°C . The values for Q_a and Q_{isp} were markedly larger and smaller, respectively, than corresponding values in the system Na_2SO_4 - NaNO_3 - H_2O over the same range of temperature.³ Uniquely, for each system there is an apparent invariance of activity coefficients at a given ionic strength and temperature. However, difficulties arise in trying to present a unified model to describe the differences in association and solubility behavior between the two systems. Attempts to resolve these difficulties are currently in progress.

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SOLUBILITY OF CALCIUM SULFATE IN BRACKISH WELL WATERS AND THEIR CONCENTRATES: EFFECT OF POLYPHOSPHATE ADDITIVES ON SOLUBILITY¹

P. M. Lantz, L. B. Yeatts, and W. L. Marshall

In the operation of water desalination plants by the process of reverse osmosis, one limiting condition for concentrating the salts in a brackish water is the point at which calcium sulfate may become saturated in the feed water and thereby form a scale on the reverse osmosis membranes. This "clogging" of the membranes must be avoided in OSW pilot plant operations at Gillette, Wyoming, and Webster, S. Dakota, for example, if good efficiencies for water purification are to be obtained for these brackish well waters. The addition of 5-15 ppm of particular additives (for example, sodium hexametaphosphate) is qualitatively effective in allowing calcium sulfate to reach a greater concentration in the feed water before precipitation, or scaling, occurs. The present study was initiated to determine (1) qualitatively the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) in representative

brackish well waters, and (2) the effect on the solubility equilibrium, if any, of the presence of trace quantities of chemicals which are customarily added. In addition, the method of computing solubilities in saline waters developed earlier at ORNL from experimental and theoretical studies²⁻⁴ would be applied to these current studies.

Presently, the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has been determined at 10, 25, and 40°C in synthetic concentrates of a Gillette, Wyoming, water and in several other related salt solutions. Preliminary studies with the addition of 5 to 50 ppm of sodium hexametaphosphate ("Calgon") have shown no detectable effect on the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The beneficial effect of this and similar additives must therefore result from an effect on the kinetics of precipitation rather than on the equilibrium process. (The related kinetic studies with reverse osmosis test "loops" presently are being performed in the Chemistry Division, and are a coordinated part of the present program.)⁵ Our previously developed computer program has provided agreement with the presently obtained solubilities, and therefore its use is supported by these experiments and calculations.

¹Study sponsored by the Office of Saline Water (OSW), Department of the Interior, Washington, D. C.

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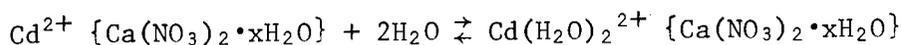
⁵R. E. Minturn, J. S. Johnson, ORNL Chemistry Division.

COMPETITIVE HYDRATION AND ASSOCIATION EQUILIBRIA IN HYDROUS MELTS

H. Braunstein and J. Braunstein

A quasi-lattice model of competitive hydration and association equilibria in highly concentrated aqueous electrolytes — hydrous melts — has been applied to the association of solute ions such as Cd^{2+} , Pb^{2+} , or Ag^+ with halide ions in solvents such as $(\text{Li},\text{K})\text{NO}_3\text{-H}_2\text{O}$ and $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$.¹ These

studies complement water activity determinations in hydrous melts obtained with the ORNL high temperature isopiestic apparatus.² The above model did not fit data for the association of Cd^{2+} and Br^- in the solvents $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and an investigation of association equilibria in the anhydrous system was carried out for clarification. Since anhydrous $\text{Ca}(\text{NO}_3)_2$ does not melt without decomposition, molten mixtures of KNO_3 or NaNO_3 with $\text{Ca}(\text{NO}_3)_2$ were employed, and the results extrapolated to pure $\text{Ca}(\text{NO}_3)_2$. Equations were derived for computing the association constants of Cd^{2+} with Br^- in charge unsymmetric molten salt solvents, containing differing numbers of cations and anions. Association constants in the anhydrous solvents were compared with those in the hydrous melts, making use of the water activities in these melts.² One possible interpretation of the observed dependence of the CdBr^+ equilibrium on water activity is that the hydration equilibrium of Cd^{2+} involves addition of two water molecules (rather than one),



with displacement of nitrate ion from the coordination sphere of Cd^{2+} . Equilibrium between contact ion pairs and solvent separated ion pairs in such melts has been postulated also on the basis of Raman spectral data.⁴

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TRANSFERENCE NUMBERS IN HIGHLY CONCENTRATED AQUEOUS CADMIUM NITRATE MELTS

H. Braunstein and J. Braunstein

Relative transference numbers of ions in hydrous melts (highly concentrated aqueous electrolytes) have been considered diagnostic of the binding strength of water molecules to ions, but have generally not been extended to water-salt compositions below 4-1.¹ The electromotive force

method of measurement is capable of accuracy exceeding the moving boundary and Hittorf methods in concentrated electrolytes, given a reversible electrode for concentration cells with transference and accurate chemical potential data. For hydrous melts of cadmium nitrate, a dilute cadmium amalgam electrode is being used, the required chemical potential data being derived from isopiestic water activity determinations.² Equations have been derived for transference numbers relative to either water or nitrate ion as the reference; (for very low water content, it becomes more convenient to choose one of the ionic constituents as the internal reference). The transference number of cadmium ion constituent falls to 0.2 (relative to water as the reference (i.e., $t_w = 0$, $t_{NO_3} = 0.8$)) at the tetrahydrate composition. Relative to nitrate ion constituent as the internal reference, the transference number of water becomes 1.6 H₂O/equivalent, or 3.2 H₂O/Cd²⁺ suggesting that the water is not all bound to Cd²⁺.

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SELF-DIFFUSION COEFFICIENTS OF Na⁺ IN POLYACRYLIC ACID-WATER MIXTURES

A. J. Shor, H. P. Phillips,* D. C. Michelson,* and R. E. Meyer*

Investigation of salt transport through organic-water solutions which act as models for hyperfiltration membranes improves our understanding of the process of salt removal. We have selected the open-end capillary method to continue our study of the self-diffusion of sodium ion in polyacrylic acid-water mixtures and to compare results previously obtained using the radiometric porous frit method.^{1,2}

In the latter method, a rectangular porous frit saturated with a solution containing a tracer of interest is placed into the center of a tube through which an identical solution not containing the tracer is pumped. The rate of removal of the tracer is monitored and diffusion coefficients

are calculated after appropriate calibration with a tracer of known diffusion coefficient. A flow regime has to be selected under which diffusional resistance in the boundary layer at the surface of the frit is small, and reproducible and appropriate allowances for this diffusional resistance must be made.

Because polyacrylic acid-water mixtures are highly viscous and because there were some questions as to the applicability of the radiometric porous frit method to highly viscous solutions, a second, independent and absolute method of determining diffusion coefficients seemed desirable. The open-end capillary method was selected for its simplicity and suitability to highly viscous solutions. In this method^{3,4} a small-bore capillary, open on one end and closed on the other, is filled with the solution containing the radioactive tracer. This capillary is immersed in a bath containing an identical but non-labeled solution. After a time interval, the capillary is removed and the reduction in total activity, C_t/C_o , is determined. The diffusion coefficient D is calculated from the relation:

$\ln(\pi^2 C_t / 8 C_o) = -\pi^2 D t / 4 L^2$ where L is the length of the capillary, t is the time interval of immersion, and C_o and C_t are the initial and final concentration in the capillary.

Table 1 shows all the solution compositions and the results we have obtained so far. Each number represents the average of the self-diffusion coefficients obtained from the capillaries used in an individual experiment, generally six. Occasionally discrepancies would occur, particularly with capillaries containing 40% and 56% PAA. Due to the extreme viscosity of these solutions, loading was often difficult and bubbles would be introduced into capillaries or would form at the tip. Results from such capillaries differed significantly from the average and were discarded in computing the final average. Until data from 40% and 56% solutions can be confirmed, the results for these solutions should be considered tentative.

The data were plotted as $\log D$ vs $1/T$ in order to obtain activation energies from the expression $D = D_o \exp(-E_a/RT)$. The values of E_a for the frit data are: 0%, 3.9 kcal/mole; 5%, 3.7 kcal/mole; and 25%, 4.4 kcal/mole. For the 25% capillary data, E_a is 4.5 kcal/mole. Thus the

activation energy appears to be slightly higher for the 25% PAA solutions as compared to the 0% (0.1 m NaCl).

In comparing the two methods for determining the diffusion coefficient, we find that the results for the frit method yielded slightly lower (5-7%) results than those obtained from the capillaries. The differences are almost within the estimated errors of the two methods ($\sim 2\%$). However, the difference seems to be consistent and worthy of continued investigation.

Viscosity measurements have not yet been completed. The viscosity of the 25% solution is, however, known to be over 180 times greater than that of pure water at 25°, and it is obvious that the viscosities of the 40 and 56% solutions are considerably greater than the 25% solution. It is interesting that the diffusion coefficients do not decrease correspondingly and that the main variables seem to be the water content and the temperature.

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*Chemistry Division, ORNL.

TABLE 1
 SELF-DIFFUSION COEFFICIENTS OF SODIUM ION IN
 PAA-WATER MIXTURES (0.1 m NaCl)

Temp. °C	<u>D x 10⁵ for 0% PAA cm²/sec frit</u>	<u>D x 10⁵ for 5% PAA cm²/sec frit</u>	<u>D x 10⁵ for 25% PAA cm²/sec frit</u>	<u>D x 10⁵ for 25% PAA cm²/sec capillary</u>	<u>D x 10⁵ for 40% PAA cm²/sec capillary</u>	<u>D x 10⁵ for 56% PAA cm²/sec capillary</u>
25	1.28	1.14	0.62	0.68	0.46	0.37
40	1.78	1.63	0.93	1.04	--	--
60	2.58	2.20	1.43	1.43	0.82	--
85	3.82	3.28	2.02	2.38	1.61	--



SURFACEINTERACTION OF GASES WITH LUNAR MATERIALS¹E. L. Fuller, Jr., H. F. Holmes and R. B. Gammage²

Continued studies of vapor sorption on lunar regolith (an Apollo 11 sample) has led to a better definition of the nature of the amorphous radiation-damaged surface. There are two concurrent modes of water penetration into this layer. First the discrete mode, characterized by the 0.8-0.9 P_0 hysteresis loop, is a constant amount as long as the temperature does not exceed 500°C. Apparently these radiation damage avenues are annealed out at these temperatures with no concomitant loss of open surface area. However 800°C in vacuo is sufficient to bring about interparticulate fusion and loss of surface area. Secondly there is a more broad, diffuse type of penetration characterized by hysteretic retention to much lower P/P_0 (initially 0.33 P_0 progressing to 0.58 P_0 on repeated cycling). The amount hysteretically retained by the latter mode increases as the maximum P/P_0 of adsorption is increased.

A third mode of interaction is the irreversible retention in vacuo which is noted when the specific penetration P/P_0 of 0.9 is exceeded for extended periods. This material is released in vacuo at elevated temperature (300°C) and is much more readily replaced, at the ambient (22°C) temperature, than initially (the 0.9 P_0 precursor state is not required).

Further studies on samples from other lunar locations are being carried on as an interagency agreement with NASA.

¹Reactor Chemistry Division Ann. Rept., for Period Ending May 31, 1971, ORNL-4717, p. 69

²Health Physics Division, ORNL.

HEATS OF IMMERSION IN THE ZIRCONIUM OXIDE-WATER SYSTEM¹H. F. Holmes, E. L. Fuller, Jr., and R. B. Gammage²

Calorimetric measurement of the heat of immersion of a series of zirconium oxide samples (having a common chemical history) has been completed. The results clearly indicate that a bare zirconium oxide surface will rehydroxylate (form surface hydroxyl groups) on exposure to liquid water. The energy involved in the rehydroxylation process is an inverse function of the specific surface area of the sample. Indications are that there are two factors involved in the slow heat process (which accounts for 8 to 36% of the total heat of immersion). These are porosity and kinetic hydrophobicity. Hydrophobicity, in this system, is kinetic in the sense that not all of the water removed during the pretreatment outgassing is replaced in the time interval (6-8 hr) of a calorimetric experiment. Kinetic hydrophobicity was also responsible for one of the samples (having the largest specific surface area) exhibiting a pronounced maximum in the heat of immersion as a function of outgassing temperature. Average net heats of adsorption calculated from the weight loss and heat of immersion data ranged from 6 to 8 kcal/mole of water. Since this is an average value for the total adsorption process, net heats of adsorption in the submonolayer region are probably several times as large as the average. Results from this work strongly suggest that the metastable tetragonal form has a much lower (at least 350 ergs/cm²) surface energy than the stable monoclinic form.

When the data are compared to corresponding data^{3,4} for the thoria-water system there are significant differences and similarities. There are clear indications that the thoria-water interface, although quite complex, is one of the simplest of such systems.

¹Modified abstract of a paper accepted for publication in J. Phys. Chem., May, 1972.

²Health Physics Division, ORNL.

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GRAVIMETRIC STUDIES OF ADSORPTION ON ZIRCONIUM OXIDE

H. F. Holmes, E. L. Fuller, Jr., and R. A. Beh¹

Adsorptive properties of a sample of nuclear grade zirconium oxide (Hf < 0.001%) have been investigated using an existing vacuum microbalance system.² Adsorbates included nitrogen, argon, and water. As was the case with thorium oxide, the surface properties of this sample were found to depend primarily on the amount of irreversibly adsorbed water the sample contained. Water was found to irreversibly adsorb on this oxide surface in amounts far in excess of that required for a classical chemisorbed monolayer, i.e., the quantity required to completely hydroxylate the oxide surface. Weight loss for this sample of zirconium oxide between 25 and 500°C, in vacuum, was equivalent to 2.3 monolayers of chemisorbed water. Replacement of this water by adsorption from the vapor phase becomes prohibitively slow after the irreversible adsorption of about 1.5 monolayers of water. In fact, a reversible water adsorption isotherm was not attained at 25°C. In contrast to this, it was relatively easy to obtain reversible water isotherms at 300 and 400°C. Similar behavior has been reported for thorium oxide.³

All three adsorbates showed that this sample of zirconia has a pore system spanning the micro to macro size range. This is another complicating factor. After outgassing at 500°C, the nitrogen (and argon) specific surface area was 23.7 m²/g. After irreversible adsorption of water the nitrogen (and argon) specific surface area was 18.5 m²/g. This reduction in surface area is real and occurs through filling of micropores by irreversibly adsorbed water. Surface areas calculated from water adsorption data ranged from 12 to 28 m²/g. These values suffer from the specificity of the interaction of water with an oxide surface and do not provide a true measure of the geometric area but can be interpreted as indicating chemisorption and specific hydrogen bonding interactions. Exploratory attempts to chemisorb carbon dioxide on this sample of zirconium oxide were unsuccessful.

¹ORAU Summer Student, 1971, from St. Ambrose College, Davenport, Iowa.

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THE HEAT OF IMMERSION OF THORIUM OXIDE AT ELEVATED TEMPERATURES

H. F. Holmes and E. L. Fuller, Jr.

Calorimetric measurement of the heat of immersion of thorium oxide in water at temperatures up to, and including, 200°C have continued. At the present time, however, there is no completely acceptable interpretation of the results. Data for three samples of thoria are given in the table.

Immersion Temperature (°C)	Heat of Immersion (ergs/cm ²)		
	Sample A (14.7 m ² /g)	Sample F (35.5 m ² /g)	Sample BB-14 (46.7 m ² /g)
25	-1220	-1355	-1232
60	-1342	-1277	-1256
100	-1450	-1254	-1232
130	-1471	-1298	-1258
150	-1657	-1316	-1269
175	(-1645)	-1402	-1257
200	-1789	-1505	-1390

Apart from the fact that there is no evident trend with immersion temperature the magnitude of the results is impressive. A heat of immersion of -1300 ergs/cm² represents an average net heat of adsorption of about 10 kcal/mole of water even if the adsorption process is spread over three monolayers. Obviously a very strong adsorption process is occurring in this system.

The dependence on immersion temperature can possibly be explained as a heat capacity effect. If the adsorbed water has only half the heat capacity of liquid water (about that for the ice transition) then 8 monolayers of water are involved in the adsorption process if one explains the data for sample A on this basis. This seems to be a large quantity of water but Derjaguin and Karashev¹ have found that liquid films in

contact with a glass or mica surface seem to be rigidified to a depth of 1000 to 1500 Å. There is no doubt that heat capacity effects play an important role in this system but at the present time there is no firm basis for making calculations or predictions.

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GRAVIMETRIC STUDIES OF ADSORPTION ON SOL-GEL THORIA

E. L. Fuller and H. F. Holmes

Sol-gel ThO₂ is prepared by dehydration of the hydrous gel which is formed from the peptized aqueous sol. Nitrogen and water vapor sorption studies reveal that 40% of the classical B.E.T. monolayer is not true physical adsorption but is taken up by a large contingent of micropores (about the size of N₂ and H₂O molecules). This persorption is very energetic as witnessed in their filling below 0.005 P₀. The presence of persorbed H₂O precludes subsequent N₂ entry to a nearly proportional degree.

At higher P/P₀ both N₂ and H₂O are sorbed into pores with somewhat restricted orifices. N₂ undergoes only a single mode of hysteretic pore filling whereas 3 modes are noted for H₂O. Both vapors are hysteretically retained in a manner consistent with the existence of minimal ports of 2-4 molecular diameters in width. The amount sorbed in these "mesopores" is quite insensitive to sample pretreatment (unlike the micropore filling).

Water vapor is reversibly adsorbed, in addition to the vacuum retention, even at high temperatures. The amount of physisorption monotonically decreases (25-300°C) to a constant, temperature invariant, amount (300-500°C). Apparently the micropore structure is quite rigid and serves as a geometric dictation for water vapor sorption. Sol-gel ThO₂ has quite a large chemisorption capacity for CO₂. Alternate CO₂ and H₂O exposures, after high temperature outgassing, lead to vacuum retentions consistent with the existence of a surface bicarbonate species. Raising the temperature above

500°C (in vacuo) leads to marked sintering culminating in a 50 fold area loss at 1000°C.

THE HEAT OF IMMERSION OF SOL-GEL THORIUM OXIDE

H. F. Holmes and E. L. Fuller, Jr.

Previously reported values¹ for the heat of immersion of sol-gel thorium oxide are seriously in error. The error arose through the use of an incorrect specific surface area (83 m²/g) in reducing the calorimetric data to a unit area basis. Use of the correct surface area (46.7 m²/g) gave more acceptable values and removed the enigma of sol-gel thorium oxide being less energetic than high-area oxalate-derived thoria in its surface reactions with water. Corrected values for the heat of immersion increased (became more exothermic) in an almost linear manner from -296 ergs/cm² for samples outgassed at 25°C to -1230 ergs/cm² for an outgassing temperature of 500°C. This compares quite favorably with the corresponding values (-325 to -1300 ergs/cm², respectively) for high-area oxalate thoria.^{2,3} Complementary experiments proved that kinetic hydrophobicity is not a complicating factor as was the case with zirconium oxide. However, this sample of sol-gel thorium oxide does have a slow component in the total heat of immersion. This slow process is almost certainly due to the porosity and microporosity of this particular sample (see section on adsorption on sol-gel thoria). The fraction of the total heat of immersion which appears in the slow process varies from 5 to 16% and is largest for samples outgassed at 300°C. This indicates that diffusion into pores containing surface hydroxyl groups is slower than diffusion into either empty pores or pores containing molecular water. The surface area error discussed above does not affect the previously reported estimate¹ of 10.4 kcal/mole for the average net heat of adsorption for the water which is lost on outgassing between 25 and 500°C.

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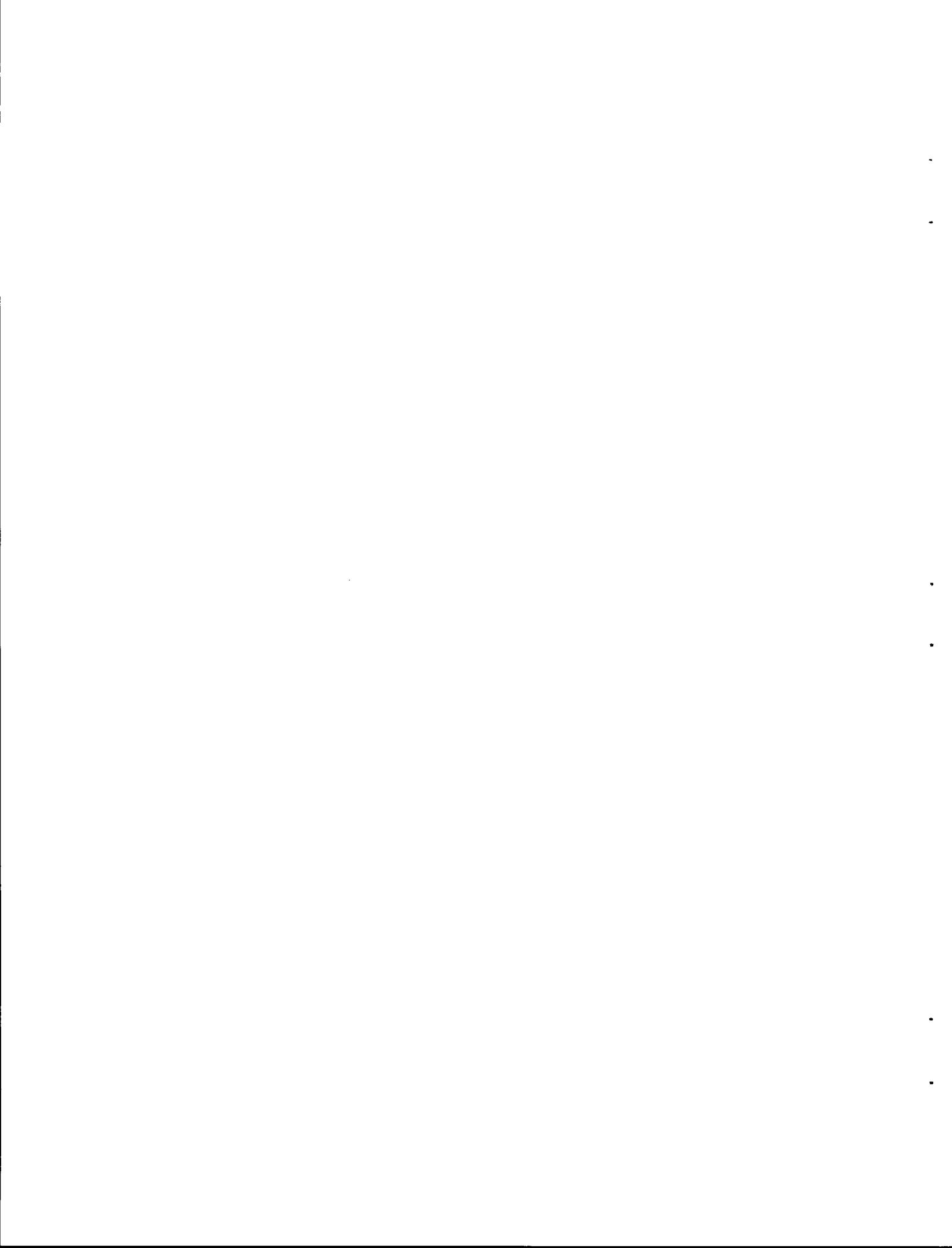
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INFRARED SPECTRA OF SURFACE SPECIES ON ZrO₂ AND SOL-GEL ThO₂

E. L. Fuller, Jr., P. A. Agron and H. F. Holmes

Spectroscopic analyses of ZrO₂ show qualitative resemblances to ThO₂. The free hydroxyl frequency is quite narrow at 3750 cm⁻¹. Three broad hydrogen-bonded hydroxyl bands occur with band heads at 3660, 3570, and 3465 cm⁻¹. The free hydroxyl exists only in vacuo or inert atmospheres (N₂, O₂, etc.) and disappears in the presence of H₂O vapor (physical adsorption). The population is decreased by cycling from vacuum to H₂O vapor and return. The hydrogen-bonded species were progressively removed at elevated temperatures in the reverse of the sequence listed above. The 1620 cm⁻¹ H-O-H bonding frequency decreases with increasing temperature and decreasing H₂O pressure.

The spectra of hydroxyl species on sol-gel ThO₂ are similar to that of the material derived from the oxalate. The free hydroxyl (3742 cm⁻¹) stretching frequency is noted only in vacuo after the initial attempt to rehydrate the surface following high temperature outgassing. The hydrogen bonded band intensities at 3660 and 3550 cm⁻¹ are quite persistent with gradual diminution as the temperature is increased. The band at 3380 cm⁻¹ is much more diffuse and thermally labile. Hydroxyl assignments were verified by D₂O exchange. An atmosphere of CO₂ grossly perturbs the 3742 and 3660 cm⁻¹ bands but shows no effect on the 3550 and 3380 bands. Removal of the CO₂ reversibly regenerates the previous vacuum hydroxyl spectrum. This sample was opaque in the 1000-1700 cm⁻¹ region and we were unable to observe the spectrum of the retained CO₂.



CORROSION

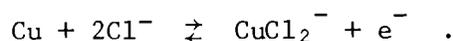
THE ANODIC DISSOLUTION OF COPPER, COPPER-NICKEL ALLOYS IN HIGH-TEMPERATURE CHLORIDE SOLUTIONS*

A. L. Bacarella and J. C. Griess

The experimental program concerned with the anodic dissolution of copper in chloride solutions was completed during the past year. It was shown that the dissolution product was CuCl_2^- at least up to 1M NaCl and that the transport of this ion to the bulk solution was the rate determining step. The following kinetic expression derived from Fick's First Law and the Nernst Equation was in excellent agreement with experimental results obtained either under static conditions up to 100°C or in flowing streams up to 175°C:

$$\log i = \log \frac{zFD_0}{\delta} + 2 \log (\text{Cl}^-) - \frac{\Delta H_D}{2.3 RT} + \frac{F\eta}{2.3 RT} .$$

In this equation i is the current density, z is the charge on the diffusing species, D_0 is a constant related to the diffusion coefficient, δ is the diffusion layer thickness, ΔH_D is the activation energy for diffusion transport, and η is the overvoltage defined as the measured potential minus the standard redox potential for



Tafel slopes were $2.3RT/F$ and the current density depended on the square of the chloride ion concentration. At an arbitrarily chosen value of $\eta = -0.450\text{v}$ plots of $\log i$ vs $(^\circ\text{K})^{-1}$ resulted in straight lines with slopes corresponding to an activation energy of 15.3 ± 1 kcal/mole. This value includes the apparent activation energy for diffusion transport of CuCl_2^- and the electrical work term, $F\eta$. At -0.450v the value of $F\eta$ is 10.4 kcal/mole which results in a value of 4.9 ± 1 kcal/mole for the apparent activation energy for diffusion of CuCl_2^- .

Experiments with 90-10 and 70-30 cupronickel and nickel were also conducted during the past year. Although complete descriptions of the anodic processes have not been obtained to this time, several interesting observations were made. At all temperatures the three materials passivated at current densities of 10^{-4} to 10^{-3} A/cm². Except for nickel at

25°C polarization curves with distinct Tafel regions were obtained prior to passivation. The polarization curves with the 90-10 alloy were very similar to those for copper at all temperature; that is, Tafel slopes were 2.3RT/F and the current density was velocity independent. The nickel curves (75 to 175°C) were independent of velocity and had Tafel slopes equal to $2/3(2.3 \text{ RT/F})$, indicating activation rather than diffusion control. The 70-30 alloy behaved like the 90-10 alloy up to some temperature between 125 and 150°C (polarization curves were velocity dependent and had Tafel slopes of 2.3RT/F) but at 150°C and above the polarization characteristics were similar to those of nickel. The behavior of other copper-nickel alloys remains to be investigated.

*Research jointly sponsored by the Office of Saline Water, U.S. Department of the Interior, and the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

THE CORROSION OF COPPER AND ITS ALLOYS IN HIGH TEMPERATURE FLOWING SALT WATER SOLUTIONS*

J. C. Griess and E. G. Bohlmann

Over the past several years the corrosion of a number of copper alloys in flowing salt water solutions at different temperatures and with different additives has been under investigation. These studies involved exposing specimens in titanium pump loops to solutions flowing at 3 to 15 fps and determining weight losses after given exposure periods. Last year's report gave information about the effect of temperature on corrosion in deaerated 1.0M NaCl between 125 and 175°C. During the past year the temperature range was extended to 100 and 200°C.

At each temperature the total exposure time was about 1500 hr with periodic interruption for specimen examination. All solutions were sparged with nitrogen and contained about 50 ppb O₂. At 200°C the pH of the solution in the loop decreased to 5.5 to 6.0 whereas in all other cases the pH of the solution was constant at 6.3 to 6.5. This slightly lower pH at 200°C may have had some influence on the results. Table 1 shows the average corrosion rates at all temperatures calculated from weight losses.

Table 1. The Average Corrosion Rates of Copper Alloys
in Deaerated 1.0m NaCl at Flow Rates of 3 to 15 fps

<u>Material</u>	<u>Corrosion Rate, mpy</u>				
	<u>100°C</u>	<u>125°C</u>	<u>150°C</u>	<u>175°C</u>	<u>200°C</u>
Copper	0.33	--	--	1.0	3.0
CDA-194 ^a	0.39	--	4	1.6	4.6
Admiralty Brass	0.35	2.7	3	1.3	7.5
Aluminum Brass ^b	0.38	--	--	--	12.4
90-10 CuNi	0.16	0.7	1	1.7	5.9
70-30 CuNi	0.08	0.2	0.4	1.7	3.7
Monel 400	0.07	0.1	0.3	2.2	2.4

^aNominal composition: 2.4% Fe, 0.024% P, bal. Cu.

^bYorkalbro from Yorkshire Imperial Metals Ltd. (21.96% Zn, 2% Al, 0.04% As, bal. Cu).

Generally the corrosion rates were independent of velocity and were constant. The corrosion rates of the nickel alloys increased with temperature whereas CDA-194 and Admiralty brass seemed to have their lowest rates at 175°C. Although copper and aluminum brass were not exposed under all conditions, their behavior seemed to be similar to CDA-194 and Admiralty brass.

Observations made in loop experiments indicated that if the 1.0m NaCl contained about 6 ppm O₂ metallic copper usually plated on specimens in highly turbulent regions. On flat coupons copper deposition occurred on the leading edge whereas light corrosion occurred on the trailing edge of the coupon; that is, the leading edge was cathodic to the trailing edge. The presence of oxygen increases the corrosion rates of copper alloys and increases the concentration of corrosion products in solution, but in deaerated solutions to which CuCl had been added copper deposition was not observed. Thus it appears that the presence of oxygen is a necessary condition. No explanation of this phenomenon is available at this time.

*Research jointly sponsored by the Office of Saline Water, U.S. Department of the Interior, and the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

CORROSION STUDIES ASSOCIATED WITH LMFBR FUEL PROCESSING

G. E. Creek and J. C. Griess

The proposed method for processing LMFBR fuel involves the high temperature oxidation of the UO_2 - PuO_2 fuel followed by dissolution in an HNO_3 - HF solution. Scouting tests of one day duration showed that of the many different materials tested only tantalum had sufficient resistance to warrant further testing. Specimens of tantalum were exposed to $8M$ HNO_3 containing between 0.05 and $0.25M$ HF in Teflon-lined autoclaves at $120^\circ C$ for 497 hr. In addition a similar series of tests was run for 340 hr in the same solution to which $1M$ $UO_2(NO_3)_2$ was added. In the absence of $UO_2(NO_3)_2$ the corrosion rate increased uniformly from 0.83 mpy with $0.05M$ HF to 60 mpy with $0.25M$ HF . In the presence of $UO_2(NO_3)_2$ the rates were lower, being 0.08 mpy with $0.05M$ HF and 21 mpy with $0.25M$ HF . In a few brief tests with titanium in the same solution prohibitively high and erratic corrosion rates (> 50 mpy) were observed.

Most of the fission product iodine is removed from the dissolver solution by gas sparging, but some of the iodine is present in a non-volatile form. This latter iodine compound is exchanged with KI at 150 to $200^\circ C$ and is subsequently removed by flashing the solution. Brief scouting tests were conducted under simulated exchange conditions with 13 different materials. The solution contained $4M$ HNO_3 , $0.5M$ $UO_2(NO_3)_2$, $0.05M$ HF , $0.2M$ H_3BO_3 , and $0.025M$ KI . Preliminary tests showed only titanium and tantalum had reasonable corrosion rates. In longer term tests (1000 hr) both of the latter two materials demonstrated adequate corrosion resistance. Titanium corroded at 2 mpy at 150 and $200^\circ C$, and no evidence of crevice corrosion or selective attack in or around welds was apparent. Tantalum, tested only at $200^\circ C$, corroded at the very low rate of 0.02 mpy.

Two methods of removing iodine and organic iodides from gas streams are by contacting with vapors from boiling concentrated HNO_3 or by scrubbing the vapors with a HNO_3 - $Hg(NO_3)_2$ solution. In tests simulating the first method it was shown that the austenitic stainless steels and Hastelloy F were severely corroded; titanium, tantalum and Zircaloy-2 had acceptably low corrosion rates of 2 , 0.02 , and 0.07 mpy, respectively.

In the $\text{HNO}_3\text{-Hg}(\text{NO}_3)_2$ method the austenitic stainless steels had adequate corrosion resistance; after 1000 hr in 14M HNO_3 containing 0.2M $\text{Hg}(\text{NO}_3)_2$ and 0.0008M HIO_3 corrosion rates did not exceed 0.2 mpy at either room temperature or 60°C.

THE STABILITY OF PROPRIETARY PROTECTIVE COATINGS ON LONG-TERM EXPOSURE TO BORIC ACID SOLUTION

G. E. Creek and J. C. Griess

Carbon steel could be used in refueling tanks for pressurized water reactors in place of more expensive alloys if suitable protective coatings could be applied. Since long-term tests of a variety of different coatings in boric acid solutions had not been made, manufacturers were invited to submit test panels of carbon steel protected with representative coatings for test at ORNL. Twelve manufacturers submitted replicate panels of 46 different coatings. Panels of each type were exposed to 0.28M H_3BO_3 (~ 3000 ppm B, pH = 4.5) in large stainless steel vats at 40, 90, and 150°F for one year. The specimens were examined in detail after 6 mo. and again at the end of the test.

Most of the coatings appeared to be unaffected by the exposure at any temperature and completely protected the carbon steel. A few developed blisters, however, and one of the coatings sloughed off the surface of the steel. The compositions of the coatings were in most cases not known by us since most designations were by trade names or numbers; therefore it was not possible to correlate composition with performance. A report containing the manufacturer's designation and the results of the examination will be issued in the near future.

Specimens of aluminum alloys 1100, 3003, 5052, and 6061 were also exposed in the same solutions with the protective coatings. During the one year exposure attack on the alloys was essentially nil; the maximum corrosion rate observed on any specimen was 0.08 mpy.

MISCELLANEOUS WORK FOR THE OFFICE OF SALINE WATER*

S. A. Reed

The following tasks were carried out during the year at the request of the Office of Saline Water. This work was reported directly by letter, informal reports and by oral presentations to the OSW staff in Washington, D. C.

1. Failure Analysis of Titanium Tubed Brine Heater on the 16-stage MSF Distillation Pilot Plant at Wrightsville Beach, N. C. - Fourteen of a total of 56 commercially pure 3/4 in. O.D. x 0.020-0.022 in. thick wall titanium tubes in the heater leaked after less than a year of cumulative on-stream time. The heater was operated intermittently with a wide variety of feedwater conditions over a temperature range of 250-350°F. Results of chemical and metallurgical examinations indicated failures occurred due to random pitting attack and localized corrosion in crevices formed between the inside tube walls and titanium plugs which were used to blank off the tubes during some periods of operation. Both types of corrosion result from essentially the same electrochemical and environmental factors. During periods of high temperature (300-350°F) operation the environmental conditions were highly conducive to localized attack where chlorides were present in crevices between scale deposits and tube walls and where plugs had been inserted in tube ends.

2. Performance of Instrumentation for Monitoring Oxygen and pH in Distillation Desalting Plants - Visits were made to all major OSW test facilities and to the International Nickel Company Corrosion Test Station at Harbor Island, N. C. to document the performance of instrumentation used for monitoring oxygen and for monitoring and controlling the pH of seawater and brine streams. An instrument based on the polarographic measurement of oxygen (e.g., Beckman Model 735X) has demonstrated reliable performance for measuring dissolved oxygen in the 0-10 ppb range.

A variety of instruments and instrument combinations of proven reliability are available for monitoring and controlling pH. Recommendations and specifications for the various instrument packages were prepared for inclusion in an OSW Instrument Guide Manual which is in preparation.

3. Evaluation of SO₂ as Feed Treatment for Alkaline Scale Control in Seawater Distillation Plants - The use of SO₂ as a substitute for H₂SO₄ as feed treatment for alkaline scale (i.e., CaCO₃ and Mg(OH)₂) control was economically evaluated. Based on a distillation plant using 100 Mgd of seawater feed containing 110 ppm alkalinity (as CaCO₃) and 5 ppm dissolved oxygen, 32,000 lb/day of SO₂ would be required. The installed cost of a sulfur burner with ancillary equipment for emission control would be \$74,000. With liquid sulfur delivered at \$18.50/ton, fixed charges at 7% and 90% plant factor, total annual charges would be ~ \$86,000/yr, i.e., 0.25¢/1000 gal of feed water or about half the cost of using conventional H₂SO₄ treatment. However additional information is needed regarding the complexity of the chemistry and solubility of calcium sulfite, the ability to operate pollution-free sulfur burners at a high availability and the probable need to oxidize sulfite (an oxygen getter) before its release to the aquatic environment.

4. Removal of Copper Ions from Distillation Plant Blowdown Brine - Copper, resulting from the corrosion of cupronickel or brass heat exchanger tubing, is normally contained in the reject brine from a distillation plant, sometimes at concentrations as high as several hundred parts per billion (ppb). Dissolved copper is known to be toxic to certain molluscs and other forms of sea life.¹ Consequently a state of the art survey was made to identify potential economic methods which might be used to remove copper from plant reject brine. The possible schemes considered included conventional ion exchange and carbon sorbates, foam fractionation, metallic aluminum traps and electrolytic removal. Of the methods considered, electrolytic removal appeared to be the most suitable method for treating large volumes of seawater brine at lowest cost.

As a result of the survey, the OSW Distillation Division funded the construction and testing of an electrolytic device designed by F. A. Posey of the ORNL Chemistry Division which employs a cathode of compressed metal turnings or wire mesh of copper or other suitable material (e.g., stainless steel). It has been demonstrated in the laboratory that the device will effectively remove up to 98 per cent of the dissolved copper

in seawater brine containing dissolved copper at concentrations as high as 1.5 parts per million (ppm). The apparatus is now being readied for shipment to the OSW Freeport, Texas test bed for in-plant testing and evaluation.

¹Disposal of the Effluents from Distillation Plants: The Effects of Copper Content, Heat and Salinity, OSW Research and Development Report No. 437 (March 1969).

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

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 to collect, index, abstract, store, retrieve and disseminate information on corrosion and performance of materials of construction used in all types of processes concerned with desalination of seawater and brackish waters. A computerized storage and retrieval system for abstracts is employed. Since December 1968, fourteen bibliographic reports, each containing from 50 to 75 abstracts, have been issued at quarterly intervals. Abstracts in the bibliographic report contain an indexed personal author and keyword listings. The keywords are used for the retrieval of specific types of information from the computerized storage system. The thesaurus of keywords developed by the Center currently numbers 839 terms. Nearly 800 entries are presently contained in the storage system.

A total of 788 Office of Saline Water research and development reports has been reviewed of which 494 contained information of pertinent interest. Current emphasis is placed on the processing of relevant worldwide literature along with newly issued Office of Saline Water research and development reports.

A computerized system for storage and retrieval of information relating to the performance and behavior of equipment in desalination

plants is operable. The system which is referred to as the Materials Performance Reporting System (MPRS) consists of a two-page form which is completed in the field and submitted to the Center for processing. Thus far a total of 1725 MPRS forms have been processed for test bed plants in Freeport, Texas, Roswell, New Mexico and Chula Vista Test Site in California.

Personnel from the Center assisted in the inspection of several test-bed plants and experimental facilities operated for the Office of Saline Water during the year.

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

POTENTIAL METHODS OF CLEANING HEAT TRANSFER TUBING IN SEAWATER DISTILLATION PLANTS*

S. A. Reed and T. H. Mauney

The heat transfer efficiency of a distillation desalting plant may be impaired by a variety of foulants which deposit on the heat transfer tubing. Fouling can occur both tubeside and steamside. Tubeside fouling may occur gradually due to the method of feed treatment used or because of the deposition of materials such as silt, organic marine life, oil, sewage plant effluent or other contaminants which enter the plant in the feedwater. Corrosion product films formed in situ due to oxidation of the tube material and corrosion products such as iron oxide resulting from corrosion of other evaporator internals can also deposit both tubeside and steam side and reduce heat transfer. Rapid tubeside fouling can also occur during periods of maloperation due to the deposition of alkaline scales or calcium sulfate.

Regardless of the cause or nature of the fouling, when the plant heat transfer performance has deteriorated to an unacceptable level the heat transfer tubing must be cleaned. Although some cleaning methods have been tested on an experimental basis in the Office of Saline Water test facilities, little attention has been directed toward the development of

the most effective and economical cleaning procedures especially for hard deposits such as calcium sulfate scale. Therefore, we are making a comprehensive survey of commercially available, cleaning methods, both chemical and mechanical, which might be used to restore high heat transfer performance at minimum cost.

There are numerous chemical and mechanical methods available for removing tubeside deposits of corrosion products, silt, organic films and alkaline scales from evaporator tubing. Solutions of hydrochloric, sulfamic or citric acids containing suitable inhibitors, wetting agents, etc., are satisfactory cleaning agents for these deposits. Tubeside deposits of gypsum and hemihydrate have been removed on some occasions by circulating ambient seawater and brine solutions. Methods employing sequestrants, e.g., EDTANa₄ and NTANa₃, which have been tested on pilot plants and in the laboratory appear effective for anhydrite scale removal as do several proprietary preparations. Test work is now in progress to verify laboratory findings and to determine overall costs. Laboratory work will be followed by field tests in pilot plants and ultimately will be extended to full scale plant cleaning demonstrations in the Office of Saline Water test beds and modules.

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

INVESTIGATION OF WASTE LINE FAILURE

E. G. Bohlmann*

During the past two years ORNL has been installing a new Intermediate Level Radioactive Waste line for transporting fluid wastes from TRU (Transuranium Processing Plant) and TURF (Thorium Uranium Recycle Facility) in Melton Valley to the waste treatment facilities in the laboratory area. The last 3300 foot section of this line, over Haw Ridge immediately southeast of the laboratory exclusion area, was installed in the late summer and fall of 1971. The two-inch seamless schedule 40 pipe used in the installation was 304L (all welded construction - 308L inert gas tungsten

arc) in view of excellent experience with 300 series stainless alloys in similar extended service. In addition the line was surrounded with ~ 6" of crushed limestone sand before the ~ 4' deep containment trench was backfilled.

Unexpectedly, in the course of final checkouts (late November, 1971) specified by the quality assurance program, it was discovered that leaks had developed in the two-inch line and in a section of three-inch pipe (same alloys, schedule 10) used for double containment under Melton Valley Road. The investigation of the leaks necessitated excavation of the entire 3300 foot section of line. Gross pitting of the three-inch pipe under and south of Melton Valley Road was found; the pipe was perforated in six places. This pitting was aggravated by the inadvertent use of crushed limestone containing ~ 4 lb CaCl_2 /ton of backfill in repairing the road; no chloride was found in the limestone sand. The attack on the bare two-inch pipe (~ 3000 ft) was more widely scattered than that on the three-inch, with some tendency to concentrate on and near welds (not restricted to the heat affected zone) and in certain sections of the line. For example, there were several areas of severe attack on the north slope of the ridge but only one minor pit on the south slope. Also, no similar problems have been encountered with a concurrently installed 1200 ft doubly contained section of the pipeline in the laboratory exclusion area or a 1900 ft bare two-inch line buried in Melton Valley a year earlier. No aggressive anions like chloride were found in the areas of severe attack on the bare two-inch line and no deleterious soil conditions or stray currents were found. Pitting could be produced in wet (deionized water) manufactured sand by anodizing to ~ 1.2 volts but did not occur when the specimen was immersed in a deionized water leach of the sand. These observations and other considerations and experience suggested that the damage may have occurred during the welding operations-- in inert gas tungsten arc welding the pipe is the anode. Examination of the welding machine revealed a faulty switch and a possible ground leak which could have resulted in electrolytic attack, but it is difficult to account for the ampere hours required for the amount of damage done.

Attempts to demonstrate that pitting initiated electrolytically would continue spontaneously have been unsuccessful except for one case in the presence of calcium chloride.

The pipe has now been replaced in part and repaired and will be buried with magnesium anode cathodic protection on all three sections of the pipeline.

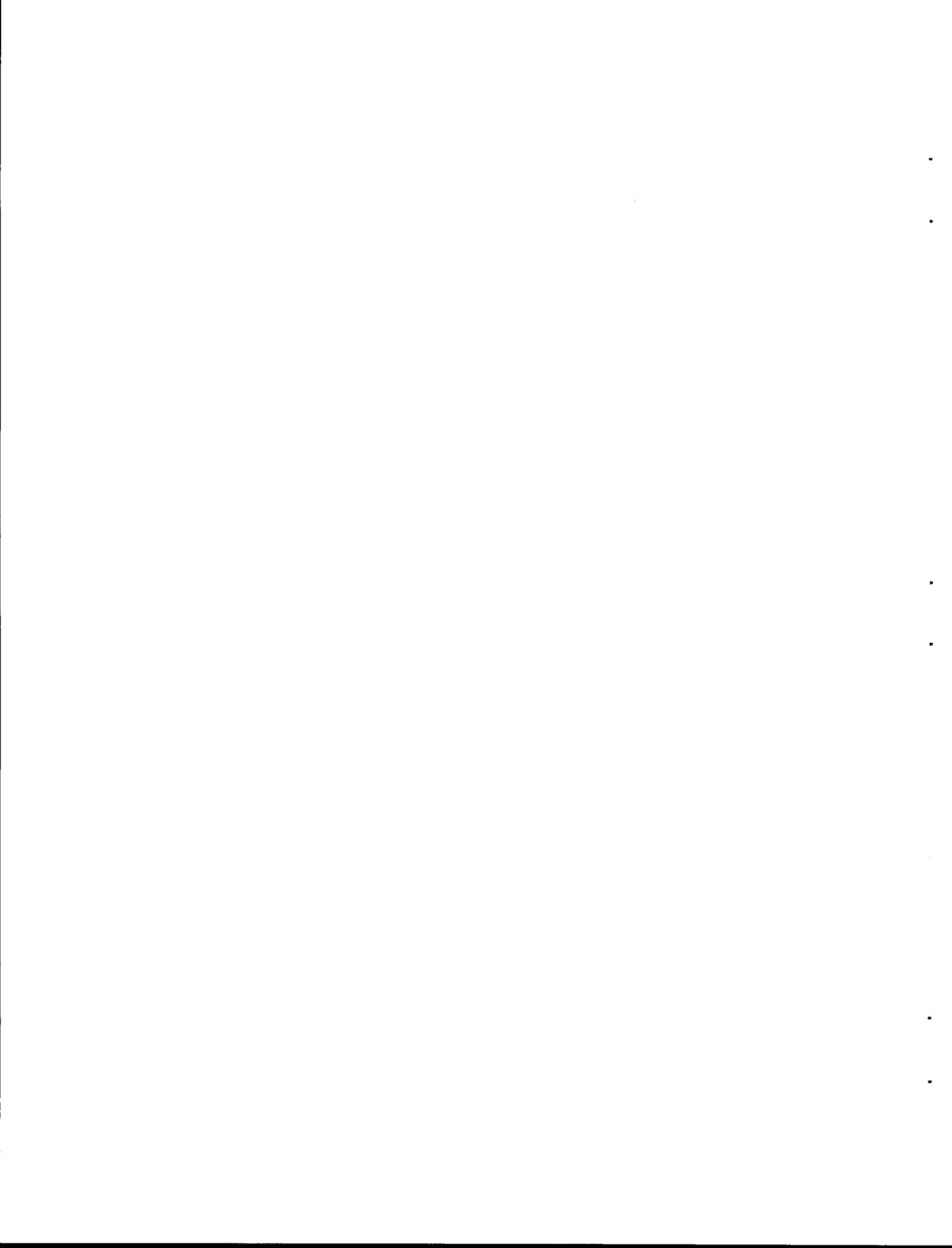
* Chairman of a task group assigned to investigate this incident:

J. C. Griess, Reactor Chemistry

J. R. McGuffey, Inspection Engineering

J. A. Steed, Jr., General Engineering

PART IV. CHEMICAL SUPPORT FOR SOLID-FUELED REACTORS



HIGH-TEMPERATURE, GAS-COOLED REACTORS

KINETICS OF THE STEAM-GRAPHITE REACTION

A. P. Malinauskas and C. M. Blood

To assess the consequences of a large ingress of steam into the core of a high-temperature, gas-cooled, nuclear reactor, as can occur from the rupture of a steam generator tube, it is necessary to provide a reasonably detailed description of both the chemical and gas kinetics associated with the steam-graphite system. However, in the situation of interest, an additional complication arises because of an interrelation between the area of graphite available for reaction and the rate of removal of the graphite. As an illustration, the rate of reaction varies proportionally with surface area, and the surface area of the graphite, in turn, typically increases with extent of reaction. An understanding of the overall phenomenon thus requires the specification of two mechanisms in order to decouple the effects mathematically, one which is addressed to the dependence of the rate of reaction on surface area without regard to changes in surface area, and a second which is concerned with the development of surface area with respect to the amount of carbon removed without regard to its rate of removal.

Mathematical models have been developed to account for both mechanisms, and a series of measurements involving H-327 graphite have been performed to provide experimental data with which the models could be tested. These measurements, which included surface area determinations and gas transport investigations, involved reaction rate studies over the temperature range 800-1000°C and steam partial pressure range 0.045-0.095 atm. Somewhat surprisingly, the data examined thus far regarding variations in the internal geometrical parameters with extent of graphite removal appear to be described fairly accurately by a simple capillary model of the graphite septa.

THE REACTION OF STEAM WITH HTGR FUEL ELEMENTS DURING IRRADIATION

S. H. Freid and H. J. de Nordwall

The objectives of these experiments are to demonstrate that rate constants measured out-of-pile can be used to describe the manner in which carbon is removed from an operating HTGR fuel element, and to observe the behavior of the fuel element in the presence of steam.

The experimental facility described previously¹ was used to expose to steam four model HTGR elements containing pyrocarbon-coated UC₂ and ThO₂ microspheres dispersed in a carbonaceous matrix and enclosed in type H-327 graphite. Surface temperatures ranged from 600 to 1000°C; the maximum fuel temperature was somewhat less than 1400°C and depended upon the power density generated by fission.

A two-zone model described elsewhere² was used to predict the relative ratio of matrix and casing oxidation using rate constants derived from laboratory investigations.³ Qualitative agreement with prediction was found. Data reduction are still incomplete.

A somewhat unexpected result was the increase in rare gas release during steam exposure, indicating broken coatings, which diminished when the steam was removed, suggesting some sintering of hydrolysis products. Metallographic examination showed that coatings had failed by a pitting process which was initiated by the products of the reaction involving UC₂ and steam. One such pit containing a fuel fragment was found to contain UC₂, UCO, and UO₂ at increasing distances from the carbon surface.

¹S. H. Freid, H. J. de Nordwall, B. F. Roberts, O. Sisman, and W. H. Montgomery, Reactor Chem. Div. Annu. Progr. Rep. Dec. 31, 1968, ORNL-4400, p. 120.

²H. J. de Nordwall, Nuclear Safety Annu. Progr. Rep. Dec. 31, 1969, ORNL-4511, pp. 89-91.

³A. P. Malinauskas and C. M. Blood, private communication.

ADSORPTION AND DESORPTION OF IODINE FROM Fe_3O_4 E. Hoinkis¹ and M. F. Osborne

Knowledge of the behavior of radioactive iodine in the coolant circuit is required to assess the safety of High-Temperature, Gas-Cooled Reactors. To this end, the adsorption and desorption of iodine from Fe_3O_4 is being investigated.²

Adsorption tests are conducted in vacuum at Fe_3O_4 temperatures of 250°C to 450°C. The iodine pressure is controlled in the range 10^{-5} to 10^{-11} atm by controlling the temperature of the iodine source. The use of 8 d ^{131}I tracer allows continuous measurement of the adsorbed iodine by conventional counting equipment. Iodine loadings on the Fe_3O_4 of 0.01 to 0.59 monolayers have been obtained, with the heavier loadings at lower temperatures. A series of equilibrium experiments are being conducted to establish the adsorption isotherms in the range of the test conditions.

After adsorption, the powder is transferred to another system for desorption studies. Both isothermal and thermal ramp desorptions have been conducted in vacuum. The desorption spectra were analyzed by the method of Smith and Aranoff.³ Iodine was found to occupy sites on the Fe_3O_4 of widely varying energy, as indicated by the complex desorption spectra, but a tendency to reorder toward sites of higher energy was shown by tests after annealing. The effect of a helium steam atmosphere on the desorption behavior will be studied by a transpiration technique.

¹Visiting Scientist, Hahn-Meitner Institute, Berlin, Germany.

²E. Hoinkis, Trans. Am. Nucl. Soc. 14, 70 (1971).

³A. W. Smith and S. Aranoff, J. Phys. Chem. 62, 684 (1958).

MASS TRANSPORT REACTIONS AS A FAILURE MECHANISM IN COATED PARTICLE FUELS

F. B. Lindemer¹ and H. J. de Nordwall

Analysis of existing data for the so-called "amoeba effect" in high-temperature, gas-cooled reactor fuel particles containing urania has led

to an extension of a model proposed by Flowers and Horsley² to account for particle coating failure. This model is based on the transport of carbon, as CO and CO₂, in a temperature gradient. Application of the model to specific data permitted the calculation of the total pressure of CO and CO₂ in the particle; these calculated pressures agreed, in the low pressure range, with measurements made by other investigators. Moreover, the pressures are in the range of CO pressures over the SiC-SiO₂-C equilibrium, indicating that this system may be chemically buffering the pressure of CO in the particle. Eventual failure of the final pyrocarbon coating as a result of access of the fuel system to this coating may be dependent on localized oxidation of silicon carbide, upon the probability of radial cracks across the silicon carbide layer, or possible silicon carbide-fission product interaction.

¹Metals and Ceramics Division

²R. H. Flowers and G. W. Horsley, "The Influence of Oxide Kernels on the Manufacture and Performance of Coated Particle Fuel," AERE-R-5949, 1968.

FISSION-PRODUCT RELEASE FROM BONDED BEDS OF BISO COATED UO₂ PARTICLES DURING POSTIRRADIATION ANNEALS AT 1250°C¹

M. T. Morgan, R. L. Towns, O. Sisman, and L. L. Fairchild

The fuel elements for high-temperature, gas-cooled, nuclear reactors will consist of bonded beds of coated fuel particles contained within a graphite moderator.

Annealing experiments were performed at 1250°C on loose BISO-type pyrolytic carbon-coated UO₂ particles and small bonded beds made from coated particles from the same batch to study the retention of Sr and Cs after burnups of 10% and 20% FIMA. Analyses indicated little holdup of Cs in the matrix of the bonded beds, therefore diffusion coefficients for Cs in the pyrocarbon coatings of the coated particles could be calculated at 1250°C from the annealing time required for Cs breakthrough.

The results are tabulated below. We see little effect of burnup on the diffusion coefficients. The fractional release was higher in the 20%

burnup samples than in the 10% burnup samples, as would be expected because of the higher concentrations of Cs inside the coating.

Cesium Diffusion in BISO-Type Pyrocarbon-Coated UO₂
Particles During Postirradiation Anneals

Sample No.	Type	Burnup (FIMA)	Diff. Coeff. (cm ² /sec)	Fractional Release After 1000 hrs at 1250°C
B-19	Bonded Bed	10%	3 x 10 ⁻¹²	4.5 x 10 ⁻³
B-21	Bonded Bed	10%	2 x 10 ⁻¹²	6.0 x 10 ⁻⁴
B-20	Loose	10%	4 x 10 ⁻¹²	7.2 x 10 ⁻³
BP-12	Loose	10%	2 x 10 ⁻¹²	4.0 x 10 ⁻⁴
B-46	Bonded Bed	20%	7 x 10 ⁻¹²	1.1 x 10 ⁻¹
B-51	Bonded Bed	20%	6 x 10 ⁻¹²	8.2 x 10 ⁻²
B-49	Loose	20%	8 x 10 ⁻¹²	1.6 x 10 ⁻¹

¹M. T. Morgan, R. L. Towns, and L. L. Fairchild, "Fission-Product Release from Bonded Beds," Gas-Cooled Reactor and Thorium Utilization Programs Annu. Progr. Rep. Sept. 30, 1971, ORNL-4760 (to be published).

FISSION PRODUCT DIFFUSION IN PYROCARBON COATINGS OF FUEL PARTICLES AT TEMPERATURES OF 1250°C to 1600°C

M. T. Morgan, R. L. Towns, O. Sisman, and L. L. Fairchild

The diffusion of cesium through pyrocarbon coatings is being studied by postirradiation anneals of high-temperature, gas-cooled reactor coated fuel particles. The effect of certain variables such as temperature, burnup, and coating type were studied. Large differences in cesium diffusion coefficients were observed between low temperature isotropic (LTI) pyrocarbon and high temperature isotropic (HTI) pyrocarbon. Effects of fast neutron damage were relatively minor. The particular variation in the coating structure (such as density, crystallite size, anisotropy, etc.) which is responsible for the better cesium retention by the HTI coatings is currently under investigation.

FISSION PRODUCT SURVEILLANCE STUDIES IN THE PEACH BOTTOM HIGH-TEMPERATURE, GAS-COOLED REACTOR

F. F. Dyer,¹ J. O. Kolb,² and H. J. de Nordwall

The concentrations of fission products and other solid impurities present in the coolant circuit of the Peach Bottom high-temperature, gas-cooled reactor are being measured using gamma-spectroscopy and gas sampling techniques. The information obtained will be used to evaluate the applicability of current mathematical models of fission product behavior in a real plant, and to provide a body of fact for utilities and HTGR vendors to use in licensing and siting arguments.

The Peach Bottom HTGR has been equipped with sampling stations up and down-stream of the steam generator. The samplers collect all circulating matter from a stream of gas that enters the sample device at the velocity of the reactor coolant, thus minimizing perturbation of flow patterns. More recent designs contain multistage impactors, as well as filters, for analysis of particle size distributions.

A second gamma-survey of activity in the primary helium circuit has been made. The results await evaluation.

Concentrations of gas-borne ^{131}I and ^{137}Cs were found to be lower in Core II than in Core I. Such strontium as was found was considered to have been derived from minute quantities ($\sim 10^{-8}$ g) of fuel rather than from rare gas precursors or strontium vapor per se.

The surface concentrations of cesium, cerium, silver, and ^{60}Co which were the principal gamma-emitters found in the primary circuit were found to fall about a hundred-fold overall. The change in surface concentration in passing through the steam generator was, however, much less than this. Data for the change in gaseous concentration between sampling points will not be available for another year.

Dust taken from the reactor dust collector was found to contain fragments of reactor thermal insulation that had lost their austenitic character and become partially ferritic. Chromium localization at the surface and carburization extending almost throughout some of these 0.002" thick foils was observed. The composition of other dust fractions was consistent with its having circulated in a strongly reducing system, i.e., free iron

and iron carbides were found by x-ray diffractometry, but no oxides.

Surveillance is being extended to cover the distribution of fission products in fuel elements.

¹Analytical Chemistry Division.

²Reactor Division.

WATER REACTORS

HIGH TEMPERATURE RUPTURE OF IRRADIATED ZIRCALOY FUEL RODS

M. F. Osborne

The extent of fuel rod deformation could significantly affect the severity of a loss-of-coolant accident in a power reactor. The expected high temperature transient would, under certain conditions, cause swelling, and possibly rupture, of some of the Zircaloy fuel rods. Two types of experiments were designed to investigate the effects of irradiation on such high temperature deformation. In the first type, some 40 fuel rods were heated to rupture in steam in single-rod tests; these tests were completed and have been reported.^{1,2}

The second type of experiment involved a 21-tube bundle in which all of the tubes were heated simultaneously by internal tungsten filaments. One such test, containing only unirradiated tubes, was conducted. The tubes were prepressurized to 100 psig and heated at 25^oF/sec. All ruptures occurred at 2200-2400^oF, and the average swelling for the center nine tubes (in the plane of maximum swelling) was 79%, which was slightly more than the 76% required for rod-to-rod contact.

In preparation for a similar test with irradiated rods, the UO₂ fuel contained within nine rods which had been irradiated to 35,000 MWd/ton was removed by dissolution. At this point, however, the program was terminated for budgetary reasons and the tubes, along with all other test components, were stored for possible future use.

¹M. F. Osborne and G. W. Parker, Reactor Chem. Div. Annu. Progr. Rep. May 31, 1971, ORNL-4717, p. 101.

²M. F. Osborne and G. W. Parker, The Effect of Irradiation on the Failure of Zircaloy-Clad Fuel Rods, ORNL-TM-3626, January 1972.

OFF-GAS FILTER SYSTEMS

THE CONSEQUENCES OF RADIOACTIVE DECAY OF FISSION-PRODUCT IODINE ADSORBED ON A CHARCOAL BED

R. J. Davis, R. A. Lorenz, W. J. Martin, and R. P. Shields

Effects of high radiation levels produced by radioactive iodine adsorbed on charcoal are being investigated. Of particular interest is a situation involving a charcoal filter bed which has been loaded with a large quantity of radioiodine and which simultaneously experiences a loss in air flow through the bed of sufficient degree that the bulk charcoal temperature of the bed approaches its ignition value. The expected consequences are desorption of the iodine and possible ignition of the charcoal. The objective is to determine safe ranges of particular design parameters for reactor containment adsorbers, specifically, safe combinations of maximum radioiodine loading (heat generation rate) and minimum air velocity (heat removal rate).

An experimental apparatus has been assembled in which approximately 4000 Ci of ^{130}I (12.5-hr half-life) will be deposited in a 1-in. diameter by 2-in. deep charcoal bed so that approximately 5 watts of radiation heat will be produced in the bed (0.2 w/cm^3 of 1 w/cm^2 frontal surface). The bed is well insulated to simulate the heat transfer conditions expected in a full-scale charcoal adsorber array. Calibration experiments using a bed of alumina bubbles and an electric disk heater at the bottom of the bed, to simulate heat due to radioactive decay of adsorbed iodine, were made to estimate the heat capacity of the container and the rate of heat loss by mechanisms other than heat transfer to the air stream. The heat capacity was found to be $12 \text{ watt-sec/}^\circ\text{C}$; the heat loss rate at an average bed temperature of 200°C was 1.6 watts. Preliminary experiments with dry air and unimpregnated coconut charcoals showed that the heat produced by slow oxidation of carbon will add significantly to radiation heating.

Experiments with low levels of radioactivity are in progress to determine the contribution of localized radiochemical effects to the desorption of iodine.

LONG-TERM EFFECTS ON I₂ AND CH₃I TRAPPING BY CHARCOAL

R. J. Davis, R. D. Ackley, and W. H. Hinds

This program pertains to the efficacy and the proof of the efficacy of iodine adsorbers at ORNL facilities. The objectives are: (1) to determine the effects of poisoning on the capability of charcoals to trap CH₃I. (2) to compare the CH₃I-trapping efficiencies measured in the laboratory with those done in-place, and (3) to initiate a study of the release of adsorbed radioiodine from charcoal.

Poisoning is considered to result from the passage of process air through a charcoal bed for extended periods of time before loading the bed with iodine. The methyl iodide trapping efficiencies of charcoal samples which had been exposed for various lengths of time to a by-pass stream on one of the laboratory containment off-gas systems were measured in the laboratory. A mass transfer model was employed to correlate these data with other data which were obtained for different gas velocities, different bed depths, and/or different granule sizes. The model is based on the assumption that the fraction of methyl iodide (or of I₂) adsorbed on a charcoal bed is controlled by the rate of mass transfer to the charcoal granules. The data correlation show that the CH₃I trapping capability of iodized charcoal decreases by about an order of magnitude faster than the I₂ trapping capability. Whereas, in typical applications, I₂ trapping efficiencies of charcoal adsorbers remain suitably high for a few years, CH₃I trapping efficiencies remain high for only a few months at most.

The laboratory and in-place measurements of CH₃I trapping efficiencies were previously found to be in disagreement. This disagreement was originally postulated to be a consequence of the large difference in CH₃I loading employed in the two test procedures. The test procedures have been modified to employ CH₃I loadings similar to each other and considerably lower than the maximum accident loading. A program of comparison tests on samples exposed to reactor off-gas streams for varying lengths of time is in progress.

A study of the literature pertaining to the release of adsorbed radioiodine revealed that the release rate is increased by: (1) organic contaminants in the gas phase, (2) organic substances adsorbed on the charcoal,

(3) elevated temperature, and (4) gamma-radiation. The magnitudes of the release rates are high enough to be of concern; the magnitudes and uncertainties are such that combinations of the above parameters can conceivably result in releases greater than the ORNL safety standard. A series of experiments has therefore been initiated to compare the effects of organic substances, either adsorbed or in the sweep gas, on the rates of release of adsorbed iodine from unimpregnated, iodized, and triethylenediamine-impregnated charcoals.

EFFECT OF EXTENDED EXPOSURE TO SIMULATED LMFBR FUEL REPROCESSING OFF-GAS ON RADIOIODINE TRAPPING PERFORMANCE OF SORBENTS

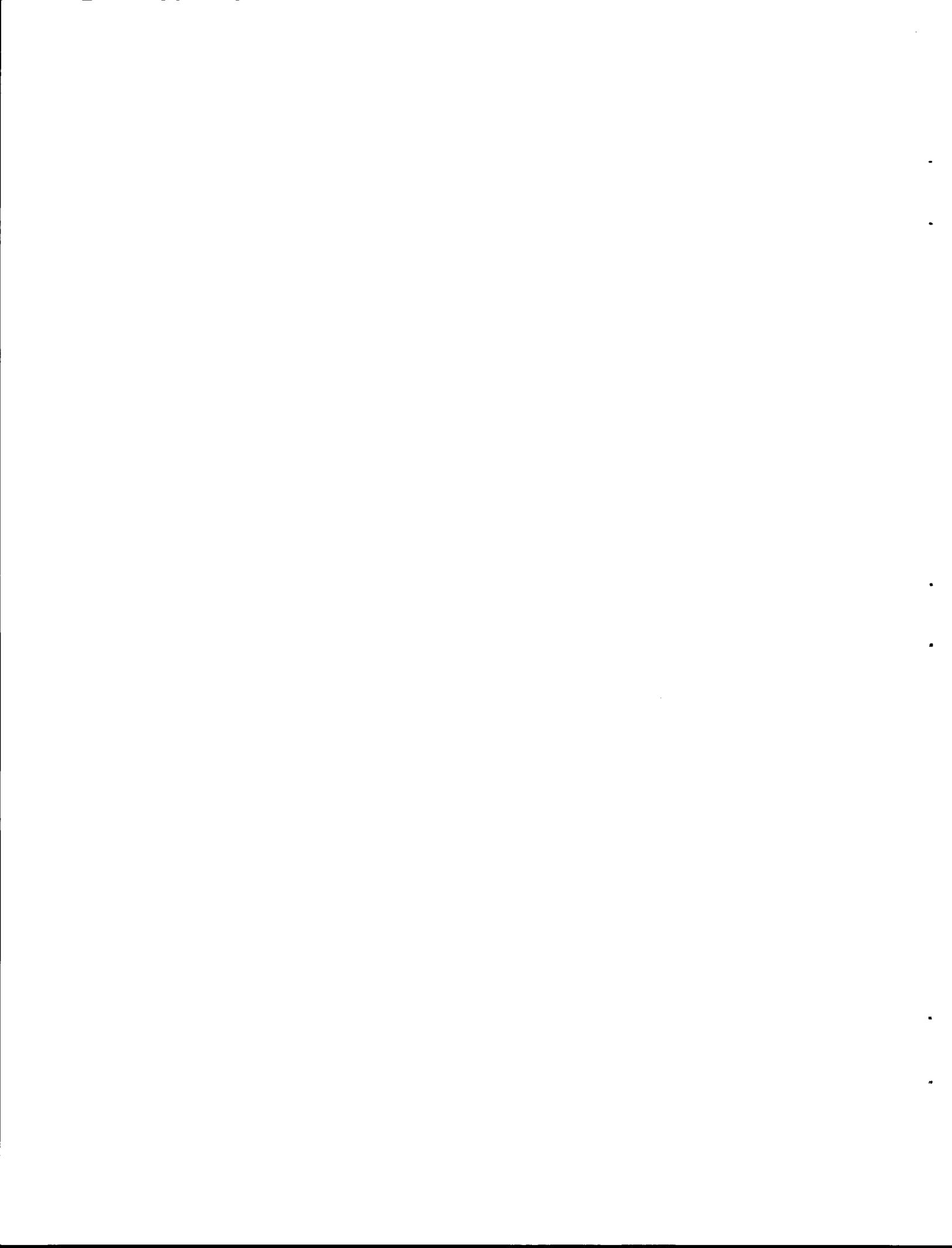
R. J. Davis, R. D. Ackley, and W. H. Hinds

In short term laboratory tests, certain silver-containing sorbents have exhibited decontamination factors greater than 10^3 for iodine as I_2 or CH_3I at $100^\circ C$ and/or $200^\circ C$, and for iodine loadings equal to or greater than estimated for one year of actual operation (around 5 mg iodine per cm^3 sorbent in a 2-in. depth).¹ Objectives of subsequent work have been to obtain information on the effective service life of such sorbents and to ascertain the desirability of locating a catalytic oxidation bed upstream of the sorbent bed to minimize poisoning by organic substances. Accordingly, a laboratory facility for exposing sorbents to simulated fuel reprocessing off-gas was constructed and is being operated.

Experimentally, the main air stream is humidified to around 85% saturation referred to room temperature. Elemental iodine (60 day ^{125}I -labeled), dodecane, and nitric oxide are continuously introduced at their projected concentrations. One group of sorbents is exposed to untreated off-gas while another group is exposed to off-gas which has traversed a Hopcalite bed at $350^\circ C$. Periodic methyl iodide (12.3 hr ^{130}I -labeled) trapping measurements are performed to yield differential results, whereas cumulative results are obtained with the I_2 . Sorbents being investigated include 26% AgX and 99% AgX (silver-sodium zeolites, where the percentages refer to the degree of Ag for Na exchange, in the form of 1/16-in. pellets) and GX135 (a silver-salt-treated alumina-silica, 8 x 16 mesh, U.S).

Thus far, the 26% AgX (at 200°C, 196 days exposure) and the 99% AgX (100°C, 105 days) have exhibited excellent CH₃I and I₂ trapping performance (i.e., the decontamination factors were $\geq 10^3$) for both the cases of with and without Hopcalite. Excellent performance has also been observed for GX135 (100°C, 119 days) without Hopcalite and for GX135 (200°C, 196 days) with Hopcalite. Poorer performances were observed for other combinations investigated, and other sorbents.

¹R. J. Davis, R. D. Ackley, Z. Combs, and W. H. Hinds, Reactor Chem. Div. Annu. Progr. Rep. May 31, 1971, ORNL-4717, pp. 96-97.



PART V. SALT MINE



RADIATION AND THERMAL CHEMISTRY OF SALT MINE BRINES

G. H. Jenks

A detailed analysis of the radiation and thermal chemistry of the salt and brines within the vicinity of a buried waste can in a waste repository has been completed.¹ Included in this work are estimates of the amounts of decomposition products which would appear within the open spaces around a can, and of the effects of these products on the design and operation of a repository. The important products are H₂, HCl, O₂, and possibly ClO₃⁻ and BrO₃⁻. No serious problems arising from these products at maximum rates of formation were recognized which could not be controlled by modifications to the design or operation of the repository.

An experimental program has been initiated to verify our understanding of the radiation and thermal chemistry, and to establish the rates at which the decomposition products will appear in, and/or diffuse from, the open spaces around a waste can.

We have also determined the concentrations of Na, Mg, Ca and Br in the brine taken from inclusions in salt from a mine at Lyons, Kansas. The results were: Mg, 2.1M; Na, 1.9M; Br, 0.04M; Ca, 0.03M. These values are in near agreement with those which we estimated previously from reported data for Hutchinson salt.¹ However, it is notable that the magnesium concentration is 2.1M, rather than the maximum of 3M, which we estimated earlier. Accordingly, the maximum rate of formation of HCl from hydrolysis of MgCl₂ is now estimated to be about 2/3 of the value used previously. We also found evidence that the pressure of gas within the brine inclusions is less than or equal to atmospheric pressure.

We are presently developing experiments to determine the steady-state concentration of radiolytic H₂ and O₂ within brine during gamma-irradiation under conditions which simulate those anticipated within the repository. Also, we are developing in situ experiments, using electrically heated waste-can mockups, to determine rates of brine migration into a burial hole and rates of evolution of the decomposition product gases from the hole.

¹G. H. Jenks, "Radiolysis and Hydrolysis in Salt-Mine Brines," ORNL-TM-3717, March, 1972.

STORED RADIATION ENERGY IN ROCKSALT

C. D. Bopp and G. H. Jenks

The rocksalt which will surround the high-level radioactive waste containers emplaced in a salt mine repository will be exposed to high gamma-ray doses and intensities (maxima of 2×10^{11} rad and 5×10^5 rad/hr) and to temperatures ranging up to about 350°C . Some of the absorbed gamma-ray energy will be stored as lattice disorder within the salt crystals. Knowledge of the amounts which will be stored in this manner is needed for evaluations of the hazards associated with rapid releases of this stored energy by thermal annealing.

Available experimental and theoretical information indicate that the amount of stored energy will depend upon dose rate, dose, and temperature, but the information is too meager to permit extrapolation to repository conditions.¹ We have therefore undertaken experimental investigations to provide information which will permit extrapolation to repository conditions. For this purpose equipment has been obtained for making experimental gamma-irradiations of salt within the target region of spent HFIR fuel elements (dose rates up to 10^8 rad/hr, doses to greater than 2×10^{10} rad, and temperatures to about 350°C), and for calorimetric measurements of the amounts of stored energy in irradiated samples. The general principles of the design and operation of the calorimeter are similar to those reported by Roux.² The sample (and container) at room temperature is dropped into the calorimeter which is maintained at a temperature above that at which the stored energy is rapidly released. This produces a transient lowering of the calorimeter temperature which is measured by a 60 -junction Pt, Pt-Rh thermopile. Roux² showed that the area under the temperature transient-time plot is proportional to the energy required to heat the sample container and sample. He also demonstrated that this method is more sensitive and rapid than differential thermal analysis at the temperatures of interest. The method is also faster than solution calorimetry, and removes the uncertainty as to the products formed on dissolution of radiation-defected material. Initial tests indicate that the sensitivity of our calorimeter, which was constructed by the ORNL Instrument Division, is similar to that reported by Roux.² However, further operational testing of the calorimeter,

as well as of the gamma-ray chambers, remains to be done.

¹G. H. Jenks, "Radiolysis and Hydrolysis in Salt-Mine Brines," ORNL-TM-3717, March 1972, pp. 13-20.

²A. Roux, "Energie Emmagasinee dans les oxydes BeO, MgO, Al₂O₃, et SiO₂ Irradies Aux Neutrons," Thesis, University of Lyon, Report No. CEA-N-4171, Translated by C. D. Bopp.

STORED RADIATION ENERGY IN HIGH-LEVEL RADIOACTIVE WASTES

G. H. Jenks and C. D. Bopp

Radiation energy can be stored in the oxides which will comprise the high level wastes in a repository, and knowledge of amounts of energy storage and of thermal annealing behavior is needed for hazard evaluations, for establishing criteria for the acceptability of solid wastes, and for establishing operating procedures. We analyzed experimental and theoretical information on radiation damage and energy storage in oxides and silicates and concluded that energy storage in the calcined-oxide-type and in the glassy-type high level wastes will result predominantly from displacements or spikes caused by elastic collisions of the heavy recoiling nuclei which are formed along with alpha particles in the alpha disintegration of the transuranic elements within the wastes.¹ The alpha rays themselves and, to a lesser extent, beta-rays will likewise cause some damage through elastic collisions. We also concluded that the radiation damage in radioactive wastes can be simulated in synthetic wastes using fast neutrons or accelerator-ion irradiations. However, the probable sample size requirements of our Roux-type calorimeter, about 100 mg, are such that accelerator irradiations are not practical. A reactor irradiation in the ORR is the practical alternative, and this experimental approach has been recommended.¹ The calorimeter should be operable to temperatures of about 1200°C, at which temperature nearly all the stored energy within the oxides will have been released.

¹G. H. Jenks and C. D. Bopp, "Types of Radiation Damage in High Level Radioactive Wastes and Simulation and Measurement of Stored Energy in Synthetic Wastes," ORNL-TM-3781, to be published.

GAS AND WATER VAPOR FLOW THROUGH CRUSHED SALT

R. B. Evans III, J. L. Rutherford, and J. Truitt

Several aspects associated with the operational safety of the radioactive waste, salt-mine repository requires that consideration be given to the gas transport characteristics of crushed salt backfill, and of the changes in these characteristics due to exposure of the backfill to water vapor. Accordingly, an experimental program of research has been undertaken to provide the requisite information.

Our first task was to ascertain whether dry crushed salt would inhibit the release of radioactive gases from defective packages soon after burial. Diffusion experiments with various size-grades of salt provided results that were interesting from an academic point of view, yet it was clear that practical size-grades of dry crushed salt would not impede gas transport in backfilled regions with any degree of effectiveness.

Since the bedded salt contains many brine-filled cavities which will migrate toward the waste packages emplaced within the salt, a second series of experiments was performed to ascertain the extent to which water vapor from the brine cavities will modify the characteristics of the backfill. In these experiments the water vapor-air system was studied using salt beds along which were maintained predetermined temperature profiles. In general, it was found that moisture condensed at predictable bed position and would accumulate and reflux until a weak consolidated seal formed, with large sacrificial voids appearing above the seal in the reflux zone. When bed temperatures were increased with time, the reflux zone moved up the bed leaving dry seals, consolidated regions, and voids behind. These results indicated that moisture aids in the permeability reduction of crushed salt in burial holes. The bench scale experiments did exclude many important effects, however, such as hole-closure compression, that are present in salt mines, so that the results must be viewed with these constraints in mind. Only sophisticated full-scale mine experiments, which are planned, will reveal the mechanism of crushed-salt consolidation in the actual situation.

HYDROGEN FLAMMABILITY LIMITS IN CRUSHED SALT

R. A. Lorenz

Hydrogen produced by possible corrosion of the waste containers emplaced within the salt mine repository and by radiolysis of migrating brine inclusions in the bedded salt will diffuse upward from the storage hole into the crushed salt backfilled burial room. It appears possible that hydrogen concentrations in air greater than four volume percent (the normally quoted flammability limit) might occur in the crushed salt backfill. The relatively large surface area and small void size in the backfill can be expected to increase the flammability limit somewhat.

A literature search revealed no information regarding flammability limits in packed beds, although many studies have been made to determine quenching distances, that is, the distance between parallel plates or the diameter of a tube below which a given explosive mixture cannot be ignited. We believe that the reported quenching distances can be compared indirectly with the characteristics of the void spaces in crushed salt beds, so that reasonable and conservative estimates can be made for flammability limits in the beds.

Evans, Rutherford, and Truitt¹ used their experimental permeability data and a capillary flow model to calculate channel diameters of 0.0081 cm and 0.057 cm for so-called fine and medium grades of Kansas crushed salt. The fine grade is clearly safe for any mixture of hydrogen in air. It would be desirable to use very coarse "as-mined" salt for backfilling the rooms, but the effects of coarse grade salts on flammability limit will require further study, and possibly some experimentation.

¹R. B. Evans III, J. L. Rutherford, and J. Truitt, private communication.

SURFACE DIFFUSION ON SODIUM CHLORIDE

B. K. Annis

The possibility of surface migration of radioactive fission products in a salt mine repository has prompted a laboratory investigation of molecular surface diffusion. The movement of lanthanum oxide on sodium chloride

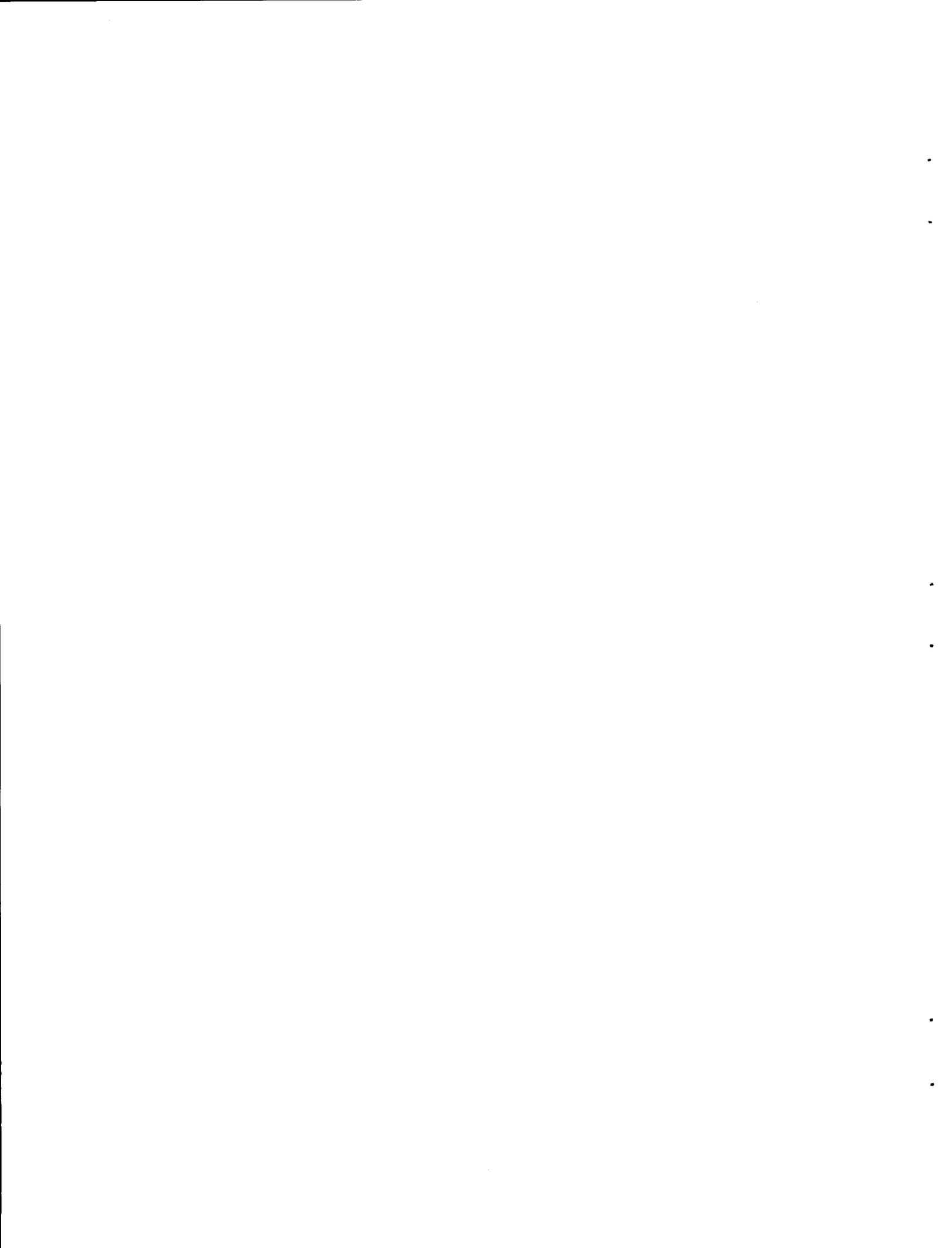
has been examined by depositing thin films of the material on salt coupons, annealing the resulting composites for various times and temperatures, and then analyzing the surface to determine the concentration profiles.

A preliminary result reported last year, which indicated a peculiar concentration profile that could not be accounted for by a diffusive mechanism, was found to be the result of inadequate masking during the deposition process. This problem was eliminated and further experiments were carried out using annealing periods ranging from two days to a week at temperatures of about 200°C. The concentration profiles of these samples were obtained through the use of two electron microprobes and an ion bombardment-X-ray fluorescence technique developed by members of the Physics Division. Also during this period, it was found that spark source mass spectrometry could provide a useful measure of the lanthanum oxide surface concentration, albeit with poor spatial resolution.

The results of these experiments, in addition to providing information on the methodology, indicated that surface diffusion, if indeed any occurred at all, was characterized by a diffusion coefficient of the order of 10^{-10} cm²/sec or less.

In an effort to make the results more definitive and the concentration profiles less ambiguous, it was decided to increase the temperature and the length of the annealing period. Consequently a number of salt coupons were partially coated with lanthanum oxide; one-third were analyzed immediately after deposition, another third were annealed at 420°C for two weeks, and the remainder were annealed for approximately five weeks at this temperature. The data collection, involving the electron microprobes, the ion bombardment technique and the spark source mass spectrometry, have recently been completed and analysis of the results is now in progress.

PART VI. SPECIAL RESEARCHES



THERMAL CREEP IN GASES¹

B. K. Annis

The development of a pressure gradient in a closed, gas-filled capillary due to the application of a temperature gradient is known as thermal transpiration. In the near continuum limit (small Knudsen number), the mechanism for the transpiration effect is a creeping motion of the gas in a thin layer adjacent to the surface. Measurements performed in the near continuum limit were compared with a number of theoretical calculations for the thermally-induced creep velocity. The experimental data which were obtained for He, Ne, Ar, Kr, and N₂ indicate that a number of calculations do not properly account for the phenomenon. On the other hand, two theories, one based on recent developments in gas kinetic theory, and another using the methods of irreversible thermodynamics, are in reasonable agreement with the data. The data were also used to test the near continuum limit of a recent calculation which attempts to describe thermal transpiration over the entire pressure range. This work is unique in that the near continuum limit is predicted to be strongly dependent upon the thermal accommodation coefficient. The experiments indicate that this prediction is in error. Finally, it was found that the value of the thermal creep coefficient can influence the evaluation of rotational collision numbers from thermal transpiration measurements.

¹Submitted for publication in the Journal of Chemical Physics.

FLOW AND DIFFUSION OF GASES IN POROUS STEEL COMPACTS

R. B. Evans III and J. L. Rutherford

Sintered compacts used in these studies were fabricated to provide specimens that would display effects of particle size of the initial powders and compaction pressure on the gas-transport characteristics of the final sintered discs. Porosimetry data indicated that the pore-size distributions of all of the discs were monodisperse and well defined. The three superficial coefficients which are required for complete gas characterization of a given specimen were obtained from a series of permeability measurements

at various pressures and a few counter-diffusion measurements.

We find good correlations of the data in terms of a simple capillary model which is consistent with the "dusty-gas" concept. In fact, reasonable estimates of the counter-diffusion behavior are provided by the relatively simple permeability measurements alone. Both porosity and average pore radii decrease as compaction pressures increase, but the number of flow channels per unit surface remain fairly constant for discs derived from a given powder.

Decreased flow admittances stem primarily from decreased pore sizes - a result which differs diametrically from impregnated-graphite results. Therefore, we note that flow admittances can be decreased in two ways other than by increasing compaction pressure. This can be accomplished either by decreasing the average particle size of the powder, or by broadening the particle size distribution, because both tend to reduce the pore sizes in the discs.

NEUTRON TRIGGERING OF CHEMICAL LASERS

S. S. Kirslis

It has been shown¹ that HF chemical laser action can be initiated by flash photolysis of a gaseous mixture of UF_6 and H_2 . An exploration was begun to evaluate the possibility of getting better laser action by more uniform triggering of chemical reaction in a large volume of $^{235}\text{UF}_6$ and H_2 with a pulse of neutrons in the Health Physics Research Reactor. First, the conditions under which neutrons would initiate the $^{235}\text{UF}_6\text{-H}_2$ reaction were explored. With 100 torr of UF_6 (93% ^{235}U) and 150 torr of H_2 at room temperature in a prefluorinated nickel vessel, there was only a trace of HF formed when a $50\mu/\text{sec}$ pulse of 10^{13} unmoderated neutrons passed through the vessel. When the pressures were increased to 400 torr of UF_6 and 600 torr of H_2 , and the initial temperature increased to 50°C , a similar unmoderated pulse caused 30% of the theoretical yield of HF to be formed. When the neutrons were moderated by immersing the nickel vessel in water at 50°C , the reaction was 70% complete. A blank run at the same temperature and

pressures in the absence of neutrons showed no HF formation.

Several attempts were made to observe lasing when $^{235}\text{UF}_6\text{-H}_2$ mixtures were irradiated with neutrons in brass tubes (14 in. long, 1.5 in. I.D.) fitted with synthetic sapphire windows. For practical reasons it was not possible to use $^{235}\text{UF}_6$ pressures above 210 torr nor initial temperatures above 34°C . Under these conditions, with unmoderated neutrons, no lasing could be detected.

A single attempt was made to observe radiation-induced laser action in one of the brass tubes using a mixture comprised of 8.1 torr F_2 , 2.7 torr H_2 and 325 torr ^3He , and employing a $50\mu/\text{sec}$ burst of about 3×10^{11} thermalized neutrons. ^3He has a collision cross section of about 5000 barns for reaction with a neutron to form a tritium atom, a proton, and 0.75 Mev of radiolyzing energy. No laser action was detected in the experiment although flash photolysis has been reported² to initiate lasing in a similar gas mixture.

¹K. L. Kompa, H. Parker, and G. Pimentel, J. Chem. Phys. 49, 4257 (1968).

²L. D. Hess, J. Chem. Phys. 55, 2466 (1971).

FEASIBILITY OF THERMOCHEMICAL OR RADIOLYTIC PRODUCTION OF HYDROGEN AS A FUEL FROM NON-FOSSIL SOURCES

F. F. Blankenship, S. S. Kirslis, and J. Braunstein

The projected exhaustion of fossil fuel resources, the desirability of conserving these irreplaceable materials for other than fuel uses, and the detrimental environmental impact of mining and burning fossil fuels provide strong incentives for searching for economically feasible methods of producing a non-polluting synthetic "convenience fuel" to supply the 80% of U.S. energy consumption from sources other than electricity. The technical consensus is that these requirements are best met by hydrogen,¹ to be produced from water using nuclear, or possibly solar, energy. It is currently feasible to produce hydrogen by the electrolysis of water, but this method suffers from the inherent inefficiencies of converting thermal to electrical energy. A survey has therefore been made of alternative methods for the

production of hydrogen from water using thermal energy or radiation.

Radiolytic methods, using either the energy of fission fragments in specially designed "chemonuclear" reactors² or the energy of radioactive fission products in spent reactor fuel elements, are severely disadvantaged by generally low radiolytic yields and the serious problem of radioactive contamination.

Although thermochemical methods are Carnot-limited, and no proposed reaction cycle has been demonstrated to be more efficient than water electrolysis, there is a definite theoretical possibility³ that reaction schemes may be devised with the necessary thermodynamic characteristics for superior efficiency. In view of this possibility and the large potential savings to be realized from even a small percentage gain in efficiency, further research on this method may be worthwhile, particularly in the following areas: (1) improvement of criteria for evaluating feasibility of proposed thermochemical cycles, especially three- and four-step processes, (2) search for reaction cycles with the required thermodynamic characteristics, (3) measurement of some thermodynamic and kinetic properties of promising reaction sequences, (4) comparison of efficiencies of thermochemical and thermomechanical topping cycles, and (5) examination of the feasibility of thermochemical processes combined with others, such as electrolysis.

¹L. W. Jones, *Science* 174, 367-70 (1971).

²M. Steinberg, *Advances in Nuclear Science and Tech.*, E. J. Henley and H. Kouts, eds., Academic Press, New York (1962), pp. 247-322.

³J. E. Funk and R. M. Reinstrom, "System Study of Hydrogen Generation by Thermal Energy," EDR 3714, Vol. II, Suppl. A, June 30, 1964, Allison Div., General Motors Corp., Indianapolis, Indiana; J. E. Funk, "Thermodynamics of Multi-step Water Decomposition Processes," Paper No. 36, Division of Fuel Chemistry, American Chemical Society, Boston, April 10-14, 1972; G. DeBeni and C. Marchetti, "A Chemical Process to Decompose Water Using Nuclear Heat," Paper No. 40, *ibid.*

RADIATION-INDUCED REACTIONS OF HYDROCARBONS

W. W. Parkinson and Ruth Slusher

The possibility of converting coal into liquid chemicals by irradiation is being investigated through studies of the irradiation of hexane and naphthalene as model compounds. The products of the radiation-induced reactions can be divided into three groups: (1) volatile compounds formed by the combination of alkyl radicals or hydrogen atoms from hexane; (2) compounds sufficiently volatile for gas chromatography, formed by addition or substitution of alkyl radicals onto a naphthalene nucleus; (3) non-volatile products formed by combination of two or more naphthalene nuclei.¹

Ten or more compounds have been identified in each of the first two groups as described previously. The last group, which constitutes the major portion of the total radiation product, has been separated into four fractions by gel permeation chromatography.^{2,3} The mass spectra of the four fractions have been measured⁴ and the general types of isomeric compounds making up each fraction have been identified.

The fraction of lowest molecular weight (Fraction 4) which was the only fraction sharply separated and the only one not resolvable into four or more constituents by thin layer chromatography, showed a mass of 219 ± 4 as the major peak. This mass corresponds to a naphthalene nucleus with one or more alkyl side groups totaling six carbon atoms and with hydrogen atoms added to the naphthalene rings to bring the mass near 219. The next heavier chromatograph fraction is largely mass 254 ± 4 , corresponding to dinaphthyl or di-hydro dinaphthyl.

The next fraction, which was the most abundant of the radiation products, appears at a chromatographic retention volume suggesting compounds of three naphthalene nuclei. However, the prominent mass peaks, 337 and 296 ± 4 , correspond to dinaphthyls with 6 and 3 carbon alkyl side groups, respectively. Either the bulky side groups reduce the retention volume to that of ternaphthyls or the original ternaphthyl compounds fragment in the mass spectrometer into ions, the heaviest of which have two naphthalene nuclei.

The heaviest fraction, which was poorly separated and contained a high mass tail, was predominantly mass 437₊₄, with small peaks at 467 and 509. The major peak was ternaphthyl compounds with alkyl side groups of 5 carbon atoms. The heavier peaks correspond to ternaphthyls with alkyl side groups totaling 7 and 10 carbons or perhaps the 509₊₄ peak arises from quaternaphthyls of 4 naphthalene nuclei and no side groups.

Additional samples have been irradiated to indicate the variation of yields with total dose and naphthalene concentration. The chromatographic separation and mass analysis of these will complete the project.

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

²N. J. Williams, Laboratory Division, Y-12, private communication.

³Ruth Slusher and W. W. Parkinson, Reactor Chem. Div. Ann. Progr. Rept., May 31, 1971, ORNL-4717, p. 120.

⁴W. T. Rainey, Analytical Chemistry Division, private communication.

THE DEVELOPMENT OF RADIATION-RESISTANT INSULATORS

W. W. Parkinson, W. J. Martin, and C. F. Weaver

It had been found earlier that polar end groups (i.e., sulfate or hydroxy) in emulsion-polymerized styrene polymers and copolymers accelerated the decay of electrical conductivity following irradiation.¹ This rapid decay of conductivity is required for insulating material in the charge storage capacitor of personnel dosimeters. To explore the influence of different types of polar groups on the postirradiation conductivity, copolymers of styrene with small fractions of methacrylic acid and maleic anhydride were procured through a related contract with Monsanto Research Corporation.

The conductivity of the methacrylic acid copolymers after irradiation was similar to that of ordinary, pure polystyrene, and the conductivity of the maleic anhydride was somewhat lower, although not consistently as low as emulsion polymers having sulfate end groups.

To increase the ionic character of the copolymers the acidic groups were neutralized with C_2H_5OK . The postirradiation conductivity of the resulting polymers appeared to be relatively low, but was masked by the extreme sensitivity, both before and after irradiation, to atmospheric moisture. Reverse currents were observed which apparently resulted from ionic conduction and electrolytic polarization.

This polarization could oppose the conduction currents measured after irradiation and this mechanism could conceivably produce the rapid decay of conductivity observed in sulfate-type emulsion polystyrenes. Successive measurements and irradiations demonstrated that electrolytic polarization did not account for suppression of conductivity in this type of polymer, however. Instead, the conductivity decreased to preirradiation values several days after irradiation, while the conductivity of pure polystyrene remained high for these periods. This behavior indicated that the trapping or recombination of charge carriers was the process active in reducing conductivity.

The styrene copolymers with methacrylic acid and maleic anhydride were then neutralized in aqueous emulsion with KOH . Specimens prepared in this manner incorporated in highly dispersed form a second phase of emulsifier and water associated with the acidic groups along the polymer chain. Post-irradiation conductivities showed some variation among specimens but were consistently lower than the conductivity of pure polystyrene and in many instances were as low as that of sulfate-type polymers.

Apparently, the emulsification step in the preparation procedure of these acidic copolymers changed the decay times of their postirradiation conductivity from the long periods characteristic of ordinary polymers to the rapid decay of the sulfate end group emulsion polystyrenes. This evidence leads to the conclusion that the trapping entity for charge carriers is an ionized or strongly polar second phase, the effective dispersal of which requires association with polar groups attached to the polymer chain.

¹W. W. Parkinson, H. H. Stone, M. J. Kelly, and Ruth Slusher, Reactor Chem. Div. Ann. Progr. Rept. May 31, 1971, ORNL-4717, p. 121.

MOLTEN SALTS AS BLANKET FLUIDS IN CONTROLLED FUSION REACTORS

W. R. Grimes and S. Cantor

The Reactor Chemistry Division is starting a research program of basic materials chemistry related to fusion reactor systems. As part of the program, we are assessing how lithium-bearing fused salts will perform as blanket coolants in fusion reactors. The following is a summary of an initial report on this subject.

The strong magnetic fields may have a considerable effect on the chemical stability and a less significant effect on the fluid dynamics of a flowing salt. A salt melt flowing across a strong magnetic field induces an electric field; which in turn produces an emf between the walls of the conduit and the adjacent salt. The emf can be lessened to minor proportions by careful design - causing the salt to flow parallel to the magnetic field wherever possible and using a system of small-bore tubes where the flow must cross the magnetic field. Although flow in a magnetic field parallel to the lines of force suppresses turbulence (which is necessary in a salt for optimum heat transfer), this effect on molten salts will be negligible owing to their low electrical conductivities.

Breeding of tritium in a molten-salt blanket is at best marginal when the lithium is in its natural isotopic abundance; however, the tritium-breeding ratio can be improved by including blanket regions of lithium or of beryllium, or by enriching the salt in lithium-6. LiF and its mixtures with BeF₂ appear to be the best molten-salt coolants in which to breed tritium in quantities adequate for fueling a reactor. Molten LiF-BeF₂ is advantageous in recovering tritium since, in contact with metallic Ni, Mo, or W, virtually all of the tritium is present as TF.

While fluorides are adequate heat-transfer agents and possess good radiation stability, neutronic transmutation of Be and F in the salt can lead to corrosion unless a redox buffer (analogous to U³⁺/U⁴⁺ in a fission reactor) is included in the melt.

In a blanket which has two coolants, one being metallic lithium, salts other than LiF-BeF₂ could be considered. For example, eutectic LiCl-KCl, melting at 354°C, may be adequate as vacuum wall coolant and as the fluid to

transport heat to the steam system of the reactor.

PARTICIPATION IN PLOWSHARE ACTIVITIES

C. J. Barton, M. J. Kelly, and R. E. Moore

Dose studies in connection with the Gasbuggy Project have been completed. They were documented in a series of topical reports¹⁻³ and in the open literature.^{4,5} Similar studies related to the Rulison Project were initiated and doses were estimated for the hypothetical introduction of one million cubic feet per day of dry, CO₂-free gas from the Rulison well into the distribution systems of two gas companies located near the Rulison site.⁶ One system provided a dilution factor of 10 or more for Rulison gas, while the other system permitted very limited dilution in the two communities that could receive Rulison gas. Production testing of the well removed most of the tritium, the radionuclide of principal concern, that was initially present in the well, but we calculated whole body doses that could have been received through inhalation and skin absorption of the gas combustion products if the gas had been used commercially instead of being burned at the well head. The maximum value for the system providing a dilution factor of 10 was 6 millirems per year, while the corresponding value for the slightly diluted gas was 39 millirems per year. Doses were also estimated for use of the gas present in the well in August 1971 following completion of the flaring program and a period of pressure building in the well. The maximum tritium whole body dose for this situation would be only 0.03 millirem per year. Computer programs have been developed to calculate the change in tritium concentration in the natural gas flowing from either a single nucleary-stimulated gas well or from a multiple well field.⁷ Other programs were formulated for calculating doses from combustion products discharged from a tall stack, such as a gas-fired electric generating plant, or for controlling exposures resulting from this situation. These programs should aid the planning of multiple well fields and the estimation of potential doses from stack discharges.

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ENVIRONMENTAL IMPACT PROGRAM

R. E. Thoma, O. Sisman, A. S. Quist, G. W. Parker, C. D. Baumann, R. J. Davis, M. J. Kelly, G. W. Keilholtz,¹ W. L. Marshall,¹ and F. F. Blankenship²

Before the U.S. Atomic Energy Commission may issue a construction permit or an operating license for a nuclear power plant it must ascertain that issuance of such a permit or license is consistent with national environmental goals as defined by the National Environmental Policy Act of 1969 (Public Law 91-190). Following an interpretation of this law

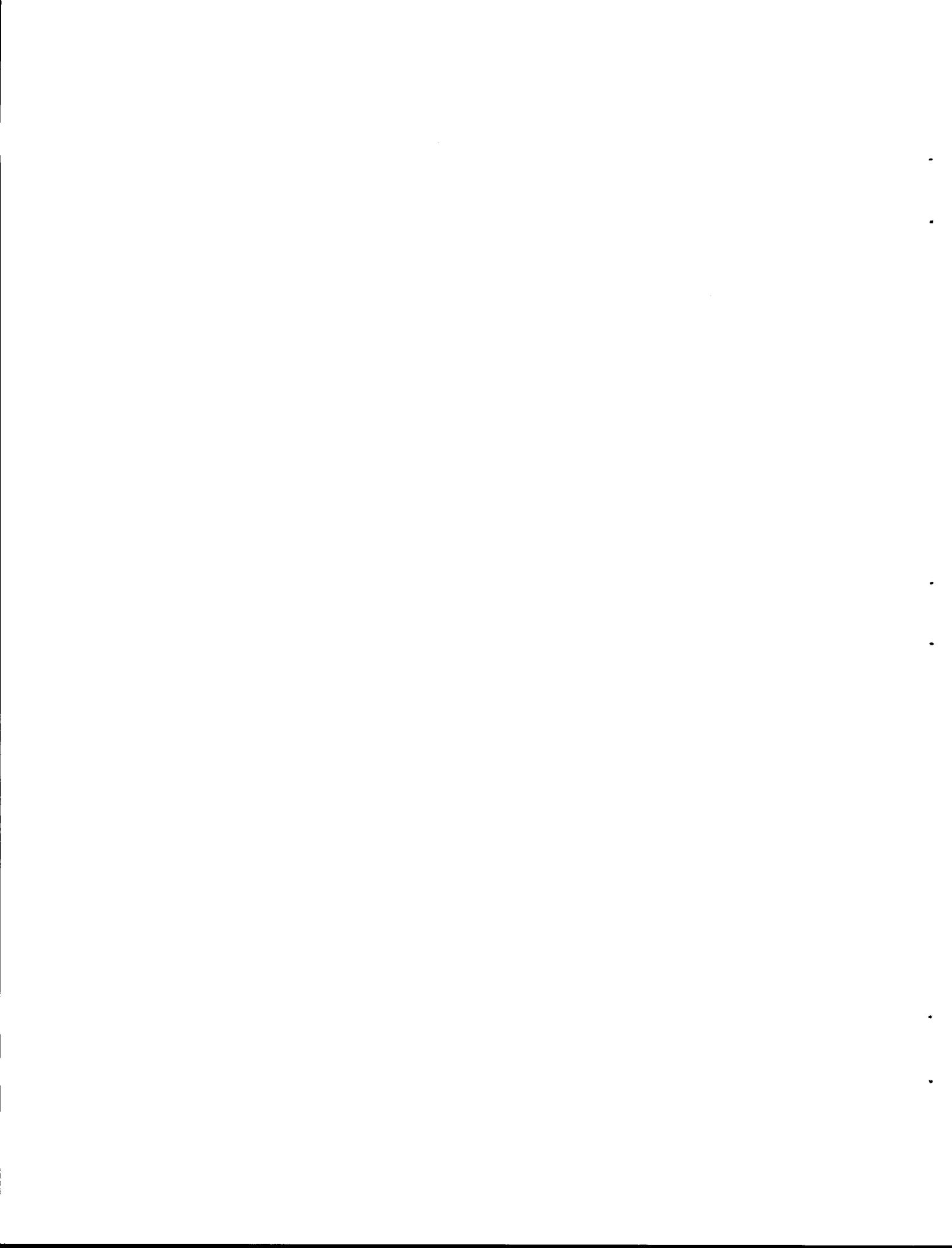
(generally called the NEPA Act) by the U.S. Court of Appeals for the District of Columbia Circuit in July 1971 in the matter of Calvert Cliffs' Coordinating Committee, Inc., et al v. United States Atomic Energy Commission et al., Nos. 24,839 and 24,871, the AEC substantially broadened the scope of its assessment of environmental impacts of all nuclear reactors in licensing and construction stages. The additional efforts were so massive that the AEC found it necessary to solicit assistance from ORNL and from others of its National Laboratories.

Since then, and as part of a team including scientists from virtually all Divisions and disciplines at the Laboratory, the Reactor Chemistry Division staff members listed above have been engaged in the Laboratory's Environmental Impact Project. This Laboratory-wide team is organized to produce detailed critical evaluations of the impact upon its environment for each individual nuclear power plant for which an operating license or a construction permit is needed. In this effort the Reactor Chemistry Division scientists have served in several capacities. Three of the above (Thoma, Sisman, and Quist) serve as leaders of Task Groups with responsibility for coordinating and writing the detailed environmental impact statements. Others serve as technical consultants, as members of these Task Groups, or as members of special Problem Position Groups who develop standard source terms for radioactive element release for use throughout the Project. Many other Reactor Chemistry Division scientists have served, and are serving, on special panels to review and comment critically upon the individual draft statements as they are developed within the Laboratory.

Both because of the monumental nature of the task, and because much of the output is still in draft form, and is subject to revision after comment by other Federal Agencies, discussion of content of the several assessments is beyond the scope of this document.

¹Half-time assignment.

²Temporary assignment.



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"Applications of Complete Constants for Geochemical Predictions," Gordon Research Conference on Geochemistry, Plymouth, N. H., Sept. 3, 1971.
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"Evaluation of Potential Exposure to Environmental Radioactivity,"
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"Stability and the Effect of Solvent on Dilute U(III)-U(IV) Mixtures
in Solution in Molten Fluorides," Gordon Research Conference on Molten
Salts, Meriden, N. H., Aug. 30-Sept. 3, 1971.
- L. M. Toth
"Spectroscopy of Molten Fluoride Salts," Department of Chemistry,
St. Mary's College, Nov. 30, 1971 under ORAU Traveling Lecture Program.
- L. B. Yeatts and W. L. Marshall
"Electrical Conductance and Ionization Behavior of Sodium Chloride in
Dioxane-Water Solutions at 300°C and Pressures to 4000 Bars," American
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- L. B. Yeatts and W. L. Marshall
"Solubility of Calcium Sulfate Dihydrate and Association Equilibria in Several Mixed-Electrolyte Salt Systems at 25°C," American Chemical Society Meeting, Washington, D. C., Sept. 12-17, 1971.
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"Experimental Results from Processing Gasbuggy Gas in a Natural Gas Processing Plant," presented at Tritium Symposium, Las Vegas, Nevada, Aug. 30-Sept. 2, 1971.

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