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Chemical Interactions During Melting of the MSRE Fuel Salt

D. F. Williams
L. M. Toth
G. D. Del Cul

MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
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Chemical Technology Division

CHEMICAL INTERACTIONS DURING MELTING OF THE MSRE FUEL SALT

D. F. Williams
L. M. Toth
G. D. Del Cul

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Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
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SUMMARY

This report describes the chemical changes that are likely to occur if the Molten Salt Reactor Experiment (MSRE) fuel salt is melted without adjustment of the salt chemistry. The radiolysis that has taken place during the last 25 years has generated a considerable quantity of fluorine gas, leaving behind metal sites in the frozen salt. Changes in the chemistry of the *molten* salt are expected because the reducing power of these metallic sites is realized only in the melt. The major conclusions that can be drawn from previous studies can be summarized as follows:

1. Because uranium and zirconium are the most reducible constituents (i.e., least active metals) in the salt and are very close together in the electrochemical series, it is likely that these minority species will be reduced by the metallic lithium and beryllium present in the melt. Uranium metal forms a relatively low-melting (740°C) intermetallic alloy with nickel (the primary metal in the Hastelloy-N wall).

2. Previous studies involving highly reduced fluoride salts have shown that significant phase segregation of both zirconium and uranium occurs after melting (usually manifested as a separate metallic phase or deposit).

3. Restoration of fluorine to the reduced salt from a F_2 blanket (i.e., "recombination," or "annealing") at subliquidus temperatures has been demonstrated on small samples, but considerable uncertainty exists about the effectiveness of this treatment for the large mass of salt that exists in the drain tanks. The annual annealing treatments conducted for 20 years were either ineffective or, at best, only partially effective.

4. Recent observations of the melting of irradiated simulant salt show that the salt melts inhomogeneously and cools to form two distinct segregated phases. On the other hand, the unirradiated salt melts uniformly, forms a clear homogeneous liquid, and cools to form a homogeneous solid with no apparent macroscopic segregation.

Support for these conclusions is provided in the following sections: (1) Thermodynamic Studies (Redox Behavior), (2) Experiments with Molten Salts Under Reducing Conditions, (3) Recombination Studies, and (4) Recent Observations.

1. THERMODYNAMIC STUDIES

The best sources of information on the redox behavior of constituents in the stored fuel salt are the investigations conducted during the Molten Salt Reactor Experiment (MSRE) program. Extensive measurement of transpiration equilibria, with various gases as redox agents, was the primary source for establishing the electrochemical series in the Li_2BeF_4 solvent. Direct measurements of reduction potential were also made, but a number of experimental complications rendered these results somewhat less accurate and reliable. In the late 1960s Baes *[1]* summarized the literature and presented a relatively complete and coherent picture of the redox behavior in this system. For our purposes we can summarize the pertinent results by displaying the electrochemical series along the reduction potential axis, as shown in Fig. 1.

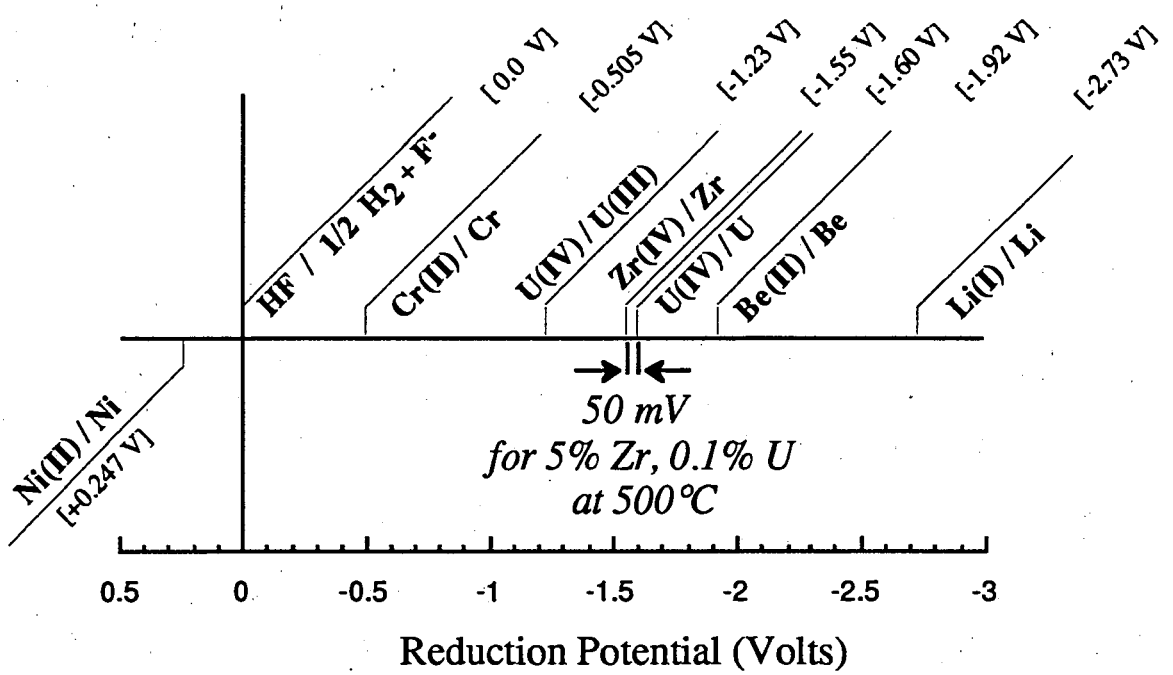

Fig. 1. Reduction potentials for the MSRE fuel salt at 500°C. Potentials referenced to HF/H_2, F^- in 0.67 LiF–0.33 BeF_2. Figure based upon data obtained from Baes, C. F., "The Chemistry and Thermodynamics of Molten Salt Reactor Fuels," *Nucl. Metal.* **15**, 617–44 (1969).

Concentration effects in Fig. 1 are accounted for by the Nernst Equation *[2]* and do not include corrections for solution-phase nonideality at high solute concentrations. Good nominal agreement between these thermodynamic predictions and the measured reduction potentials was achieved *[3-4]*. Exact agreement between predicted and

measured reduction potentials cannot be expected because of the lack of a stable and unbiased reference electrode for this system. Despite these limitations, use of quasi-reference electrodes and bounding corrections gave agreement between measured and predicted values that was within 5% (100 mV), and the basic reduction sequence was the same as that predicted by Baes.

The implication of the reduction sequence depicted in Fig. 1 for the stored MSRE fuel salt is relatively straightforward. Previous irradiation studies on alkali halides *[5-6]* showed that the metallic sites associated with the loss of fluorine exist as a distribution of Li°, Be°, and Be^{+}. These sites will reduce the less active U(IV) and Zr(IV) species in the molten salt. Uranium(IV) will be preferentially reduced to U(III), and if sufficient reductant is present, Zr° and U° will be formed. Based upon the present assay of 290 equivalents of reductant (i.e., 145 mol F_2 liberated from the salt as F_2 and $UF_4 \cdot F_2$) and a uranium inventory in the fuel drain tanks of 31.3 kg, all of the uranium will be reduced to U(III) and a significant amount of uranium and/or zirconium metal will be formed by the remaining 155 equivalents of reductant. Preferential reduction to Zr° will result in 3.5 kg of zirconium metal, while preferential reduction to U° (not indicated in Fig. 1) will result in 12 kg of uranium metal.

It must be emphasized that these predictions can only provide guidance, and a number of important factors may influence the amount of uranium that is reduced to the metal. The projected reduction potentials of uranium and zirconium are very close, and small errors in our estimates or neglect of previously unknown species or interactions may act to increase the amount of uranium metal that is formed. The presence of strong reducing sites (e.g., Li°) can be envisioned as a large reduction overpotential that is capable of driving a number of reduction reactions even though they are not favored in the eventual equilibrium distribution. The potential for alloying interactions with the wall and other specific mechanisms that are not accounted for in this treatment must be recognized and addressed by a review of the experimental literature and operational experience. A review of pertinent experiments is contained in the remaining sections of this report.

The basic character of the interaction between zirconium or uranium metal with the Hastelloy-N vessels and piping is a reflection of the tendency of the Group IVA metals to form intermetallic bonds with nickel. For the nickel-uranium system, this is manifested by the formation of a low-melting (740°C) alloy at 33% nickel *[7]*. Zirconium also forms a number of intermetallics with nickel and the lowest melting alloy occurs at 75.9% Zr and 960°C *[8]*. It is likely that any zirconium or uranium metal formed will eventually

plate on the nickel-rich Hastelloy-N surfaces due to a combination of physical and chemical interactions. The phase diagram for uranium-zirconium indicates that these metals form nearly ideal solutions with one another over a very large range of compositions *[9]*. No mixtures melting lower than the pure metals exist.

2. EXPERIMENTS WITH MOLTEN SALTS UNDER REDUCING CONDITIONS

2.1 Melt-out Experiment (Materials Testing Reactor MTR-47-4 Capsule 36)

The MTR-47-4 melt-out trial *[10-14]* is the closest approximation to the conditions we expect to exist upon "simple" melting of the stored MSRE fuel salt (i.e., without simultaneous chemical adjustment). This trial subjected 25 g of $LiF-BeF_2-ZrF_4-ThF_4-UF_4$ (71-22.6-4.7-1-0.7 mol %) salt to extensive in-pile irradiation* and resulted in considerable radiolysis of the cooled salt during the decay period after irradiation. Table 1 compares the reduced condition of capsule 36 salt with that from a previous benchmark trial and with the limits we expect to apply to the stored MSRE fuel salt.

Table 1. Comparison of fluorine removal from selected irradiated MSRE salts

Salt origin	Fluorine removal	
	mmol F_2/g salt	% F removal (or % damage)
MTR-47-4 capsule 36	0.35	2.1
Toth 1977 gamma irrad.[a]	0.37	2.0
MSRE drain tanks[b]		
Lower bound	0.033	0.18
Upper bound	0.13	0.72

[a]*Source*: Toth, L. M., and Felker, L. K., "Fluorine Generation by Gamma Radiolysis of a Fluoride Salt Mixture," *Radiat. Eff. Def. Solids* 112, 201–10 (1990).

[b]Bounds are based upon measured and maximum projected values. *Source*: Williams, D. F., Del Cul, G. D., and Toth, L. M., *A Descriptive Model of the Molten Salt Reactor Experiment After Shutdown: Review of FY 1995 Progress*, ORNL/TM-13142, Oak Ridge National Laboratory, 1996.

After irradiation, cooling, and measurement of the gaseous product from radiolysis, a melt-out recovery of the contents of capsule 36 was conducted to help establish the chemical condition of the radiolyzed salt. The apparatus for this operation was first tested with the unirradiated control capsule 3A and worked flawlessly. The analytical values for the recovered salt were exactly as expected. However, when removal of the

* Here in-pile irradiation refers to the actual fissioning of a salt specimen in a test reactor. The decay radiation is therefore most similar to that of the actual stored fuel salt and includes α, β, γ, and neutron sources.

contents of capsule 36 was attempted, only half of the salt was obtained and the recovered fraction exhibited a 34% reduction in uranium concentration and a 50% reduction in the expected reducing power (based upon the fluorine removal value in Table 1). These findings are summarized in Table 2. Analysis of a solid sample (i.e., not melted) recovered from capsule 24 of MTR-47-4 gave good agreement between the measured uranium content, 3.82 wt %, and the expected value of 3.89 wt %.

Table 2. Summary of melt-out experiment results on MTR-47-4 Capsule 36

Measurement	Observation or value	
Volume of recovered melt	~ 50% of total charge	
Appearance of recovered melt	Pale green	
	Before melting	In melt
Uranium content (wt %)	3.89	2.56
Reducing power (meq/g salt)	0.7	0.34

It was concluded that substantial reduction of uranium (and possibly other species) must have occurred in the melt and that this reduction produced a high-melting heel that would not drain. The pale green color of the salt drained from capsule 36 indicates that most of the uranium in the melted fraction was present as UF_4. The presence of UF_4 in the melt means that reduction did not proceed to equilibrium — portions of the salt were reduced completely, while other parts remained unchanged. The residual reducing power remaining in the recovered fraction also indicates that the sample did not reach equilibrium in the melt. Unfortunately no analysis of the high-melting heel was reported.

2.2 Thermal Cycling During In-Pile Tests (MTR-47-5)

During the in-pile trials *[15-16]*, irradiated salt specimens were intermittently cooled from the molten state to ~35°C during periods when the Materials Testing Reactor was shut down. These cool-down cycles permitted fluorine generation due to radiolysis. During the MTR-47-5 trial, fluorine generation was measured as a pressure rise and swept-gas samples were taken periodically for chemical analysis. Since this cooling and the subsequent heating during restart of the reactor caused a reduced fuel to be melted, the post-irradiation examination of the frozen capsules may yield some useful information about the chemical interactions that occur in a reduced molten salt. As with almost all of the early irradiation tests, graphite surfaces were included in the test specimen because of materials compatibility questions regarding the use of graphite as a moderator in the MSRE core.

The quantitative results from the post-irradiation examination of capsules 3 and 4 from MTR-47-5 are summarized in Table 3. The reduction, expressed as percentage fluorine removal, accumulated during the seven cooling cycles is extensive, and we should expect significant chemical effects during melting. The primary influence of this reduction was manifested as a selective deposition of uranium on graphite to a depth of ~2 mils and generalized attack on graphite by fluorine. Although the surface concentrations appear low (5–7 mg/cm^2), this deposition accounts for about 10% of the uranium in the specimen. Similar concentrations of uranium on graphite were measured during examination of reduced fuel specimens from MTR-47-4. The chemical form of the deposit was never determined, but it was believed to be UC_2. Examination of the fuel and Hastelloy-N container showed no distinct evidence of reduction, corrosion, or formation of a new phase. The amount of uranium deposition is less than that expected based upon the melt-out experiment results, but it is far larger than that measured during examination of the unreduced MTR-47-5 irradiation specimens. While these results do not directly confirm the behavior seen in the melt-out experiment, neither do they contradict the previous observations. Any uranium reduced to the metal is expected to react with the graphite wall to form UC_2 deposits. It is quite likely that the presence of a large surface of graphite in contact with reduced fuel will alter the reduction events that occur during the melting process.

Table 3. Characteristics of reduced fuel specimens from MTR-47-5

Capsule no.	% Fluorine loss from salt	Uranium surface concentration [mg/cm^2]	% U deposited on graphite
3	0.177	5	13.9
4	1.08	7	10.1

2.3 Reductive Extraction into Liquid Bismuth

Extensive research into separation of molten salt species by reductive extraction into liquid bismuth (or metallic bismuth alloy) began in 1965 *[17-18]* and continued until the end of the MSRE program. The focus of this work changed as the separative goals (e.g., rare earth removal, ^{233}Pa scavenging), flowsheets, and proposed salt chemistries evolved. A few of these studies address the ease with which uranium is reduced relative to the other molten salt components (especially zirconium) and help to form a more complete picture of the redox chemistry of the stored salt. In the absence of zirconium all studies show that uranium is the most readily reduced element in the salt *[19]*. In mixtures that contain both uranium and zirconium, it was found that comparable amounts of each of these elements are transferred to the metal phase under a wide range of reducing conditions, as shown in Fig. 2 *[20]*. Despite the extra complications of solute/solvent and solute/solute interactions in the metal phase, these results support the basic thermodynamic predictions that uranium and zirconium have very similar redox potentials in molten fluoride salts *[1]*.

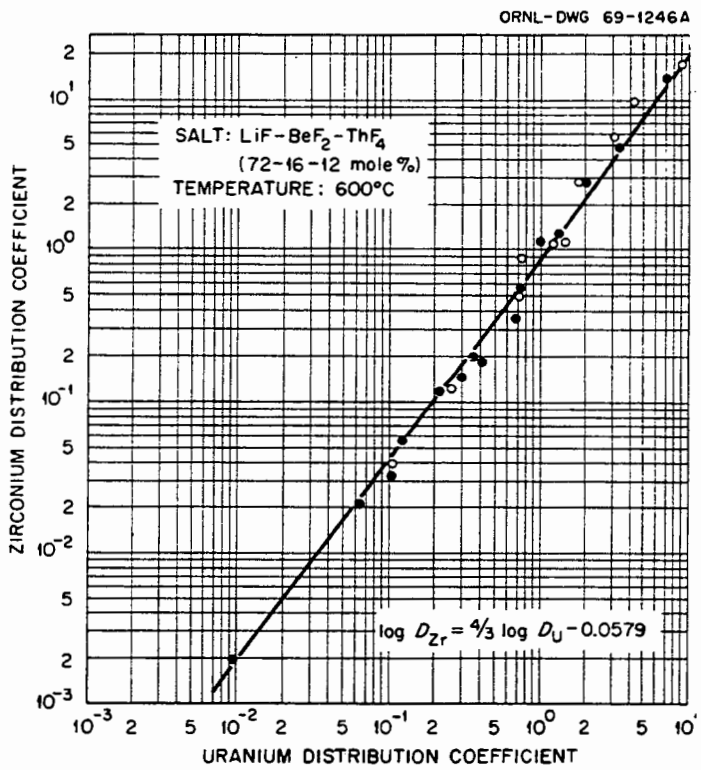

Fig. 2. Equilibrium distribution of uranium and zirconium between LiF-BeF_2-ThF_4 (76-16-12 mol %) and bismuth solutions at 600°C. (*Source:* Ferris, L. M., et al., "Measurement of Distribution Coefficients in Molten-Salt/Metal Systems," p. 281 in *Molten Salt Reactor Program Semiannual Progress Report for Period Ending February 28, 1969*, ORNL-4396, Oak Ridge National Laboratory, August 1969.

2.4 Early Flow-Loop Tests with Reductant Additions

The first generation of molten salt reactors was developed during the 1950s as part of the Aircraft Nuclear Propulsion Program and explored the use of $NaF-ZrF_4$ mixtures and alkali metal fluorides (e.g., LiF-NaF-KF, or FLINAK) as solvents for UF_4. During flow-loop corrosion experiments, various reductants (usually ZrH_2) were added to the salt to suppress the redox potential for corrosion of chromium in the Inconel piping *[21-22]*. These additions were effective in preventing corrosion of chromium, but they also caused reduction of Zr(IV) and U(IV) to the metal. The addition of ZrH_2 to $NaF-ZrF_4-UF_4$ (56-46-4 mol %) caused two distinct changes: (a) loss of uranium from the salt during reductant addition in the 700°C make-up vessel and (b) deposition of metallic zirconium (and perhaps some uranium) on the inner wall of the Inconel flow loop. Noticeable uranium losses in the make-up vessel and transfer filters were evident for ZrH_2 additions corresponding to a 0.5 wt % contribution, and one-half of the uranium remained in the make-up vessel/filter after an addition of 2% ZrH_2. After circulation of the reduced salt for 500 h at 815°C, significant deposits were detected on the inner pipe walls, as shown in Fig. 3. Microspark spectrographic measurements indicated that the deposit was primarily zirconium metal, but the presence of some uranium could not be excluded by this type of analysis.

Reduced alkali metal fluorides of various strengths were prepared by controlling the concentration of trivalent uranium during the salt production process. During circulation of salts with more than 2% of the uranium as U(III), a metallic deposit formed that was judged to be uranium by its metallographic appearance. This deposit is shown in Fig. 4. In a separate trial, addition of TiH_2 to a circulating alkali fluoride salt resulted in a thin metallic deposit containing the intermetallic compound Ni_3Ti *[21]*. This deposition occurred well below the 1380°C melting point of Ni_3Ti.

These studies support the assertion that significant quantities of zirconium and/or uranium are likely to form in molten MSRE fuel salt if fluorine is not restored to the salt before or during melting. However, this work does not sort out the uncertainty that exists regarding the preference for reduction between uranium and zirconium. In the $NaF-ZrF_4$ system, the zirconium concentration is 10 times higher and the uranium concentration is 20 to 40 times higher than that of the MSRE fuel salt. Even with such a high concentration of zirconium fluoride, substantial losses of uranium were experienced. For the case of the alkali fluoride salt, no ZrF_4 was present to compete with uranium for the reductant and only uranium metal deposits were reported.

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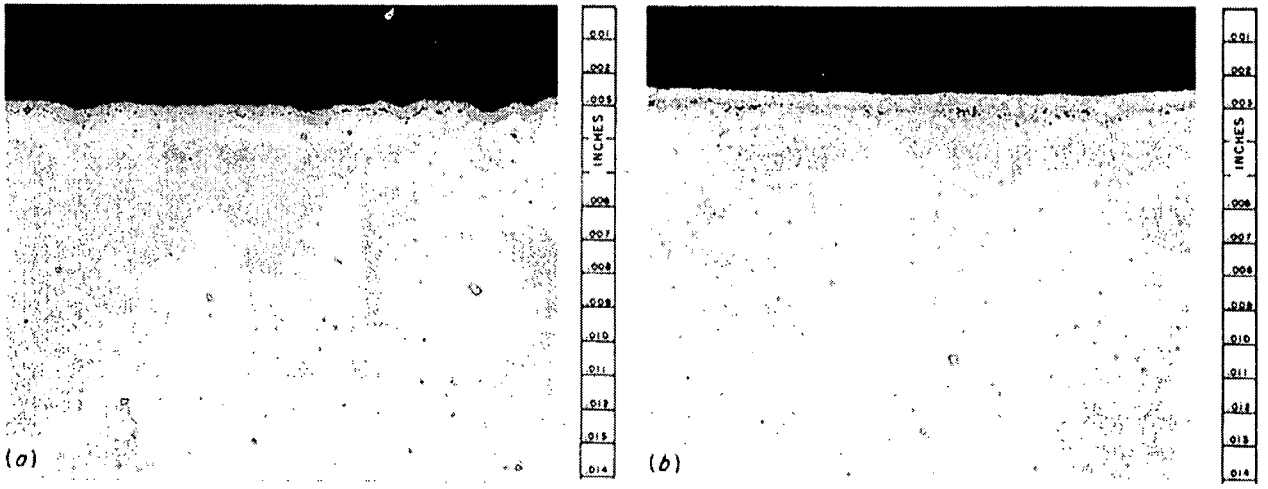

Fig. 3. Deposits in hot legs of loops with zirconium hydride additions to NaF-ZrF_4-UF_4 (56-46-4 mol %). ***(a)*** **0.8 % ZrH_2;** ***(b)*** **2% ZrH_2.** (Source: Adamson, G. M., Crouse, R. S., and Manly, W. D., *Interim Report on Corrosion by Zirconium-Base Fluorides,* ORNL-2338, Oak Ridge National Laboratory, January 1961, p. 51.)

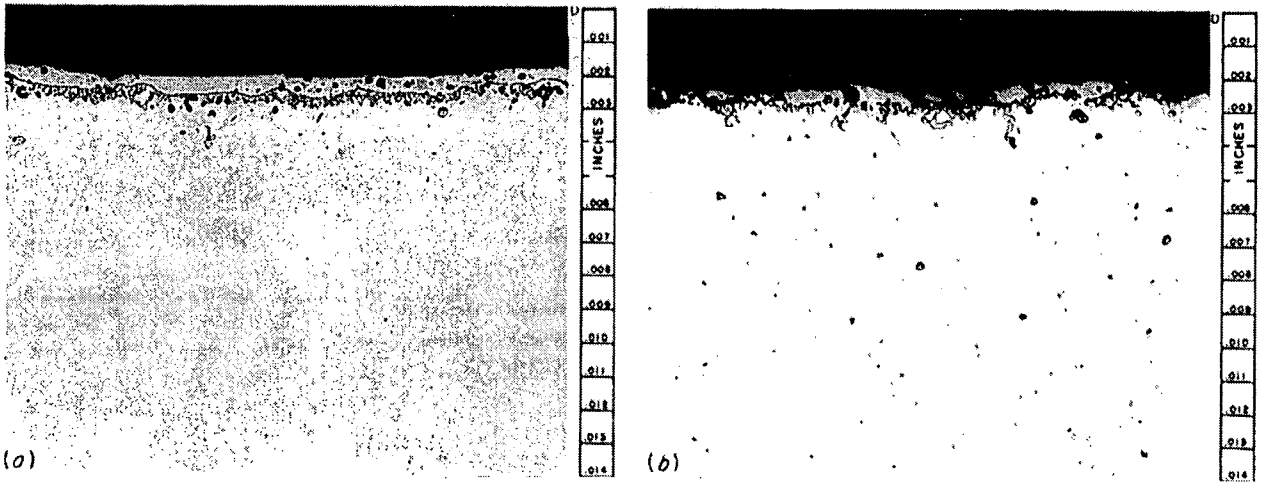

Fig. 4. Typical hot-leg sections from loops circulating alkali-metal fluorides with larger amounts of trivalent uranium. ***(a)*** **5.3% U(III), 500 h at 1500°F;** ***(b)*** **5.6% U(III), 1000 h at 1500°F.** (Source: Adamson, G. M., Crouse, R. S., and Manly, W. D., *Interim Report on Corrosion by Zirconium-Base Fluorides,* ORNL-2338, Oak Ridge National Laboratory, January 1961, p. 56.)

3. RECOMBINATION STUDIES

Previous studies sought to find the temperature at which the recombination back-reaction just counterbalances the generation of fluorine by radiolysis and thus establish the lowest temperature that would inhibit the generation and release of fluorine. Recombination of fluorine with reduced metal sites was measured by noting the rate of fluorine pressure loss over reduced fuel at various temperatures. Comparison of this back-reaction rate with the radiolysis rate gave reasonably good predictions of the inhibition temperature (~150°C). These predictions agreed with the observations made during and after in-pile irradiation of fuel — only moderate heating of the fuel (to >100°C) was required to suppress fluorine evolution.

However, the primary importance of recombination in the present context derives from the desire to *completely* anneal the damage that has accumulated in the reduced fuel salt. In this context, annealing refers to the restoration of the original salt chemistry by recombination of trapped or gaseous fluorine with the metal sites in the salt. The ability to inhibit further fluorine evolution by heating is well established and is of secondary importance in this discussion. The general issue of annealing radiolytic damage encompasses more variables than inhibition predictions and requires a more thorough understanding of the governing phenomena. Except for one investigation *[23]*, all of the previous studies *[24-26]* have measured recombination rates only during the very earliest stages of annealing.

Our present knowledge of recombination in MSRE salt is based upon four rather limited investigations: one study of "synthetic" reduced fuel (generated by metal addition, not radiolysis), one investigation of recombination after in-pile irradiation, and two studies of recombination of reduced fuel generated by external gamma radiation. The pertinent details of these studies are summarized in Tables 4 and 5 and in Fig. 5.

Table 4. Parameters in recombination studies

Study	Sample size	Sample form	Extent of reduction	Extent of recombination
Synthetic reduced fuel[a] (1963)	360 g	1.8-in.-ID x 3.6-in. cylindrical plug	50% UF_3	Complete
In-pile irradiation[b] (MTR-47-5, 1963)	25 g	0.5-in. x 1-in. annular U-tube plug	2–4 % damage	< 15%
^{60}Co irradiation[c] (Savage, 1964)	35 g	0.78-in.-ID x 3.2-in. cylindrical plug	0.24% damage	< 30%
HFIR-pool irradiation[d] (Toth, 1986)	30 g	0.78-in.-ID cylindrical powder bed	2% damage	Minor

[a]*Source*: Briggs, R. B., et al., *Molten Salt Reactor Program Semiannual Progress Report for Period Ending January 31, 1963*, ORNL-3419, Oak Ridge National Laboratory, May 1963, p. 136

[b]*Source*: Briggs, R. B., et al., *Molten Salt Reactor Program Semiannual Progress Report for Period Ending July 31, 1963*, ORNL-3529, Oak Ridge National Laboratory, December 1963, p. 86.

[c]*Source*: Savage, H. C., et al., "Gamma Irradiation of a Simulated MSRE Fuel Salt in the Solid Phase," pp. 27–31 in *Reactor Chemistry Division Annual Progress Report for Period Ending January 31, 1964*, ORNL-3591, Oak Ridge National Laboratory.

[d]*Source*: Toth, L. M., and Felker, L. K., "Fluorine Generation by Gamma Radiolysis of a Fluoride Salt Mixture," *Radiat. Eff. Def. Solids* **112**, 201–10 (1990).

Table 5. Results from recombination studies

Study	Temp. (°C)	Recombination rate: Measured (psig/h)	Molar (μmol/h)	Volumetric (μmol/h•g)	Surface (μmol/h•cm^2)
Synthetic reduced fuel[a] (1963)	≤ 300	0	0	0	0
	400	—	> 640	> 1.8	> 155
^{60}Co irradiation[b] (Savage, 1964)	110	0.001–0.004	0.1–0.34	0.0035–0.01	0.04–0.11
	130	0.002–0.006	0.18–0.5	0.005–0.015	0.057–0.17
	150	0.019–0.021	1.5–1.8	0.043–0.053	0.5–0.6
HFIR-pool irradiation[c] (Toth, 1986)	100	0.007	1.4	0.046	0.00038
	150	0.03	5.7	0.19	0.0016
	200	0.11	20.2	0.67	0.0056

[a] The "zero"values reported for < 300°C correspond to no detected recombination in 3 h. *Source*: Briggs, R. B., et al., *Molten Salt Reactor Program Semiannual Progress Report for Period Ending January 31, 1963*, ORNL-3419, Oak Ridge National Laboratory, May 1963, p. 136.

[b]*Source*: Savage, H. C., et al., "Gamma Irradiation of a Simulated MSRE Fuel Salt in the Solid Phase," pp. 27–31 in *Reactor Chemistry Division Annual Progress Report for Period Ending January 31, 1964*, ORNL-3591, Oak Ridge National Laboratory.

[c]*Source*: Toth, L. M., and Felker, L. K., "Fluorine Generation by Gamma Radiolysis of a Fluoride Salt Mixture," *Radiat. Eff. Def. Solids* **112**, 201–10 (1990). For this study, 120 cm^2/g was used for the surface area of 0.02-cm powder.

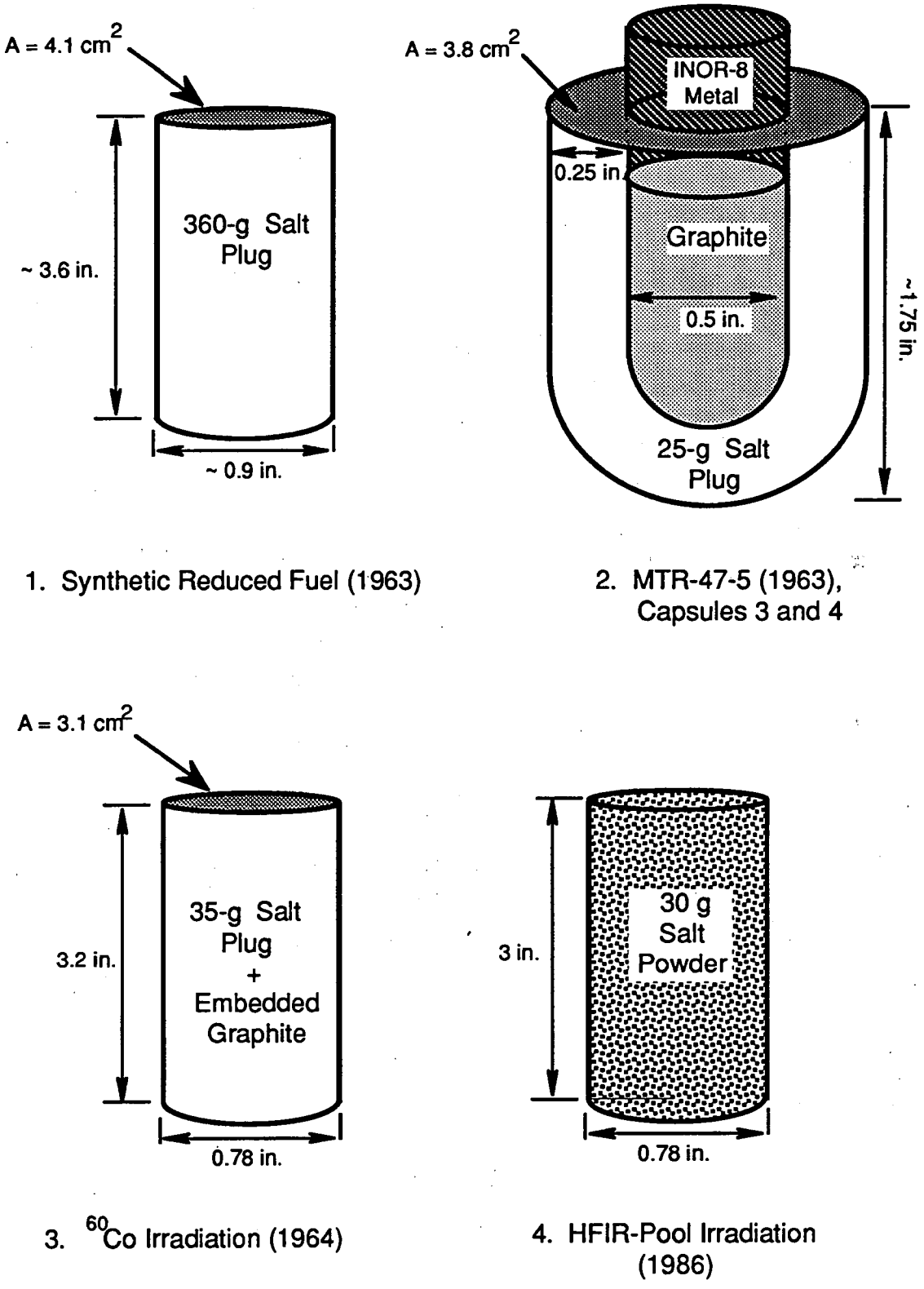

Fig. 5. Specimen configurations for recombination studies.

4. RECENT OBSERVATIONS

During the past 3 months, preliminary trials involving the melting of radiolyzed (i.e., "reduced" or fluorine-deficient) MSRE simulant fuel salt were conducted. In the first set of trials, direct observation of the melting process was conducted by flame heating a small platinum crucible contained in a helium-purged quartz chamber. For these direct observations the salt from the 1995 irradiation in the HFIR cooling pool was used (0.1% fluorine deficiency), and recovery of the melted salt from the crucible was achieved manually (i.e., without additional melting) in a fume hood after the salt had come to room temperature in the helium atmosphere of the quartz chamber. For comparison purposes a sample of the unirradiated simulant salt was also melted in the same apparatus.

The unirradiated salt melted uniformly to a nonwetting translucent green liquid and cooled to its original appearance — a macroscopically homogenous greenish-white microcrystalline solid. The grey-black irradiated salt eventually melted to a form an opaque pool that appeared to be completely liquid and to wet the container wall. Experience has shown that this wetting is indicative of the net reducing character of a salt. Upon freezing a light yellow-green solid appears that becomes the dominant phase upon repeated or prolonged melting. However, a considerable volume of dark-phase remnant was present in the frozen salt even after repeated and extensive melting.

X-ray diffraction and X-ray fluorescence(EDX) measurements were made on the unirradiated salt, the untreated irradiated salt, and the melted irradiated salt. Diffractograms for the two untreated samples (irradiated and unirradiated) were almost identical — showing strong peaks corresponding to Li_2BeF_4, Li_2ZrF_6 and no other uncorrelated or unmatched features. The diffractogram for the melted sample had strong "new" peaks which could not be identified in the International Center for Diffraction Data (ICDD) library of standards. Because EDX did not reveal any differences in elemental composition between the three samples, we do not expect the new peaks to be an artifact due to contaminants. These unidentified features probably reflect the presence of a "new" compound formed in the reducing melt.

Additional studies on the melting of fluorine-deficient salt in a furnace are under way. For these trials the more highly reduced salt (~2% fluorine deficiency) from the first 1996 irradiation in the HFIR cooling pool is being used and is contained in Monel tubes that more closely resemble the Hastelloy-N wall of the drain tanks. In the previous tests Xray diffraction did not show evidence of a macroscopic metallic phase; therefore, we are

planning to use Auger electron spectroscopy to help resolve the identity of metallic species distributed in the salt. Because previous petrographic investigations of irradiated salt specimens during the MSRE program were not successful in characterizing the chemical changes in the irradiated salt *[27–31]*, microscopic examination of the salt is not our primary focus for resolving the remaining salt chemistry issues. The assembly of a remotely operated X-ray diffraction apparatus for examination of irradiated fuel during the MSRE program was a response to the limited results obtained from petrography *[31]*. Unfortunately, very few results were obtained with this apparatus because of the difficulties of hot-cell operation and waning support for this activity.

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