

Radiolytic Processes During Intermediate Stages of ^{233}U Removal from the Oak Ridge Molten Salt Reactor Experiment

L. D. Trowbridge, A. S. Icenhour, G. D. Del Cul, and D. W. Simmons
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6224, USA

ABSTRACT

An ongoing project at Oak Ridge National Laboratory has the goal of removing ^{233}U from the Molten Salt Reactor Experiment (MSRE) and ultimately converting it to a stable form for storage. The high activity of ^{233}U and ^{232}U creates physical and chemical vulnerabilities that must be addressed during processing and interim storage of the uranium prior to ultimate conversion to a stable oxide. This paper discusses two such vulnerabilities deriving from radiolytic processes.

At present, the uranium from the MSRE is partitioned into three primary locations. The majority has been removed as UF_6 and is chemically complexed with NaF pellet beds. This material is in interim storage awaiting conversion to U_3O_8 . A substantial fraction (perhaps one third) remains in the fuel and flush salts in three tanks at the reactor site. This material is to be converted to UF_6 and also complexed with NaF. A small fraction of the uranium was captured by an activated charcoal trap in the reactor off-gas system. That material has been removed from the charcoal trap and is in a shielded storage container at the MSRE site. Both the NaF/ UF_6 traps and the activated charcoal material are undergoing radiolytic processes that could lead to difficulties if not attended to. These processes, their consequences, and ameliorating measures are the subject of this paper.

INTRODUCTION

The Oak Ridge Molten Salt Reactor Experiment (MSRE) was a fluoride salt ($\text{LiF}\text{-BeF}_2\text{-ZrF}_4\text{-UF}_4$) reactor operated in the mid-to-late 1960s. The final series of experiments used a ^{233}U -based fuel. When the reactor was shut down in 1969, the fuel salt was drained into two tanks where it remains to this day. Due to radiolytic generation of F_2 from the frozen salt, the salt was periodically annealed,

that is to say, heated to a temperature (below the melting point) at which F_2 recombination with the salt took place. In the 1990s, radiation readings in piping remote from the fuel drain tanks indicated that uranium had migrated from the salt. A remediation effort was begun at that time with the overall goal of removing the uranium from the piping systems, fuel and flush salt and other areas of significance (notably an activated charcoal bed) and converting the uranium to a stable form suitable for long-term storage or final disposition. The remediation effort as a whole is discussed in more detail in a separate paper at this conference. The focus of this paper is to examine in greater detail observations on two radiolytic processes that have had an impact on the processing and interim storage of uranium during this remediation effort.

RADIOLYSIS OF NaF-COMPLEXED UF_6

The discovery of radiation attributable to uranium daughter products in piping remote from (but in communication with) the fuel drain tanks suggested that uranium had migrated from those tanks as gaseous UF_6 . The tanks had been observed to pressurize due to buildup of F_2 generated by radiolysis in the salt proper. This effect was known in the 1960s and led to periodic annealing to a temperature (150–230°C) that could recombine F_2 with the (now fluorine-deficient) salt [1]. Gas sampling in 1994, however, indicated that the gas present in the MSRE off-gas system contained not only the expected F_2 but also UF_6 near its saturation vapor pressure. Early remediation efforts were aimed at the removal of the F_2 and UF_6 from the off-gas system. The removal scheme passed the gas through three pellet-bed scrubbers (“chemical traps”) in series containing, in order, NaF, activated alumina, and molecular sieve. The UF_6 was captured in the first of these traps, reacting to form the complex $2\text{NaF}\cdot\text{UF}_6$. The gas-removal system ultimately

generated 26 NaF traps containing a total of approximately 23 kg U, with individual traps containing between 130 and 1100 g U. A single NaF trap has bed dimensions of approximately 8 cm in diameter and 36 cm long and contains an initial load of about 1.8 kg of pelletized NaF.

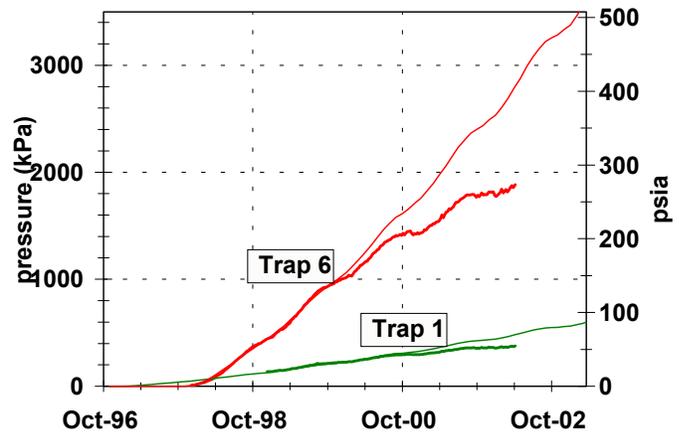
Trapping of UF_6 in pelletized NaF is a form of gas scrubbing used extensively in the uranium enrichment industry. Prior to the MSRE remediation project, there had been no documented experience with NaF-trapping of $^{233}UF_6$ and storing the resultant material for an extended period of time. Alpha radiolysis of UF_6 in the gaseous and solid state is known to occur [2 – 4], forming F_2 and reduced uranium fluorides (e.g., UF_4 and UF_5). No corresponding radiolysis experience was known for the $2NaF \cdot UF_6$ complex, however. At the relatively low activities found even in highly enriched uranium, only an insignificant degree of decomposition would be expected to occur. However, ^{233}U has an activity orders of magnitude greater than ^{235}U . Therefore the question of radiolysis of UF_6 in the trapped form is of significance in this application. The MSRE uranium assay also has a trace (presently ~ 150 ppm) of ^{232}U , which approximately triples the activity from that of the ^{233}U alone.

The immediate consequence of radiolysis of this complex is the pressurization of the gas-tight chemical traps during interim storage. In anticipation of radiolytic pressure buildup, the NaF traps were designed as pressure vessels and were constructed from F_2 -compatible materials. The operational effect of the pressure rise is that conversion processing for each trap must begin before its pressure rating is exceeded. When the traps are removed for processing for purposes of conversion of the UF_6 to U_3O_8 , the high-pressure F_2 must be vented. The loss of fluorine from the UF_6 implies that a substantial fraction (perhaps one third) of the uranium will be present as a reduced fluoride (e.g., $NaF \cdot UF_5$), which will require refluorination to allow transfer of uranium as UF_6 out of the NaF trap. Both these factors are considered in the uranium conversion process design.

To date, 26 traps have been placed in interim storage. The rate of radiolytic pressure buildup was not known prior to this project, so trap design and pressure ratings were targeted at the worst-case rate estimates. In addition, two of the traps have pressure-monitoring instruments attached. Readings from these sensors have indeed shown

an increase in pressure over the past few years (see Fig 1). This has been the subject of considerable interest and analysis. The goals of this analysis are to characterize the radiolysis process of the NaF/ UF_6 complex and to predict the future course of pressure rise for the two instrumented traps as well the remaining uninstrumented ones.

Figure 1: Pressure in monitored NaF/ UF_6 traps showing observed (heavy) and predicted (light)



pressure.

One of the instrumented traps (Trap 1) has a uranium load near the minimum for any trap in storage, while the other (Trap 6) is near the maximum. Both were loaded early in the gas-removal campaign. The general course of pressurization seen in both traps showed an initial period of little or no pressurization (i.e., an induction period, which is common in radiolytic processes in solid-state materials), followed by a transition to a fairly constant rate of pressure increase. Superimposed upon the basic increasing trend is a cyclic up-and-down variation related to seasonal temperature swings in the storage facility. Recent pressure data show a decline in the rate of pressurization. Factors that might reduce the net F_2 production include target depletion, lower G-factors for reduced uranium fluorides, and back-reaction of F_2 . Ultimately the (net) generation of F_2 must cease, but there is not yet sufficient information to quantitatively predict the resulting upper pressure limit.

When UF_6 was first deposited in the NaF traps, it was separated from its daughter products, since

none form volatile fluorides at the prevailing conditions. For that reason, nearly all the radiation energy initially deposited in the trap (>99%) is attributable to alpha particles. With the build-in of daughter products, this fraction decreases, but remains high (~96% four years after initial capture of UF₆). Unless alpha radiolysis is completely ineffective at decomposition of NaF or UF₆, it will dominate any radiolytic pressurization. A simple computational model of this system was developed to interpret the available pressurization data. The model has also been applied to the remaining (un-instrumented) traps in order to predict their pressurization.

When normalized for uranium-load, the initial pressure trends in the two instrumented traps were found to be reasonably consistent with one another. This is not particularly surprising, since the UF₆-trapping kinetics and dynamics for the conditions that apply to this system are such that an incompletely loaded NaF trap will, to a reasonable approximation, consist of a zone of UF₆-saturated NaF followed, after a short transition zone, by a zone of essentially uranium-free NaF. A highly loaded trap will thus have a larger volume of UF₆-saturated NaF while a lightly loaded trap will have a smaller volume of such material. Both volumes, however, will have about the same density of uranium in the loaded region.

Several potential fluorine-generating radiolytic interactions might be considered in a model, namely alpha, beta, and gamma particles interacting with 2NaF@UF₆ or with uncomplexed NaF. The very small fraction of radiation energy due to beta and gamma, however, makes the gas generation insensitive to G-factors for beta and gamma. Only the alpha vs 2NaF@UF₆ interaction is important in this system.

The model devised had the following features:

1. Uranium (of 1998 MSRE assay) was assumed deposited on the date the trap was loaded. Daughter products are assumed to build in from that date.
2. Energy from all major radioactive decay modes (alpha, beta, and gamma) is calculated at intervals from the date of uranium loading in the trap for all nuclides present.
3. Energy deposition is apportioned among the various target species proportional to their electron density.
4. UF₆-loaded NaF is assumed to have a loading

density of UF₆ typical of UF₆-saturated NaF. Traps not loaded to this level are assumed to have a zone of pure NaF, which does not participate in radiolysis other than to occlude gas volume.

5. The G-factor for alpha vs 2NaF@UF₆ is treated as an adjustable parameter.

6. G-factors for beta and gamma vs 2NaF@UF₆ and NaF are set to a nominal value (0.02 molecule F₂/100 eV deposited energy) typical in other inorganic fluoride systems.

7. Generation of F₂ gas is calculated by summing the contributions from all decay modes interacting with all species.

8. An empirical induction period was imposed based on instrumented trap observations during which gas generation smoothly increased to its nominal rate.

9. Pressure is predicted by treating F₂ as an ideal gas.

Factors not considered include geometric effects such as edge effects, depletion of reactants, differing G-factors for reduced uranium fluorides, back reaction, and upper damage limits.

In spite of the seeming complication of the model briefly described above, it had, in effect, only two adjustable parameters (the length of the induction period and the key G-factor). The early pressure rise data for the two instrumented traps were best represented by an (alpha vs 2NaF@UF₆) G-factor of 0.44 molecule F₂/100 eV alpha energy deposited in trapped UF₆. This represented the available data quite well for 3 years after the date of loading the instrumented traps. The model's predictions for the two instrumented traps are shown in Fig. 1, along with the observed pressures.

Recently, the pressurization has declined noticeably from the rate predicted by this G-factor (at present to about 50% of the original value. While, from an operational standpoint, it would be convenient if this could be proven to represent the onset of an upper damage limit, it is premature to predict any useful upper limit to gas generation in these traps.

G-factors deduced from trap pressurization are shown in Table 1, along with literature values for gas-phase UF₆. Two values are shown for the MSRE NaF traps: one, which represents the data well from 6 months to 3 years after the trap was loaded and the second, which represents the characteristic of more-recent observations.

Table 1. G-factors for gaseous UF₆ from literature and those inferred from MSRE trap pressurization for UF₆ complexed with NaF. G-factors are in units of molecules F₂ generated per 100 eV deposited energy

Species	Rad type	G-factor	Ref.
UF ₆ (gas)	Rn alpha	0.53	[2]
UF ₆ (gas)	Rn alpha	0.17	[3]
2NaF·UF ₆	MSRE U	0.44	to 3 yrs
2NaF·UF ₆	MSRE U	0.22	5 yrs

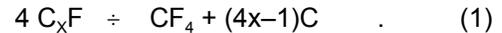
This model has been used to predict the pressurization in the 24 uninstrumented traps. On the basis of two traps of significantly different loading, it is, of course, difficult to categorically state what the trap-to-trap variability in pressurization may be. Ultimately, as the other traps are taken from storage and vented prior to uranium removal and conversion, we will have a measure of the final pressures in the uninstrumented traps for comparison with the model predictions.

NH₄F RADIOLYSIS

A second radiolytic process has also had a significant impact on another aspect of MSRE remediation, namely that portion that deals with the uranium-loaded activated charcoal.

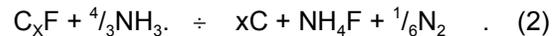
The off-gas system in the MSRE passed through an activated charcoal bed consisting of four packed beds in series with a diameter of approximately 15 cm and a cumulative bed length of 26 m. This bed was designed to intercept volatile fission and decay products prior to discharge of off-gas to facility stacks. During the three decades after shutdown, a closed but slightly leaking valve allowed a portion of the F₂ and UF₆ in the off-gas piping to enter the charcoal bed. Estimates of charcoal loading varied from 50 to 550 g-mol of F₂ (based on mass balance and fuel salt radiolysis projections) and 2.6 kg uranium (based primarily on radiation measurements near the charcoal bed). From reactivity considerations, both the uranium and fluorine would be expected to deposit in the inlet region of the charcoal bed, the uranium occupying the first 30-40 cm and the fluorine perhaps the first 1 to 1.5 m [1].

At moderate temperatures, activated charcoal exposed to F₂ produces a fluorinated carbon of variable composition, C_xF. The composition of this material depends on the temperature of formation. At room temperature, the typical composition was found to be approximately C_{2.6}F. When heated or mechanically agitated, C_xF materials have been reported to deflagrate. The deflagration is due to the exothermic disproportionation of the material as follows:



Activated charcoal exposed to UF₆ forms intercalation compounds, effectively immobilizing the UF₆ as a reduced fluoride. Experiments simulating the formation of C_xF in the charcoal bed (both with and without the presence of UF₆) were performed, which demonstrated that the fluorine-laden charcoal could be thermally or chemically induced to deflagrate but that the presence of UF_x inhibited the reaction. [5]

Because the planned method for removal of the uranium from the charcoal bed involved mechanical operations that could possibly initiate the deflagration reaction, a means of ameliorating this hazard was sought. A process was developed that involved controlled exposure of the C_xF to NH₃. This abstracted the fluorine from the C_xF to form NH₄F and N₂ as follows:



This process is exothermic and thus must be carried out in a carefully controlled manner to avoid an exothermic runaway of this reaction itself or the deflagration reaction. After lab development and scale-up [6], the process was carried out in the MSRE charcoal bed in early 1998.

When reaction (2) is carried out at low temperature, the NH₄F formed remains in the vicinity of the original C_xF. Since much of this was also in the immediate vicinity of the ~ 2.6 kgU in the bed, it experiences a high radiation field. Radiolysis of crystalline NH₄F by gamma radiation is reported by Orlov [7] to have a G-factor of about 0.7 molecule NH₄F destroyed per 100 eV deposited energy. G-factors for alpha and beta radiation were not found for NH₄F, but G-factors for gamma vs liquid NH₃ are of similar magnitude [8]. G-factors for alpha, beta, and gamma interactions with gaseous NH₃ are similar to one another and 3 to 5 times higher than gamma vs

liquid NH₃ [9].

Radiolysis of NH₄F in activated charcoal was confirmed by several means.

1. Experimental exposures of NH₃-treated C_xF to a ⁶⁰Co source yielded a pressure increase that is interpreted as a G-factor of 0.22 molecule NH₄F destroyed per 100 eV deposited gamma energy.

2. Gas sampling in the MSRE charcoal bed after NH₃ treatment showed that H₂ and N₂ generation was taking place. The rate, after taking into account probable diffusion from the source area, is interpreted to correspond to a G-factor of 0.4 molecule NH₄F per 100 eV.

3. After removal of the uranium-laden portion of the charcoal to an intermediate storage container, time-integrated gas-flow measurements during periodic venting of the storage container suggest that radiolysis is occurring at a rate consistent with a G-factor of 0.9.

The first of these methods is the most quantitatively accurate but may underestimate radiolysis by neglecting adsorption of radiolysis products. The potential significance of this factor is indicated by the fact that in venting gas from the storage container (item 3), approximately three times as much gas is observed to be vented (as determined by time-integrated flow during venting) as is nominally accounted for by the pressure drop during venting.

The second and third lines of evidence are approximate in that the derived G-factors rely on several assumptions whose accuracy cannot be gauged, [partitioning of radiation energy deposition, composition of the U-laden charcoal, and diffusion of product gases from the source location (item 2)]. Nevertheless, the three observations are, given these uncertainties, quite consistent with one another and have proven adequate to form a basis for safety and operational decisions regarding storage and handling of the material.

These G-factors for NH₄F and NH₃ are listed in Table 2. The target species and radiation type are listed in the first two columns. The phrase "NH₄F in MSRE AC" refers to the actual charcoal bed deposit, presumed but not definitely known to be similar to the synthetic NH₃-treated uranium-laden fluorinated charcoal used in the ⁶⁰Co exposure. The MSRE AC deposit was self-irradiated by the

decay energy of the ²³²U/²³³U mixture and daughters, calculated to be ~96% due to alpha radiation. Two G-factors for the material in interim storage are presented, one based on ideal gas interpretation of observed rate of pressurization and the second based on a time integration of gas flow during venting. The second is favored.

Table 2. G-factors (all expressed as molecules destroyed per 100 eV energy deposited) reported in literature and deduced from MSRE observations

Species	Rad type	G-factor	Ref.
NH ₄ F	gamma	0.7	[7]
NH ₃ (l)	gamma	0.4	[8]
NH ₃ (g)	alpha	3 – 4.2	[9]
NH ₃ (g)	beta	3	[9]
NH ₃ (g)	gamma	3 – 4.7	[9]
UF _x /NH ₄ F/C	gamma	0.22	⁶⁰ Co
NH ₄ F in MSRE- AC	MSRE U	0.4	in situ
NH ₄ F in MSRE- AC	MSRE U	0.3 pressure	interim storage
NH ₄ F in MSRE- AC	MSRE U	0.9 flow x t	interim storage

Having characterized the magnitude of radiolysis in the uranium-laden treated charcoal, it must be said that the precise nature of the radiolysis products is not fully known. Although H₂ and N₂ are definitely observed, the fate of the fluorine atom in radiolyzed NH₄F is not known. A plausible product is HF, which readily adsorbs on activated charcoal. If, however, atomic fluorine were formed in the radiolysis process, a portion of it might well find a carbon surface and regenerate C_xF. From the predicted overall NH₄F radiolysis rates, a worst- case rate of 3% C_xF regeneration per year is predicted. After considering the consequences of runaway exothermic reaction of the regenerated C_xF via either reaction (1) or (2), it was decided that the charcoal material will be periodically re-treated with NH₃, especially prior to any operation that could lead to localized heating. Supporting the notion that C_xF regeneration is not entirely a hypothetical proposition, 9 months after

the initial treatment, a sudden gas-generation event occurred during a mechanical intrusion operation. The gas release was minor (~7 L) and was contained, but suggested that sufficient C_xF regeneration had taken place to allow an exothermic runaway of reaction (2) to occur when triggered by localized heating.

Two additional NH_3 treatments have been performed on the charcoal since that time and the uranium-laden material has now been removed to a shielded interim storage container awaiting final processing.

CONCLUSIONS

Radiolytic processes have had a significant impact on plans and operations in the remediation of the Oak Ridge MSRE facility. This paper has discussed the research and analysis conducted on two such cases that apply to intermediate stages of uranium removal from the facility, namely radiolysis of UF_6 complexed with NaF and radiolysis of NH_4F in activated charcoal, the product of a treatment designed to safely desensitize potentially explosive, U-laden, carbon fluorides. From available data and limited research, these problems have been analyzed in sufficient depth to serve the need for safe and predictable performance of operations involved in the MSRE remediation effort.

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