

**WASTE STREAM GENERATED AND WASTE DISPOSAL PLANS  
FOR MOLTEN SALT REACTOR EXPERIMENT  
AT OAK RIDGE NATIONAL LABORATORY**

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**ABSTRACT**

The Molten Salt Reactor Experiment (MSRE) site is located in Tennessee, on the U.S. Department of Energy (DOE) Oak Ridge Reservation (ORR), south of the Oak Ridge National Laboratory (ORNL) main plant across Haw Ridge in Melton Valley. The MSRE was run by ORNL to demonstrate the desirable features of the molten-salt concept in a practical reactor that could be operated safely and reliably. It introduced the idea of a homogeneous reactor using fuel salt media and graphite moderation for power and breeder reactors. The MSRE reactor and associated components are located in cells beneath the floor in the high-bay area of Building 7503 (Figure 1).

The reactor was operated from June 1965 to December 1969. When the reactor was shut down, fuel salt was drained from the reactor circuit to two drain tanks. A "clean" salt was then circulated through the reactor as a decontamination measure and drained to a third drain tank. When operations ceased, the fuel and flush salts were allowed to cool and solidify in the drain tanks. At shutdown, the MSRE facility complex was placed in a surveillance and maintenance program.

As a result of the S&M program, it was discovered in 1994 that gaseous uranium ( $^{233}\text{U}/^{232}\text{U}$ ) hexafluoride ( $\text{UF}_6$ ) had moved throughout the MSRE process systems. The  $\text{UF}_6$  was generated when radiolysis of the fluorine salts caused the individual constituents to dissociate to their component atoms, including free fluorine. Some of the free fluorine combined with uranium fluorides ( $\text{UF}_4$ ) in the salt to form  $\text{UF}_6$ .  $\text{UF}_6$  is gaseous at slightly above ambient temperatures; thus, periodic heating of the fuel salts (which was intended to remedy the radiolysis problems) and simple diffusion had allowed the  $\text{UF}_6$  to move out of the salt and into the process systems of MSRE.

Currently, MSRE is undergoing the D&D process to remove the fuel and salt from fuel drain tanks and fuel flush tank. During the D&D activities the uranium will be separated and recovered from the salts and residual salts containing fission products, other uranium daughter radionuclides, and residual uranium in the salts will be disposed of as waste. Recently, the majority of the uranium-laden charcoal material residing within the auxiliary charcoal bed (ACB) has been removed and is currently awaiting process and disposal. In addition, the Reactive Gas Removal System (RGRS) has been deployed at MSRE since 1996 to remove reactive gases containing uranium material (i.e.,  $\text{UF}_6$ ) and other reactive gases (i.e.,  $\text{F}_2$ ,  $\text{MoF}_6$ ,  $\text{HF}$ , etc.) from the MSRE off gas systems and capturing them on sodium fluoride (NaF) and alumina traps, respectively. The uranium material in these NaF traps will be recovered and the residual



**Fig. 1 Aerial view of the MSRE facility**

NaF traps that contain the  $^{233}\text{U}/^{232}\text{U}$  daughters will be disposed of as waste. Due to these D&D activities at MSRE, a variety of waste streams are generated (aside from the routine operation low level radioactive waste), and each encompasses its own waste management and disposal issues. Plans are being developed at MSRE for safe final disposal of these different waste streams at different off-site disposal facilities.

## **INTRODUCTION/BACKGROUND**

The MSRE is an 8 MW reactor that was operated at Oak Ridge National Laboratory (ORNL) from 1965 through 1969 as a demonstration of the technology needed to develop a large scale Molten Salt Breeder Reactor. The reactor used a unique liquid fuel, formed by dissolving  $\text{UF}_4$  fuel in a carrier salt composed of a mixture of LiF, BeF, and ZrF. The fuel salt circulated through a reactor vessel, a fuel salt pump, and a primary heat exchanger at temperatures above  $600^\circ\text{C}$  ( $1112^\circ\text{F}$ ). In the reactor, the salt was forced through channels of graphite to provide the geometry and moderation necessary for a nuclear chain reaction. Heat was transferred from the fuel salt to the secondary coolant salt in the primary heat exchanger. The coolant salt is similar to the fuel salt, except that it contains only LiF (66%) and BeF (34%). The coolant salt passed from the primary heat exchanger to an air-cooled radiator, a coolant salt pump, and then returned to the primary heat exchanger. Each of the salt loops was provided with drain tanks, located such that the salt could be drained out of either circuit by gravity. A single drain tank was provided for the nonradioactive coolant salt. Two drain tanks were provided for the fuel salt. The fuel salt drain tanks were provided with a system to remove the intense heat generated by radioactive decay immediately after an emergency reactor shutdown and fuel salt drain. A third drain tank connected to the fuel salt loop was provided for storing a batch of flush salt. This batch of salt, similar in composition to the coolant salt, was used to condition the fuel salt loop after it had been exposed to air and to flush the fuel salt loop of residual fuel salt and contaminants before accessing the reactor circuit for maintenance or experimental activities. All three tanks are located in the drain tank cell, a stainless steel lined below grade cell that could be covered by two layer of concrete shield blocks.

The MSRE was originally fueled by adding ~218 kg of uranium, consisting of 30%  $^{235}\text{U}$  and 70%  $^{238}\text{U}$ , to the carrier salt. In 1968 this initial charge of uranium was stripped from the salt using a fluoride volatility process wherein the molten salt was sparged with fluorine gas to convert  $\text{UF}_4$  to the volatile  $\text{UF}_6$  which was subsequently recovered by chemisorption on sodium fluoride (NaF). The reactor was refueled with ~37 kg of uranium, consisting of - 83%  $^{233}\text{U}$  (with ~250 ppm of  $^{232}\text{U}$ ). When reactor operations were terminated in December 1969, the fuel, flush, and coolant salts were drained into their respective drain tanks. The fuel salt was divided between the two fuel-salt drain tanks.

The  $^{233}\text{U}$  isotope makes for a particularly difficult fuel to handle because high levels of gamma radiation are associated with it. A small percentage of  $^{232}\text{U}$  is included in  $^{233}\text{U}$  as an impurity. The decay chain of  $^{232}\text{U}$  includes  $^{208}\text{Tl}$ , which is a strong gamma radiation emitter (2.6 MeV gamma energy and 100% emission rate). This daughter product builds up rapidly, causing exposure rates of up to approximately ~37 R/hour per gram of salt. Because of the high exposure rates (as well as fission and activation products in the plant), much of the work at MSRE and in subsequent processing steps is done remotely or in hot cells.

Following reactor shutdown, several activities were performed to evaluate the performance of the materials of construction and to improve containment of the stored salts. Prior to reactor operation, it had been discovered that irradiation of the solid salt produced fluorine gas, presumably by providing the energy to release fluorine radicals (or atomic fluorine) from the salt molecules. This atomic fluorine could then combine to form  $\text{F}_2$ . Experiments indicated that at sufficiently high temperatures the effects of radiolysis were reversed. An annual annealing process was instituted in which the salt was heated to temperatures above 149° C (300° F), but below the melting point, for periods of about two weeks so that radiolytic fluorine would recombine with the lithium or beryllium in the salt. This procedure was carried out through December 1989. After this time annealing procedures were halted in part because a high radiation area in a remote section of the facility was postulated to be caused by the migration of radioactive material and this migration may have been caused by the annealing procedure.

In 1994, a gas sample was withdrawn from the off-gas system. It was found that the gas sample contained  $\text{UF}_6$  near its saturation pressure, smaller but significant quantities of  $\text{MoF}_6$ , and about 50% fluorine. A review was promptly undertaken to assess the extent of uranium migration, and a deposit of uranium (~2 to ~3 kg) was identified on the auxiliary charcoal bed (ACB). (In 2001, after the removal of the ACB uranium and a reduction in the radiation field in the area, less than 1 kg of uranium was also found in the four other main charcoal beds, which were connected to the drain tank off-gas piping.) Since the identification of these findings a Remediation project was undertaken to remove the uranium material from the off-gas system; remove the highly contaminated fuel and flush salts from fuel drain tanks and fuel flush tank; and uranium material from ACB.

Since 1996 the MSRE has been undergoing the D&D process using the Reactive Gas Removal System (RGRS) to remove reactive gases containing uranium material (i.e.,  $\text{UF}_6$ ) and other reactive gases (i.e.,  $\text{F}_2$ ,  $\text{MoF}_6$ , HF, etc.) from the MSRE off gas systems and capturing them on sodium fluoride (NaF) and alumina traps, respectively. Recently, the majority of the uranium-laden charcoal material residing within the auxiliary charcoal bed (ACB) has been safely and successfully removed using the uranium deposit removal system, remote equipment, and long-handled tools. This material is awaiting processing and disposal by a down-blending process. In addition, salt removal equipment has been designed and installed at MSRE to remove and dispose of the fuel and salt from fuel drain tanks and fuel flush tank after recovering the uranium from these tanks. During the salt removal activity the uranium will be separated as  $\text{UF}_6$  from the salt and will be recovered on NaF traps using the MSRE RGRS system.

### Reactive Gas Removal System (RGRS)

The reactive gas removal system is connected to the MSRE off-gas system via sampler-enricher hardware, which was used during reactor operation to withdraw salt samples for analysis or to add enriching salt to a well-mixed location in the pump bowl. In addition it provides an enclosed access point to one of the MSRE off-gas system lines. The RGRS (Figure 2) consists of a glove box, which houses the RGRS system valves and piping that allows the system to withdrawal reactive gases (including  $UF_6$ ) from the MSRE off-gas system. The RGRS system uses a NaF trap for uranium ( $UF_6$ ) removal from the MSRE gases, followed by an alumina trap for removal of the fluorine. Beyond the alumina trap a molecular sieve trap is used to absorb residual moisture, which possibly contains HF generated from the alumina trap. This prevents the corrosion of the other system components. Gas coming out of the last trap is sent to a holdup tank and after allowance for the decay of  $^{220}Rn$  (one of the  $^{232}U$  daughters) it is discharged via the MSRE ventilation system through  $F_2$ -resistance HEPA filters. The RGRS is also equipped with a Fourier-transform infrared spectrometer system that monitors  $UF_6$  concentration at various locations between the traps.

To date approximately 23 kg of the 37 kg of  $^{233}U$  have been removed from the salts by purging the off-gas piping and trapping the gaseous  $UF_6$  on 26 NaF traps using the RGRS system. The recovered materials have been transported to their interim storage facility at ORNL, awaiting conversion to a stable form.

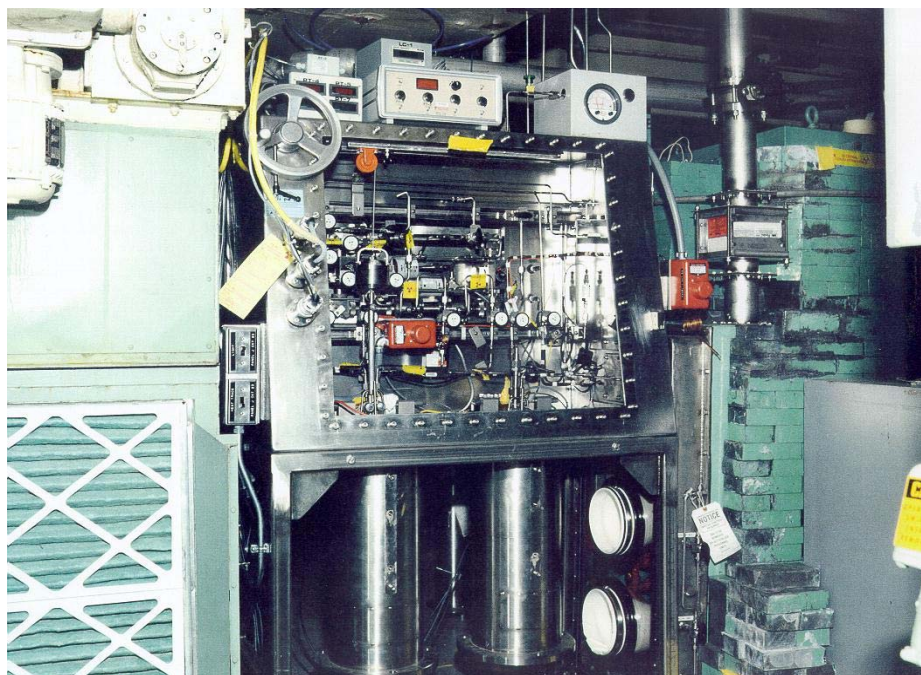


Fig. 2. The MSRE RGRS System

### Uranium Deposit Removal (UDR)

As mentioned earlier due to radiolysis process in the fuel salt it is estimated that ~2-3 Kg of the  $UF_6$  migrated to the MSRE ACB and another ~1 Kg migrated to the other four charcoal beds via MSRE off-gas system. The majority of the uranium in the ACB was identified to reside in the top ~14 in of the bed. To remove the uranium-laden charcoal material in the ACB, an elaborate remote-handled charcoal removal system was designed, fabricated, tested, and installed at MSRE ACB (Figure 3). Using this

system and remote equipment, the ACB top was removed. Then the diffuser residing top of the charcoal was removed to gain access to the uranium-laden charcoal within the ACB and the top ~14 in of the uranium-laden charcoal was vacuumed into the shielded charcoal canister. As mentioned in the case of the salt, this material is highly radioactive with exposure rates of ~500 R/h at the side of the collection canister. This material could contain as much as ~30 Ci of  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$  as well. This material is planned to be down-blended with urinal nitrate and disposed of as waste.



**Fig. 5. UDR charcoal removal equipment at ACB**

### **Uranium Recovery from Salts and residual Salts Removal**

The fuel salt in the two fuel drain tanks and flush salt in the flush tank will be melted for removal using a process known as “pool melt.” A heated probe, which melts the salt and supplies gases for sparging, will be lowered onto the middle of the salt block. A pool of liquid salt will be created at the point of contact between the probe and the salt. While the pool of salt is melting and slowly expanding, it will be sparged with a mixture of hydrogen fluoride (HF), hydrogen ( $\text{H}_2$ ) and helium (He). This hydrofluorination process restores the chemical balance in the salt and ensures that the uranium is in the form of  $\text{UF}_4$ . Without this chemistry adjustment, the reduced uranium could precipitate, preventing its recovery. The melting and chemical processing will continue as the probe is lowered into the salt. The pool of melted salt will expand and become deeper until all of the salt is molten.

After all of the salt has reached a liquid form, the molten salt will be sparged with a fluorine-helium mixture, which oxidizes the dissolved  $\text{UF}_4$  to form volatile  $\text{UF}_6$ . The gaseous  $\text{UF}_6$  will escape the salt and be carried away by the circulating helium and excess fluorine. These gases will then move into a refrigerated collection vessel (cold trap) where the  $\text{UF}_6$  will be trapped as a frozen solid. Afterward, the cold traps will be warmed to ambient temperature to render the solid  $\text{UF}_6$  back to a gaseous state. The gaseous  $\text{UF}_6$  will then be collected on NaF traps using the RGRS and packaged for transportation to an interim storage area or to the conversion facility at ORNL. Approximately 1 kg of  $\text{UF}_6$  will be collected

on each NaF trap. This operation will continue until all of the  $UF_6$  from a specific drain tank has been recovered on the NaF traps.

Once uranium is separated from the salts, the residual salts will be transferred into storage containers (~10 canister with a total of 8 metric tons of residual salts from flush and fuel salt tanks). A chemically active “getter” will be added to the salt packages to capture any fluorine gas that may be generated. Currently, these cans are planned to be loaded into a shielded container and staged at an interim storage area at ORNL pending final disposal off-site. The majority of the salt removal equipment has been designed, fabricated and installed at MSRE facility and equipment check out and integrated testing are on-going(Figure 4).



**Fig. 4. Salt removal equipment, installation of pool melt probe glove box in the drain tank cell**

## Conversion and Disposition of Uranium

The uranium hexafluoride collected in the NaF traps is not in a stable form suitable for long-term storage. Unless preventive action is taken, radiolysis will continue to separate free fluorine from the  $UF_6$ , generating gas pressure and reducing the uranium. A process will therefore be employed to convert the  $UF_6$  to the more stable  $U_3O_8$  form. Although this conversion process is common in the uranium industry, a modification tailored to a small-scale remote chemical operation will be applied in this case. The  $^{233}U$  will be processed in a hot-cell at ORNL.

The conversion process for the NaF traps consists of a recovery scheme interconnected with the oxide conversion unit. Most of the equipment is common to the two steps. The first step of the conversion process is to transfer the uranium hexafluoride from the NaF traps to a conversion reaction vessel. In the second step, the resulting solid  $UF_6$  is step-heated and subsequently exposed to pressurized steam, which allows the hydrolysis reaction to take place. The reaction steps are repeated until the temperature of the system reaches as high as  $850^\circ C$  as necessary. Moist air is introduced at the end of the hydrolysis process to complete the conversion to an oxide. The vessel is then heated to up to  $950^\circ C$  to produce a good quality  $U_3O_8$  (<0.5% moisture content). At the completion of conversion, the vessel containing the  $U_3O_8$  is allowed to cool. The lines are evacuated and filled with an inert gas, and the vessel is disconnected, capped, placed into an overpack, removed from the hot cell, and transported to a permanent storage area. The residual NaF traps containing all of the  $^{233}U/^{232}U$  and possibly other radionuclides (i.e.  $^{137}Cs/^{137m}Ba$ ) will be transported to an interim storage location at ORNL for staging and shipping to an off site disposal facility.

## MSRE Wastes Generated during D&D Activities

Important waste streams generated by the MSRE D&D project include the spent NaF traps, the uranium-laden charcoal, and the residual salt.

The main waste stream generated during the conversion operation is the spent NaF trap. Less than 1% of the original uranium content is expected to be present after processing. The residual content will be determined for each trap by weight loss in the trap, on-line instrumentation, and weight gained in the conversion vessel. Essentially all of the uranium daughters produced by radioactive decay and most transuranium species will remain in the NaF trap. For this reason, the level of radiation emanating from the trap will remain very high (~ 100s of R/h at contact) for several years. These radiation levels will decline as  $^{228}Th$ , along with its associated daughters, decays with a half-life of 1.9 years. Current plans are to transport the residual NaF traps using a shielded carrier to a temporary storage facility where radioactive decay will occur, and then to a final disposal site. The current selected off-site facility for these traps is the Nevada Test Site. Plans and documentation are being prepared to achieve this goal.

The HF produced during the transformation of the  $UF_6$  into  $U_3O_8$  will be trapped as a solid. Several HF trapping materials have been tested; the one found to be the most effective is a granulated grout made with blast furnace slag and lime. The spent HF trapping material, which is contained in plastic cartridges, will be removed and discarded as solid low-level waste (SLLW). The spent trapping material consists of a mixture of highly insoluble calcium, aluminum, and silicon fluorides and is not a hazardous waste.

The exhaust gases are filtered by a combination of solid traps in series. A NaF trap placed before the off-gas system will trap traces of  $UF_6$  that could migrate to the plant off-gas system. This trap will be treated at the end of the conversion campaign to recover any accumulated traces of uranium. Alumina or soda lime traps follow in series to trap reactive gases such as  $F_2$  or HF. Alumina or soda lime will also trap  $UF_6$ ; hence, they offer redundant protection. A hold up volume is also present to ensure a residence time for the exhaust gases of about 10 minutes to allow for radon decay. The spent alumina or soda lime traps

will be discarded as SLLW. They may be sent as a unit, including the stainless steel container, or emptied to allow for reuse of the trap.

The uranium-laden charcoal currently stored in the charcoal canister in a shielded container is planned to be chemically processed, down blended, and pH-adjusted to an acceptable level to be added to the Melton Valley storage tanks (MVST). The second alternative is to solidify the material after chemical processing and dispose of the material in the Nevada Test Site as a monolith. MSRE has conducted preliminary work on the process and proof of principle and successfully adjusted the pH to the MVST requirement in order to keep the material in a uniform liquid form once introduced to the tanks. At the same time experiments were conducted to show that the same material can successfully and safely be solidified into a monolith appropriate for waste transport.

The end-point location for disposal of the stripped salts or components of the salts will be the Waste Isolation Pilot Plant (WIPP) in New Mexico. Currently MSRE has developed a white paper and an acceptable knowledge package to characterize the waste for WIPP disposal. The waste is considered to be a defense-related transuranic (TRU) waste. Evaluation and selection of WIPP for disposal of the MSRE residual salts will be documented upon completion of the necessary documentation/requirement and negotiation among MSRE, DOE and WIPP site. Therefore, decisions about waste acceptance criteria cannot be made yet. As a result, the WIPP alternatives developed can not be fully implemented at this time. Selection of a disposal of residual salts at WIPP must wait until WIPP questions about the acceptance of MSRE salts for disposal can be evaluated. In the interim, fuel and flush salts will be removed from the MSRE facility and placed in interim storage at another ORNL facility. The salt remaining after the uranium removal process will be stored until it is shipped to a disposal location.