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Remediation Activities.

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OVERVIEW OF THE RECOVERY AND PROCESSING OF ^{233}U FROM THE OAK RIDGE MOLTEN SALT REACTOR EXPERIMENT (MSRE) REMEDIATION ACTIVITIES

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ABSTRACT

The Molten Salt Reactor Experiment (MSRE) was operated at Oak Ridge National Laboratory (ORNL) from 1965 to 1969 to test the concept of a high-temperature, homogeneous, fluid-fueled reactor. The discovery that UF_6 and F_2 migrated from the storage tanks into distant pipes and a charcoal bed resulted in significant activities to remove and recover the ^{233}U and to decommission the reactor. The recovered fissile uranium will be converted into uranium oxide (U_3O_8), which is a suitable form for long-term storage. This publication reports the research and several new developments that were needed to carry out these unique activities.

Keywords: Molten salt reactor, uranium-233, remediation, conversion

1 - INTRODUCTION

The Molten Salt Reactor Experiment (MSRE) was operated at Oak Ridge National Laboratory (ORNL) from 1965 to 1969 to test the concept of a high-temperature, homogeneous, fluid-fueled reactor. When the reactor was shut down, the fuel salt ($\text{LiF}\text{-BeF}_2\text{-ZrF}_4\text{-}^{233}\text{UF}_4$) was drained into two tanks at the reactor site, where it remains today.¹ Uranium-233 containing about 220 ppm of the impurity isotope ^{232}U was used in the final fuel charge. The presence of high radiation readings in some of the reactor piping systems and the results from the analysis of gas samples led to the determination in 1994 that some of the ^{233}U had migrated throughout the piping system as uranium hexafluoride (UF_6). Additionally, it was discovered that about 3.9 kg of the UF_6 had leaked past a faulty valve and deposited onto a charcoal bed. Because fluorine (F_2) was also present in the gas, it was estimated that about 1 meter or two of fluorinated charcoal (C_xF) extended beyond the uranium front.²⁻⁴ These discoveries resulted in the initiation of an extensive remediation program to remove and recover the ^{233}U , to convert the recovered uranium into uranium oxide (U_3O_8) for long term storage, and to decommission the reactor. Targeted research and several new developments were needed to carry out these unique activities. These targeted investigations grew from our Basic

Energy Science research program, which has sustained our capabilities in molten salt chemistry, spectroscopy, and actinide chemistry.

2 - URANIUM REMOVAL AND RECOVERY

The main tasks were to remove the uranium deposit from the charcoal bed, to remove UF_6 from piping and tank head space, and to remove uranium and salt from storage tanks.

2.1 - REMOVAL OF THE URANIUM DEPOSIT IN THE CHARCOAL BED

During the prolonged storage of the fuel salt, radiolytically generated fluorine F_2 and $^{233}UF_6$ migrated from the fuel storage tanks through gas piping to a charcoal bed. Fluorinating gases such as F_2 and UF_6 are known to react with activated charcoal to produce carbon fluorides of varying composition. Of particular concern was the potential for the explosive decomposition of carbon-fluorine compounds when heated or mechanically shocked. In order to understand the problem and remove the hazards, a thorough investigation of the activated charcoal-fluorine-uranium chemistry was undertaken via laboratory tests designed to reproduce as closely as possible the conditions present in the beds. Laboratory analyses of the reaction products were extensive and included ESCA, NMR, FTIR and Raman spectroscopy, TGA-DTA, as well as a host of other techniques.²⁻⁴

It was determined that the primary product from the reaction of F_2 with activated charcoal is fluorinated charcoal (C_xF). The carbon:fluorine ratio (x) is a reproducible function of the fluorination temperature and ranges from ~ 4 at $-80^\circ C$ to ~ 0.95 at $350^\circ C$. Charcoal fluorinated at room temperature has a composition of about $C_{2.6}F$. Spectroscopic measurements (ESCA and NMR) indicate that the nonintegral stoichiometry is a reflection of the distribution of discrete carbon-bonding possibilities (C-C, C-F, C- F_2 , and C- F_3) and that the lamellar structure of graphitic carbon plays a critical role in determining the extent of charcoal fluorination at any temperature.

Decomposition of near-explosive characteristics to carbon tetrafluoride (CF_4), hexafluorethane (C_2F_6), tetrafluorethylene (C_2F_4), carbonyl fluoride (COF_2), carbon monoxide (CO), and carbon dioxide (CO_2) can be triggered by any process or reaction that would rapidly elevate the temperature. The increased temperature would initiate a positive feedback. Once the thermal excursion is initiated, the generation of heat and gases will propagate unless there is a mechanism to dissipate the heat

The uranium deposited in the activated charcoal from a UF_6/F_2 gas stream is in the form of nonvolatile uranium fluorides and uranium oxyfluorides, mainly UF_4 , that are intercalated in the micrographitic structure of charcoal.

The MSRE ACB contains a volume of approximately 506 L of activated charcoal (6–16 mesh). The top 30

cm of the ACB were known, by gamma scan and thermal analysis, to contain about 2.6 kg of ^{233}U ; and from mass balance considerations, a meter or two of fluorinated charcoal was estimated to extend beyond the uranium front.

To remove the potential for sudden decomposition of C_xF , it was necessary to develop a process to chemically convert the reactive C_xF into a more stable material.⁵ Various gases and some high-vapor-pressure liquids were considered for their potential for halogen exchange. As a result of a comprehensive series of scoping tests, it was determined that ammonia [$\text{NH}_3(\text{g})$] was the best reagent. After full-scale testing of the process in the laboratory, it was successfully applied to the actual charcoal bed. The process consisted of the injection of NH_3 and helium mixtures of increasing NH_3 concentration (2% to 50%) followed by the injection of pure NH_3 . This process resulted in the conversion of the C_xF to carbon and ammonium fluoride (NH_4F). Following the NH_3 treatment, the top 50 cm of the charcoal bed were mechanically removed. This material is awaiting further processing to recover and convert the uranium-laden charcoal into U_3O_8 for long term storage.

2.2 - RECOVERY OF URANIUM FROM PIPING SYSTEM

A trapping system was used to remove and trap the UF_6 and F_2 from the piping system and tank head space. Sodium fluoride (NaF) traps were used to chemisorb UF_6 and these traps were followed by an activated alumina trap to capture the F_2 . A third trap containing molecular sieve was used to trap a small amount of hydrogen fluoride (HF) that formed as residual water was released from the alumina trap when reacting with F_2 . A vacuumed tank and flow controllers were used as the driving force to suction the gases from the reactor piping system in a safe and controlled manner. In addition to measurement of the weight gained by the traps, in-line infrared absorption spectroscopy was used to quantify the amount of UF_6 and other species being trapped. Chlorine trifluoride (ClF_3) was also injected to remove uranium deposits (uranium oxyfluorides and fluorides).

2.3 - URANIUM REMOVAL FROM FUEL SALT

The salt will be melted using a heated rod that will be slowly lowered from the surface of the salt toward the bottom of the tank. The melt will start at the center, and will then slowly propagate radially out and downward. The salt will be sparged while melting with a HF/H_2 mixture in order to transform all of the radiolytically reduced species into UF_4 at a controlled redox potential to avoid corrosion of the tanks.⁶ The UF_4 will then be removed as UF_6 using a fluorination process.

3 - CONVERSION TO URANIUM OXIDE

The two main streams of materials to be processed are (1) the NaF -traps that contain the UF_6 recovered from the piping system, tank head space, and fuel salt; and (2) the uranium-laden charcoal. Of the 37 kg of uranium

at MSRE, about 23 kg (as UF_6) have already been removed from the piping system and sorbed onto NaF pellets in 25 NaF traps. The planned recovery of ~11 kg of uranium from the fuelsalt will generate another 15 to 19 NaF traps. The processing of the uranium-laden charcoal will generate 3 or 4 additional NaF traps.

3.1 - RECOVERY OF THE URANIUM LADEN IN CHARCOAL

A process was developed and tested at full scale to recover the uranium from the activated charcoal matrix.⁷ The first step of processing includes the heating of the charcoal under helium flow to remove NH_4F . The uranium-laden charcoal is then burned in oxygen. The combustion gases, mostly CO_2 , are filtered using NaF and alumina traps before being exhausted through HEPA filters. The NaF retains any UF_6 , while the alumina captures reactive impurities such as HF and F_2 . When burning is complete, as determined by in-line infrared analysis, the remaining ashes are then fluorinated in a closed recirculation loop that includes the NaF traps. The UF_6 that is generated by fluorination of the ashes is chemisorbed onto the NaF.

3.2 - CONVERSION OF THE UF_6 CHEMISORBED ON NaF TO URANIUM OXIDE

The unique aspect of this conversion process is the requirement to handle a uranium assay consisting of ^{233}U contaminated with ^{232}U . This mix of isotopes is much more radioactive than the typical natural or enriched assays of uranium, and produces very high levels of airborne activity. Many industrial-scale continuous and semi-continuous processes exist to convert uranium-containing materials into an oxide. However, these processes are not adequate to process relatively small batches under gas-tight conditions. They are not easily adaptable to hot-cell operations, they produce a significant volume of secondary liquid wastes, and they include open transfers between vessels. As a consequence, a conversion process was developed to remove the UF_6 from the NaF traps and then to convert the UF_6 to U_3O_8 .^{8,9} The major design considerations for this process were: closed system to avoid the spread of contamination, no moving parts for stirring, mixing, or transferring between vessels, simplicity and adaptability to small-scale hot-cell operation, minimization of uranium losses, and minimization of secondary wastes. As shown in Fig. 1, the conversion process for the NaF traps consists of a recovery unit interconnected with the oxide conversion unit. Most of the equipment is common to the two units. All components have a critically safe geometry.

UF_6 is desorbed from the heated NaF trap (at 300–450°C) in a F_2 atmosphere and transported in a closed loop to a cooled conversion vessel in which the UF_6 condenses. A small volume of F_2 is continuously recirculated

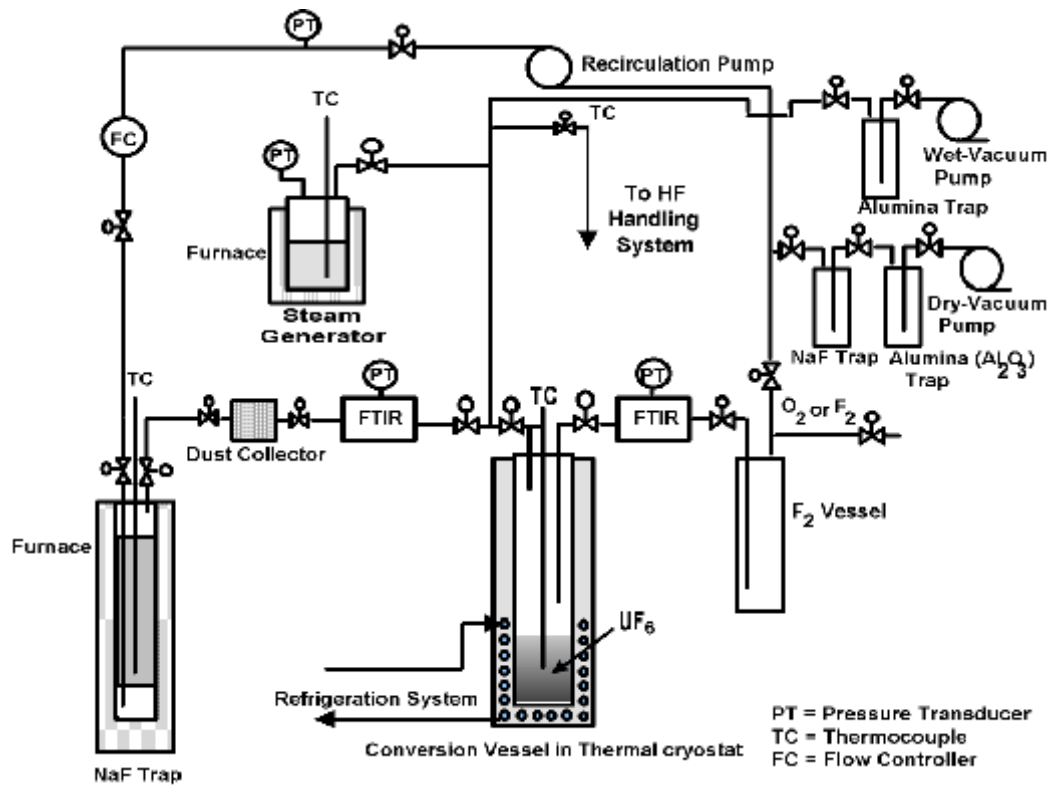


Figure 1: Diagram of the major components of the uranium recovery and conversion process.

within the system by using a double-sealed metal bellows pump. The pressure inside the system is maintained below atmospheric pressure to minimize the possibility of uranium release. Any trace of UF_6 , which escapes condensation in the conversion vessel, will be recirculated and trapped and the fluorine carrier will be recycled and reused.

The frozen UF_6 is converted to U_3O_8 inside the same conversion vessel. Initially, a stoichiometric excess of water vapor is condensed as ice on top of the frozen UF_6 . The conversion vessel is then allowed to warm to room temperature, thus resulting in the formation of solid $UO_2F_2 \cdot xH_2O$ and HF. A freeze-thawing cycle is repeated two or three times to ensure complete hydrolysis of the UF_6 and to promote cracking of the solid cake.

The cake is step-wise contacted with fresh steam at increasing temperatures until nearly all the fluorine is removed from the solid and transported as HF to a condenser. When the temperature reaches 750–800°C, the introduction of pressurized steam is discontinued. Wet air at atmospheric pressure is then flowed to remove fluoride traces and convert the uranium oxides formed at lower temperatures into U_3O_8 . After a final bake-out of the oxide in dry air at about 900°C, the conversion is completed.

Full scale prototype testing showed that the processes can efficiently recover and convert the uranium laden in the NaF traps and charcoal. No significant problems were encountered during the testing and the minor

corrections needed were transferred to the conversion system design. The results showed that in all cases greater than 99 wt % of the uranium was recovered from the NaF pellets. The design of the system is such that the possible paths for uranium losses were eliminated or minimized. Since the system is a closed-loop, any traces of uranium carried over between batches will be eventually recovered in a following batch.

The actual system was constructed as a mock-up unit and fully tested before installation inside the hot-cell. Auxiliary systems include: shielded carrier, pressure relief system, calibration system, liquid nitrogen delivery system, gas delivery system, weighing station for mass balance, welding station, decontamination system, and an off-gas system. Most systems inside the hot-cell have redundancy and were designed to be easily serviced and repaired. Three full operational tests will be conducted using depleted or natural UF_6 before starting the actual conversion operations for the MSRE $^{233}UF_6$. These tests will include a thorough examination of the entire system including all auxiliary operations, and they will serve to train and qualify personnel.

4 - CONCLUSIONS

The presence of high radiation readings and the results from the analysis of gas samples showing the presence of significant amounts of F_2 and UF_6 led to an urgent program to remove and recover the fissile uranium from the MSRE and to convert it into U_3O_8 for long-term storage. Because of the uniqueness of the problems, the planning and execution of almost all of the removal and recovery operations required research and modeling that enabled the understanding of the situation. These activities were followed by lab scale simulations that led to practical solutions, sometimes requiring the development of new processes. This graded approach allowed for a very successful program that met all of the remediation needs at the reactor site.

Of the 37 kg of uranium at the MSRE, about 23 kg (as UF_6) have already been removed from the piping system and sorbed onto NaF pellets in 25 NaF traps. The fluorinated charcoal bed was treated with NH_3 to convert the C_xF to carbon and NH_4F , removing the deflagration concern. Following the NH_3 treatment, the top 50 cm of the charcoal bed were mechanically removed. The planning and development for the removal of the remaining uranium from the fuel salt has been completed. The conversion process has been developed and deployed. The results of full-scale testing of the conversion process showed that in all cases greater than 99 wt % of the uranium was recovered from the NaF pellets. A full-scale process for the recovery of uranium from the activated charcoal has been developed and successfully tested with greater than 99% of the uranium recovered.

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