

Present Status of the Recovery and Processing of ^{233}U from the Oak Ridge Molten Salt Reactor Experiment
Remediation Activities

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PRESENT STATUS 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 was operated in the sixties at Oak Ridge National Laboratory to test the concept of a high-temperature, homogeneous, fluid-fueled reactor. The discovery that UF_6 and F_2 had migrated from the storage tanks into distant pipes and a charcoal bed resulted in significant multiyear 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 present status of these remediation activities.

INTRODUCTION

The Molten Salt Reactor Experiment (MSRE) was operated at Oak Ridge National Laboratory 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 ($\text{LiF}-\text{BeF}_2-\text{ZrF}_4-^{233}\text{UF}_4$) 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 m 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.

REMOVAL OF THE URANIUM DEPOSIT IN THE 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. 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°EC to ~ 0.95 at 350°EC . Charcoal fluorinated at room temperature has a composition of about $\text{C}_{2.6}\text{F}$.

Decomposition of near-explosive characteristics can be triggered by any process or reaction that would rapidly elevate the temperature. The increased temperature would initiate a positive feedback. 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. It was determined that ammonia [$\text{NH}_3(\text{g})$] was the best reagent for this conversion.⁽⁵⁾ After full-scale testing in the laboratory, the process was successfully applied to the actual charcoal bed. This process resulted in the conversion of the C_xF to carbon and ammonium fluoride (NH_4F). Following the NH_3 treatment, the top 50cm of the charcoal bed was mechanically removed and transferred into a shielded container that is periodically vented to release the gaseous species formed by radiolysis.⁽⁵⁻⁸⁾

This material is awaiting further processing to recover the uranium from the charcoal and convert it into U_3O_8 .⁽⁹⁾

RECOVERY OF URANIUM FROM PIPING SYSTEM

Sodium fluoride (NaF) traps were used to chemisorb the UF_6 removed from the piping system and tank headspace. These traps were followed by an activated alumina trap to capture the F_2 . Molecular sieve was used to trap a small amount of hydrogen fluoride (HF) that formed as residual water was released from the alumina trap upon reaction with F_2 . The entire system, including the traps and the process and analytical instrumentation, were contained in a glove box with local shielding. A vacuumed tank was used to suction the gases from the reactor piping systems. 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).

REMOVAL OF URANIUM FROM THE FUEL SALT

The fuel salt, containing about 11 kg of uranium, 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.⁽¹⁰⁾ While melting, the salt will be sparged 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 prevent corrosion of the tanks. The UF_4 will then be removed as UF_6 using a fluorination process. The UF_6 will be trap by cooling and then chemisorbed onto NaF traps for temporary storage.

CONVERSION TO URANIUM OXIDE

A conversion process was developed to remove the UF_6 from the NaF traps and then convert it to U_3O_8 .^(11,12) 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.

The major design considerations for this process were as follows: a closed system to prevent 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. 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.

The 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 vessel in which the UF_6 condenses. A small volume of F_2 is continuously recirculated within the system by using a double-sealed metal bellows pump. The system is maintained

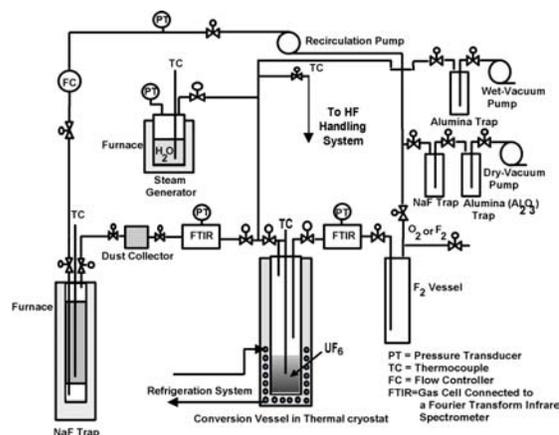


Fig.1. diagram of the major components of the uranium recovery and conversion process.

below atmospheric pressure to minimize the possibility of uranium release. Any trace of UF_6 that escapes condensation in the conversion vessel is 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 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.

The cake is then stepwise 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, wet air at atmospheric pressure is then flowed over the product to remove traces of fluoride and convert the uranium oxides formed at lower temperatures into U₃O₈.

After a final bake-out of the oxide in dry air at about 860°C, the conversion is completed. After cooling, the vessel containing the oxide is disconnected from the system, shut with a welded cap, and overpacked for long-term storage.⁽¹³⁾

Full-scale prototype testing showed that the processes can efficiently recover and convert the uranium in the NaF traps and charcoal. In all cases greater than 99 wt % of the uranium was recovered from the NaF pellets.

Two full-scale operational tests were successfully conducted using natural UF₆ before starting the actual conversion operations for the MSRE ²³³UF₆. These tests, which included a thorough examination of the entire system including all auxiliary operations, also served to train and qualify personnel.

Between the first and second operational tests, the process was adjusted to reduce the processing time and to enhance the quality of the product. The analysis of the oxide produced during the second test, which involved the recovery and conversion of about 1 kg of uranium, showed a recovery better than 99.9%, while the removal of fluorine was 99.8%.

At present, the major efforts relate to the completion of approved documentation and procedures in preparation for the upcoming operational readiness review.

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