

OAK RIDGE
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FOR THE DEPARTMENT OF ENERGY

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**Prototype Tests for the Recovery
and Conversion of UF_6
Chemisorbed in NaF Traps for the
Molten Salt Reactor Remediation
Project**

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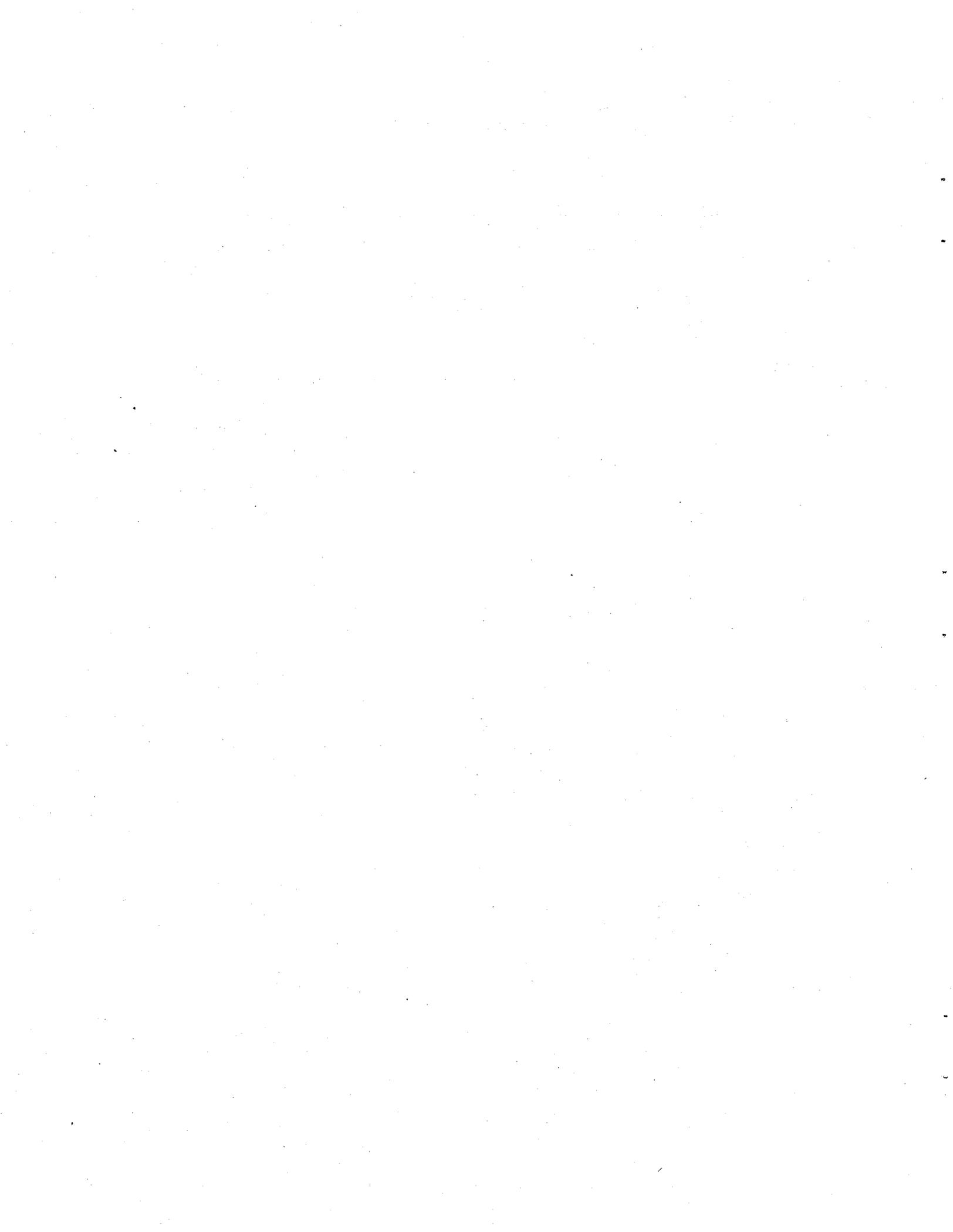
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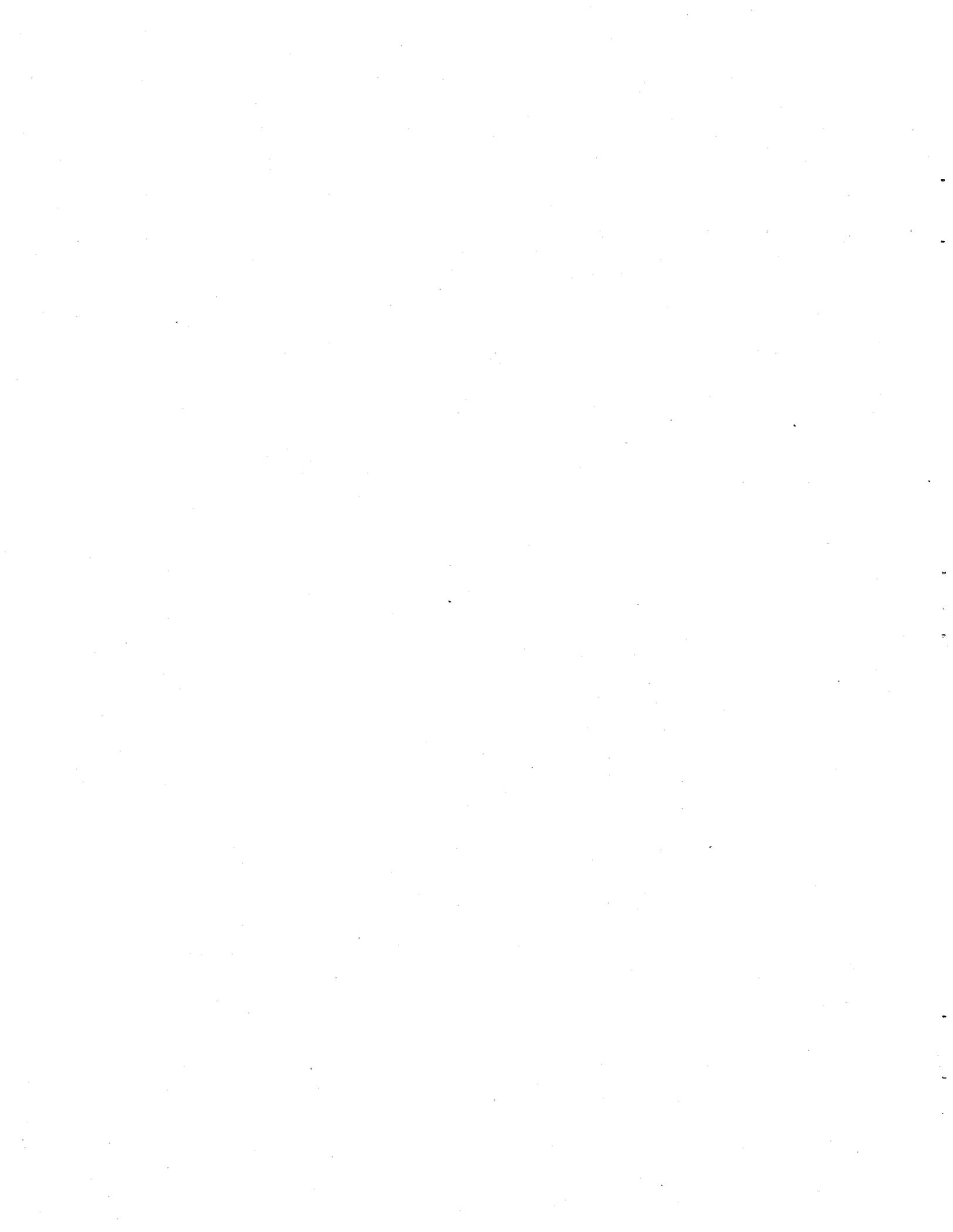
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ACRONYMS

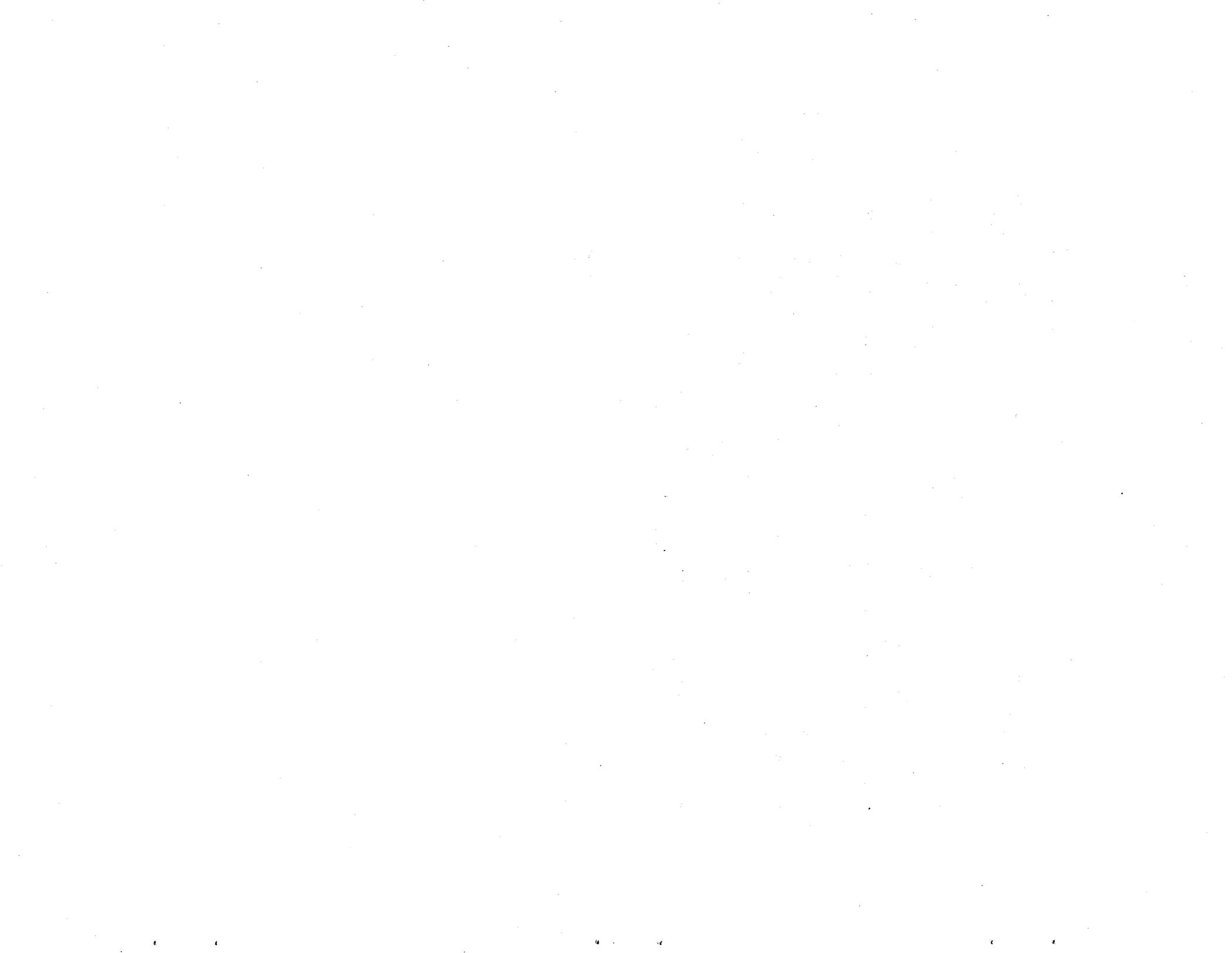
DOE	U.S. Department of Energy
DU	depleted uranium
FTIR	Fourier Transform Infrared
HEPA	high-efficiency particulate air
MSRE	Molten Salt Reactor Experiment
ORNL	Oak Ridge National Laboratory
RGR	reactive gas removal
UPS	uninterrupted power supply

ABSTRACT

The remediation of the Molten Salt Reactor Experiment (MSRE) site includes the removal of about 37 kg of uranium. Of that inventory, about 23 kg have already been removed from the piping system and chemisorbed in 25 NaF traps. This material is being stored in Building 3019. The planned recovery of ~11 kg of uranium from the fuel salt will generate another 15 to 19 NaF traps. The remaining 2 to 3 kg of uranium are present in activated charcoal beds, which are also scheduled to be removed from the reactor site. Since all of these materials (NaF traps and the uranium-laden charcoal) are not suitable for long-term storage, they will be converted to a chemical form [uranium oxide (U_3O_8)], which is suitable for long-term storage.

This document describes the process that will be used to recover and convert the uranium in the NaF traps into a stable oxide for long-term storage. Included are a description of the process, equipment, test results, and lessons learned. The process was developed for remote operation in a hot cell. Lessons learned from the prototype testing were incorporated into the process design.

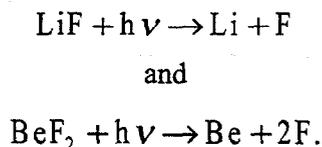
This work was performed for the MSRE Remediation Project, which is managed by Bechtel Jacobs Company, LLC, for the U.S. Department of Energy (DOE), under contract DE-AC05-98OR22700. This work was performed by UT-Battelle at Oak Ridge National Laboratory (ORNL) under contract DE-AC05-00OR22725.



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. An overview of the MSRE system is shown in Fig. 1.1. The reactor was fueled with a molten salt mixture of LiF-BeF₂-ZrF₄-UF₄ (with a composition of 64.5-30.4-4.9-0.14 mol % for a ²³³U-fueled reactor and 64.1-30.0-5.0-0.81 mol % for a ²³⁵U-fueled reactor), which melts at about 450°C and which served as both the fuel and the primary coolant (Compere et al. 1975). This fluid was circulated by a large impeller pump, which was located between the reactor core and the primary heat exchanger. A secondary coolant of LiF-BeF₂ (66-34 mol %), circulated by a similar impeller pump, transferred heat from the primary heat exchanger to an air-cooled radiator. About 4,350 kg (~2 m³) of fuel salt constituted the fuel charge circulating in the fuel-salt circuit. Originally, the MSRE was fueled with ²³⁵UF₄; however, after successful operation using this isotope, the ²³⁵U was removed by fluorinating the tetrafluoride to the volatile hexafluoride, UF₆. Afterward, the fuel was reconstituted with ²³³UF₄ (containing 220 ppm ²³²U, an impurity isotope) to demonstrate that the system could function equally well on the product of a ²³²Th thermal breeding cycle. After the successful completion of this campaign, reactor operation was terminated Dec. 12, 1969, when the fuel salt was drained from the reactor circuit and solidified in two drain tanks at a lower level of the facility. This fuel salt has remained in these tanks for the past 30 years.

During the MSRE operation, no radiolysis of the fuel salt was ever observed. However, radiolysis of the fuel salt was recognized as a problem if the salt were solidified and then held below 100°C—with the net effect that F₂ would be liberated from the frozen salt mixture and cause corrosion or overpressurization of the drain-tank containment system. The relevant radiolysis reactions are (Williams, Del Cul, and Toth 1996; Toth and Felker, January 1990):



To prevent the accumulation of F₂, the frozen salt (which was normally at about 40°C because of the self-heating by fission product decay) was heated to 200°C annually. This frequency was selected because of the experimentally observed induction period before any release of F₂ from the salt matrix (Savage, Compere, and Baker 1964). Hence, it was believed that any generated F₂ would be trapped in

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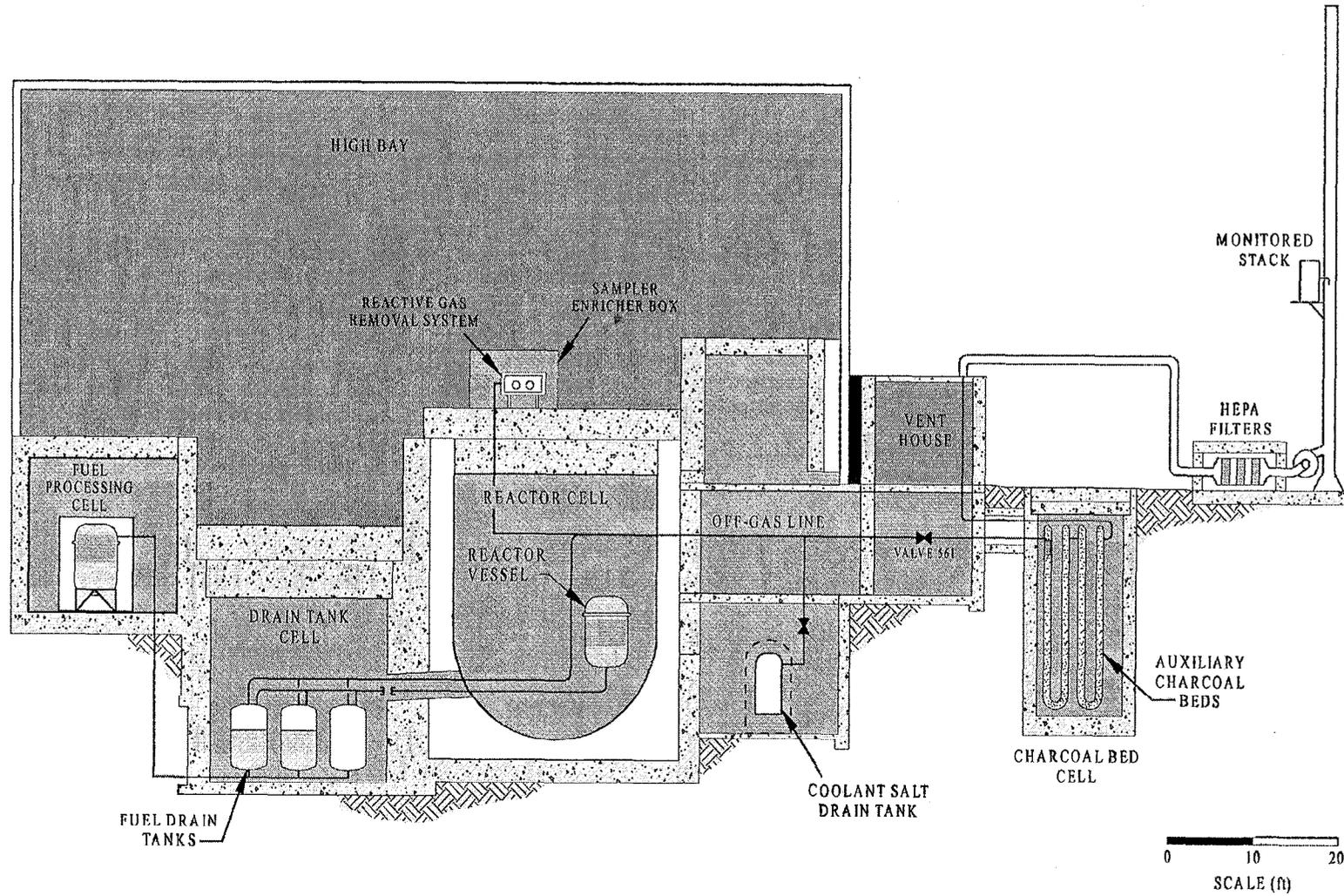
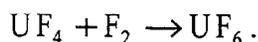


Fig. 1.1. Overview of the MSRE system.

the matrix and that heating would lead to the recombination of the F₂ with the reduced metal sites in the salt. The fluorine pressure in the drain tanks before and after annealing was not monitored; therefore, the effectiveness of this annual procedure was never established.

In the late 1980s, an increase in radioactivity in one of the gas-line protrusions into the North Electrical Services Area, a room adjacent to the drain-tank cell, was suspected as coming from UF₆. Because the annual annealing operation would drive this condensable gas from the drain tanks to cooler surfaces, such as the gas-line protrusion into the North Electrical Services Area, the annual annealing operation was postponed until a better understanding of the fuel salt under long-term storage conditions was obtained.

In early 1994, two 1,000-mL gas samples were withdrawn (from a vent house gas line that was connected to the drain tanks) and analyzed. Surprisingly, 350 torr of F₂, 70 torr of UF₆, and smaller amounts of other gases were found in both of the samples (Table 1.1)—confirming that the annual annealing operations had not been successful in recombining the fluorine with the fuel salt and, more importantly, that the temperature gradient created during the annealing operation had definitely (as was later shown by Williams, Del Cul, and Toth 1996) contributed to the formation and displacement of UF₆ from the fuel salt. The UF₆ was formed by the following reaction (Williams 1999):



Upon further investigation, it was found that the gas line from the drain tank also ran to large charcoal beds (U-tubes that were 6-in. in diameter and 24-ft in length), which could not be isolated because a shutoff valve had failed in the open position. Gamma scans and thermal analyses indicated that about 2.6 kg of the uranium from the drain tanks had been deposited at the charcoal-bed inlet. Because F₂ was also present with the UF₆, it was believed that the charcoal bed containing both carbon-fluorine reaction products (C_xF) and uranium presented both chemical and radiological hazards. The C_xF was an explosive compound that could result in major dispersion of the ²³³U contained in the charcoal bed. In November 1995, the shutoff valve was closed to prevent any further movement of uranium and fluorine onto the charcoal bed. Steps were taken to minimize (and ultimately eliminate) the possibility of explosive decomposition of the C_xF in the charcoal beds.

Table 1.1. Gas analysis of two samples taken from the off-gas MSRE system

Species	Gas composition (torr)	
	First sample	Second sample
UF ₆	70 (0.9 g/L)	68 (0.9 g/L)
HF	1200 ppm	1000 ppm
MoF ₆	10	10
CF ₄	5	5
F ₂	<i>a</i>	350
He, Ar, N ₂ , O ₂ ^b	305	305

^aQuantity not determined analytically but assumed to be the same as second sample

^bQuantity determined by difference from total sample pressure. Qualitative identification by mass spectroscopy.

The remediation of the MSRE site will include removing the total uranium inventory of about 37 kg. Of that inventory, about 23 kg have been removed from the piping system and sorbed onto NaF pellets (as a 2NaF•UF₆ complex). The containers for the NaF pellets are referred to as NaF traps, and 25 such traps have been produced. The traps are being stored in Bldg. 3019 at ORNL. The planned recovery of ~11 kg of uranium from the fuel salt will generate another 15 to 19 NaF traps. The remaining 2 to 3 kg of uranium are located in the activated charcoal beds, which are also scheduled to be removed from the reactor site. Since all these materials (NaF traps and the uranium-laden charcoal) are not suitable for long-term storage, they will be converted to a chemical form (U₃O₈) which is suitable for long-term storage.

This document describes the prototype testing of the process that will be used to recover and convert the uranium in the NaF traps into a stable oxide for long-term storage. Included are the process description, a description of major components, and results from prototype testing. The process was conceived and developed to maximize the recovery of uranium while minimizing any radiation exposure to operators, keeping waste disposal to a minimum, satisfying criticality concerns, and maintaining safeguards security. During the engineering design, efforts were made to satisfactorily fulfill these goals.

2. PROCESS DESCRIPTION

The main objective of the conversion process is to transform all the uranium-containing materials reclaimed from the MSRE site to a stable oxide. Many industrial-scale continuous and semicontinuous processes exist to convert uranium-containing materials into an oxide. However, these processes are specific only to a particular material, and they are not adequate to process relatively small batches of diverse materials. Also, they are not easily adaptable to hot-cell operations, and they produce a significant volume of secondary liquid wastes.

A specially-developed conversion process will be used to remove the UF_6 from the NaF traps and then to convert the UF_6 to U_3O_8 . Because there is a large radiation field caused by the ^{232}U (an impurity isotope in the ^{233}U), the material will be remotely processed in a hot cell. The major design considerations for this process were:

- minimization of uranium losses
- minimization of secondary wastes and contamination
- simplicity and adaptability to small-scale, hot-cell operation
- no moving parts for stirring, mixing, or transferring between vessels
- ability to meet minimal product-purity requirements

The conversion process for the NaF traps consists of a recovery unit interconnected with the oxide conversion unit (Fig. 2.1). Most of the equipment is common to the two steps, and descriptions of these two units are provided in Sects. 2.1 and 2.2.

2.1 RECOVERY OF UF_6 FROM THE NaF TRAP

The first part of the process relates to the recovery of the uranium contained in the NaF traps and is shown in Fig. 2.2. As mentioned, the UF_6 from the MSRE system is chemisorbed onto NaF traps, where the UF_6 forms a complex ($2NaF \cdot UF_6$), which decomposes at higher temperatures ($>300^\circ C$).

UF_6 is desorbed from the heated NaF trap (at $300\text{--}450^\circ C$) and is transported in a closed loop to a liquid-nitrogen-cooled conversion vessel, in which the UF_6 condenses. A component, called a thermal cryostat, allows the conversion vessel to be cooled to liquid-nitrogen temperatures and to be heated to about $900^\circ C$. A small volume of fluorine gas is continuously recirculated 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.

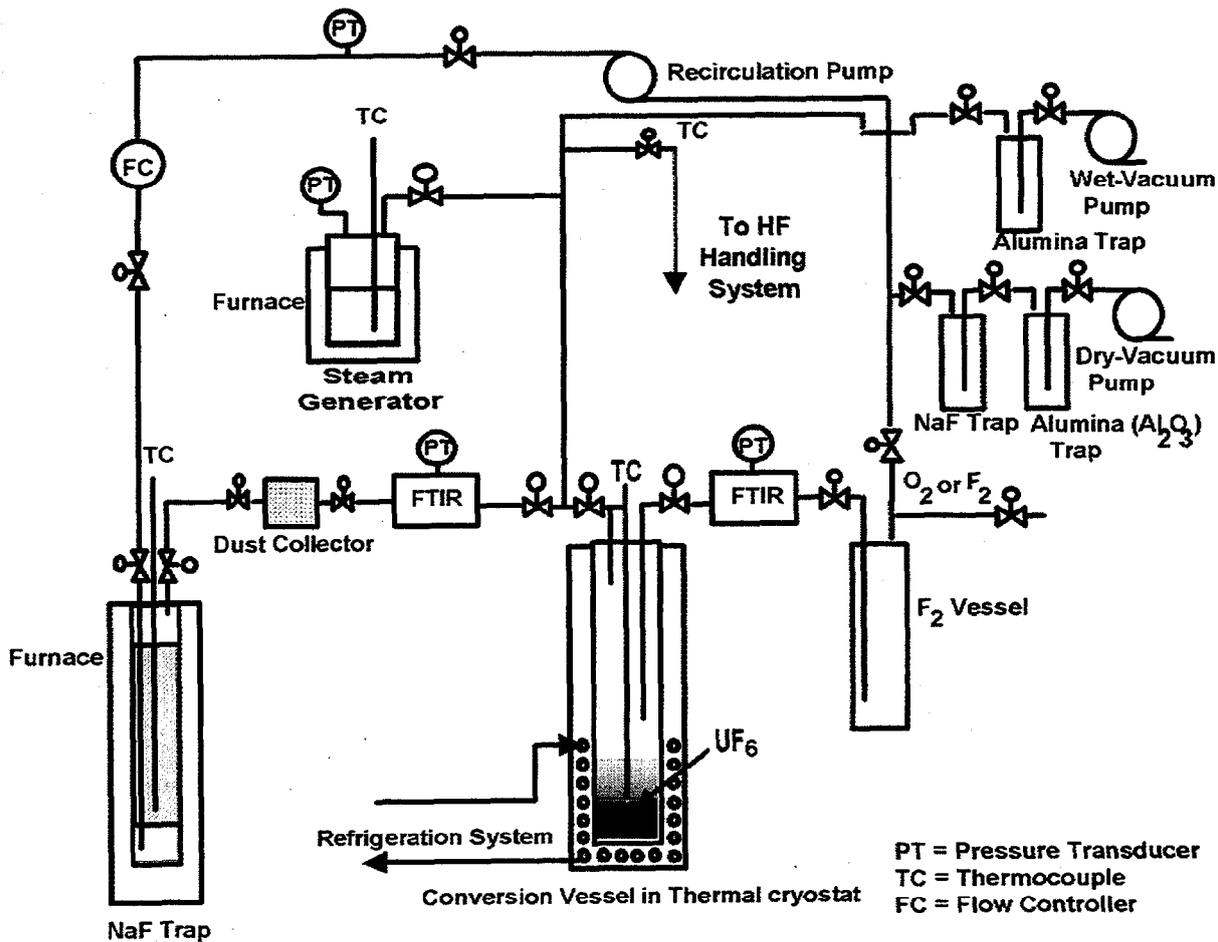


Fig. 2.1. Diagram of the major components of the uranium recovery and conversion process.

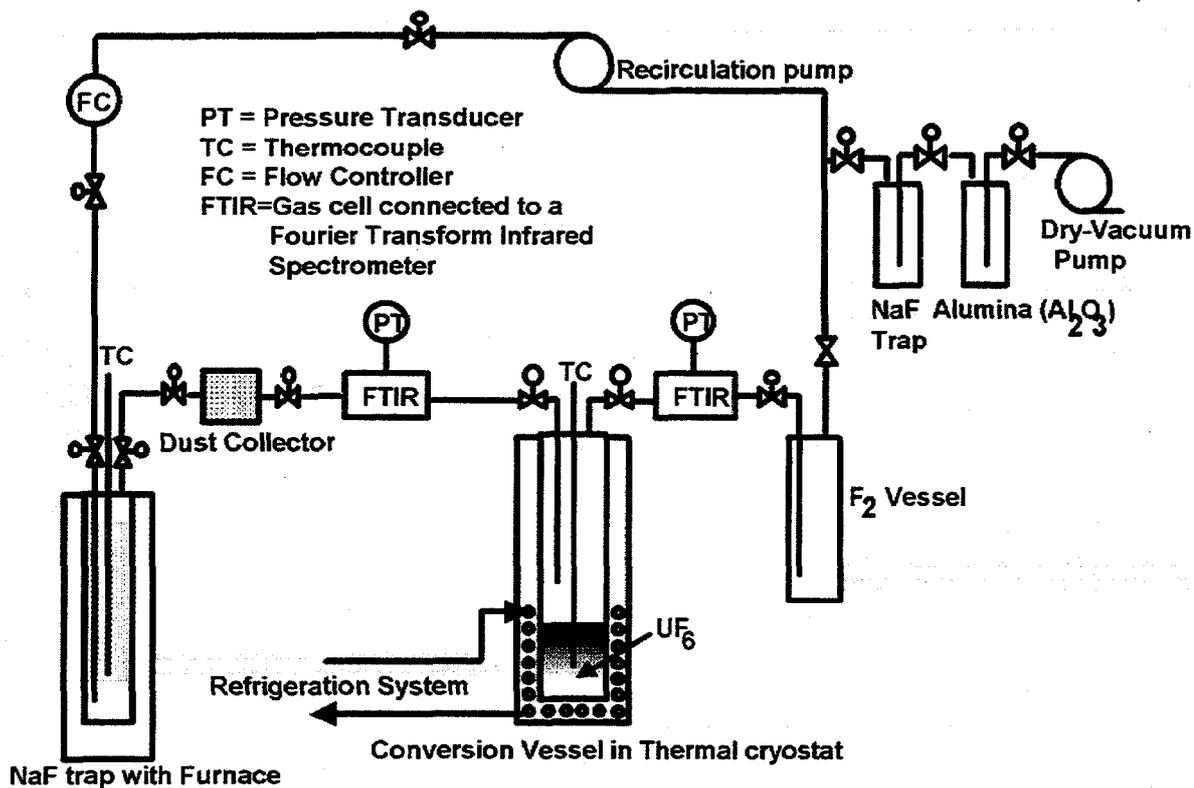


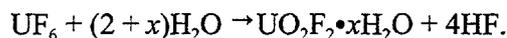
Fig. 2.2. Diagram of the closed-loop recovery of UF₆ from a NaF trap.

The circulating F_2 serves as (1) a carrier gas and (2) a fluorination agent, which can recover any oxyfluorides or lower fluorides in the trap. Two Fourier Transform Infrared (FTIR) spectrometers, which are located before and after the conversion vessel, are used to monitor the completeness of the recovery and condensation. Any trace UF_6 , which escapes condensation in the conversion vessel, will be recirculated and trapped afterward. Most of the fluorine (except for the volume of the piping loop) will be recycled and reused.

To ensure that no uranium or F_2 leaves the processing system, a NaF scrubber and an alumina trap are installed before the vacuum pump to prevent a release. The NaF scrubber will be treated at the end of the conversion campaign to recover any accumulated traces of uranium. A holdup volume will allow for the decay of Radon (Rn) and other radioactive daughters.

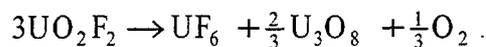
2.2 CONVERSION OF UF_6 TO U_3O_8

The frozen UF_6 , which is recovered from the NaF trap, is next converted to U_3O_8 . Initially, a slight excess of water vapor (as determined by the amount of water needed to stoichiometrically react with the UF_6) is condensed as ice on top of the frozen UF_6 (Fig. 2.3). 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 as shown in the reaction:



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 cracking facilitates further exposure to water vapor during the steam treatment.

The resulting solid cake is step-wise heated (in $\sim 50^\circ C$ steps) and contacted with pressurized steam (~ 200 psi), which penetrates into the cake and gradually reacts with the oxyfluoride-oxide mixture. Treatment of the oxyfluoride with pressurized steam slowly removes the fluorine (as HF), thus promoting the conversion to uranium oxide. When heated, the UO_2F_2 slowly decomposes according to the following reaction:



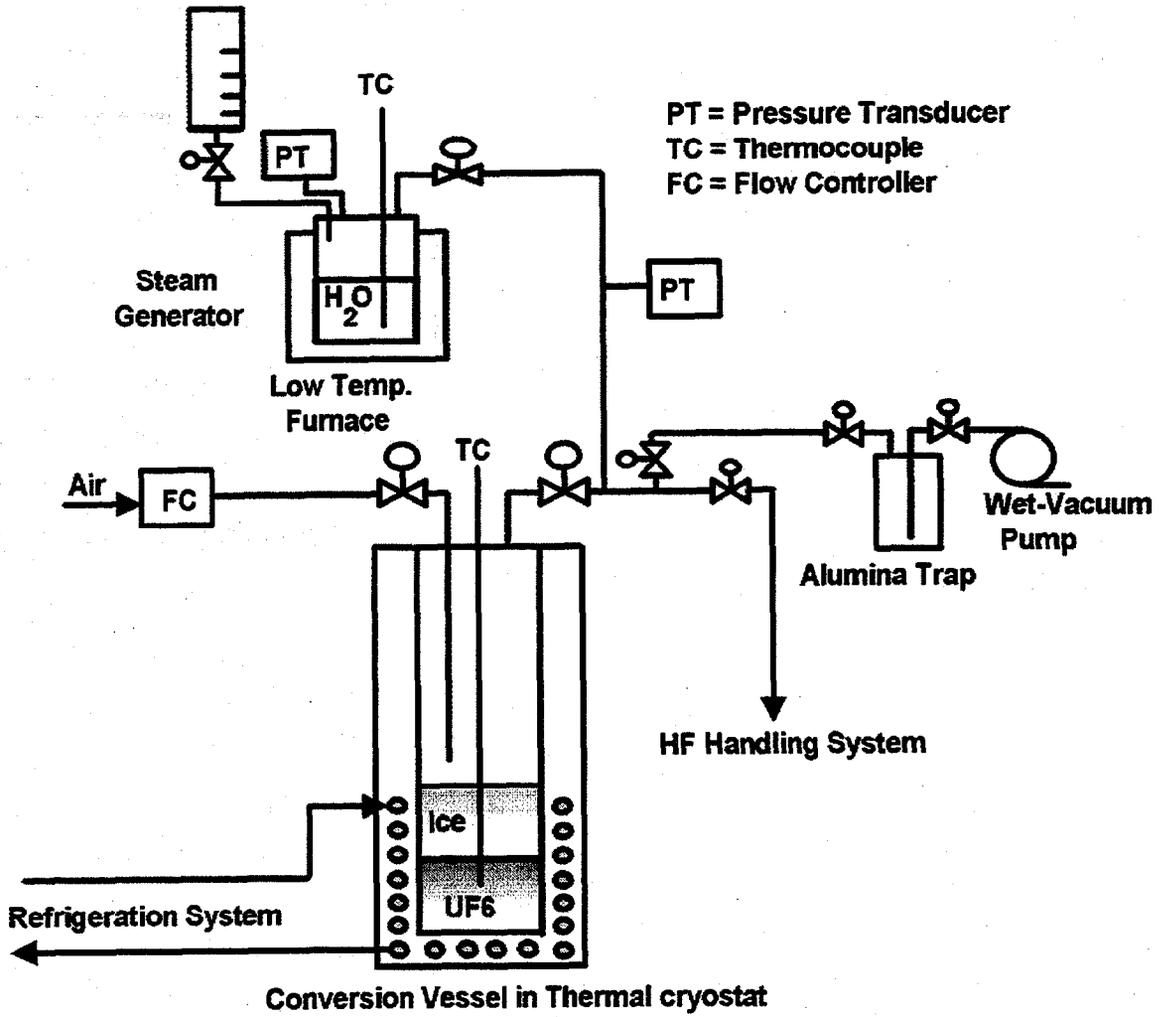
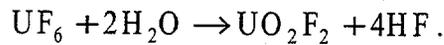


Fig. 2.3. Diagram of the process for converting UF_6 to U_3O_8 .

First, the UF_6 (produced by the decomposing UO_2F_2) reacts with the water to form UO_2F_2 and HF, as shown in the following reaction:



The newly produced UO_2F_2 can then decompose (again producing UF_6 and U_3O_8), and the cycle is then repeated. This cycle continues, slowly reducing the amount of oxyfluoride in the material. After a 15–30-min reaction time, the remnant steam, which carries dissolved HF, is transported to another vessel (the condenser), in which it is condensed by cooling. The HF handling system is described in Sect. 3.6. The cake is step-wise contacted with fresh steam at increasing temperatures until nearly complete hydrolysis of the uranium oxyfluorides is achieved. When the temperature reaches 750–800°C, the introduction of pressurized steam is discontinued. Wet air at atmospheric pressure is then allowed to flow through the conversion vessel, filtered through alumina, and then released to the off-gas system. This wet air will remove fluoride traces and convert the uranium oxides formed at lower temperatures into the air-stable higher oxide of uranium, U_3O_8 . After a final bake-out of the oxide in air at about 900°C, the conversion is completed. The conversion vessel is then allowed to cool to room temperature. All lines are evacuated and filled with inert gas. The conversion vessel is disconnected, capped, placed in an overpack, and removed from the cell.

3. DESCRIPTION OF THE MAJOR COMPONENTS

The NaF traps will be processed, one at a time, in a hot cell in Bldg. 4501 at ORNL. The major components for the process will be arranged on a table inside the hot cell and will be interconnected with valves and tubing. The conversion process will be remotely controlled—either by the use of master-slave manipulators or by remote-operated components such as air-operated valves, pumps, or flow controllers. In this section, the major components or systems required for operation of the conversion process are described.

3.1 IN-CELL CRANE

The lifting and movement of components inside the hot cell using the manipulators will be limited to small tools and objects weighing less than 20 lb. An in-cell crane will be used to move larger and heavier components (e.g., NaF traps and conversion vessels).

The limited space between the manipulator arms and the cell ceiling requires a unique compact configuration. The design criteria includes a 500-lb capacity hoist with a maximum 12-in. hook distance from any wall. Additionally, limit switches are installed to prevent the collision of the crane or its load with the manipulators. The crane can be operated from outside the cell window using a standard push-button pendant.

3.2 LOAD-IN STATION

The NaF traps to be processed will enter hot-cell D through a 6-in.-diam hole in the top of the hot cell. The trap will be contained inside an overpack. The overpack, containing a trap, will be lowered into the cell and will then be moved into a shielded load-in station. The purpose of this station is to provide (1) a shielded location to store the trap, and (2) a means by which the trap can be removed from the overpack. The station consists of a cylindrical cavity, which extends below the table top. The bottom of the load-in station has a male key, which matches a female key in the bottom of the NaF trap overpack. This key holds the overpack in place while the cap is rotated for removal. Once the cap is removed, then the NaF trap will be removed from the overpack and moved into the desorb station. The shielding protects electronic components from radiation damage, particularly the FTIR instruments. The shielding will also

minimize exposure in the unlikely event of a cell entry by personnel while the NaF trap is in the load-in station.

3.3 DESORB STATION

The desorb station will be used to heat the NaF traps above 300°C to recover the UF₆. The station consists of a cylindrical cavity, which extends under the table, with the top of the cavity even with the table top. The station is encircled by ceramic-fiber heaters and then by lead shielding. The heaters are used to evenly heat the NaF trap from room temperature to about 500°C. The heaters are controlled using a thermocouple probe with independent type K junctions in each heating zone (one for controlling, one for emergency shutoff if the temperature exceeds 600°C, and one for a spare). A low-flow N₂ gas purge will be maintained inside the desorb station during heating to protect components from corrosion. The shielding protects all the electronic components from radiation damage, particularly the FTIR instruments. Additionally, the shielding will minimize exposure in the unlikely event of a cell entry by personnel while a NaF trap is in the desorb station.

3.4 CONVERSION VESSEL

The conversion vessel is a heavy-walled, cylindrical vessel. To minimize the attack of HF produced during the conversion of the UF₆ to U₃O₈, the inside of the vessel is coated with gold on top of a nickel base. The vessel will be designed to withstand pressures up to 300 psi at about 900°C. At the end of the conversion process, the inlet and outlet tubes of the conversion vessel will be capped, and the entire top of the vessel will be covered by a welded cap to provide a leak-tight primary enclosure. As envisioned, the conversion vessel will then be enclosed in a leak-tight overpack with a freeze plug and sent to Bldg. 3019 for long-term storage.

3.5 THERMAL CRYOSTAT

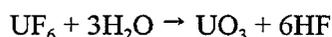
The thermal cryostat consists of a jacketed cavity, which houses the conversion vessel. The jacket is divided into three zones. The bottom and middle zones can be independently cooled by liquid nitrogen. During the desorption of UF₆ from the NaF trap, the bottom and middle zones are kept cold to collect and freeze the incoming UF₆. After recovering and freezing all the UF₆, the middle zone is then warmed to

concentrate the UF₆ deposit at the bottom of the conversion vessel in preparation for the conversion of the UF₆ to an oxide.

The conversion vessel is encircled by three ceramic-fiber heaters, which cover the top, center, and bottom sections of the thermal cryostat. By using these heaters, one can heat each zone independently. During the final stages of conversion the bottom zone will be heated in the presence of air to about 900°C to generate a good quality U₃O₈. The heaters are controlled using a thermocouple probe with three independent type K junctions in each heating zone (one for controlling, one for emergency shutoff if the temperature exceeds the maximum set value, and one for a spare). A very low-flow N₂ gas purge will be maintained during the heating stages to protect heaters and metal parts from oxygen corrosion.

3.6 HF HANDLING SYSTEM

The overall conversion process can be summarized by the following global reaction:



(The UO₃ is not stable at higher temperatures, and it transforms spontaneously in air to U₃O₈). A total of 6 mol of HF are produced for each mole of UF₆ that is converted. The HF is generated in the form of a concentrated aqueous solution and may include traces of uranium and other impurities (e.g., Ni, Cr, Fe, Mo, and W). The concentrated aqueous HF is a dangerous and extremely corrosive product. To avoid the handling of HF, it will be reacted with soda lime to produce an inert solid, CaF₂. To avoid transporting trace amounts of uranium into the soda lime, the process will include a distillation step for the HF. As shown in Fig. 3.1, initially the HF aqueous solution will be condensed in a cooled vessel (condenser 1). At the end of the conversion process, the condensed HF will be warmed and transferred to an evaporator. The purpose of the evaporator is to distill, under vacuum, a pure HF solution. Any dissolved solids will remain in the evaporator, and the purified HF solution will condense in the second condenser. The evaporator will be periodically treated with F₂ or ClF₃ to fluorinate and recover (as UF₆) the accumulated traces of uranium. The clean HF, which is in the second condenser, will then be slowly allowed to flow into the HF trap, which is basically a removable plastic cartridge that is filled with soda lime. The HF will react with the soda lime, producing CaF₂ particles that stay in the cartridge, while the water is collected at the bottom and evaporated. An indicator that changes color as the pH changes is used to visually determine when the cartridge is exhausted and needs to be replaced.

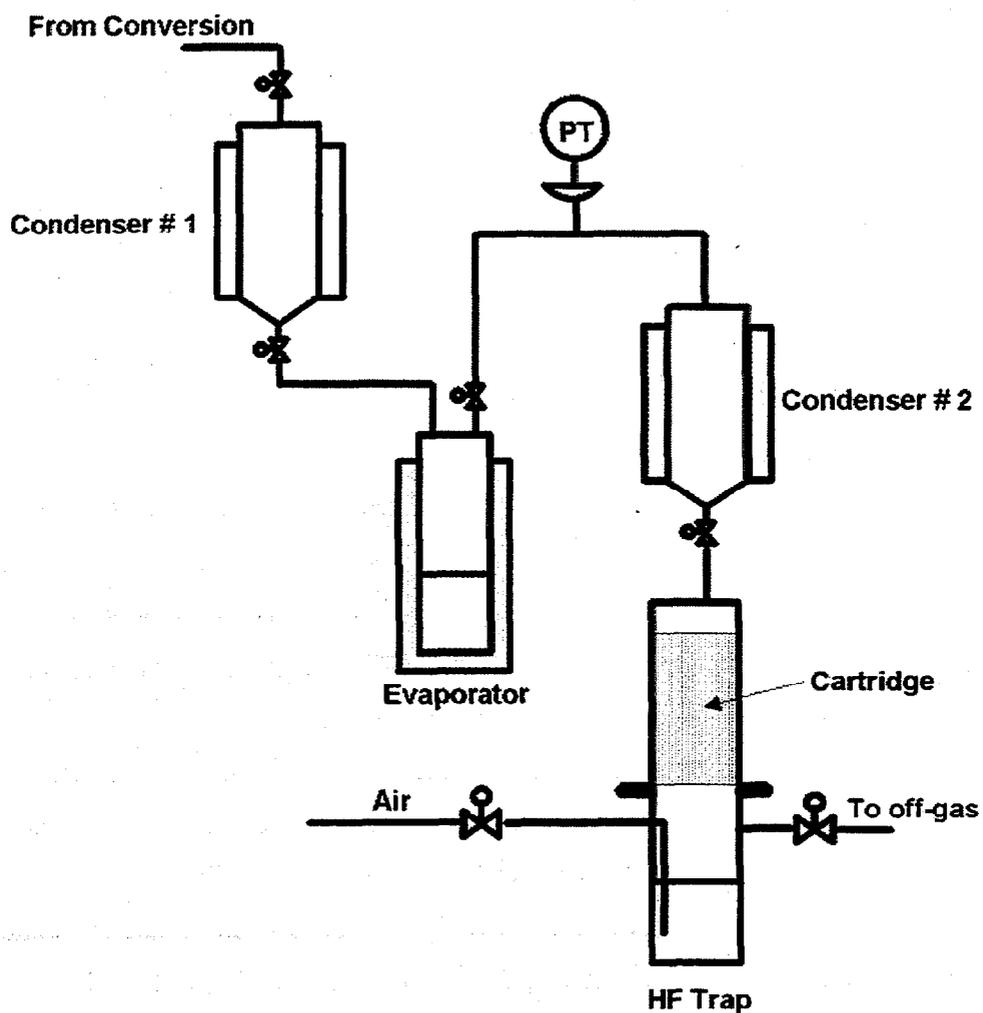


Fig. 3.1. Diagram of the HF handling system.

3.7 STEAM GENERATOR

The steam generator will be used to transfer water vapor to the conversion vessel, where an ice layer will form on top of the frozen UF_6 . Additionally, the steam generator will be used to produce pressurized steam (~200–220 psi), which will be used in the steam treatment of the uranium oxide–oxyfluoride. A pressure relief valve, set at 300 psi, is connected to the steam generator to prevent overpressurization of the conversion process.

3.8 DUST COLLECTOR

Potentially, NaF dust in the trap can be transported throughout the process piping and collected in areas where there is a change in flow direction (e.g., the FTIR cells and the conversion vessel). A dust collector will be used at the outlet of the NaF trap to collect the NaF dust. The collector is to consist of a tortuous flow path, which allows the dust to settle out of the gas stream. The dust collector will be heated with a heating mantle to prevent condensation of UF_6 inside the collector.

3.9 FTIR SPECTROMETERS

The conversion system has two in-line cylindrical gas cells before and after the conversion vessel. They are 2.54-cm in diameter, and they have 8-mm-thick ZnSe windows on each end. The distance between the two windows is 100 mm. Both cells are placed in the optical path of FTIR instruments in order to measure the light absorption in the infrared region. These instruments will be used to monitor the amount of UF_6 being desorbed and trapped and to monitor and quantify other gaseous impurities that are infrared active (e.g., MoF_6 , HF, CO_2 , COF_2 , CF_4 , and H_2O). Local shielding and the stationary shielding around the desorb and load-in stations will be used to protect the electronic components of the FTIRs.

3.10 RECIRCULATION PUMP

The recovery of UF_6 will be achieved by heating the NaF trap in a closed-loop recirculating system, wherein the UF_6 will be desorbed from the NaF and is then condensed in the cooled conversion vessel. A small amount of F_2 will be continuously circulated using a metal-bellows-diaphragm pump. The F_2 is

a carrier gas for UF_6 and also serves as a fluorinating agent to convert oxyfluorides or lower fluorides, which may be present, to UF_6 .

Senior Flexonics, Inc., designed and built the double-contained metal-bellows pump (model MB-111), which will be used to flow F_2 and UF_6 gases through the conversion loop. The MB-111 can be used continuously to pump heated F_2 and UF_6 (at $\sim 100^\circ\text{C}$) with a variable flow rate between 0 and 11 slm when the inlet and outlet pressures are near atmospheric pressure. The leakage rate is less than 10^{-8} scc/s of helium at 1 atm differential.

A pressure switch will sense the pressure between the internal and external seals and will be used to actuate an alarm in case the internal seal is broken. If this were to happen, the external seal will still contain the UF_6 and F_2 . In such an event, the NaF trap will be isolated and by-passed to remove the source of UF_6 . The flow will be maintained for a short period to allow full condensation of the UF_6 in the cooled conversion vessel, as indicated by the FTIR gas cells. Then, the system will be evacuated and refilled with helium to safely remove and replace the recirculation pump.

3.11 PRESSURE BUFFER TANKS

The NaF traps to be processed are stored in Bldg. 3019. According to the planned schedule for the conversion operations, some of the traps will have been stored for about four years before processing. During this time, the pressure in the traps will have increased as a result of the formation of F_2 , which is caused by radiolysis. After connecting a trap to the conversion system, the pressure in the trap will be reduced by expansion of the gas into a set of tanks called the pressure buffer. The gas (mostly F_2) will then be vented through a NaF scrubber and alumina trap to the cell off-gas system. The NaF scrubber will remove and retain any traces of UF_6 , while the alumina will remove the F_2 and other reactive gases that could be present.

The pressure buffer has enough capacity to handle a pressurized NaF trap at its maximum design pressure of 800 psi. The pressure will be reduced by about a factor of 20 (from 800 psi to less than 40 psi). The pressure buffer will consist of four cylinders 4-in. diam and 30-in. long with a total volume of ~ 24 L (~ 6 L each). The use of 4-in.-diam cylinders is consistent with a criticality safe geometry for all components in the system.

Pressurized steam (200 to 220 psi) will be used to process the materials into an uranium oxide. The conversion vessel, in which all chemical reactions take place, is rated to at least 300 psi at 900°C . Test runs show that the pressure in the conversion vessel goes down after each injection of steam; in addition, the conversion vessel and connecting lines are protected from a potential overpressurization by a rupture

disc in series with a relief valve, which is set at 300 psi. The pressure relief line is also connected to the pressure buffer tank. In the event of a release from the conversion vessel, the gases will be contained by the pressure buffer. A line connecting the bottom of all four tanks allows any liquid to be recycled into the evaporator. The pressure buffer can also be connected to the recirculation loop and fluorinated to recover any traces of uranium.

All valves in the process loop are normally closed—except for one that is normally open, the valve connecting the pressure relief valve from the conversion vessel to the pressure buffer tanks. The only time that this valve will be closed is during the initial NaF trap depressurization or during fluorination of the pressure buffer vessels. Administrative controls will be used to ensure that the valve is open during the conversion operations (i.e., when performing pressurized steam treatments).

3.12 FLUORINE TANK

The fluorine tank will be a cylinder 4-in. in diameter and 30-in. long with a volume of ~6 L. The use of a 4-in.-diam cylinder is consistent with a criticality safe geometry for all components in the system. The fluorine tank will be identical to the four tanks that constitute the pressure buffer. The tank is rated at 300 psi, but it is normally operated at subatmospheric pressure. The purpose of this tank is to store sufficient fluorine for each batch. Most of the fluorine (except the volume in the piping loop) will be recycled and reused by isolating the fluorine tank and opening a bypass valve.

3.13 VACUUM PUMPS

The conversion system has two vacuum lines connected to the hot-cell, off-gas system. One line (referred to as the *dry line*) is used to evacuate the system when no water is present; this line is connected to a corrosion-resistant oil vacuum pump. The second line (referred to as *wet line*) is used to evacuate the system when in the presence of water, and it is connected to a diaphragm vacuum (oil-less) pump. Gases that are evacuated from the conversion system pass through a radon-decay holdup volume, and a high-efficiency particulate air (HEPA) filter prior to release to the hot cell off-gas system.

To prolong the life of the oil in the “dry” vacuum pump, the system has a four-way valve, which allows for two modes of operation. In one mode (parallel), both pumps work independently (i.e., the wet pump evacuates the wet line and the dry pump evacuates the dry line). In the second mode (series), both pumps are connected in a series, and the diaphragm pump evacuates the exhaust of the oil pump. When

operating in series, any volatile substances that are dissolved or entrapped in the oil are removed by the diaphragm pump.

Alumina traps are connected before the vacuum pumps in each line (wet and dry) to protect the pumps and to ensure that no UF_6 , F_2 , or HF leaves the system. The alumina traps are filled with pelletized activated alumina and possibly also may contain soda lime. The dry vacuum line has a NaF scrubber before the alumina trap to collect and recover any traces of UF_6 . The wet line cannot accommodate a NaF scrubber because NaF is incompatible with the presence of water. The alumina trap is quite effective to trap UF_6 , but such trapping is essentially irreversible. As a result, any UF_6 trapped in alumina will be disposed of as waste.

3.14 NAF SCRUBBER AND ALUMINA TRAP

The NaF scrubber and alumina traps are essentially of the same design. However, different materials of construction are required because the NaF scrubber will be processed in the conversion system to remove any trace UF_6 which is trapped by the scrubber. To be compatible with the conversion system, the NaF scrubbers are then limited to 3.5-in. in diameter. The bed length for the NaF scrubber and alumina trap is about 16 in. Because the NaF scrubber may collect traces of uranium during conversion processing, it will be contained inside a shielded station to protect personnel and equipment.

3.15 TUBING AND VALVES

Either Monel[®], Hastelloy[®], or Inconel[®] tubing will be used to connect process components. Hastelloy will be used in the portions of the system that will be in contact with HF. Flexible Inconel tubing will be used in some sections to allow for the remote connection of NaF traps, conversion vessels, and FTIR gas cells.

Air-operated valves will be used throughout the system. Selected valves will be manually operated (using manipulators). Valves will be fabricated from Monel.

Selected portions of tubing and valves will be gold-plated to provide further protection from HF corrosion. The system was designed with redundant valves for all of the most critical components.

3.16 GAS SUPPLY

Inert gases, He and N₂, will be used in the conversion system for pressure checks and purging of the lines. Fluorine is used as a carrier gas in the recirculation loop and in the fluorination of uranium fluorides and oxyfluorides to UF₆. ClF₃ will be used periodically to clean trace uranium deposits from process lines. Plant air is used (a) to operate valves, (b) to evaporate water from the HF trap, (c) to facilitate the final oxidation step of the process, and (d) to provide a supply of air to a purge-air generator for the purge of the FTIRs.

Manifolds, which will be located outside the hot cell, will supply gases to the system. Check valves, which are located on either side of the hot-cell wall, will be used to prevent backflow of contamination. The F₂-ClF₃ cylinders will be contained inside a ventilated cabinet outside the hot cell. The F₂-ClF₃ supply line will be doubly-contained to prevent release of these gases.

Argon or an argon-helium mixture will be used to provide an inert atmosphere for the automatic welder.

3.17 LIQUID NITROGEN SUPPLY

Liquid nitrogen will be used to cool the conversion vessel and the condensers. Two liquid nitrogen dewars will be placed inside the hot cell. One dewar will supply liquid nitrogen through the components to be cooled, and the liquid nitrogen will then return to the second dewar. After the first dewar is depleted and the second is filled, three-way cryogenic valves will be used to switch their roles (i.e., the second dewar will then become the supply dewar). A larger dewar, which is to be located outside the hot cell, will be used to supply the dewars inside the hot cell. The supply dewar inside the hot cell may also be pressurized with N₂ gas—either from a cylinder or the gas from the large dewar outside the hot cell.

3.18 INSTRUMENTATION AND CONTROL

Various types of instrumentation will be used to monitor and control important aspects of system operation such as gas composition, pressure, temperature, and flow rate. All vessels have thermocouple probes, which include spare thermocouple junctions for redundancy. Heaters will have dual-control thermocouples along with an independent safety shutoff system, which will turn off the heater if the maximum preset temperature is reached. Pressure transducers will be used to continuously monitor the

pressure throughout the system. Flow controllers will be used to monitor the flow of helium and fluorine into the system along with the flow speed of the gases in the fluorination loop.

All air-operated valves have a visual indication showing valve position. Both mechanical and electrical indications are available. The position of all manual valves will be visually indicated on the control panel by selecting the position of individual switches assigned to each valve.

A computerized data acquisition system will be used to provide real-time indication of system parameters and to record data for later analysis.

An emergency scram switch will interrupt power to heaters and remotely-operated valves. As a consequence, all system components will be isolated and will cool, leaving the system in a safe condition.

In the event of a power failure, computers and part of the data acquisition system will remain operational because they are connected to an uninterrupted power supply (UPS).

3.19 BALANCES

Two balances are used in the process. One balance will weigh NaF traps and conversion vessels for material accountability. A second balance will weigh the amount of water introduced into the hot cell. The water will be used during hydrolysis and steam treatments.

3.20 CAMERAS

Radiation-resistant cameras will be used to provide additional viewing capability for the process operators. One camera will be located above the table, while the other will be placed below the table. The cameras will have pan, tilt, and zoom capability.

4. RESULTS OF TESTS

Bench- and full-scale tests have been conducted to demonstrate the conversion process flow sheets. These tests are described in Sects. 4.1 and 4.2. Lessons learned from the testing are described in Sect. 4.3.

4.1 BENCH-SCALE TESTS

Initially, small tests were conducted using gram amounts of UF_6 and glass equipment. The objective of these tests was to observe the behavior of UF_6 during the cold trapping and subsequent initial hydration of the UF_6 to UO_2F_2 . It was observed that freezing UF_6 at liquid nitrogen temperatures, followed by freezing an ice cap from water vapor, was an effective way for creating a solid UO_2F_2 cake at the bottom of the vessel.

During the deposition of ice on top of the UF_6 , a small degree of reaction occurred at the ice- UF_6 interface, as shown by the appearance of a yellow tint. However, the bulk of the UF_6 deposit and ice remained pristine white. The reaction between UF_6 and water is exothermic, and to generate a solid cake and avoid projection of material (i.e., spattering), the thawing needs to proceed slowly. To reach a "soft landing", the system should be allowed to warm very slowly when the temperature is approaching the range -15 to $-10^\circ C$. Under these conditions, the reaction front slowly moves down, forming orange and yellow regions until the entire mass is reacted. Any excess of water appears as a yellow solution on top of the solid cake. The tests demonstrated that the ice needs to be on top of the UF_6 ; otherwise, the reaction will occur all over the vessel causing projections and splashes. For large batches, a small amount of ice could be added initially (before the UF_6) so as to produce a "sandwich", which has then the bulk of the water on top of the UF_6 deposit. This will ensure a complete reaction at the bottom of the vessel and facilitate further conversion of the UF_6 to an oxide. Cycles of freezing and thawing will generate cracks in the solid cake, thus allowing complete reaction to uranyl fluoride, and enhance the surface area for the following steam hydrolysis to form an oxide.

A simplified proof-of-principle, closed-loop conversion system at 1/10 scale was performed using ~ 100 g of depleted uranium (DU). The uranium was converted to an oxide using steam hydrolysis at elevated temperatures up to $700^\circ C$ and pressures up to 150 psi. The HF generated during the conversion was trapped in a sodium hydroxide scrubber. The final product from this test was a black uranium oxide, which contained about 290 ppm of residual fluoride. This bench-scale test demonstrated that a simple,

closed-loop system (as envisioned) could produce an acceptable oxide. Since no major problems were identified, full-scale tests were planned and conducted.

4.2 FULL-SCALE TESTS

Four full-scale prototype tests have been conducted to evaluate the flow sheet and the operating procedure. A fifth conversion operation was performed on UF_6 removed as part of a charcoal-processing test. Either DU or natural uranium was used in each of the tests, which are described in Sects. 4.2.1–4.2.5.

4.2.1 Test 1

For Test 1, a NaF trap, which was identical to the traps used in the MSRE Reactive Gas Removal (RGR) system, was used. The estimated UF_6 loading on the trap was about 650 g. The conversion vessel was cooled by immersing the bottom of the vessel in a liquid nitrogen dewar. For heating, the vessel was surrounded by Watlow heaters. A small bellows pump was used to circulate gases in the system.

The desorption cycle involved heating the NaF trap while circulating F_2 at subatmospheric pressure through the loop. The UF_6 was transferred to the conversion vessel, in which the UF_6 condensed. The NaF trap was heated for 20 h over a 4-d period to temperatures between 300 and 460°C to desorb the UF_6 . After desorption, the NaF trap was weighed and found to be 622 g lighter.

The hydrolysis of the UF_6 was accomplished by first transferring 320 g of water on top of the frozen UF_6 as ice. The amount of water was calculated by allowing 10 mol of water per mole of UF_6 . This amount of water is well in excess of that required to stoichiometrically react with the UF_6 . As the frozen mass was allowed to slowly warm, the UF_6 began reacting with the water, forming $UO_2F_2 \cdot xH_2O$ and HF. The temperature inside the conversion vessel peaked at about 90°C. To more thoroughly expose the material to water during subsequent steam treatments, the conversion vessel was cooled with liquid nitrogen to freeze the UO_2F_2 . The material was then allowed to thaw. This freeze-thaw cycling promoted cracking in the material, and such cycling was repeated. The HF, which was produced, was evacuated to an HF trap, which contained NaOH. The hydrolysis and freeze-thaw cycling operations took about 7 h to conduct.

To convert the UO_2F_2 to uranium oxide, steam was introduced into the conversion vessel at pressures ranging from 170 to 240 psi. After the steam was introduced into the vessel, it was held from 5–45 min to allow for reaction. The average hold time was approximately 10 min. Between each of the

16 steam shots, the conversion vessel was evacuated to the HF trap, and the temperature set point for the conversion vessel heaters was raised by 50°C. The steam shots were conducted over a period of about 4 h, and the maximum temperature reached within the conversion vessel was about 623°C.

To complete the oxidation, 30 psi of air was introduced into the conversion vessel and the vessel temperature was then held at 624°C for 2.5 h. After the conversion vessel cooled, it was transferred to a dry box. The vessel was then opened, and its contents were removed. About 527 g of material was recovered; this material was found to have a fluoride content of about 1.4 wt % using spark source mass spectroscopy. Based on the estimated trap loading of 650 g of UF₆, about 520 g of U₃O₈ would be expected to be recovered. However, considering that the change in the NaF trap mass was about 622 g (presumably as UF₆) and that slightly more U₃O₈ was recovered than expected, the initial starting mass of UF₆ is somewhat suspect. Additionally, some of the mass of the recovered material may be attributed to corrosion products.

4.2.2 Test 2

For the second test, the NaF trap used in test 1 was reloaded with UF₆. About 1,712 g of UF₆ (1,157 g U) was loaded onto the NaF pellets in the trap. A new thermal cryostat, which was manufactured by Abbess, was tested. This cryostat provided the capability to heat and cool various zones of the conversion vessel. Additionally, a new data acquisition system, which was programmed in LabView®, was implemented. The same conversion vessel as that used in test 1 was used in this test.

To initiate the desorption of the UF₆, 500 torr of fluorine was added to the loop and recirculated. About 100 mL of ethanol was added to the annular region between the thermal cryostat and the conversion vessel to promote the cooling of the vessel. The temperature of the NaF trap heater was then set to 400°C, and the desorption of UF₆ was first seen with the FTIR when the trap temperature was just above 100°C. Fluorine continued to be recirculated during the first 4 h of desorption as the trap temperature peaked at 350°C. The system was then powered down and allowed to cool overnight. The following day, the UF₆ was vacuum-transferred (i.e., no fluorine recirculation) for 2 h at 370°C. On the third day, UF₆ was again vacuum-transferred for 5 h at 380°C. Finally, on the fourth and fifth days of operation, the system was operated in recirculation mode, and fluorine (~300 torr) was circulated through the NaF trap at 400–450°C for 10 h. The total desorption time was about 21 h.

About 750 mL of water was added to the steam generator to be transferred to the conversion vessel. After completing the transfer, the vessel was allowed to warm, producing UO₂F₂·xH₂O and HF. Three valves in the HF-steam transfer lines were observed to be leaking because of HF corrosion. These valves had to be replaced before proceeding with the test. The configuration of the tubing in the system allowed

the HF to reflux in the lines, thereby accelerating the corrosion of the valves. The valves were replaced with Nupro® “U-series” valves. This leakage pointed out the need to make the connections between the conversion vessel, steam generator, and HF trap as short and straight as possible. Additionally, the Cajon® VCR connection at the top of the conversion vessel began leaking. This was the second use of this vessel, but the leakage was likely because of the HF reflux. The head on the conversion vessel was removed and replaced with a new head. Samples of the material in the vessel were taken for analysis during the head replacement and determined to be primarily $UF_4 \cdot H_2O$ and UO_2F_2 . After reassembly, a total of 39 steam shots were applied to the material in the vessel over a period of 6 d. These steam treatments are summarized in Table 4.1. A Cajon seal on the conversion vessel outlet line began leaking, again because of HF reflux in the line, and it was decided to discontinue the test rather than proceed with the final oxidation step.

Results from the material recovery proved to be very good because ~1,159 g U were recovered as compared with the original 1,157 g U in the NaF trap. Again, there may have been some corrosion products in the material. The recovered material was submitted for characterization and determined to have 700–1,000 ppm fluorine. The Abbess thermal cryostat system was determined not to be reliable for long-term processing in the hot cell. Heaters in the unit failed. The configuration of the unit also made maintenance difficult.

Table 4.1. Summary of steam shots for test 2

Day	Number of steam shots	Average hold time between shots (min)	Maximum temperature reached in conversion vessel (°C)
1	9	60	650
2	6	15	850
3	8	25	810
4	6	45	790
5	8	45	880
6	2	120	855

4.2.3 Test 3

The third test was set up in a California-style hood, which allowed for layout of major system components in a manner that is close to the expected layout in the hot cell. Five remote-operated valves were installed to test the control of the steam shots and the removal of the HF. A new, simplified

thermal cryostat was designed and installed in the system. A new NaF trap, which allows for both loading and unloading of pellets, was fabricated. This trap configuration allowed uranium loadings on NaF pellets to be compared before and after desorption. The NaF trap was loaded with pellets containing about 858.8 g U. A variable speed, double metal-bellows recirculation pump (manufactured by Senior Flexonics) was installed.

For the desorption step of the process, 300 torr of helium and 200 torr of fluorine were introduced into the loop and recirculated. Ethanol was added to the annular region between the thermal cryostat and the conversion vessel to promote freezing. The bottom two zones of the thermal cryostat were cooled with liquid nitrogen, while the top zone was heated to about 50°C. The NaF trap heater was set to about 200°C for 1 h. During this time, the first UF₆ began to desorb from the trap, and the temperature on the heater was increased to 400°C. Some plugging occurred in the system, but desorption continued over the next 3 h, and the NaF trap reached a maximum temperature of 380°C. On the following day, the NaF trap was heated for a total of 7 h at furnace temperatures ranging from 200–500°C. The maximum temperature reached in the centerline of the trap was 420°C. The gas composition was monitored both before and after flowing through the conversion vessel using FTIR spectrometers. No UF₆ was seen in the FTIR gas cell after the conversion vessel, indicating that all of the UF₆ was trapped in the conversion vessel. Heating at 450°C continued for an additional 8 h, when it was determined that the UF₆ desorption was complete. The total desorption time was about 19 h.

To prepare for the initial hydrolysis reaction, 650 mL of water was transferred on top of the frozen UF₆ based on the estimated amount of UF₆ present. The conversion vessel was then warmed to allow the hydrolysis reaction to occur.

The steam generator was filled with 1.5 L of water in preparation for the steam shots. Nitrogen gas was allowed to flow around the exterior of the conversion vessel while heating to prevent oxidation of the external wall of the vessel and to protect the heaters. Steam was introduced into the conversion vessel and held there for about 20–30 min before the steam-HF mixture was evacuated to the HF trap. The set point for the thermal-cryostat furnace was then increased by 50°C before another shot of steam was injected. The steam shots are summarized in Table 4.2. The final temperature reached after the last steam shot was 650°C.

To perform the final oxidation, wet O₂ was introduced into the conversion vessel by allowing O₂ to flow through a water bubbler. Initially, 600 torr of wet O₂ was introduced into the conversion vessel and held for ~20 min at a temperature of 660°C. The vessel was then evacuated to the HF trap, and 990 torr

Table 4.2. Summary of steam shots for test 3

Steam pressure (psi)	Hold time (min)	Thermal cryostat furnace setpoint (°C)	Conversion vessel bottom, center-line temperature ^a (°C)
100	20	150	53
180	20	200	106
203	19	250	128
195	23	300	136
182	18	350	148
181	29	400	143
225	29	450	157
230	21	500	176
180	20	550	170
160	28	600	175
170	30	650	208
200	22	700	243
189	19	750	385
183	43	750	560

^aTemperature is at the time of the steam shot.

of wet O₂ was introduced. This atmosphere was held for 30 min at 690°C before being evacuated to the HF trap. Wet O₂ was introduced at ~1,000 torr six more times (with a hold time of about 20 min) as the conversion vessel temperature slowly increased to 855°C. The thermal cryostat heaters were then turned off, and the conversion vessel was allowed to cool while an O₂ atmosphere was maintained inside it.

The weight of material collected from the conversion vessel was 984 g. If all of this material were U₃O₈ and were based on the estimated starting weight of 858.8 g of U in the NaF trap, there was a recovery of 97% of uranium. Pellets were removed from the NaF trap and examined after desorption. The pellets were white—in contrast to the yellow color of uranium-loaded pellets. Pellets, both before and after desorption, were analyzed by Davies-Gray titration to evaluate the amount of uranium recovery. The results of the Davies-Gray titrations (performed for prototype tests 3 and 4) are presented in Table 4.3. These results show that greater than 99 wt % of the uranium was recovered from the NaF pellets. One very small yellow sample consisted of a larger amount of uranium, but this sample was not

Table 4.3. Results of Davies-Gray analyses of NaF pellets before and after desorption

Material	Sample weight (g)	Uranium content (mg U/g)
Uranium-loaded NaF pellets	0.9754	323.39
Uranium-loaded NaF pellets	0.9754	323.92
Uranium-loaded NaF pellets	0.5152	332.64
Desorbed NaF pellets from test 3	0.5253	1.22
Desorbed NaF pellets from test 3	0.0332	1.82
Desorbed NaF pellets from test 3	0.5069	0.81
Desorbed NaF pellets from test 3	0.0489	45.45
Desorbed NaF pellets from test 4	0.4997	2.07
Desorbed NaF pellets from test 4	0.1555	1.76
Desorbed NaF pellets from test 4	0.5016	2.12
Desorbed NaF pellets from test 4	0.2040	0.88

representative of all of the NaF pellets. The fluorine content of the material was determined by spark source mass spectroscopy and was found to be 910–3,100 ppm.

4.2.4 Test 4

The fourth full-scale test was similar to the third test in that the same NaF trap was used, which allowed for loading and unloading of NaF pellets. The trap was loaded with pellets containing an estimated 1,250 g of UF_6 . Before desorption, 20% of the required water was added to the conversion vessel as ice to form a layer of water both above and below the UF_6 , which should provide a better reaction area. About 100 mL of ethanol was added to the annular region between the conversion vessel and thermal cryostat to enhance the cooling of the conversion vessel. The recirculation loop was evacuated and then filled with 300 torr of helium. Zone-three temperature was set at 100°C and allowed to warm to 12.5°C before the NaF trap heaters were set to 200°C. The temperature set point of the NaF trap heaters was then increased in increments of ~20°C every 5–10 min until the furnace temperature reached 390°C. The trap was held at this temperature for 35 min and then turned off because of plugging. The system was evacuated and refilled with a mixture of helium and fluorine twice before the heaters were turned on again. The furnace temperature was slowly increased to 500°C, at which point it

was held for 6 h. Fluorine was added to the system each time the pressure dropped below 400 torr for the first 4 h and ~500 torr for the last 2 h. The total desorption time was about 11 h.

An additional 520 mL of water was added to the steam generator for transfer to the conversion vessel, where the water froze on top of the UF_6 . After warming of the conversion vessel and the initial hydrolysis reaction, two freeze-thaw cycles were performed. Water (1.5 L) was added to the steam generator in preparation for the steam shots, which are summarized in Table 4.4. The HF-steam mixture was evacuated to the HF trap between each steam shot.

After completion of the steam shots, the final oxidation of the uranium oxide was accomplished by introducing air (at atmospheric pressure) and low-pressure steam into the conversion vessel. The thermal cryostat temperature was increased by 50°C about every 20 min. The low-pressure steam was used in place of wet air. Between air-introduction cycles, the air-steam mixture was evacuated to the HF trap. The final temperature set point for the thermal cryostat was 950°C , and the centerline temperature in the conversion vessel (i.e., the uranium oxide temperature) reached about 820°C .

After cooling to room temperature, the conversion vessel was filled with helium and placed in a dry box to have the contents removed. About 525 mL of water was removed from the steam generator, and 750 mL of an acidic green liquid was recovered from the HF trap. Apparently, some of the HF-steam mixture by-passed the trapping material (i.e., by-passed the seals), and, as a result, did not react with the HF solid trapping material. The NaF trap lost 1,338.7 g during the desorption phase of the test compared to the estimated 1,249.8 g UF_6 (845 g uranium) loaded on it. Some of the weight difference can be attributed to NaF dust, which collected throughout the process system, especially in the FTIR cells. A mass of 1,181 g was recovered from the conversion vessel. Assuming all of this material was present as U_3O_8 , this would indicate a recovery of about 1,000 g of uranium. Some of the difference between the estimated uranium removed from the NaF trap and that recovered may be attributed to weight gain from oxidation of the conversion vessel itself; as a result, the recovered material may contain some corrosion products. It is not likely that the entire difference can be attributed to corrosion products; thus, the discrepancy therefore remains unresolved. However, examination of the Davies-Gray analysis results (Table 4.3) indicate that the recovery of uranium from the pellets is greater than 99%. The fluorine content of the material was determined by spark source mass spectroscopy and found to be about 3,800 ppm. The appearance of the material was very good (i.e., a black powder). The relatively high fluorine content is most probably the result of NaF dust carryover into the conversion vessel.

Table 4.4. Summary of steam shots for test 4

Steam pressure (psi)	Hold time (min)	Thermal cryostat furnace set point (°C)	Conversion vessel bottom, center-line temperature ^a (°C)
90	40	150	53
110	25	200	102
185	30	250	128
210	30	300	100
210	29	350	113
200	29	400	159
<i>b</i>	33	450	181
203	24	500	240
200	30	550	<i>b</i>
205	25	600	331
205	20	650	531
200	19	700	626

^aTemperature is at the time of the steam shot.

^bData not recorded.

4.2.5 Conversion of a Partial Batch Recovered from Uranium-laden Charcoal

The first full-scale prototype test of the recovery and conversion of the uranium laden in activated charcoal was interrupted when the internal membrane that held the charcoal as a bed was plugged because of severe corrosion of the sintered material. The UF_6 , which had been recovered up to that point, was converted to an oxide. The pressurized-steam treatment was stopped at about 742°C. The temperature was raised to ~900°C, while air was allowed to flow through the conversion vessel. The objective was to produce a high-quality oxide with a very low fluorine content. At the end of the process, 99.2 g of oxide was recovered with a fluorine content of only 4 ppm. This result indicates that a longer treatment at higher temperatures produces a high-quality oxide.

4.3 LESSONS LEARNED FROM TESTING

The overall flowsheet was successfully operated during the prototype tests. However, there were a number of lessons learned that need to be incorporated either into the design or the operating procedure. These lessons learned are described in this section.

4.3.1 HF Handling System

A major product of the conversion process is HF, which must be removed from the conversion vessel and neutralized. The bulk of the HF is produced during the initial hydrolysis of the UF_6 . After this hydrolysis, two freeze-thaw cycles are conducted to break up the solid UO_2F_2 cake, which is formed. Based on the prototype tests, it has been determined that the HF should be removed as part of the second freeze-thaw cycle. While the UO_2F_2 , H_2O , and HF are still frozen, the conversion vessel is connected to a condenser, which is under vacuum. As the conversion vessel slowly warms, the HF evaporates and is transported to the liquid-nitrogen-cooled condenser, where it freezes. This slow transportation of the HF should limit the transport of uranium contamination.

Between steam shots, during the conversion of the UO_2F_2 to uranium oxide, the pressurized HF-steam mixture is removed from the conversion vessel. Originally, in the prototype testing, this mixture was introduced directly into the HF trap. However, it was found that in some cases, the pressurized mixture by-passed the seals on the trap cartridge; hence, the HF was not neutralized. The second condenser allows the HF to flow slowly at low pressure through the HF trapping media.

Additionally, to limit the potential for uranium contamination of the HF trapping media, the HF handling system, which is shown in Fig. 3.1, is used. The HF is condensed in the first condenser, and it is then transported to the evaporator. The HF is then distilled and travels to the second condenser and then is slowly pumped through the HF trapping media. Any uranium contamination should be left in the evaporator, which can be later removed by treatment with F_2 or ClF_3 . The flow sheet for the HF handling system allows for decoupling of the HF processing from the main process (i.e., such processing can be performed at any time after the removal of the HF from the conversion vessel), reduces the possibility of contamination of the trapping media, and allows for recovery of uranium in the system.

4.3.2 Materials and Plating

Portions of the system that are in contact with wet HF should be made from Hastelloy or be gold-coated. Additionally, gold plating should be used in this part of the system and in other parts of the conversion system as is practicable. The gold plating provides an extra barrier of protection from

corrosion and also should ease the decontamination of the system during both operations and decommissioning.

4.3.3 Water Transfer from Steam Generator to Conversion Vessel

After the desorption of the UF_6 from the NaF trap is completed, water is transferred from the steam generator to the conversion vessel, where it forms an ice layer on top of the frozen UF_6 . Before the transfer, the UF_6 in the conversion vessel should be moved to the bottom of the vessel. This move is achieved by maintaining the bottom of the vessel at liquid nitrogen temperatures, while heating the middle and top zones of the vessel to $\sim 50^\circ C$. Next, the steam generator is connected to the conversion vessel, and the steam generator furnace is then energized and the water is slowly heated. Water vapor is then slowly transported to the conversion vessel, where it freezes.

4.3.4 Desorption

Before desorption of the UF_6 from the NaF trap, about 100 mL of ethanol should be added to the annular region between the thermal cryostat wall and the outer wall of the conversion vessel. The ethanol increases the heat transfer across the gap of the annular region and results in lower temperatures being reached more quickly inside the conversion vessel.

It was found that in some tests, dust from the NaF pellets was transported from the trap and deposited in other areas of the process. The majority of the dust was found in the FTIR gas cell at the inlet to the conversion vessel. The change in flow direction in the cell resulted in the deposition of most of the dust inside the cell. To trap this dust, a dust collector has been installed at the outlet of the NaF trap. The collector is heated to prevent UF_6 deposition and provides a tortuous flow path for the gas to pass through. The multiple changes in flow direction inside the dust collector allows for NaF dust particles to settle before the gas exits the collector.

4.3.5 Vacuum System

Two different types of vacuum pumps are used to evacuate the system. An oil-less vacuum pump is used for operations involving wet HF, while an oil-type pump is used for all other types of operations. The pumps can be operated either independently (i.e., in parallel) or in a series—with the oil-less pump following the oil pump.

During testing, it was found that water could collect in the discharge line from the oil-less pump, resulting in damage to the pump. Consequently, it was necessary to place a water trap at the discharge of the pump. The trap is equipped with vent and drain lines to allow for periodic emptying.

5. SUMMARY AND CONCLUSIONS

The main conclusions from the prototype tests are that (a) the developed process can efficiently recover and convert the uranium laden in the NaF traps and (b) no significant problems were encountered during the testing. The problems were corrected as they were identified, and the changes were transferred to the conversion system design.

Summaries of the test results and of the time required to perform major process steps are provided in Tables 5.1 and 5.2, respectively. The mass balance by weight difference of input and output vessel is somewhat complicated by a series of factors. One significant factor is the change in weight of the vessels resulting from oxidation by ambient air of the heated external surfaces and by internal corrosion. The second major factor is the redistribution and deposit of impurities. These changes can affect the weights from a few grams to tens of grams. This uncertainty in the weights of the empty vessels introduced an uncertainty of the order of ± 10 g in the content of material obtained by weight difference.

Despite this problem, 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 liquid stream, mainly aqueous HF, is distilled, and nonvolatile impurities are left in the evaporator before the trapping of the purified HF by soda lime. The evaporator will be periodically fluorinated to recover accumulated traces of uranium.

The gaseous exhaust is filtered by NaF and alumina. Traces of uranium sorbed in the NaF trap will be recovered at the end of the campaign. The other two outputs are the emptied NaF traps and the conversion vessels containing the uranium oxide. Our prototype tests indicate that a removal of 99% or better from the NaF traps is reasonably achievable. Once removed from the NaF trap, the recovery of uranium is near 100% for the reasons explained, while the carryover between batches is 1% or less. The nature of the recirculation loop precludes any significant buildup of uranium in the system. Still, periodic cleaning of the system with ClF_3 and trapping of the UF_6 traces will ensure the cleanliness of the system.

Table 5.1. Summary of results of prototype tests

Test	Estimated UF ₆ loaded on NaF (g)	Estimated U loaded on NaF (g)	Weight loss of NaF trap after desorption (g)	Mass of material recovered from conversion vessel (g)	Estimated U recovered in conversion vessel ^a (g)	Estimated wt % U recovered and converted	Peak temperature reached during steam shots (°C)	Peak temperature during final oxidation (°C)	Estimated fluoride content (ppm)
1	650	439	622	527	447	101.7	623	624	14,000
2	1,712	1,157	1,708	1,367	1,159	100.1	855	<i>b</i>	700–1,000
3	1,270	859	1,197	984	834	97.2	650	855	910–3,100
4	1,250	845	1,339	1,181	1,001	118.5	661	820	3,800
5	<i>c</i>	<i>c</i>	<i>c</i>	99.2	84	<i>c</i>	742	897	4

^a Assumes all recovered material is U₃O₈.

^b Final oxidation step not performed because vessel was leaking at the Cajon seal.

^c Not applicable. Uranium removed by partial fluorination of uranium-laden charcoal.

Table 5.2. Summary of time required to perform major process operations

Test	Estimated UF ₆ loaded on NaF (g)	Time of operation (h)			
		Desorption	Initial hydrolysis and freeze-thaw cycles	Steam shots	Final oxidation
1	650	20	7	4	2.5
2	1,712	21	<i>a</i>	28	<i>b</i>
3	1,270	19	13	5.7	2.8
4	1,250	11	6	5.6	2
5	<i>c</i>	<i>c</i>	3	13.4	15.7

^a Transfer and reaction times not meaningful because water refluxed in the transfer line.

^b Final oxidation step not performed because vessel was leaking at the Cajon seal.

^c Not applicable. Uranium removed by partial fluorination of uranium-laden charcoal.

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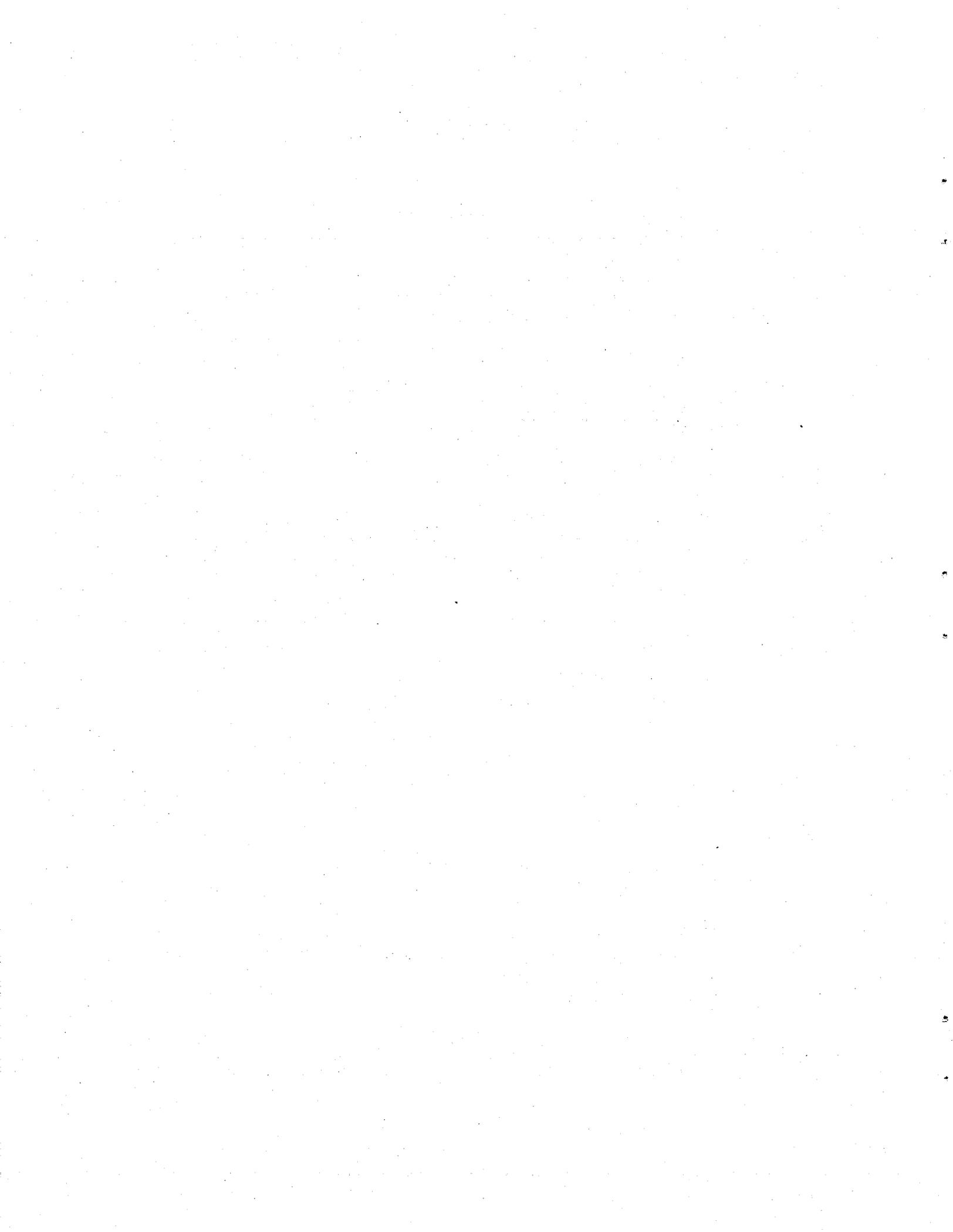
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