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# Conversion of Uranium-Containing Materials Retrieved from the Molten Salt Reactor Experiment into Stable Oxides for Final Storage or Disposition: Results of the First Full-Scale Prototype Test of Burning of Uranium-Laden Charcoal in Oxygen

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# Conversion of Uranium-Containing Materials Retrieved from the Molten Salt Reactor Experiment into Stable Oxides for Final Storage or Disposition: Results of the First Full-Scale Prototype Test of Burning of Uranium-Laden Charcoal in Oxygen

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## ACRONYMS

| | |
|---|---|
| ACB | auxiliary charcoal bed |
| FTIR | Fourier Transform Infrared |
| MSRE | Molten Salt Reactor Experiment |
| ORNL | Oak Ridge National Laboratory |
| XRD | X-ray diffraction |

## EXECUTIVE SUMMARY

The most significant remediation activities for the Molten Salt Reactor Experiment (MSRE) include the removal and recovery of the fissile uranium from the off-gas system, the removal of the uranium-laden charcoal from the charcoal bed, and the removal of the stored fuel salt. All of the retrievable materials (i.e., $2NaF \bullet UF_6$ complex, uranium-laden charcoal, and fluoride salt) are not suitable for long-term storage and must be converted to a more stable form. Furthermore, the high energy gamma (2.6 MeV) radiation released from $^{208}Tl$, a daughter of $^{232}U$, requires the conversion to be performed in a hot cell.

This report summarizes the results of the first full-scale, integrated test of the recovery of uranium laden in activated fluorinated charcoal. The test was conducted in July 1998 and includes (1) removal of the ammonium fluoride ($NH_4F$) from the charcoal, which was produced during the ammonia passivation; (2) combustion of the uranium-laden charcoal in subatmospheric oxygen; (3) transfer of the fluorinated uranium to the conversion vessel as $UF_6$; and (4) conversion of the uranium to uranium oxide.

Several problems were encountered during the testing; each of these problems can be corrected by changes in the design and operational mode. It is quite clear that continuous operation is needed during the oxygen combustion because most of the problems originated from condensation of solids in the inlet and outlet of the charcoal container during the periodic shutdown of the system. The combustion of the charcoal using oxygen will need 48 to 60 h of continuous operation.

The charcoal trap will have to be modified to permit a higher operational temperature. A redesigned, more efficient $NH_4F$ trap is already being built. The thermal cryostat will be replaced with a newly designed system, which is much simpler and more efficient than the current system. A radon-decay coil tube will be added to the system exhaust to test the combustion of the charcoal by using open-loop fluorination of the charcoal.

# 1. INTRODUCTION

The most significant remediation activities for the Molten Salt Reactor Experiment (MSRE) include the removal and recovery of the fissile uranium from the off-gas system, the removal of the uranium-laden charcoal from the charcoal bed, and the removal of the stored fuel salt. The uranium hexafluoride ($UF_6$) from the off-gas system is chemisorbed onto sodium fluoride (NaF) traps, where the $UF_6$ forms a complex ($2NaF \bullet UF_6$), which decomposes at higher temperatures (>300°C). The uranium-laden charcoal was pretreated with ammonia to prevent deflagration of carbon-fluoride $C_xF$ compounds, which could occur if there was localized heating during the charcoal-removal process. The charcoal will then be removed into one large vessel and then will be divided into smaller portions (about six), which will be stored in Building 3019 wells for further processing.

The removal of the fuel salt is still in the planning stages. Two major alternatives are being considered. The first alternative is the removal of the uranium as $UF_6$ by fluorinating the salt. The $UF_6$ will then be chemisorbed onto NaF. The second option includes the removal of the molten salt and its ensuing storage in a number of small containers for further uranium recovery and processing. All of the retrievable intermediate materials (i.e., $2NaF \bullet UF_6$ complex, uranium-laden charcoal, and fluoride salt) are not suitable for long-term storage and must be converted to a more stable form. Furthermore, the high-energy-gamma (2.6-MeV) radiation released from $^{208}Tl$, a daughter of $^{232}U$, requires the conversion to be performed in a hot cell. A process has been developed for converting the different MSRE uranium streams into a uranium oxide that is suitable for long-term storage or disposition. A full-scale prototype has been built to test this process. Depleted or natural uranium surrogates of the MSRE materials are being used for process testing in a laboratory walk-in hood.

The conversion process, developed at Oak Ridge National Laboratory (ORNL), originally was designed to process both uranium-laden NaF traps and uranium-laden charcoal. Full-scale tests of the NaF processing system were completed and are described in Ref. 1. A full-scale test of the charcoal-conversion process was conducted in June 1998. This report summarizes the results of the first full-scale integrated testing of the recovery of uranium laden in activated fluorinated charcoal. The test includes (1) removal of the $NH_4F$ from the charcoal that was produced during the ammonia passivation; (2) combustion of the uranium-laden charcoal in subatmospheric oxygen; (3) transfer of the fluorinated uranium to the conversion vessel as $UF_6$, and (4) conversion of the uranium to uranium oxide.

## 2. EXPERIMENTAL

Two process options are being considered for testing: (1) closed-loop combustion of the charcoal with oxygen followed by fluorination of the residue to recover the uranium as condensed $UF_6$ and (2) open-system combustion of the charcoal with fluorine ($F_2$) followed by recovery and condensation of the uranium as $UF_6$. The test described in this report is based on the closed-loop burning (Option 1). Figures 2.1 and 2.2 show, respectively, the experimental layout used for the recovery and conversion of the uranium-laden charcoal.

The MSRE charcoal trap was designed with the dual purpose of interim storage and charcoal processing for conversion. As shown in Fig. 2.1, the charcoal trap is connected to the Fourier Transform Infrared (FTIR) gas cells and the conversion vessel. An intermediate trap is present during the initial heating of the passivated charcoal to allow for the condensation of the sublimed $NH_4F$. Figure 2.3 shows a picture of the actual equipment used in the test. The manifold in the back of the hood is not part of the conversion system.

The charcoal trap was initially filled with 406.8 g of dried 8–16 mesh "Calgon" coconut activated charcoal. This material is believed to be essentially the same as the charcoal present in the MSRE auxiliary charcoal bed (ACB). A 5-to-1 gas mixture of $F_2$ and $UF_6$ (5 mol of $F_2$ per mole of $UF_6$) was slowly flowed through the trap containing the charcoal while the temperature was maintained slightly above room temperature. The gas mixture was flowed until uranium breakthrough. The weight gained by the charcoal during the loading of the $F_2$ and $UF_6$ was 313.5 g. The $UF_6$ laden in the charcoal was calculated to be about 195 g. The uranium-laden fluorinated charcoal was then treated with ammonia following the same procedure as that used for the passivation of the MSRE ACB.

As mentioned, the initial step of the test consisted of burning the charcoal with oxygen at a temperature in the range of 400–600°C in a closed system. The charcoal was preheated to about 250°C and helium (He) was flowed in a closed loop to remove the $NH_4F$. Helium flow was maintained, and the temperature was raised to 400°C to complete the removal of the $NH_4F$, which was condensed in the intermediate trap. This trap was cooled using the gas exhaust coming from the Dewar flask, which received the liquid nitrogen leaving the thermal cryostat (Fig. 2.1). Once the $NH_4F$ removal was completed and the temperature reached 400°C, the He gas was replaced with oxygen. In the temperature range between 400 and 600°C, the combustion of the charcoal produces carbon dioxide ($CO_2$) and only traces of carbon monoxide (CO). The $CO_2$ formed was condensed as a frozen solid in the conversion vessel. After an appropriate holding time (~10 min.) for radon decay, the $CO_2$ can be released.

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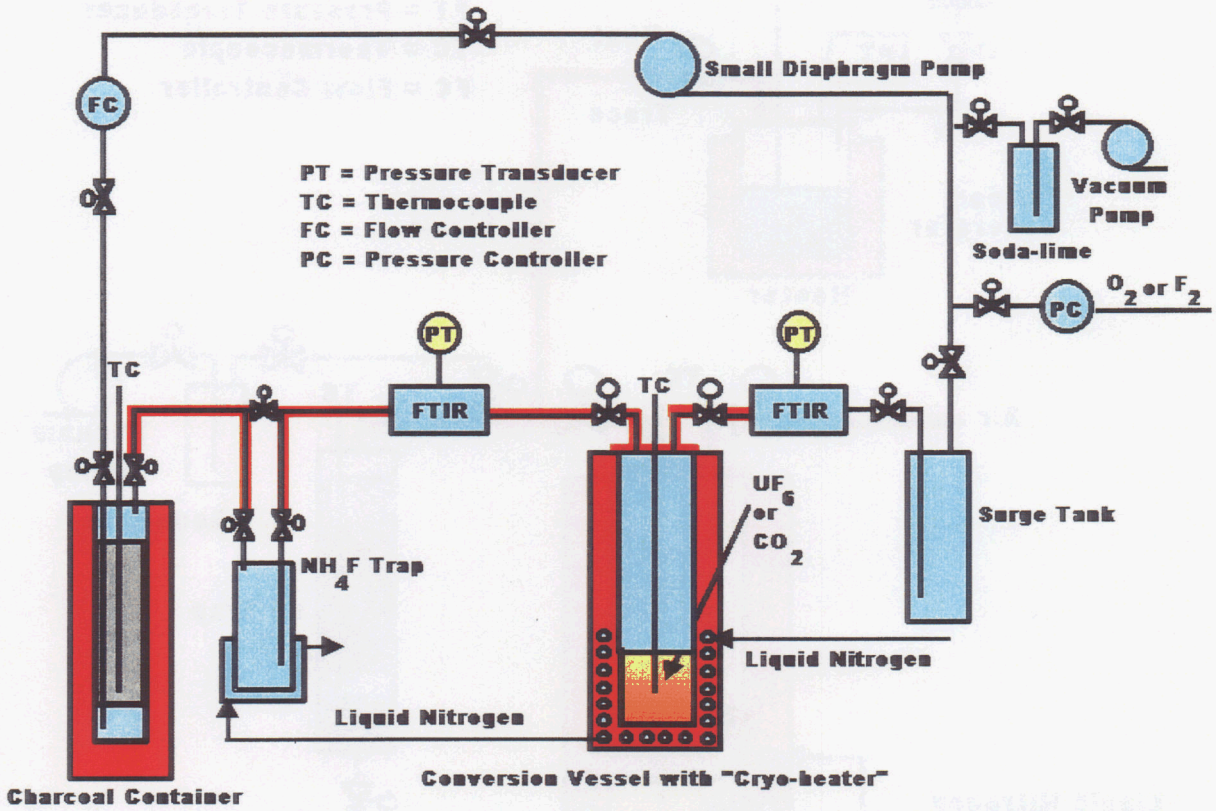


**Fig. 2.1. Diagram showing the experimental setup for the sequential $O_2$-$F_2$ burning of the uranium-laden activated charcoal.**

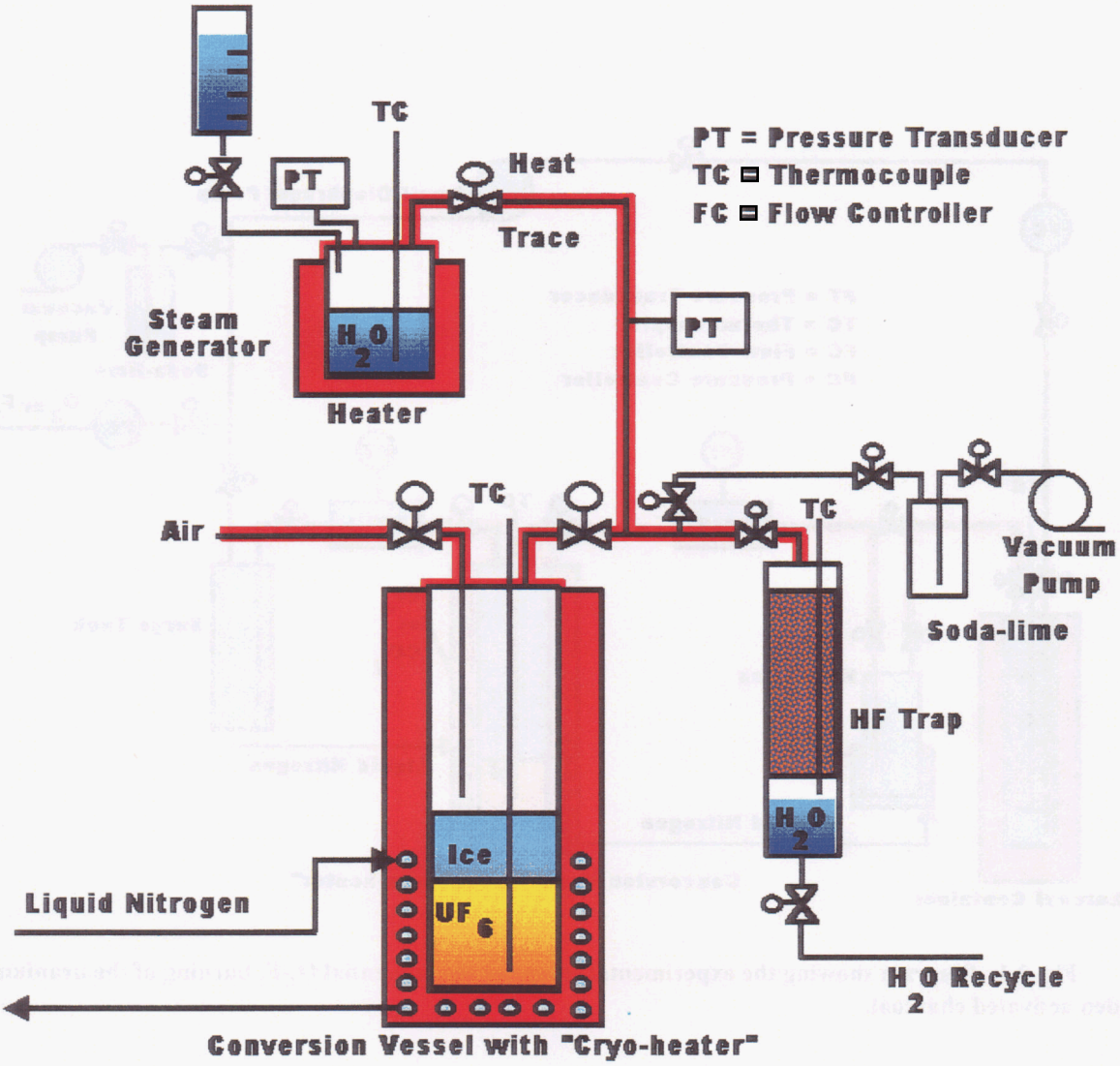


**Fig. 2.2. Diagram showing the experimental setup for the conversion of the uranium recovered from the uranium-laden activated charcoal.**

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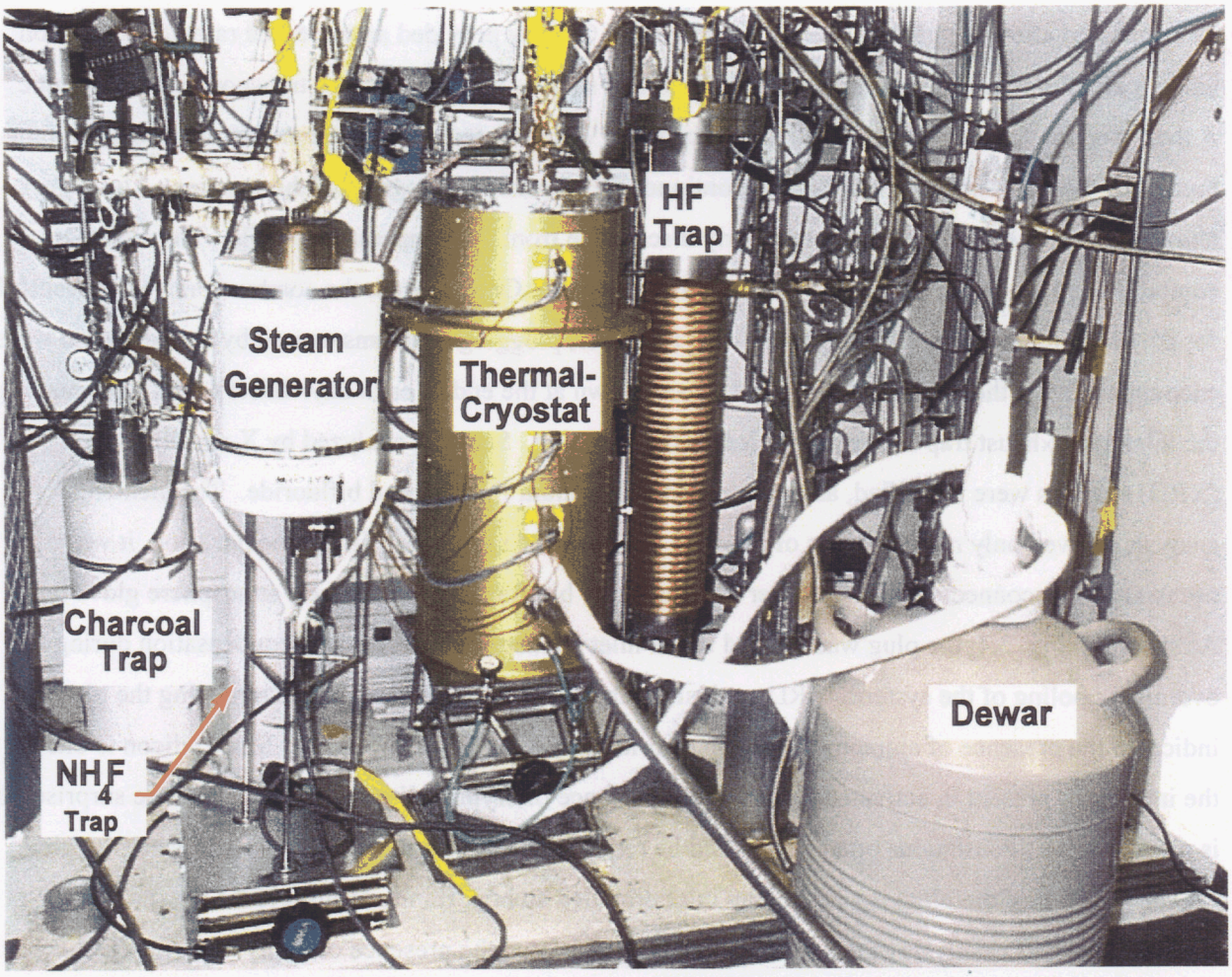


**Fig. 2.3. Picture of the equipment used in the test.**

A flowmeter-controller (Tylan® Model 2900), which was controlled with a pressure transducer, was used to inject the oxygen ($O_2$) gas while maintaining a constant reaction pressure of about 600 Torr (subatmospheric). Once the combustion started, the temperature ranged between 400 and 600°C, and the average oxygen flow rate was between 200 and 400 sccm. This $O_2$ injection was automatically controlled by the flowmeter-controller, which maintained the set constant pressure. The clam-shell-type "Watlow" furnace, which surrounded the charcoal trap, was turned off and opened to increase vessel heat dissipation to allow a higher $O_2$ flow. The increased $O_2$ flow provided an increased rate of combustion while maintaining reaction temperatures low enough such as to prevent vapor transport of the uranium. A thermocouple probe containing 10 thermocouples, which were each located at 1-in. intervals from the bottom of the charcoal trap, was used to continuously monitor the progress of the reaction. The higher temperature of the reaction zone was clearly discernible from the temperature profile. The charcoal combustion required several 8-h days to reach completion. Once started, the combustion was uneventful for the entire day of uninterrupted operation. However, plugging problems caused by condensation were encountered after the system was allowed to cool down at the end of each day. Most of the time, heating the inlet and exhaust trap connections cleared the plugging. Samples analyzed by X-ray diffraction (XRD) analysis were identified, as expected, as ammonium fluoride and bifluoride. The elemental analysis showed only minute traces of uranium in one of the samples. Still on one occasion, it was necessary to disconnect the trap in order to remove the blockage inside the inert atmosphere glove box. As shown in Fig. 2.4, the plug was located in the inlet connection as a result of condensation during the overnight cooling of the system. XRD analysis of the substance recovered while removing the plug indicated the presence of ammonium silicon fluoride [cryptohalite, $(NH_4)_2SiF_6$]. Since silicon is one of the impurities present in activated charcoal, the presence of cryptohalite is an understandable surprise. It is obvious than a continuous operation would be required for this treatment option to prevent plugging.

The removal of the plugging at the trap inlet provided an opportunity to inspect the trap and its contents. An XRD analysis of the charcoal residues indicated the presence of uranyl fluoride ($UO_2F_2$) as the major component with $UO_3$ and other uranium oxides as minor components. The visual inspection showed that the trap was still in excellent condition. The picture (shown as Fig. 2.5) displays a view of the opened bottom of the trap showing the intact annular porous-Monel® membrane (i.e., the frit) and the partially burned uranium-laden charcoal.

The periodic FTIR analysis of the gases showed occasional bursts of ammonia and ammonium compounds during the burning process. This fact was probably due to the $NH_4F$ (deeply trapped in the charcoal matrix) being released as the combustion progressed. At the end of the $O_2$ combustion, the

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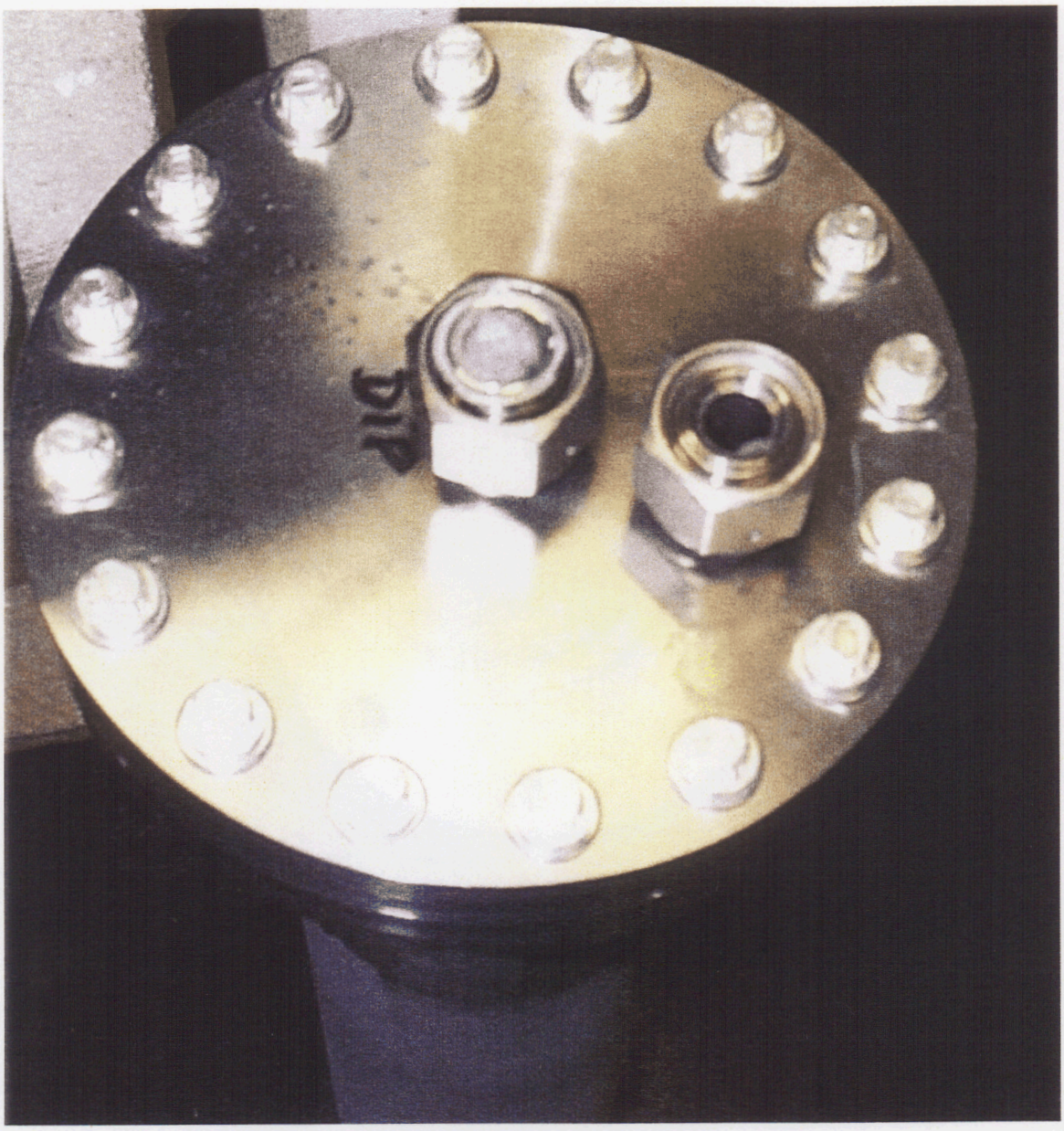


**Fig. 2.4. Picture of the charcoal trap showing the $(NH_4)_2SiF_6$ plug on the inlet Cajon® 4 connection.**

ORNL Photo 6346-2000

**Fig. 2.5. View of the opened bottom of the charcoal trap showing the intact annular porous-Monel® membrane and the uranium-laden charcoal.**

heating was reestablished to ensure completion. When the FTIR analysis of the gases showed only trace levels of $CO_2$, the process was stopped, and the oxygen was replaced with fluorine.

Before starting the closed-loop fluorination of the combustion residues, the charcoal trap was removed from the system and opened inside the glove box. The visual inspection showed that the trap was still in excellent condition. The XRD analysis of the charcoal residues indicated, as before, the presence of uranyl fluoride as the major component, and $UO_3$ and other uranium oxides as the minor components.

To retain any fine particles during the uranium transfer, Cajon gaskets with a 5-μm porous-nickel membrane at the center were used to reconnect the trap. However, the pressure drop caused by the membranes did not allow an acceptable flow of fluorine for the closed-loop fluorination, and the gaskets were removed and replaced with standard Cajon gaskets. More porous Cajon gaskets (50 and 100 μm) were ordered and will be evaluated in future prototype tests.

The initial fluorination was performed at temperatures in the range of 400–600°C, and it progressed uneventfully at a good rate, as shown by the continuous $UF_6$ present in the FTIR analysis of the gases. However, the rate of uranium recovery decreased significantly with time. The temperature was raised in steps up to 700°C. The fluorination rate improved and continued without problems for several hours. Then, the backpressure started to increase, and the recirculating pump could not maintain an acceptable flow rate. The process was stopped to examine the charcoal trap. As shown in Fig. 2.6, the membrane plug at the bottom of the trap was severely damaged, and the plug disintegrated when tapped with a spatula. The annular part of the membrane (welded to the wall of the trap) was still in good condition. Uranyl fluoride was still clearly visible. Since the repair of the bottom of the charcoal trap would require at least two weeks, it was decided to continue with the conversion of the uranium (~102 g), which was already recovered in the conversion vessel.

Water was slowly transferred to the conversion vessel, onto the frozen $UF_6$, in a 10 $H_2O$-to-1 $UF_6$ molar ratio (52.7 g). Then the system was warmed slowly to allow for a smooth formation of the solid $UO_2F_2 \cdot xH_2O$ and hydrogen fluoride (HF) gas. A freezing-thawing cycle was repeated three times to ensure complete hydrolysis of the $UF_6$ and to promote cracking of the solid uranyl fluoride cake. The cracking aided the reaction during the following steam treatment.

The conversion vessel was then evacuated to the HF trap to remove the bulk of the HF. The resulting solid cake was sequentially contacted with pressurized steam and heated in 50°C increments. At each step, the volatile reaction byproducts (mainly $H_2O$ and HF) were then allowed to expand into the silica-gel sorbent (16–40 mesh), which was contained in the HF trap. The manifold connecting the steam generator, conversion vessel, and HF trap was evacuated between steam cycles using the corrosion-resistant, oil-less vacuum pump. This evacuation was done to minimize the residence time of wet HF in the heated manifold to in turn minimize corrosion.

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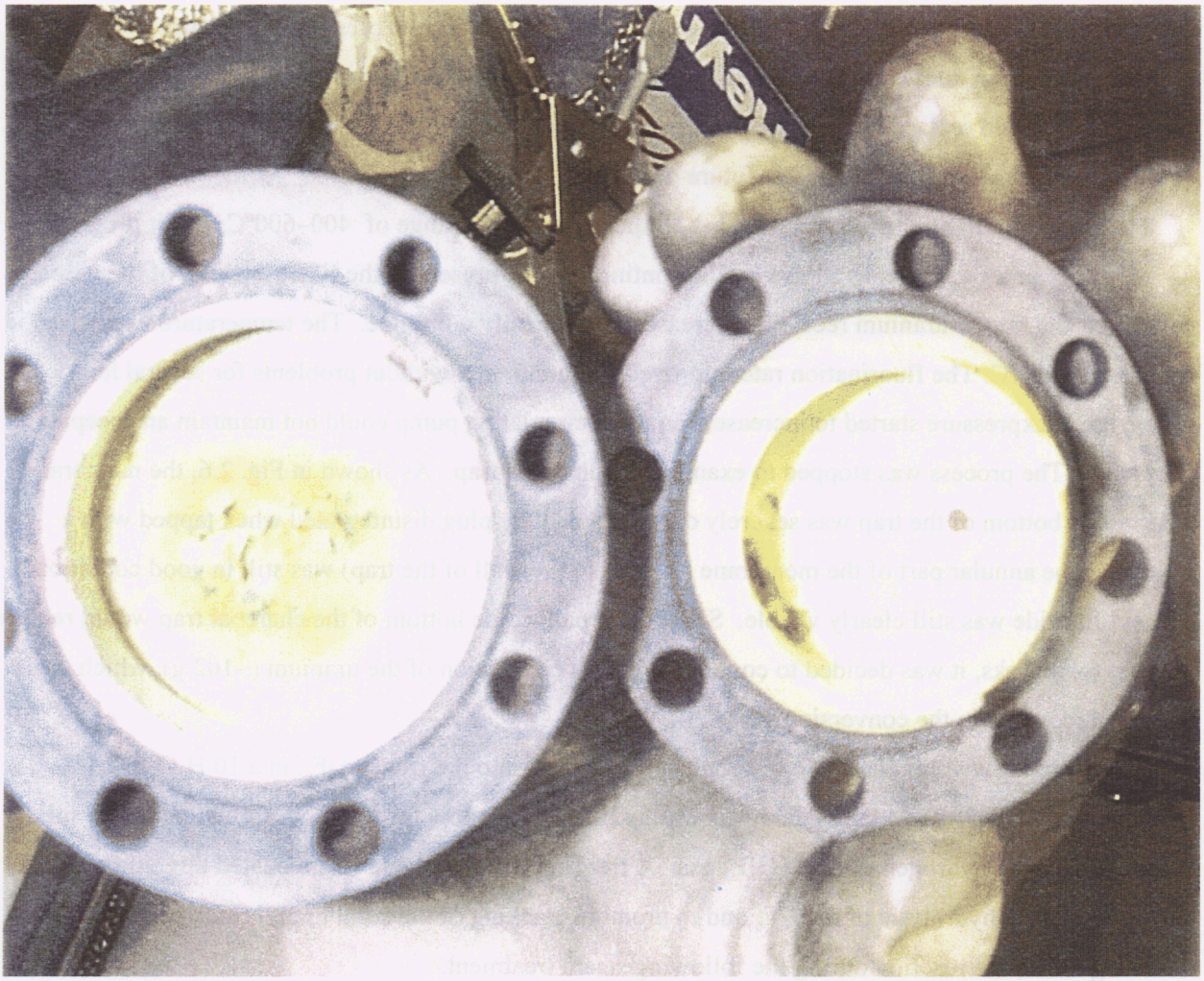

**Fig. 2.6. Picture of the severely damaged membrane which was welded to the bottom of the trap. It disintegrated when knocked with a spatula. The annular part of the membrane welded to the wall of the trap was still in good condition.**

Room air was injected at the end of the oxidation process at a temperature of 700°C to complete the reaction. The vessel was then heated to about 900°C under air to produce $U_3O_8$. At the end, the vessel was allowed to cooldown. The lines were evacuated and filled with an inert gas. Samples of the final product will be sent for analysis.

## 3. CONCLUSIONS AND FUTURE WORK

Several problems were encountered during the testing. However, none of these problems is a "show-stopper", and all can be corrected by changes in the design and operational mode. It is quite clear that continuous operation is needed during the oxygen combustion since essentially all the problems originated because of the condensation of solids in the inlet and outlet of the charcoal container during the periodic shutdown of the system. The combustion of the charcoal using oxygen will need 48 to 60 h of continuous operation. The charcoal trap will have to be modified to permit a higher operational temperature. The bottom membrane plug is currently being repaired. Three Monel screens (two coarse and a very fine one) are going to be sandwiched and welded on top of a perforated monel plate to replace the sintered monel membrane. Larger tube bore Cajon fittings (Cajon 8, ½ in.) should replace the present Cajon (4, 1/4 in.) connectors. A redesigned, more efficient $NH_4F$ trap is already being built. The thermal cryostat will be replaced by a newly designed system which will be much simpler and more efficient than the current one. A radon-decay coil tube will be added to the system exhaust to test the combustion of the charcoal by using open-loop fluorination of the charcoal (Option 2). The volume of this coil is such that it provides adequate time (~10 min.) for the radon to decay before reaching the hot-cell off-gas system.

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1. G. D. Del Cul, A. S. Icenhour, and D. W. Simmons, *Prototype Tests for the Recovery and Conversion of $UF_6$ Chemisorbed in NaF Traps for the Molten Salt Reactor Remediation Project*, ORNL/TM-2000/92, UT-Batelle, LLC, Oak Ridge National Laboratory, Oak Ridge, Tennessee, April 2000.

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