

MSRE REMEDIATION PROJECT SALT MELT, TRANSFER, AND PROCESS DEMONSTRATIONS

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ABSTRACT

Three demonstrations of the process to melt and remove the fuel salt stored at ORNL's Molten Salt Reactor Experiment were performed. (1) The secondary coolant salt was melted and transferred into storage vessels. (2) Coolant salt in one of the vessels was melted, using the poolmelt process developed for the fuel salt. (3) A simulated fuel salt mixture, irradiated to a damage level similar to that in the reactor fuel salt, was melted and treated with hydrogen fluoride to obtain a clear melt. The effectiveness of the fuel salt melt and transfer process was demonstrated, and key process operating parameters were defined.

INTRODUCTION

The Molten Salt Reactor Experiment (MSRE) was an 8-MW, fluid-fueled test reactor that operated from 1965 through 1969 in support of a program to develop a thermal breeder power reactor using the thorium-uranium fuel cycle. The fuel consisted of a mixture of lithium, beryllium, and zirconium fluoride salts, to which uranium was added as UF_4 . The molten salt circulated through a reactor vessel, pump, and heat exchanger at temperatures above $600^\circ C$; the salt, however, is solid at room temperature. After reactor shutdown, the salts were returned to their drain tanks and allowed to freeze. The 4650 kg of fuel salt was divided between two drain tanks, and another 4265 kg of flush salt, slightly contaminated with fuel salt, was left in a third drain tank. A single batch of 2610 kg of coolant salt was left in another drain tank. The coolant salt was not contaminated with either fuel or fission products, but it contained a small amount of tritium.

Over the years, fluorine was released from the fuel and flush salt matrix as a result of radiolysis. This fluorine, in turn, oxidized UF_4 to volatile UF_6 and thus provided the means to spread ^{233}U throughout an off-gas system and into a charcoal bed. The MSRE Remediation Project was formed to recover and stabilize uranium from the MSRE and to remove and process the fuel and flush salt for safe storage and ultimate disposition.

The loss of fluorine from the matrix leaves the salt in a net reducing state. The addition of fluorine during the melting process is necessary to completely melt the salt and to prevent the remaining uranium salt from precipitating or interacting with the vessel walls. Salt expands when it melts, and heat must be supplied in such a way that excess stress on the vessel walls is avoided. A progressive poolmelt process has been developed to melt the salt with an internal thermal probe while treating a growing pool of molten salt with HF/H_2 to restore the chemical balance in the salt as it is melted. The insertion of a melt probe in one of the fuel salt drain tanks is depicted in Fig. 1. Three demonstrations were performed to demonstrate the technology of safe melting and transfer of the MSRE fuel and flush salts.

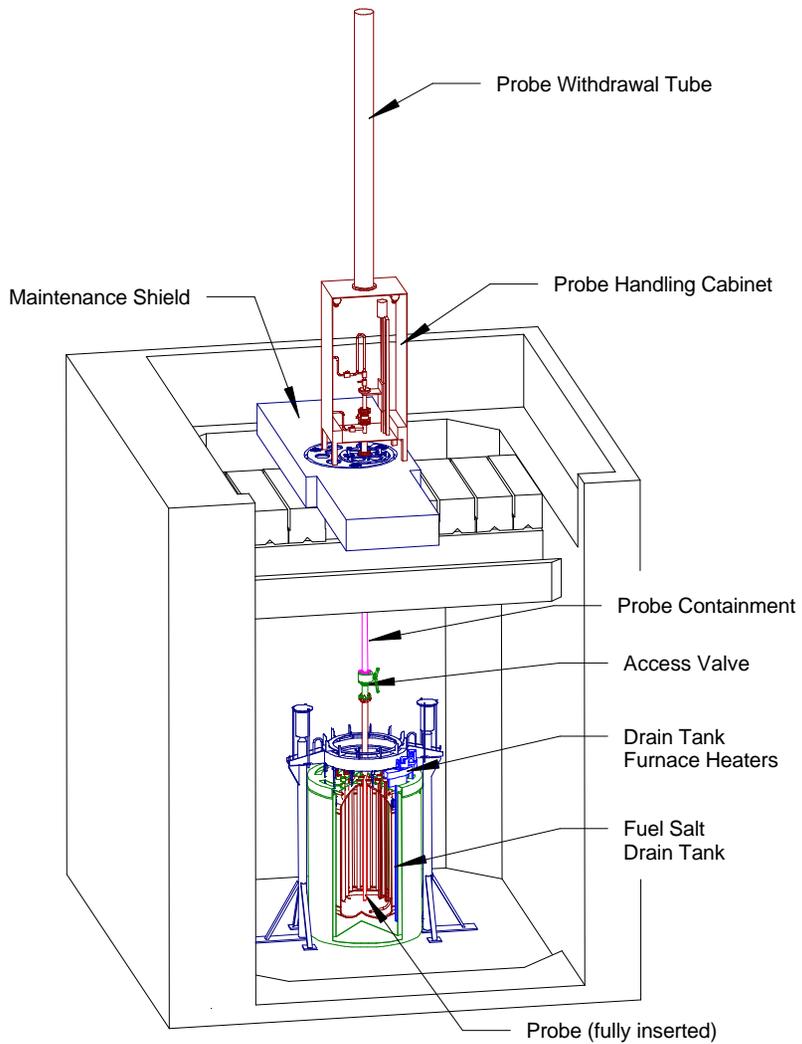


Fig. 1. Fuel salt drain tank with probe inserted.

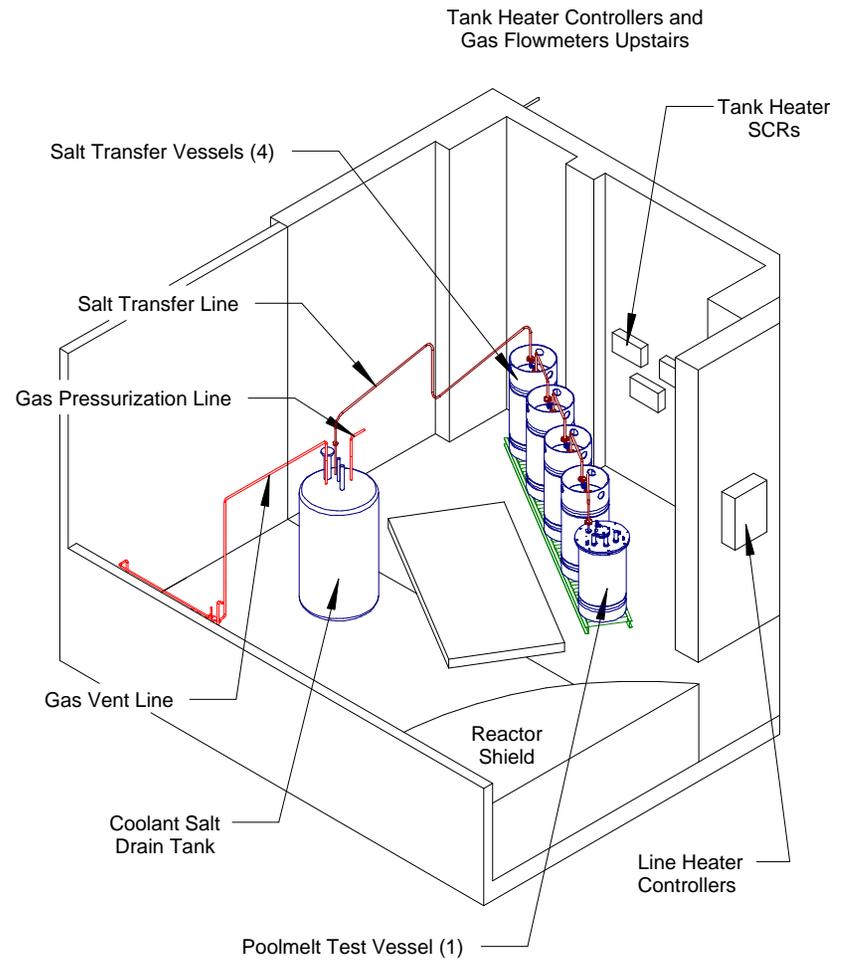


Fig. 2. Coolant salt transfer equipment.

COOLANT SALT TRANSFER DEMONSTRATION

The coolant salt transfer demonstration had four objectives: (1) to demonstrate the safe melting of a large tank of salt, (2) to demonstrate the transfer of a large quantity of salt, (3) to prepare a vessel of coolant salt for use in the poolmelt test, and (4) to provide experience in reactivating one of the original molten salt systems.

System Description

The coolant salt drain tank, shown in Fig. 2, is very similar to the fuel and flush salt drain tanks but is slightly smaller. The main difference is that the coolant salt drain tank is wrapped with horizontal heating elements and directly covered with insulation, whereas the fuel and flush salt tanks have vertical heating panels lowered between the drain tank and a separate furnace enclosure. Molten salt is removed by pressurizing the tank with gas, causing salt to flow from a dip tube that extends to the bottom of the tank. Five new vessels were obtained, each holding about 530 kg or about 240 L of salt. The existing drain tank fill tube was extended to provide a connection to the first transfer vessel.

The five vessels were connected in series, with dip tubes extending only to the intended level of elevation for molten salt in the filled vessels. Salt was added to each vessel until the level of the exit dip tube was reached, at which time it flowed on to the next vessel. The last of the five vessels was provided with a central access flange and a series of thimbles, analogous to the cooling thimbles in the fuel salt drain tank, for use in the poolmelt demonstration. Each of the five transfer vessels was wrapped with an insulating blanket containing heater elements and thermocouples, and insulation was placed on the top and bottom. Salt transfer lines were wrapped with heater tape and covered with insulation. Thermocouples were provided at regular intervals along the transfer lines.

To avoid excessive stress on the drain tank walls, it was necessary to melt the salt in such a way that expansion can be directed to a free surface. Because the coolant salt tank was provided with horizontal heating elements wrapped around the tank shell, the use of an internal heater probe was not required. The existing heater elements were rewired so that heat could be progressively applied in three horizontal zones and a bottom zone, with the first zone near the top elevation of the salt. The existing power supplies, thermocouples, and wiring were found to be serviceable. Solid-state controllers were provided to allow fine control of the heating operation during the melt.

A nitrogen system was provided to supply purge and transfer gas to the system. Before the melt, the gas flow was used to dry the tank and ensure that interactions of salt and moisture did not occur. Valving was provided to allow pressurization of the tank, with a relief path to stop the salt transfer.

Results

Wall temperatures on the coolant salt drain tank throughout the demonstration are shown in Fig. 3. The nitrogen purge began on January 29, 1999, and heating of the salt began on February 2. To avoid excessive initial temperature increases, the solid salt was heated to 400°C in three steps. The purge was maintained for several weeks to ensure removal of moisture and to allow completion and testing of salt transfer equipment before the salt was melted.

Melting of the salt began on March 9. A four-stage sequence was used to ensure that the melt would progress from the top down. In the first stage, the power to all but the upper zone of heaters was held at a level that maintained a temperature of 400°C. Power in the upper heater zone was increased, and the salt quickly passed the 459°C melt temperature at the tank side near the salt surface. This configuration was maintained until the melt temperature was exceeded at the tank midplane. The controller for the upper

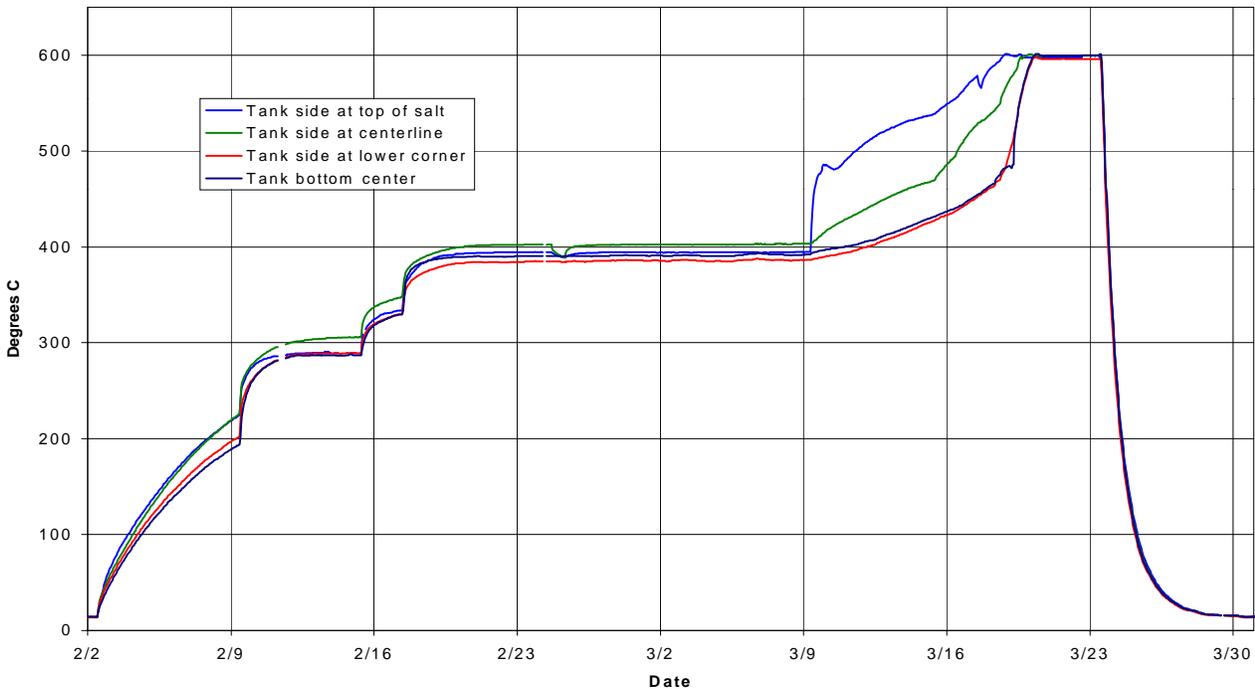


Fig. 3. History of coolant salt drain tank temperature during heating, melting, and transfer.

zone was then set to maintain 600°C, and power to the middle zone was increased. A similar transition took place when the lower corner of the tank indicated melt temperature. Finally, when indications of a complete melt were obtained, all controllers were set to maintain 600°C.

Late in the melt process, the thermocouple at the tank bottom lagged behind the one at the lower-side corner. Some erratic indications were seen, and then the temperature quickly rose to near the temperature of the lower-side thermocouple. This was caused by the melting of the last pieces of solid salt at the bottom of the tank. The sudden rise in temperature provided a clear indication that the melt was complete. This took place on March 19. In the following days, the tank temperature was stabilized at 600°C.

The transfer vessels were then warmed to 600°C, and the transfer piping, to 550°C. Salt transfer was performed on March 23. A valve on the gas outlet to the drain tank was closed, allowing the feed gas to pressurize the tank and initiate transfer. Thermocouples on the transfer line soon indicated an increase in temperature, as the warmer salt entered the line. After about 30 min, a conductivity probe inserted into the first transfer vessel indicated that the vessel was nearly full. Soon afterward, a temperature rise in the jumper between the first and second vessels indicated that salt was flowing into the second vessel. Similar indications were observed as the salt progressively flowed out of the second, third, and fourth vessels. In no case did the higher conductivity probe indicate salt above the desired fill level. As expected, the fifth vessel did not fill to the level of the lower conductivity probe before the drain tank was emptied. When all the transfer lines were clear, the pressure equalized across the transfer system.

The transfer system included gas flowmeters at the inlet to the drain tank and the outlet to the fifth transfer vessel. Although the controlling flowmeter at the inlet appeared to function well, the flowmeter at the outlet provided erratic data. A variable-resistance probe was inserted into one of the vessels in an attempt to provide continuous monitoring of the salt level over several inches near the intended final salt level. Although the output of this probe did rise somewhat as the vessel filled, the parameter was not quantitative. All other instrumentation performed as desired, and the transfer was complete in about 2.5 h.

Following the salt transfer, power was cut to all heaters. The salt vessels, piping, and empty drain tank were then allowed to cool. The poolmelt vessel was disconnected and moved to another facility for the test. Later, a visual examination of the interior revealed that the drain tank was empty. No problems were encountered in removing the jumpers between the tanks, and an internal examination of one of the transfer vessels again showed no problems. The four remaining salt vessels were removed from the coolant drain tank cell for storage.

POOLMELT DEMONSTRATION

The poolmelt demonstration had four objectives: (1) to determine the main operating parameters for the heating probe, including insertion depth and power as a function of time; (2) to estimate the melt profile from the thermal data and compare it with measured data; (3) to determine (or confirm) melt completion from thermal data and compare it with independent measures and heat balance estimates, and (4) to assess the suitability of the melting probe with respect to thermal performance, durability, and control characteristics.

System Description

These trials were conducted with a prototypical central melting probe and a tank containing MSRE coolant salt. This tank is roughly one-half the dimensions of the MSRE drain tanks but has internal thimble tubes positioned at the depth and radius that occur in the actual tanks. The basic poolmelt apparatus provides (1) blanket heaters on the tank wall, with two separately controlled heater zones; (2) a heating probe inserted through the central access flange and isolated by an elastomer bellows for vertical travel; (3) a 1/4-in. stainless steel dip tube inserted through the fill-line flange to measure the melt interface, sparge the tank, and take salt samples; and (4) provisions for inert-gas flow for purging the melt probe, the dip tube, and the bellows.

The tank used for the poolmelt trial contained about 350 kg of coolant salt and had Type K thermocouples arranged on the tank surface and in the thimbles. Eighteen thimble thermocouples were inserted into the interior of the three thimble tubes by means of three stringers containing six thermocouples spaced 4 in. apart. The stringers were assembled by DELTA-M Corporation by mounting Type K thermocouples off a central threaded rod with Inconel-strip springs to press the sensor tip against the thimble wall. Stringer thermocouples were attached to the Inconel strips with high-temperature cement.

The blanket heaters and control system were those used during the removal of salt from the coolant drain tank; however, the wiring was slightly different to permit two-zone control of the tank temperature. The probe, of double-pipe construction, provided a central sparge tube and an annular heating region. For this development work, only a 12-in. heated length was provided (in two 6-in. zones of 1.3 kW each). Consequently, the heated length was only one-half the entire salt depth. A nylon-reinforced neoprene bellows isolated the probe and linked it to the tank. Water-cooling coils attached to the central access flange kept the bellows cool. The probe was suspended from a framework, and a simple hand-operated chain hoist was used to control the probe position. With the exception of the upper portions of the heater probe, the dip tube, and the hoist, the entire apparatus was enclosed within a well-ventilated hood. Exhaust gases were routed to the radiochemical stack.

Results

To explore the effects of different operating parameters, the salt was melted twice. In the first trial the probe was inserted as rapidly as possible to ensure that melting could be effected in a rapid and practical

manner. The tank was stabilized at 400°C, the blanket heaters were switched to manual, and the melting probe elements were checked. The lower 6-in. element was set to 750°C, which is below the upper limit established by earlier tests to ensure burnout protection. At this temperature the lower element was fully inserted into the salt in about 1 h. After the lower element was immersed in the melt, the temperature rapidly dropped to ~600°C, and the full element power could not raise the probe temperature much above this level. A very similar behavior was observed when the upper element was inserted into the salt.

After 9 h of probe heating, the bottom of the probe was 3.5 in. from the bottom of the tank. This position was maintained for 10 h, after which time the probe was allowed to melt its way to the bottom and then pulled up 1 in. from the bottom for the remainder of the trial. The probe heating elements were run at full capacity for most of the 37 h required to melt the salt. Within the errors associated with the estimation of tank heat losses, this corresponds to the expected melt time using 120 cal/g as the heat of fusion and 0.57 cal/g-°C as the salt heat capacity.

The temperature response of the thimble and heating blanket thermocouples indicated when a melting front was passing a particular location. The passing of a front, as shown in Fig. 4, is marked by a change in the slope of the line indicating temperature response. Significant superheat (in excess of the 459°C melt temperature) is obvious only when the entire tank inventory is molten, after an elapsed time of 151 h.

The dip tube, the thimble thermocouples, and the tank sidewall thermocouples all indicated melting in a consistent pattern. Completion of melting was unmistakably indicated by the rapid rise in temperature above 450°C at the bottom of the tank, as was the case when the salt in the coolant salt drain tank was melted.

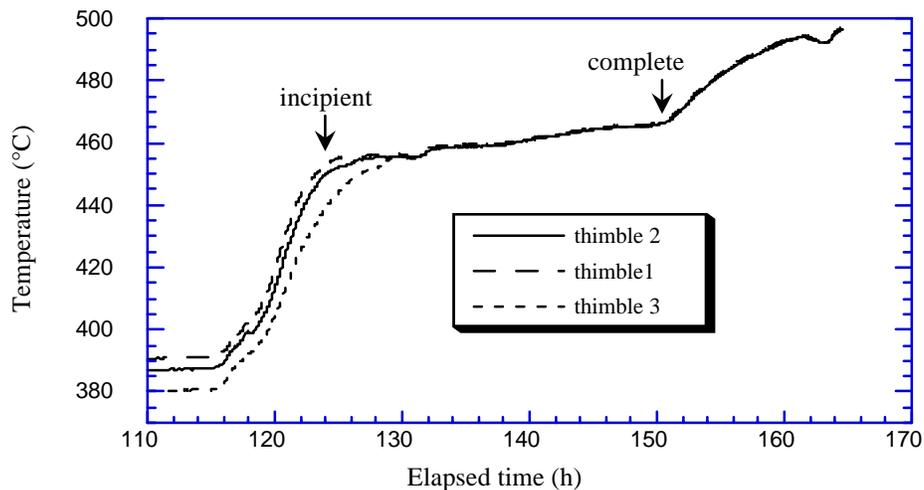


Fig. 4. Typical thimble temperature measurements.

In a second poolmelt trial, the probe was inserted at a lower temperature (650°C). This temperature is likely to be used in the fuel salt melt to provide further margin from local overheating in the probe plenum region. In this run, the probe was inserted to its full length in 6 h. In this second trial the salt was also melted in two stages: (1) first, with the probe inserted only to its heated length (12 in.) until the melt interfaces at the thimble and wall were below the probe, and (2) with complete immersion of the probe to within 1 in. of the bottom of the tank. The basic characteristics and consistency of the melt data are similar to those of the first trial. Some key features of the melt are worth noting. Even in this two-stage regime, a significant melting cavity was established and it is clear that at least a surface crust of salt remained long after the pool was well established. This “cavity” effect may have been caused by heat loss

through the relatively poorly insulated top of the vessel. When the melt interface progressed below the probe, the melting at the wall progressed faster than the melting at the thimbles. These differences in melt behavior did not pose any difficulty in safely melting the salt and following the melt progression.

In summary, we can conclude (1) that the prototype probe demonstrated basic suitability of design and performance and (2) that it is possible and practical to establish and follow a progressive melt generated from a central melting probe.

HYDROFLUORINATION DEMONSTRATION

The MSRE fuel salt is fluorine deficient due to the radiolysis that has occurred over the past 30 years. A process that restores fluorine is required to completely melt the salt while avoiding undesirable reduction of zirconium and uranium. This demonstration was performed to show that fluorine can be restored to the salt by hydrofluorination and that the process is practical and can be followed in a straightforward manner by analysis of the off-gas for HF or H₂.

System Description

The 800-g salt sample used in this trial was identical to the MSRE fuel salt except that it did not contain activation or fission products. A radiolytic damage of 0.24 meq/g-salt was induced by exposure of this salt to the intense gamma field in a spent-fuel element from the High Flux Isotope Reactor. This damage is somewhat greater than that expected to be present in the actual MSRE fuel salt (~0.15 meq/g-salt).

The hydrofluorination chamber was constructed of Monel. The 3-in.-OD × 6-in.-long monel insert from the irradiation capsule, containing the radiolyzed salt, was positioned inside the chamber with a nickel funnel insert to minimize salt splash to other parts of the container. Metered flows of Ar-4%H₂ and HF were directed down a 1/8-in.-OD nickel tube that could be raised or lowered through a compression fitting. Exhaust gas traveled up through an annulus outside the sparge tube and through a Fourier transform infrared (FTIR)-analyzer gas cell and an aqueous scrubber. Provisions for illumination and viewing of the salt were provided by two sapphire windows. The windows provided very useful feedback during the trial, but the quality of the image was not suitable for reporting purposes. Post-treatment photographs were taken to document the condition of the salt and container.

Results

The trial was conducted by establishing a standard Ar-4%H₂/HF flow mixture in the system at room temperature. This standard, 100 sccm Ar-4%H₂ and 4 sccm HF, was chosen because it was very noncorrosive toward the container yet afforded a practical means of restoring fluoride to the salt. After a stable HF concentration was established, the chamber was heated to a maximum wall temperature of 620°C.

The progress of chemical adjustment of the salt is shown in Fig. 5. During the initial heating a transient increase in the HF content of the exhaust gas occurred because the heating of surfaces (previously saturated with HF at a lower temperature) resulted in desorption of HF. Once the salt began to melt and the sparge tube was inserted, the HF concentration dropped rapidly to a value corresponding to consumption of 75% of the HF fed. This level of HF utilization was maintained for the next 18 h until the adjustment neared completion, the characteristic breakthrough curve developed, and the feed concentration was reestablished. Excellent correspondence of the FTIR results and the titration values was obtained. The number of equivalents of HF consumed during treatment was very close to that associated with the fluoride deficiency estimated to be in the radiolyzed salt (~0.2 equiv).

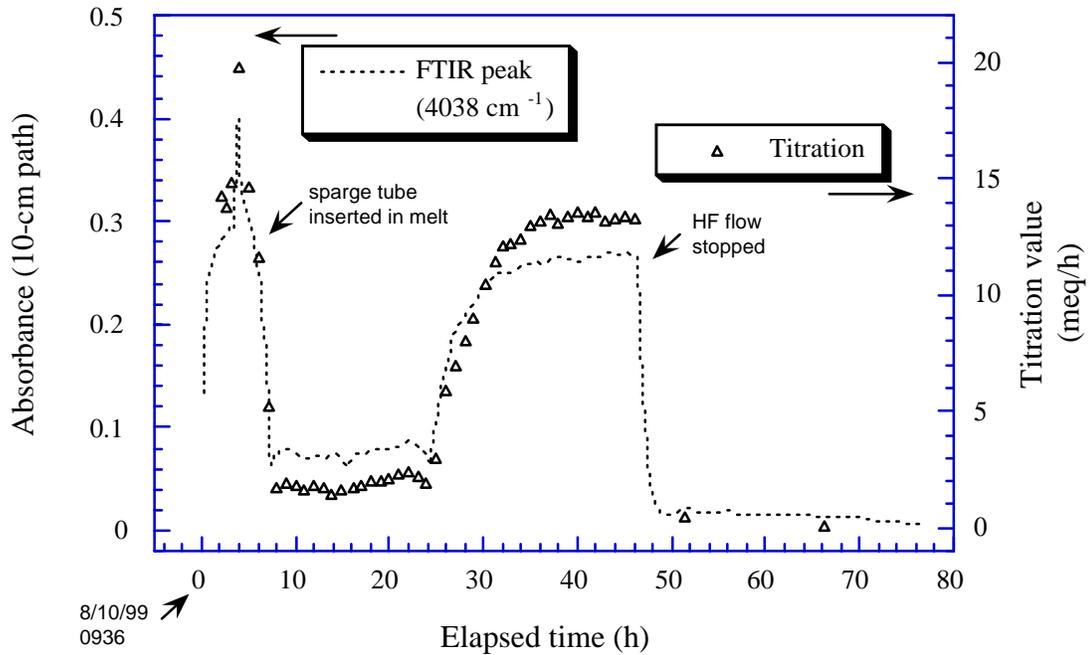


Fig. 5. Hydrofluorination results—exhaust gas analysis.

Examination of the solid salt after cooling showed that the final state of the salt is that of a complete and homogeneous melt. Black graphite deposits (remnants from the preparative crucibles) were seen on top of the salt boule. A superficial black film was also apparent on the side walls and, to a small extent, on the bottom. Because this black film dissolved completely in strong acid while the graphite deposits on top did not, the film was judged to be a mixture of reduced metals and salt. When the boule was cleaved, nearly all of the salt was of a uniform green appearance, demonstrating complete restoration of the salt chemistry. The empty salt container was found to be free from significant corrosion, and the metallic finish was marred only by a thin black film, which is either graphite or a small amount of metallic deposit.

Concentrations of corrosion products in the bulk salt were below detection limits of the analyses. The dark films at the side and bottom of the salt were found to contain about 500 ppm nickel, 2000 ppm copper, and 475 ppm iron. Because these features represented only a very minor fraction of the salt inventory (< 0.01%), the total quantity of corrosion products in the salt was small. In the bulk salt sample, the presence of lithium, beryllium, zirconium, and uranium was in the same proportion as in the original preparation.

CONCLUSIONS

These demonstrations provide confidence in the overall plan to safely melt and transfer the MSRE fuel and flush salts. They confirm the chemistry and provide data for use in flowsheet and procedure development, as well as in equipment design. They also provide operating experience that will be useful in preparation for the actual melting of the fuel and flush salts.