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ENVIRONMENTAL RESTORATION PROGRAM

Identification and Evaluation of Alternatives for the Disposition of Fluoride Fuel and Flush Salts from the Molten Salt Reactor Experiment at Oak Ridge National Laboratory, Oak Ridge, Tennessee

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ORNL/ER-380

Energy Systems Environmental Restoration Program

Identification and Evaluation of Alternatives for the Disposition of Fluoride Fuel and Flush Salts from the Molten Salt Reactor Experiment at Oak Ridge National Laboratory, Oak Ridge, Tennessee

F. J. Peretz

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PREFACE

This report on the *Identification and Evaluation of Alternatives for the Disposition of Fluoride Fuel and Flush Salts from the Molten Salt Reactor Experiment at Oak Ridge National Laboratory, Oak Ridge, Tennessee*, (ORNL/ER-380) was prepared as part of the Decontamination and Decommissioning activities taking place at Oak Ridge National Laboratory under the auspices of the Environmental Restoration Program. It was prepared under Work Breakdown Structure 1.4.12.6.2.01.05.06, Activity Data Sheet 3701, "ORNL Decontamination and Decommissioning Program" in support of the CERCLA feasibility study being prepared by Jacobs Engineering Group, Inc.

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ABBREVIATIONS

ANL-W	Argonne National Laboratory--West
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CEUSP	Consolidated Edison Uranium Solidification Project
CFR	<i>Code of Federal Regulations</i>
CH-TRU	contact-handled transuranic
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EIS	environmental impact statement
EPA	U.S. Environmental Protection Agency
FFA	Federal Facilities Agreement
GMODS	Glass Material Oxidation and Dissolution System
HEPA	high-efficiency particulate air
ICPP	Idaho Chemical Processing Plant
INEL	Idaho National Engineering Laboratory
MSBR	Molten Salt Breeder Reactor
MSRE	Molten Salt Reactor Experiment
MTR	Materials Test Reactor
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
RCRA	Resource Conservation and Recovery Act
RDF	Radiochemical Development Facility
RH-TRU	remote-handled transuranic
SRS	Savannah River Site
TDEC	Tennessee Department of Environment and Conservation
WIPP	Waste Isolation Pilot Plant
WTWBIR	WIPP Transuranic Waste Baseline Inventory Report

EXECUTIVE SUMMARY

This document presents an initial identification and evaluation of the alternatives for disposition of the fluoride fuel and flush salts stored in the drain tanks at the Molten Salt Reactor Experiment (MSRE) at Oak Ridge National Laboratory (ORNL). It will serve as a resource for the U.S. Department of Energy contractor preparing the feasibility study for this activity under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). This document will also facilitate further discussion on the range of credible alternatives, and the relative merits of alternatives, throughout the time that a final alternative is selected under the CERCLA process.

On the basis of the review prepared under this study, the following sequence of preferences was defined:

If reuse of the fuel and/or flush salts is a serious option, then it should be selected.

If *any* of the geologic disposal alternatives prove technically and programmatically implementable, every reasonable effort should be made to implement that alternative. In particular, efforts should be made to resolve the regulatory and programmatic obstacles to disposal in the Waste Isolation Pilot Plant (WIPP).

At the present time, only the interim storage option is likely to be implementable. It does provide adequate protection of human health and the environment, but at some time an ultimate disposition must be identified to end the cost of perpetual care and monitoring. Storage of fluorinated, stabilized salt can meet the quantitative requirements for disposal at WIPP or can serve as the feed for any of the other processes evaluated. Thus, interim storage is recommended as being consistent with ultimate disposition and being fully implementable at this time.

Permanent disposal of the salts in their drain tanks is not recommended. The long-lived actinides in the salt should be placed in geologic disposal; the penetrating radiation from fission products and uranium decay daughters will require that the waste be remote-handled. Specific scenarios for handling and disposition of the salt include a potential for the reusing the salts at Los Alamos National Laboratory; separating the uranium and chemically stabilizing the salt; calcining and possibly eventually vitrifying the salt at Idaho National Engineering Laboratory; blending the salt into the feed stream to the Defense Waste Processing Facility at the Savannah River Site; and constructing an electrorefining system or other new process at ORNL or at another site. Interim storage opportunities exist at any of the above sites.

Chapter 1 of this report presents background information on MSRE, the salts, and the methodology used to define and evaluate alternatives for the disposition of the MSRE fuel and flush salts. Chapter 2 identifies potential ultimate end points for the key contaminants in the salts. Chapter 3 summarizes the technologies available for removal, processing, and stabilization of the salt. The disposition alternatives are identified in Chap. 4 and evaluated in Chap. 5. Chapter 6 summarizes the key uncertainties identified during these evaluations and recommends actions to resolve the uncertainties.

1. OVERVIEW

1.1 OVERVIEW OF THE MOLTEN SALT REACTOR EXPERIMENT FUEL SALT DISPOSITION TASK

1.1.1 Facility Description

The Molten Salt Reactor Experiment (MSRE) is an 8 MW reactor that was operated at Oak Ridge National Laboratory (ORNL) from 1965 through 1969 as a demonstration of the technology needed to develop a commercial Molten Salt Breeder Reactor (Robertson 1965). The reactor used a unique liquid fuel, formed by dissolving UF_4 fuel in a carrier salt composed of a mixture of LiF , BeF_2 , and ZrF_4 . The fuel salt circulated through a reactor vessel, a fuel salt pump, and a primary heat exchanger at temperatures above 600°C (1112°F). In the reactor, the salt was forced through channels of graphite to provide the geometry and moderation necessary for a nuclear chain reaction. Heat was transferred from the fuel salt to the secondary coolant salt in the primary heat exchanger. The coolant salt is similar to the fuel salt, except that it contains only LiF (66%) and BeF_2 (34%). The coolant salt passed from the primary heat exchanger to an air-cooled radiator, a coolant salt pump, and then returned to the primary heat exchanger. Each of the salt loops was provided with drain tanks, located such that the salt could be drained out of either circuit by gravity. A single drain tank was provided for the nonradioactive coolant salt. Two drain tanks were provided for the fuel salt. The fuel salt drain tanks were provided with a system to remove the intense heat generated by radioactive decay immediately after an emergency reactor shutdown and fuel salt drain. A third drain tank connected to the fuel salt loop was provided for storing a batch of flush salt. This batch of salt, similar in composition to the coolant salt, was used to condition the fuel salt loop after it had been exposed to air and to flush the fuel salt loop of residual fuel salt and contaminants before accessing the reactor circuit for maintenance or experimental activities.

As seen in Figs. 1.1 and 1.2, the reactor circuit is located in a large cylindrical cell. The coolant circuit, including the coolant salt drain tank, is located to the south of the reactor cell. The two fuel salt drain tanks and the flush salt drain tank are located in a rectangular cell north of the reactor cell. The coolant salt circuit, including the salt-to-air radiator, is located south of the reactor cell. Blowers force outside air through the radiator and up the large diameter coolant stack attached to the south exterior wall of the building.

The design of the fuel salt drain tanks is shown in Fig. 1.3. The tanks were constructed of Hastelloy N (referred to as INOR-8 in the MSRE design documentation), as were all components that were in contact with molten salt. An array of heat transfer thimbles penetrates the head of the fuel salt drain tanks. Bayonets, attached to a steam drum assembly, are inserted into these thimbles. Cooling water was fed through a tube inside the bayonets and evaporated by the heat transferred out of the drain tank; steam was collected in the steam dome. The flush salt tank is similar, except that it does not have a cooling system. Each of the salt drain tanks was suspended in a furnace assembly with resistance heaters provided to maintain the salt above the solidus temperature. Each tank is sized to hold the entire inventory of fuel or flush salt, respectively. Thus, there is one redundant fuel salt tank. The drain tank cell (Fig. 1.4) is at a low elevation in the facility so that salt could drain by gravity from the reactor circuit into the tanks. A system of freeze valves, in which cooling air was blown across a flattened section of salt piping to form a plug of frozen salt, were used to isolate the reactor circuit from the drain tank system, the drain tanks from each other, and the drain tanks from the salt processing system. Salt was transferred back to the reactor circuit, or on to the salt processing facility, by freezing salt plugs in

Fig. 1.1. Arrangement of the principal components of the MSRE.

Fig. 1.2. Plan view of the MSRE facility.

Fig. 1.3. Sketch of an MSRE fuel drain tank.

1-5

Fig. 1.4. Cross-section through the MSRE drain tank cell and adjacent areas.

the appropriate freeze valves, closing valves in the off-gas system, and pressurizing the tank with helium. This forced salt through one of the dip legs reaching the bottom of the tank. The drain tanks are provided with a set of thermocouples on the side and bottom of the tank. In the case of the fuel salt drain tanks, an additional set of thermocouples is located in a vertical thimble that extends down into the salt. The tanks are suspended in the furnace assemblies from weigh cells. The tank wall is 0.5 in. thick. The thimbles are constructed of 1.5-in. Schedule 40 pipe. Each tank is provided with a 3 in. access pipe and flange at the top center. In the case of the fuel tanks, this pipe extends up through a gap in the center of the steam dome.

The salt processing facility was constructed in the fuel processing cell, just south of the drain tank cell. This process (Fig. 1.5) was used to remove oxides and corrosion products from the salt by sparging with a mixture of H_2 and HF and to remove UF_4 by oxidation to UF_6 with a F_2 gas sparge. The sparging operation took place in the fuel storage tank, which was sized to hold the entire inventory of fuel salt or flush salt with enough freeboard that salt carryover would not be a problem during gas sparging operations. In the fluorination configuration (depicted in Fig. 1.5), the sparge gas flowed through a high-temperature NaF trap to remove volatile fission products; a bank of NaF traps in the high bay to remove the uranium; a caustic scrubber to neutralize the excess fluorine; and an array of mist, high-efficiency particulate air (HEPA), and charcoal filters. Most of the filter system is located in the spare cell.

The reactor and drain tank cells were designed as a sealed containment system. Both are lined with stainless steel and are covered with two layers of shield blocks (Fig. 1.6). A stainless-steel seal pan between the two shield block layers is welded to the cell liner, completing the containment boundary. The cells are designed for remote maintenance (Blumberg and Hise 1968). A maintenance shield (Fig. 1.7) is used to access the cell. The shield consists of a frame and track assembly on which stationary and sliding concrete shield elements are placed. Some of the shield elements have rotating work plugs, with tool bushings and viewing ports. To place the shield, the appropriate upper shield blocks are removed and the seal pan is cut away to expose the lower shield block. The track and shield blocks are set up around the lower block, and the operators move to the shielded remote maintenance control room (or a similar safe area). The lower block is lifted out through the opening in the frame with the building crane. A motor is used to move the sliding shield element over the gap; this allows the operators to reenter the high bay. The shield elements are then positioned so that tools can reach the component being worked on. The shield was also used to access the drain tanks by placing a module through one of the shield ports that couples onto the flange on top of the drain tank. The arrangement that added most of the ^{233}U to the fuel carrier salt is shown in Fig. 1.8.

1.1.2 Operating History

Production of fluoride mixtures for the flush and coolant salts began in March 1964 and was completed in September (Shaffer 1971). These salts were used in the checkout of reactor and coolant systems, and the flush salt was purified by using the MSRE fuel processing system after initial circulation in the reactor circuit (Lindauer 1969). Processing of the fuel carrier salt began in November 1964 and was completed in March 1965. The original uranium charge, consisting of 30% ^{235}U and 70% ^{238}U , was then added to the fuel carrier salt. Although the design documents indicated that salt would be added from a station in the high bay and through components of the fuel processing system, it was actually added directly into the drain tanks from an addition station set up on top of the drain cell shield blocks. The tanks were hot when salt was melted in furnaces and fed into the tanks. During the operations phase of the MSRE, the salts were maintained in the molten state.

Fig. 1.5. Flowsheet of the MSRE salt processing system.

Unclassified
ORNL-DWG 64-2502

Fig. 1.6. Shield block arrangement on top of the drain tank cell.

Fig. 1.7. Typical plan view of setup of the maintenance shield.

Fig. 1.8. Arrangement of the equipment used to add ^{233}U directly into an MSRE fuel drain tank.

The reactor achieved initial criticality on June 1, 1965, and reached full power early in 1966. In 1968, the initial charge of uranium was stripped out of the fuel and flush salts by using the fluoride volatility process (Lindauer 1969). Residual uranium was 7 ppm in the flush salt and 26 ppm in the fuel salt. Uranium recovered from the salt was sent back to the uranium enrichment facility in Portsmouth, Ohio. Each batch of salt was then sparged with an HF/H₂ mixture to precipitate corrosion products that resulted from the fluorination process, and the salt was filtered as it was returned to the drain tanks. A second fuel charge, consisting of ~80% ²³³U and 20% ²³⁵U, was then used for the balance of reactor operations. The uranium concentrate salt was again added directly into one of the drain tanks by using the equipment depicted in Fig. 1.8. Late in the operating campaign, the fuel was enriched with relatively small quantities of ²³⁹Pu (as PuF₃). In December 1969, reactor operation was terminated, and the fuel, flush, and coolant salts were drained into their respective drain tanks. The fuel salt was divided between the two fuel salt drain tanks. As the fuel salt was drained, activity was observed in the drain tank cell atmosphere. This activity was traced to a minor leak in freeze valve 105, leading to fuel drain tank 2. All of the salts were allowed to freeze, but the fuel salt was held at an elevated temperature for about a year to control the effects of radiolysis in the salt. This is the only time the salts were allowed to freeze in the MSRE drain tanks, and they have not been melted since. Throughout the operation of MSRE, a detailed record of the chemical behavior of the salts was maintained, and a summary of the chemical aspects of MSRE operation was prepared following the postoperation examination period (Thoma 1971).

1.1.3 Postoperation History

In the 2 years that followed reactor shutdown, a number of activities were performed to evaluate the performance of materials used to construct the reactor and to improve the containment of the salts stored in the drain tanks (Rosenthal et al. 1971). The latter included the isolation of salt and off-gas lines between the drain tank cell and the reactor system and removal of the failed freeze valve (and adjacent freeze valve 106) for examination. Mechanical devices were used to press copper plugs into the end of the severed salt lines. These plugs were also provided with leak detection lines.

During a series of experiments to test the chemical compatibility of metal and graphite materials with the MSRE salts, the production of fluorine gas was observed (Briggs et al. 1964). It was found that irradiation of solid salt produces fluorine radicals, which can then combine to form F₂ and diffuse to the salt surface. Some of the irradiation experiments were reconfigured to explore this phenomena. It was found that lower temperatures favored the formation of F₂; whereas at higher solid salt temperatures, the back reaction of fluorine with the lithium and beryllium from which it had been dissociated was favored. No uranium was observed in the gas above the salt. To prevent the accumulation of fluorine in the drain tanks after the reactor was shut down and the salts were solidified, a procedure was instituted for an annual annealing of the fuel salt to prevent the release of radiolytic fluorine from the fuel salt (Guymon 1971). In the annealing operation, the salt was heated with the furnace heaters to a temperature above 149°C (300°F), but well below the melting temperature, and held at this temperature for about a week.

Following reactor shutdown, the reactor operations crew was disbanded, and monitoring of key MSRE parameters was established at the central ORNL waste management center. A number of studies addressed the disposition of the fuel and flush salts and the decommissioning of the MSRE facility. Final disposition of the fuel and flush salts was put on hold pending the opening of a geologic repository. In 1985, a review was performed of the issues associated with extended storage of the fuel and flush salts in their drain tanks (Notz 1985). This review extended the radionuclide decay models out to repository time frames and included a review of fluorine production predictions. Additional salt irradiation experiments were carried out to provide a better basis for fluorine generation predictions (Toth and Felker 1990).

Over the years, indications were noted of migration of radioactive materials in the piping connected to the drain tank cell and the off-gas system. In particular, increased radiation levels were observed in the north electrical service area adjacent to the drain tank cell. In addition to electrical penetrations, this service area houses components of the helium addition system that had been used to pressurize the drain tanks for salt transfers. Maintenance activities on the off-gas system indicated the presence of alpha activity. Gamma scans indicated the presence of ^{208}Tl , a product of the decay of ^{232}U . The annual annealing procedure was halted after December 1989 in part because of concerns that this procedure may have aided the migration of radioactive material out of the drain tank cell.

In March 1994, a gas sample was taken from the auxiliary off-gas system, which was connected to the gas space above the drain tanks. Expectations were that fluorine might be detected in part per million quantities. An analysis of the gas (Table 1.1) revealed that fluorine composed about half of the gas sample (Williams et al. 1996). Even more unexpectedly, UF_6 was a major component of the gas stream. At a partial pressure of 69 mm Hg, the amount of UF_6 identified was just below the 79 mm Hg saturation pressure of UF_6 at the sampling temperature of 21°C (69.8°F).

Table 1.1. Results from analysis of Molten Salt Reactor Experiment off-gas samples taken in 1994

Component	Partial pressure (mm Hg)
F_2	350
Inerts	305
UF_6	69
MoF_6	10
CF_4	5
HF	0.74
N-F compounds	trace

The auxiliary off-gas system was in communication with the vapor space above the drain tanks; this provided a migration path for UF_6 and F_2 that had been liberated from the salt. A detailed review of the off-gas system (Fig. 1.9) was undertaken to identify all locations to which uranium might have migrated. It was also recognized that the auxiliary charcoal bed was in communication with the drain tanks because valve 561 had failed in the open position. Radiation and thermal surveys were used to identify a uranium deposit in the auxiliary charcoal bed (Fig. 1.10). These data indicated that 2.6 kg of uranium was deposited in a 1 ft section of bed near the inlet pipe. It was also discovered that reactions of fluorine with carbon at low temperatures can result in the formation of potentially reactive carbon-fluorine compounds. Laboratory investigations determined the likely stoichiometry of these compounds to be that of C_2F . On the basis of volume estimates of the piping and vessels in communication with the drain tanks and the measured concentration of UF_6 in the off-gas, at least 1.8 kg of uranium is believed to exist as vapor in the vessels and piping. Because the measured UF_6 concentration is so close to the saturation pressure, solid deposits of UF_6 may exist in the off-gas system. Thus, the amount of uranium present in the system could exceed 1.8 kg.

Fig. 1.9. Principal components of the MSRE off-gas system.

Fig. 1.10. Location of the uranium deposit in the auxiliary charcoal bed.

1.1.4 MSRE Remediation Project

1.1.4.1 Organization of the MSRE Remediation Project

Following this discovery, the MSRE Remediation Project was initiated to assess, control, and reverse the consequences of the migration of uranium. These activities are being planned and executed according to the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). In November 1989, the U.S. Department of Energy (DOE) Oak Ridge Reservation was placed on the National Priorities List, and a Federal Facilities Agreement (FFA) was established between DOE, the U.S. Environmental Protection Agency (EPA), and the Tennessee Department of Environment and Conservation (TDEC). A 1995 revision to the FFA established that the MSRE Remediation Project is to be conducted and documented in accordance with the requirements of CERCLA. This ensures that a risk-based process is used to identify appropriate actions and that both the state of Tennessee and EPA Region IV are involved in the decision making process. The MSRE Remediation Project is organized into three CERCLA projects. The first of these, a time-critical removal action, is further divided into two sets of activities (Lingle 1995). The first, called interim corrective measures, addressed various aspects of containment, criticality control, and protection against chemical reactions. This phase of the project, discussed further in Sect. 1.1.4.2, is now complete. The second phase is trapping uranium and fluorine in the off-gas system, converting the uranium to oxide, and placing it in storage. These activities are discussed in Sect. 1.1.4.3.

The second CERCLA project, classified as a non-time critical removal action,^{*} will remove the deposit of uranium that has been trapped on the auxiliary charcoal bed. It is summarized in Sect. 1.1.4.4.

The third CERCLA project is the fuel salt disposition task, which is the subject of this report. The fuel salt disposition task is classified as an interim remedial action. This classification defines the CERCLA documentation that must be prepared before conducting remedial activities. In particular, a feasibility study is being prepared to define the risk and the remediation goals, to identify the remediation alternatives, to screen potential remediation technologies, and to conduct an overall evaluation of the alternatives. The feasibility study will be followed by a proposed plan, which details the specific activities to be used to conduct the task. The selection process will culminate in the issuing of a Record of Decision, agreed to by all of the parties in the Oak Ridge FFA.

Uranium left in the MSRE following reactor shutdown also has been included within the scope of the Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 94-1, which addresses material left "in-pipeline" following shutdown of nuclear facilities without complete decommissioning activities. The implementation plan for this recommendation carries the milestone that the salts will be removed from the drain tanks by May 2002. The implementation plan also states that the uranium will be separated from the salt and converted into an oxide form for long-term storage. Completion of these activities is contingent on the remedial action alternative documented in the CERCLA Record of Decision.

^{*}"Action Memorandum for Uranium Deposit Removal at the Molten Salt Reactor Experiment, Oak Ridge National Laboratory, Oak Ridge, Tennessee," June 1996.

1.1.4.2 Interim corrective measures

At the time the uranium deposit was discovered in the auxiliary charcoal bed, the concrete charcoal bed cell in which the main and auxiliary charcoal beds are located was flooded with water. This water was removed to keep the potential neutron moderator out of the charcoal beds. Water sources throughout the facility were either removed or isolated from potential uranium deposits to prevent a nuclear criticality.

Reaction of the carbon-fluorine compounds in the charcoal bed cell could lead to a significant release of energy that could rupture the auxiliary charcoal bed vessel and generate a pressure in the cell to lift the concrete cell lid and disperse radioactive materials into the environment. To prevent this, a lid restraint ring was installed. The cell was inerted with CO_2 so that, should the carbon-fluorine compounds react, the burning of charcoal in air will not add to the internal pressure in the cell.

Valve 561, which had previously failed in the open condition, was repaired and is now closed. This isolates the auxiliary charcoal bed from the drain tanks. New, calibrated pressure transmitters were installed on the helium lines leading from the north electric service area to the two fuel drain tanks (PT 572 and PT 574 shown in Fig. 1.9) and on the off-gas line downstream of the auxiliary charcoal bed (PT 562). Along with a transmitter installed previously upstream of the charcoal bed (PT 518) and another installed as part of the reactive gas removal system (PT 542), these instruments allow the trending of pressures throughout the system. Readings are as high as 10 psig and indicate that plugs exist in the system between the drain tanks and the reactive gas removal system and between the reactive gas removal system and the branch of the off-gas system ahead of the charcoal bed cell. Before closing valve 561, it was observed that readings upstream and downstream of the charcoal bed cell (PT 518 and PT 562) were identical. A new, computerized data collection system was installed to record these pressures, along with temperatures and other key data points throughout the system (including drain tank and drain tank cell temperatures). A general review of facility data collected over the past few years was performed and documented (Shor 1996).

A detailed survey of the rest of the facility was performed to identify any other potential migration paths for uranium or other radionuclides. Gamma radiation from ^{208}Tl , a decay product of ^{232}U , was identified in the fuel processing cell and a salt distillation experiment located in the spare cell. Apparently, the freeze valves on the salt lines do not provide a gas-tight seal, allowing migration of the pressurized gas above the tanks into these areas. An analysis of data collected in these cells indicated that the total amount of uranium present is <700 g and possibly as little as 20 g (DeVore et al. 1996).

1.1.4.3 Reactive gas removal

The sampler-enricher hardware, used during reactor operations to withdraw salt samples for analysis or to add enriching salt to a well-mixed location in the pump bowl, also provides an enclosed access point to line 542 in the off-gas system. A glove box facility has been attached to the sampler-enricher enclosure to allow the withdrawal of gas into a trapping system. The major components of this system are shown in Fig. 1.11. A sodium fluoride trap is used to remove UF_6 from the MSRE gas, followed by an alumina trap for the removal of fluorine. A molecular sieve trap is used to trap residual moisture, possibly containing HF from the alumina trap, and to prevent corrosion of other system components. Gas from the traps is sent to holdup tanks for the decay of ^{220}Rn and its daughters before it is discharged into the MSRE ventilation system through fluorine-resistant HEPA filters. A Fourier-transform infrared spectrometer system is used to monitor UF_6 concentrations between the NaF and alumina traps and at the outlet of the trapping system. Thermocouple data and gamma transmission measurements are used to monitor the loading of the traps. As of the writing of this document, the

Fig. 1.11. Flowsheet of the reactive gas removal system.

reactive gas removal system is nearing operation. When the uranium has been trapped on the NaF, it will be placed in temporary storage until a conversion facility is constructed. This facility will be used to convert the UF_6 absorbed on the NaF to U_3O_8 for long term storage at ORNL. A report recommending the uranium conversion flowsheet has been written (Advanced Integrated Management Services 1995), but design of the conversion facility has not yet begun.

The reactive gas removal system will be operated in batch mode by evacuating the holdup tanks downstream of the traps to a pressure that will allow a predetermined amount of gas to flow through the traps. As batches of process gas are removed, the off-gas system will drop below atmospheric pressure. Eventually, the off-gas system will be evacuated and backfilled with helium. Initial operation of the reactive gas removal system will remove process gas from that part of the off-gas system that is not in some way isolated from line 542. As noted earlier, pressure differentials as high as 8 psi occur between segments of the off-gas system, indicating that the piping is plugged in some way. Because the UF_6 partial pressure is so near saturation, the system may be plugged with solid UF_6 . If so, evacuating the system will cause the plugs to sublime, and access may be gained to the rest of the system. If not, jumper lines may be installed to access other parts of the system. Line extensions may also be installed to remove gas from the salt processing system and distillation experiment in the fuel processing and spare cells.

1.1.4.4 Charcoal bed uranium deposit removal

Studies are now underway to establish the performance of an approach to passivate carbon-fluorine compounds by flowing a reactive gas through the auxiliary charcoal bed. If the studies yield a gaseous treatment approach, little additional equipment will be required for the passivation operation, and risks during other operations will be reduced.

After the charcoal is removed, the container will be transferred to a hot cell where the contents will be divided into several containers suitable for temporary storage. The charcoal will be placed in interim storage until the uranium conversion facility is available and will then be converted from UF_4 to U_3O_8 for long-term storage. Conversion is expected to take place in the same facility used to convert the UF_6 collected by the reactive gas removal system, with appropriate modifications made to the head-end of the process.

1.1.5 Fuel and Flush Salt Disposition Task

The fuel and flush salt disposition task addresses the activities needed to place these salts, and the key contaminants in the salts, in an appropriate condition that provides for the long-term protection of human health and the environment. The primary objectives of the fuel salt disposition task are to reduce risk as identified in the CERCLA process and to stabilize material identified as part of DNFSB Recommendation 94-1. Secondary objectives are to reduce or eliminate maintenance and surveillance costs associated with storing the salts in MSRE and to allow the final decommissioning of the MSRE facility to proceed as soon as funding is available for the task. The key contaminants include fissile materials, radioactive materials, and any chemicals in the salts or salt by-products that are identified as posing a significant risk to human health and the environment.

The scope of this task clearly includes the salt in the fuel and flush drain tanks. The evaluation currently underway will establish the extent to which residual salt in those MSRE systems that have contained salt are in the scope of this task, including residual salt left in the drain tanks after removal. This task does not include the ultimate decommissioning of the drain tank cell or of MSRE as a whole. Locations of residual salt will be defined, and recommendations will be made on whether residual salt

in the reactor, drain tank, or salt processing and experiment systems will be removed and disposed of in this phase or as part of the ultimate facility decommissioning.

This task will assess whether a truly permanent disposition can be achieved in the near term. Ideally, the salts and the key contaminants in the salts should be placed in an appropriate permanent disposal site or should be made available for productive reuse. If it is not possible to commit to permanent disposal at this time, interim storage must be shown to provide adequate protection to human health and the environment. Definition of credible end points is discussed in Chap. 2.

At the start of salt disposition operations, the reactive gas removal system will have purged out the off-gas system, and the amount of uranium and fluorine removed from the off-gas system will be known. In the course of evacuating the off-gas system, which includes the upper part of the drain tanks themselves, the integrity of the system will become better defined. Significant leaks will be identified if the system cannot be fully evacuated. Plugs in the off-gas system will be identified and likely removed, and the operating condition of other valves in the system (such as the off-gas system valves in the drain tanks) may be established. The last pressure transducer in the north electric service area, attached to the helium line leading to the flush salt drain tank, will be replaced. The charcoal bed deposit removal operation will also be well underway, if not completed. The amount of uranium and fluorine in the charcoal bed should be quantified. Even if operations at the charcoal bed cell are not complete, they are physically isolated from activities at the drain tank and salt processing cells.

This report is part of the preparation of a CERCLA Feasibility Study. The CERCLA document is scheduled to be transmitted to TDEC and EPA Region IV at the end of February 1997. A conceptual design of the recommended alternative will be prepared next and will serve both as the basis for the CERCLA Proposed Plan and the planning base budget for the project. Studies into the behavior of irradiated salt have also begun and will continue into next year. Work to access the drain tank cell, and possibly inspect the interior of a fuel salt drain tank, will also begin next year. Assuming the salt is to be removed, current plans call for removal operations to be completed by 2002, and separation, stabilization, and storage activities to be completed in the following year.

1.2 CHARACTERIZATION OF THE MSRE FUEL AND FLUSH SALTS

1.2.1 Inventory and Composition of the Fuel and Flush Salt

The coolant and flush salts were initially prepared as 66 mol % ^7LiF and 34 mol % BeF_2 , using isotopically pure ^7Li . In the case of the coolant salt, no changes to the composition occurred during reactor operation. Although some contamination with tritium is likely as a result of diffusion from the fuel salt across the hot heat exchanger tubes, this salt remains as a stable, largely nonradioactive solid in the coolant salt drain tank.

The carrier salt for the fuel was initially prepared as 65 mol % ^7LiF , 30 mol % BeF_2 , and 5 mol % ZrF_4 . Zirconium fluoride was added to the fuel salt so that if the salt became contaminated with oxygen-containing contaminants (e.g., water or oxygen), zirconium oxides would precipitate ahead of uranium oxides. Enough zirconium was added so that the precipitate would be observed before precipitation of uranium began. Fuel was added to the carrier salt as a 73 mol % ^7LiF - 27 mol % UF_4 low-melting eutectic enriching salt. The bulk of the fuel was added directly into the molten carrier salt in one of the drain tanks. Final approach to criticality was made by adding small batches of enriching salt to the fuel and carrier salt using the sampler-enricher, while the salt was circulating through the reactor. The initial ^{235}U fuel charge was diluted with about 70% ^{238}U to increase the amount of uranium in the salt until

experience was gained with maintaining chemical control of the system, especially with respect to maintaining the desired UF_3/UF_4 ratio. The total mass of uranium in the initial charge was about 220 kg.

The composition of the fuel salt did not remain constant. The quantity of uranium changed as fuel was burned and additional enriching salt was added. Enriching salt also added small amounts of LiF to the system. Plutonium was produced by transmutation of ^{238}U . Each time the system was opened for maintenance, flush salt was circulated through the reactor circuit before the fuel salt was returned. It was estimated that about 20 kg of salt remained in the reactor circuit following a drain; this amount of fuel salt was lost to the flush salt and the same amount of flush salt was added to the fuel salt each time the system was opened.

In 1968, the initial charge of uranium was removed by fluorination, down to 26 ppm uranium. A second charge of uranium, about 80% ^{233}U and 20% ^{235}U , was then added. By this time it had been determined that uranium chemistry control was not a major concern, and no ^{238}U diluent was used. The total charge of uranium used for ^{233}U operations was about 40 kg. Again, burn up, additions of enriching salt, and cross-contamination with flush salt contributed to minor changes in salt composition. Late in the ^{233}U campaign, enriching salt containing $^{239}\text{PuF}_3$ was used to demonstrate reactor operation using that isotope.

Changes in the composition of the flush salt are similar to those in the fuel salt, except that burn up and the addition of enriching salt do not apply. Seven cross-transfers with fuel salt occurred during ^{235}U operations. The flush salt was fluorinated in 1968, and then returned to its drain tank with a heel of 7 ppm uranium. Two more cross-transfers took place under ^{233}U operations. Thus, the fraction of uranium that is ^{235}U is greater in the flush salt than it is in the fuel salt.

Throughout reactor operations, a meticulous sampling and analysis program tracked both the fuel and flush salts. Data from this program is summarized in Thoma (1971) and has been reviewed by Williams et al. (1996). The latter includes estimates of the effects of cross-contamination of the flush salt each time the reactor was opened for maintenance.

The final mechanism that changed the composition of the fuel salt is the production of F_2 and UF_6 by radiolysis during the time the salt was stored as a radioactive solid. Because the amount of UF_6 present in the off-gas system (especially the amount that may be present as solid deposits) and in the auxiliary charcoal bed is only approximately known, this represents the major uncertainty in the present composition of the fuel salt. It is assumed that loss of uranium from stored salt is an issue for the fuel salt only. However, it is also possible that the flush salt could contain deposited UF_6 on the salt surface that migrated over from the fuel salt. The current estimates of the inventory and composition of the fuel and flush salts stored in the drain tanks are given in Tables 1.2 and 1.3.

1.2.2 Fissile Material Inventory

As noted in the previous section, fissile material inventories were meticulously tracked by a program of sampling and analysis throughout reactor operations. Thus, inventories in the fuel and flush salt discharged into the drain tanks in December 1969 were very well documented. The major uncertainty is the amount of UF_6 that has left the fuel salt as a result of radiolysis. The fissile material inventories in the fuel and flush tanks, both with and without the migration of 4.4 kg of uranium from the fuel salt, are shown in Table 1.4.

Table 1.2. Inventory of salt stored in the fuel and flush drain tanks

Tank	Mass (kg) ^a	Volume (m ³) ^a	Density (g/mL at 26°C)
<i>Fuel salt</i>			
Fuel salt drain tank 1	2479	1.00	2.48
Fuel salt drain tank 2	2171	0.88	2.48
Total fuel salt in drain tanks	4650	1.88	
<i>Flush salt</i>			
Flush salt drain tank	4265	1.92	2.22

^aMass and volume estimates that best correspond to process history.

Table 1.3. Composition of the fuel and flush salts

	Fuel salt	Flush salt
<i>Current salt composition, mol %</i>		
LiF	64.5	65.9
BeF ₂	30.4	33.9
ZrF ₄	4.9	0.18
<i>Mass of fissile elements in salt, kg</i>		
Uranium	<33.2 ^a	0.5
Plutonium	.724	.013
<i>Current distribution of fissile element isotopes, wt %</i>		
²³² U	160 ppm	75 ppm
²³³ U	83.92	39.4
²³⁴ U	7.48	3.6
²³⁵ U	2.56	17.4
²³⁶ U	0.104	0.245
²³⁸ U	5.94	39.4
²³⁹ Pu	90.1	94.7
²⁴⁰ Pu	9.52	4.8
other Pu	0.35	0.50

^aAssumes that at least 1.8 kg of uranium has migrated to the off-gas system, and at least 2.6 kg of uranium is loaded onto the auxiliary charcoal bed.

A summary of key criticality safety parameters, including the "always safe" mass, is given in Table 1.5. The fuel salt, of course, contains sufficient ²³³U to achieve criticality. The total mass of ²³⁵U and ²³⁹Pu also exceeds the always safe mass. In evaluating criticality safety, the combined effects of all fissionable isotopes must be considered. If all uranium is removed from the fuel salt, the 0.65 kg of ²³⁹Pu is still above the always safe mass. However, any further division of the fuel salt (such as into the two drain tanks) results in a ²³⁹Pu inventory below the always safe mass. In the case of the flush salt, the sum of ²³³U, ²³⁵U, and ²³⁹Pu is about 0.3 kg. This is well below the always safe mass for any of the three isotopes, and criticality is not an issue with the flush salt unless a significant quantity of uranium is found to have migrated over from the fuel salt.

Table 1.4. Mass of uranium and plutonium in fuel and flush salt, kg

Isotope	Assuming no losses			Assuming 4.4 kg U lost from fuel salt ^a		
	Mass in fuel salt	Mass in flush salt	Total mass	Mass in fuel salt	Mass in drain tank 1	Mass in drain tank 2
Total U	37.1	0.5	37.6	32.7	17.4	15.3
²³² U	^b					
²³³ U	31.1	0.2	31.3	27.4	14.6	12.8
²³⁴ U	2.8	0.02	2.8	2.4	1.3	1.1
²³⁵ U	1.0	0.09	1.0	0.84	0.45	0.39
²³⁶ U	0.04	0.001	0.04	0.03	0.02	0.02
²³⁸ U	2.2	0.2	2.4	1.9	1.0	0.9
Total Pu	0.72	0.013	0.74	0.72	0.39	0.34
²³⁹ Pu	0.65	0.013	0.66	0.65	0.35	0.30
²⁴⁰ Pu	0.069	0.0006	0.070	0.069	0.037	0.032
Other Pu	0.003	0.0001	0.003	0.003	0.001	0.001

^aBased on transport of 2.6 kg to the auxiliary charcoal bed and presence of 1.8 kg as UF₆ vapor in the off-gas piping and vessels.

^bAs of 1995, there was 160 ppm total uranium in the fuel salt and 75 ppm total uranium in the flush salt. The ²³²U/²³³U ratio is assumed to be the same in both the fuel and flush salts.

Table 1.5. Some key criticality safety parameters for fissionable isotopes present in the MSRE salt^a

	²³³ U	²³⁵ U	²³⁹ Pu
"Always safe" mass	500 g	700 g	450 g
Solid metal sphere, reflected with water	6 kg		
Aqueous solution of UO ₂ F ₂ or Pu(NO ₃) ₄	540 g	760 g	480 g
Safe diameter for solution of UO ₂ F ₂ or Pu(NO ₃) ₄	10.5 cm	13.7 cm	15.4 cm

^aSource: ANSI/ANS-8.1

Later in this document, a package size that divides the fuel and flush salt into 24 packages will be considered. A package containing fuel salt (assuming 4.4 kg lost from the total fuel salt inventory) would contain about 1.2 kg of ²³³U, 36 g of ²³⁵U, and 27 g of ²³⁹Pu. Only the ²³³U would raise a criticality concern, even if these packages are grouped in sets of three. Even without uranium separation, the 8 g of ²³³U in a flush salt package would be of no concern.

1.2.3 Radionuclide Inventory

Fission product inventories have been estimated using computer codes that track burn up and decay, especially the ORIGEN code. Decay products from uranium and transuranic isotopes are tracked using the fissile material analyses above and computer codes to track decay. Transfers of radionuclides between the fuel and flush salts are tracked in the same way as transfers of fissile material, and fissile material analysis provides supporting information for estimates of material transfers between the salts. Because the MSRE was a fluid-fueled reactor, volatile fission products were not retained in the fuel. Initial estimates of the fission product inventory considered the transport of noble gases, iodine, and other volatile elements to the off-gas system. Since in many cases these transport mechanisms can only

be estimated, an additional uncertainty is introduced to inventory estimates for radionuclides with volatile precursors. In some cases, measured data was available to compare against predictions (Williams et al. 1996).

Table 1.6 lists the half-life and inventory of those fission and activation products that are present in quantities greater than 0.1 Ci, as of 30 years after reactor shutdown (about the beginning of the year 2000). It is seen that the inventory is dominated by ^{90}Sr , ^{137}Cs , and their daughter isotopes. There will be a total of 24,400 Ci of fission and activation product isotopes at the start of the year 2000.

Table 1.6. Inventory of fission and activation product isotopes^a

Isotope	Half life	Curies	Inventory in fuel salt (98.3%)	Inventory in flush salt (1.7%)
^{90}Sr	28.5 y	6,670	6,557	113
^{90}Y	2.7 d	6,670	6,557	113
^{137}Cs	30 y	5,600	5,505	95
$^{137\text{m}}\text{Ba}$	2.6 m	5,290	5,200	90
^{151}Sm	90 y	117	115	2
^{147}Pm	2.62 y	13.4	13.2	0.2
^{155}Eu	4.96 y	4.4	4.3	0.1
^{154}Eu	8.8 y	3.1	3.0	0.1
^{152}Eu	13.3 y	1.1	1.1	0.0
^{99}Tc	2.1×10^5 y	0.5	0.5	0.0
^{125}Sb	2.73 y	0.3	0.3	0.0
^{93}Zr	1.5×10^6 y	0.3	0.3	0.0
Total		24,400	23,985	415

^aBased on decay to December 1999.

Actinide radionuclide inventories are dominated by the ^{232}U and ^{233}U decay chains and a few other key isotopes. The ^{232}U and ^{233}U decay chains are shown in Fig. 1.12. The ^{232}U chain is a single chain until near the end, where it takes two paths to the end point of ^{208}Pb . One of these branches includes ^{208}Tl , which emits a distinctive 2.6 MeV gamma. The ^{232}U chain also includes ^{220}Rn , a gaseous isotope with a 56 s half-life. The ^{233}U chain is a bit more complex, but the two branches have yields of only 1% and 2%. Thus, only the main chain contributes isotopes with activities near 1 Ci at the present time. Radon is only present in the 1% branch, and thallium in the 2% branch. The parent uranium isotope for the ^{232}U chain has a 70 year half-life, and the thorium daughter has only a 1.9 year half-life. Thus, this chain of daughter isotopes is already in equilibrium with the parent, and is decaying with the half-life of the parent. The parent uranium isotope for the ^{233}U chain has a 1.6×10^5 year half-life, and its thorium daughter has a half-life of 7,300 years. Thus, the thorium daughter has yet to build to equilibrium, and decay of the parent is not noticeable. Daughters of the ^{229}Th daughter are short-lived, and are in equilibrium with ^{229}Th . This daughter chain is only radiologically significant at present because of the relatively large quantity of the ^{233}U parent in the salt. Each of the other uranium and transuranic isotopes decays to another long-lived isotope, and their daughter chains are not radiologically significant compared to ^{232}U and ^{233}U . The inventory of the significant actinide isotopes is shown in Table 1.7.

Table 1.8 lists those radionuclides present in significant quantities in the salt along with a general factor for dose at 1 m from an unshielded point source of 1 Ci. It also lists the activity of each nuclide in a postulated package, in which the fuel and flush salts are each divided into 24 packages. The dose

Fig. 1.12. Decay chains for ^{232}U and ^{233}U .

at 1 m from an unshielded point source is then summarized for the activity in a fuel salt package and a flush salt package. It is seen that the external dose is dominated by ^{137}Cs . The ^{208}Tl daughter from ^{232}U decay is also a significant contributor, and because of its higher energy gamma, is more difficult to shield. These values indicate that, without significant shielding, a fuel salt package will exceed 200 mrem/h at the surface and will be classified as remote-handled. However, a flush salt package (possibly with minor shielding beyond the thickness of the container wall) is likely to be a contact-handled package.

Table 1.7. Inventory of actinide isotopes^a

Isotope	Half life	Curies	Activity in fuel salt (Ci)	Activity in flush salt (Ci)
<i>^{232}U and its daughter chain</i>			<i>27.4 kg ^{233}U</i>	<i>0.2 kg ^{233}U</i>
^{232}U	70 y	129	113	0.81
^{228}Th	1.9 y	132	116	0.83
^{224}Ra	3.66 d	132	116	0.83
^{220}Rn	55.6 s	132	116	0.83
^{216}Po	150 ms	132	116	0.83
^{212}Pb	3.25 h	132	116	0.83
^{212}Bi	1.01 h	132	116	0.83
^{212}Po	45 s	84.8	74.3	0.53
^{208}Tl	3.05 m	47.6	41.7	0.30
<i>^{233}U and its primary daughter chain</i>				
^{233}U	1.59×10^5 y	302	265	1.90
^{229}Th	7300 y	0.8	0.70	0.01
^{225}Ra	14.8 d	0.8	0.70	0.01
^{225}Ac	10 d	0.8	0.70	0.01
^{221}Fr	4.9 m	0.8	0.70	0.01
^{217}At	32 ms	0.8	0.70	0.01
^{213}Bi	45.6 m	0.8	0.70	0.01
^{213}Po	4 μs	0.8	0.70	0.01
^{209}Pb	3.25 h	0.8	0.70	0.01
<i>Other significant uranium and transuranic isotopes</i>			<i>2.5 kg ^{234}U</i>	<i>0.02 kg ^{234}U</i>
^{234}U	2.45×10^5 y	17.4	15.2	0.11
			<i>98.2% Pu</i>	<i>1.8% Pu</i>
^{238}Pu	87.7 y	0.89	0.87	0.02
^{239}Pu	24,110 y	41.7	40.9	0.75
^{240}Pu	6,540 y	15.3	15.0	0.28
^{241}Pu	14.4 y	212	208	3.82
^{241}Am	433 y	23.2	22.8	0.42
<i>Summary of actinide inventories</i>				
Total actinide activity, Z<92		931	815	5.9
Total uranium activity		448	393	2.8
Total transuranic activity		293	288	5.3
Total activity		1,672	1,496	14.0

^aBased on decay to December 1999; all uranium present except that which has migrated from fuel salt.

^bTotal inventory of 31.3 kg ^{233}U and 2.8 kg ^{234}U . $^{234}\text{U}/^{233}\text{U}$ ratio assumed to be constant.

Table 1.8. Dose at 1 m for unshielded radionuclides in postulated fuel and flush salt packages

Isotope	Dose at 1 m for 1 Ci (R/hr)	Fuel salt		Flush salt	
		Activity in package (Ci)	Dose at 1 m (R/hr)	Activity in package (Ci)	Dose at 1 m (R/hr)
¹³⁷ Cs	0.33	229	76	3.97	1.309
¹⁵² Eu	0.58	0.045	0.026	0.0008	0.0005
¹⁵⁴ Eu	0.62	0.13	0.079	0.0022	0.0014
¹⁵⁵ Eu	0.03	0.18	0.005	0.0031	0.0001
²³² U	1.3	4.7	6.1	0.034	0.044
²³³ U	0.029	11.0	0.32	0.079	0.0023
²³⁴ U	0.078	0.64	0.050	0.0047	0.0004

Notes:

Fuel and flush salt divided into 24 packages, each; includes uranium except that which migrated to off-gas system.

Dose values for fission products from Radiological Health Handbook, January 1970, p. 131.

^{137m}Ba radiation included in ¹³⁷Cs above.

⁹⁰Sr/⁹⁰Y have no gammas.

⁹⁹Tc has no gamma.

¹⁵¹Sm has only a weak gamma (0.022 MeV at 4% yield).

¹⁴⁷Pm has no gamma.

Values for uranium isotopes from ORNL/MD-45 (given as rem/h in air).

Value for ²³²U includes daughter chain, in equilibrium.

Figures 1.13 and 1.14 depict the fission product and the actinide and transuranic activities over time. Cesium and strontium will continue to dominate the fission product activity until several hundred years after discharge, at which time these 30 year half-life isotopes will have decayed away. Then, ⁹³Zr and ⁹⁹Tc will dominate the fission and activation product dose into geologic time frames. However, once the ⁹⁰Sr and ¹³⁷Cs isotopes have decayed away, the total fission and activation product activity will be about 10 Ci.

Similarly, the ²³²U decay chain will dominate the actinide activities until it is overtaken by ingrowth of ²³³U daughters after a few hundred years. Hundreds to thousands of curies of actinide activity will be present out into geologic time frames. Were the uranium separated from the salt at the time it is removed from the tanks, the ²³³U chain will not grow in to any significant extent, and the ²³²U daughter products would decay with the 1.9 year half-life of ²²⁸Th. The long term inventories would then be represented by the plutonium and americium chains, and would remain below 100 Ci after about 50 years. Thus, separation of uranium can have a significant impact on the long-term radionuclide inventories in salt packages. Of course, the inventories associated with uranium and its daughters are not eliminated, but rather transferred to a uranium package.

1.2.4 Chemical Characteristics

Today, both the fuel and flush salts are a mixture of LiF, BeF₂, ZrF₄, UF₄, and trace quantities of the fluorides of other corrosion products, fission products, actinides and transuranics. The phase diagram for the system LiF-BeF₂-ZrF₄ is shown in Fig. 1.15; adding UF₄ to the system necessitates a three-dimensional representation (plastic models have been used to depict such systems in the past). A series of experiments was performed to quantify the crystallization sequence of the MSRE salt. Table 1.9 summarizes the crystallization sequence for MSRE fuel salt (Thoma 1971).

ORNL DWG 85-438

Fig. 1.13. Fission product activity of MSRE fuel and flush salts.

ORNL DWG 85-439

Fig. 1.14. Actinide and daughter activity of MSRE fuel and flush salts.

Fig. 1.15. Phase diagram of the LiF-BeF₂-ZrF₄ system.

Table 1.9. Crystallization sequence for Molten Salt Reactor Experiment fuel salt

Crystalline form	Onset temperature (°C)	Volume fraction
Li_2BeF_4	434	0.735
Li_2ZrF_6	431	0.204
LiUF_5	416	0.032
BeF_2	complete ~350	0.029

Note: Crystals of pure BeF_2 are generally not expected. The last liquid solidifies as a glass which incorporates variable amounts of the phases listed above with BeF_2 .

An experiment was performed in which simulated fuel salt was frozen at rates that would approximate the cooling rate in the drain tanks after reactor shutdown. The objective of this experiment was to determine whether uranium segregation could take place as crystalline phases began to form but most of the salt was still liquid. Uranium samples taken from the frozen salt plug ranged from 2.94 wt% near the top to 5.74 wt% at the bottom. This degree of segregation was considered small enough to not affect criticality safety in the drain tanks.

One key reason these salts were selected for use in MSRE is that there is very little volume change between the solid and liquid phase. It has been estimated⁵ that, on melting Li_2BeF_4 , the density is reduced only about 2.07%.

Other physical properties for liquid salt were measured as part of the MSRE development program, and are documented in the literature. Data found in the MSRE literature for the physical properties for solid salt is more sparse, but open literature data for components in the salt can be used along with the data that is available for the MSRE salt to obtain reasonable estimates for the key properties over the necessary range of temperatures.

The UF_6 and F_2 gas that has migrated away from the salt has left the salt in a net reducing condition. It has been estimated that at least 115 mol of fluorine was generated by radiolysis and removed from the solid (Williams et al. 1996). This represents a net 230 equiv of reductant present in the form of isolated metal sites (Li° and Be°). The present reducing potential of the stored salt is latent in the solid form, but once the salt is melted the reducing potential of these sites can be realized, and the metal species will react according to their redox potentials, $\text{Li} > \text{Be} > \text{U} \sim \text{Zr}$. The following reactions are a consequence of this reduction series:

The reduction of beryllium by lithium is expected to be kinetically favored and the cascade of subsequent reduction steps probably eventually converts all of the uranium to U^{3+} and some fraction of the uranium and zirconium to the metallic state. By using a lower bound of 230 equiv of reductant (based only on UF_6 detected in the vapor phase) and an estimate of 142 mol of uranium in the fuel salt, it can be projected that after all UF_4 is converted to UF_3 , 88 equiv of reductant remains. The close proximity of uranium and zirconium makes it difficult to predict the subsequent reduction of these metals. Were the remaining reductant to reduce uranium preferentially, a mass of 6.8 kg of uranium metal would be formed. Other concerns include plating of uranium on the tank walls, and precipitation or disproportionation of UF_3 . Thus, adjustment of the redox chemistry of the salt will likely be required before or during melting.

Preliminary experiments have indicated that production of fluorine is the result of beta-gamma, not alpha, radiation. Using the the fission product decay energy and the most reasonable fluorine yield curves measured (Williams et al. 1996), the amount of fluorine that will be generated in the future is depicted in Fig. 1.16. This curve is most representative of a case in which uranium is separated from the salt after the salt is removed. If the uranium remains with the salt, production of UF_6 must also be considered, and the gamma radiation from the ^{232}U and ^{233}U daughter chains must be taken into account.

The present storage of the salts has been evaluated relative to Resource Conservation and Recovery Act (RCRA) regulatory status (Nix 1992a,b). It has been concluded that the salts, in their present form, are neither listed nor characteristically RCRA hazardous waste. In particular, Skipper (1992) determined that beryllium fluoride is not a listed waste and, as a solid, does not exhibit the characteristics of ignitability, corrosivity, reactivity or toxicity as defined in the RCRA legislation. This determination only applies to storage in its present form, and must be reviewed in the context of any processing performed on the salt.

1.2.5 Summary of All Locations Containing Fuel or Flush Salt

Table 1.10 provides a list of all locations in the MSRE that contain fuel or flush salt, along with estimates of the quantity of uranium present in the salt. A review of the components likely to contain salt was made, and process history was used to determine the type of salt that was last circulated through that component. The largest quantity of salt outside the fuel and flush (and coolant) drain tanks is a salt heel left in the fuel storage tank after the fuel salt was fluorinated in 1968. When the fuel salt was returned to the drain tank prior to the addition of the ^{233}U enriching salt, a quantity of salt was left in the fuel processing cell for transfer to a distillation experiment in the spare cell. When salt was transferred to the spare cell, measurements indicated that only a fraction of the desired amount could actually be transferred. Although a number of reasons were postulated, it was generally assumed that this indicated that a hole had appeared in the dip leg during the corrosive fluorination operation. Based on the available measurements, it was assumed that 190 kg of salt remained in the fuel storage tanks. This salt would contain essentially no uranium (after fluorination), and would contain the fission products that existed at the end of ^{235}U operations. More recent investigations into the conditions in the fuel processing cell (DeVore et al. 1996) did not identify radiation fields that would correspond to the expected cesium inventory. Thus, the actual amount of salt in the fuel storage tank may be substantially less.

Projection of Fluorine Accumulation
Based Upon $G_{F_2} = 0.02$ molecules/100eV

Fig. 1.16. Projected fluorine generation resulting from fission product decay.

Table 1.10. Summary of Molten Salt Reactor Experiment salt inventory

Location	Type of salt	Mass of salt (kg)	Mass of uranium (kg)
Fuel drain tanks	Fuel salt	4,650	<32.7
Flush drain tank	Flush salt	4,290	0.5
Fuel storage tank	Fluorinated fuel salt	190	negl.
Distillation experiment	Fluorinated fuel salt	36	negl.
Reactor cell	Flush salt	20	negl.
Drain tank cell piping	Flush or fluorinated fuel salt	12	negl.
Release into drain tank cell	Fuel salt	0.1	negl.
Fuel processing cell piping	Fluorinated fuel or fresh salt	9	negl.
Coolant drain tank	Coolant salt	2,610	none

Other estimates of salt volumes were made in a similar manner. Most of the salt in the piping systems was that left in the freeze valves. Drawings for freeze valves were reviewed, and process history was used to determine the type of salt that last flowed through the freeze valve. In all cases, the last salt in the valve was either flush salt or fluorinated fuel salt, and again no valve contains any significant uranium inventory. Salt in the distillation experiment is the same as that in the fuel storage tank, with some separation between salt in the feed and receiver vessels in the experiment. It had been estimated that 20 kg of salt remained in the reactor circuit after the salt was drained into the drain tanks; again, the last salt circulated in the reactor was flush salt. When the failed freeze valve 105 was removed, visual examination was used to estimate that only a few cubic inches of salt were left in the cell. Although this was actual fuel salt, the low quantity again means there is no significant uranium inventory associated with the spill. Thus, none of the known inventories of salt outside the fuel and flush drain tanks contains any significant quantity of uranium. If the inventory in the fuel storage tank is substantially <190 kg, there may be only about 100 kg of salt outside the tanks. The fission product inventory in this quantity of salt may be about 260 Ci of fission products.

In performing the CERCLA feasibility study, a review will be made as to whether the selected salt removal technology (assuming the salt is removed) is readily adaptable to removing any of the salt outside the fuel and flush tanks. If so, that salt removal will be recommended for inclusion into the scope of the task. If not, the salt will be left for disposition as part of the overall decommissioning of the facility.

1.3 PRESENT CONDITION OF THE MSRE FACILITY

The MSRE experiment was ended in calendar year 1969 so that funding for the following year could be used instead for the design of a prototype Molten Salt Breeder Reactor. Thus, at shutdown, a few key safety signals were tied into a remote monitoring station at the ORNL Waste Operations Center, and the facility operations staff was disbanded. After the radionuclides in the salt had decayed for a year, a small staff was reassembled for post-operation examinations and to implement a number of additional containment measures. The reactor cell was opened, test specimens and pieces of reactor components were removed for examination, a visual inspection of the reactor assembly was made, and the cell was sealed closed again. One of the control rods was left permanently inserted in the reactor assembly.

A heavy accumulation of dust (about $\frac{1}{2}$ in. deep on flat surfaces) was observed inside both the reactor and drain tank cells (Cagle and Pugh 1977). An ordinary water hose was used to flush the dust onto the cell floor. By keeping the cell wetted, no contaminated dust was allowed to escape.

At the same time, the drain tank cell was opened for inspection and for removal of failed freeze valve 105 and the nearby freeze valve 106. Copper plugs were inserted into the ends of the salt lines leading back to the fuel drain tanks, using a mechanical clamping mechanism. A blind flange was inserted between the flange faces of a connection in the off-gas line leading from the tanks to the pump bowl in the reactor cell. The cell was then sealed closed, and has not been opened since. Various penetrations into the cell were cut and capped, including the helium addition lines that had been used to pressurize the tanks for salt transfers.

The reactor cell was opened one more time in 1977 to measure radiation levels at the top of the reactor graphite and at various other locations in the cell (Cagle and Pugh 1977). The effective tenth-value layer of lead was determined to be 1.4 in.

All MSRE equipment except the items required for surveillance and operation of the drain tank and salt processing systems was placed on a surplus materials list and made available to other projects. Control and electrical panels for the drain tank and salt processing systems were eventually painted pink or yellow to make it obvious that equipment was not to be removed. The process computer was transferred to the TVA Bull Run steam plant, and the control rooms were dismantled. The coolant salt pump and piping were removed for use in a molten salt reactor component development test loop. The 5 in. coolant lines were welded shut where they exit the reactor cell.

The scope of surveillance and maintenance activities over the years was generally limited to monitoring the overall status of the facility. Checks were made by a waste operator making rounds through that part of ORNL and entered into the log. The annual annealing procedure was performed, through 1989, as dictated by the procedure (Guymon 1971). A reactor operator from the adjacent High Flux Isotope Reactor performed the annealing operation.

Other spaces in the MSRE complex were used to house personnel and equipment from the Health Sciences Research Division at ORNL. The most use was made of the offices in Buildings 7509 and 7503, but areas such as the high bay and open areas on the lower floor of Building 7503 were used for storage as well. The buildings were maintained as needed for this occupancy. At one point, a fence was placed in the high bay to prevent casual entry to the reactor, drain tank, and fuel processing cells.

Some required facility maintenance was performed once the MSRE Remediation Project was formed. Improvements were made to the data collection system that read, among other parameters, the temperatures in the drain tanks and the drain tank cell. Routine trending of data is now taking place. Facility maintenance has included repair of the roof at several locations, including over the electrical equipment in the switch house, repairs to the steam system, and similar activities. The building cranes have been recertified. More significantly, the facility is now staffed with knowledgeable operations, maintenance, and health physics personnel. Portal monitoring and access control has been improved, and the spare cell and fuel processing cell have been accessed for inspection. Some of the techniques used to inspect these cells might be applicable to a preliminary inspection of the drain tank cell.

The drain tanks are thought to be in good condition. A continuous review of corrosion product concentrations in the salt during reactor operations did not indicate any significant damage to the Hastelloy-N tank and thimble walls. The recent sample taken from the off-gas system did not contain large quantities of volatile fluoride corrosion products. Furnace heaters have been operated annually until

December 1989, and no operational difficulties have been observed. Equipment for removing shield plugs over the drain tank cell remains at the facility. The maintenance shield is in place over one of the other cells, and is used periodically to access irradiated materials specimens stored in the cell by another ORNL division. The condition of the off-gas system, including valves in the system, will be determined as the off-gas system is evacuated by the reactive gas removal system. Once the reactive gas removal system has purged the gases out of the tanks and refilled the system with helium, the tanks themselves can safely be opened. The reactive gas removal system will remain as an operating trapping system for use during salt removal operations.

The solidified salt in the tanks has never been inspected. It is thought to be a monolithic mass, although some fracturing may have taken place during cooling. A thermal model of the salt* has replicated the measured temperatures in the drain tanks using thermal conductivity values for solid salt, indicating that gross degradation of the salt block, to the extent that additional thermal resistance is introduced, has not happened.

The condition of existing salt processing equipment is less certain than that of the drain tanks. Corrosion rates during the fluorination operation conducted in 1968 were significant (Lindauer 1969). Operational difficulties have suggested that a dip leg in the fluorination vessel had corroded through; however, recent inspections into the cell did not identify radiation levels consistent with the projected salt inventory in the fuel storage tank (DeVore et al. 1996). Visual inspections of the cell contents indicated that, at least on the exterior, equipment in the fuel processing and spare cells is in remarkably good condition. There is no dust layer; the impression is that much of the equipment had only recently been installed. Radiation levels in the fuel processing cell are moderate. Radiation levels on the side of the spare cell that contains the salt processing off-gas equipment are quite low, and personnel have entered the cell for further survey work and to replace a filter near the cell floor. No contamination has been observed on the exterior of equipment in either cell.

Other systems that might be needed for salt transfer and processing operations have been removed, and would have to be replaced. This includes the helium system used to pressurize the tanks to transfer salt, and the fluorine station used during the fluorination operations in 1968. The migration of uranium to the fuel processing and spare cells indicates that the freeze plugs do not provide a tight seal, although remelting and then freezing the plugs might restore the seal. A general survey of the activities needed to reactivate existing drain tank and salt processing systems is underway.

General building systems are available to support operations at the drain tanks and at the salt processing system. These include electrical and other utilities, the building ventilation systems, monitoring systems (including criticality and radiation monitors), and fire protection systems. The flowrate on the building ventilation system had been reduced to the requirements of storage and surveillance to limit the power consumption and increase the service life of the stack fans. The original flow might have to be restored before shield plugs are removed from the drain tank cell. The building is adequate in terms of protecting equipment and workers from weather, and reasonable truck and crane access is available in the high bay. The high bay confinement was constructed as a separate structure inside an existing Building 7503. At present, there are multiple openings in this structure as a result of minor architectural modifications and the removal of equipment for salvage. The ventilation system does maintain airflow into the structure. Repairs to this confinement barrier could improve the negative pressure in the high bay relative to the rest of the building.

*DAC-EA-020794-A019 N.d. *Thermal Analyses of MSRE Fuel Drain Tanks*, in preparation.

1.4 BASELINE RISK ELEMENTS

A streamlined risk assessment is being prepared to evaluate the potential human health risks associated with the fuel and flush salts at the MSRE, assuming no actions are taken to remove the salts or mitigate contaminant concentrations or exposures (personal communication from P. Howell to F. J. Peretz, Oak Ridge National Laboratory, July 24, 1996). This assessment is being prepared to the guidance generally applied to CERCLA feasibility studies for an interim remedial action. Most probable pathways to exposure have been identified for the near term and the long term.

In the near term, the most probable exposure pathway is the continued production of F_2 and UF_6 , collection of these gases in the off-gas system, and a sudden release due to a failure of a component in the off-gas system. This risk exists today (until operation of the reactive gas removal system begins). An approximate assessment of the consequences of such an event can be obtained by reviewing the system safety analysis for the reactive gas removal operation (SSA/7503-ERP/003/R0 1996). According to a scenario in which a component of the now pressurized off-gas system suddenly fails and releases the entire gas inventory in the off-gas system, 50% of the gas is retained in the building, the rest is lost as a ground level release, and typical conservative atmospheric conditions are assumed. A dose commitment of 24 rem is projected for a member of the public at the nearest accessible location on Bethel Valley Road just outside of the main ORNL complex. Over time, the generation rate of fluorine (and probably UF_6) will decline. This pathway will be of far less concern once the primary gamma source, $^{137}Cs/^{137m}Ba$, has decayed away in a few hundred years.

For the long term (hundreds to thousands of years), the exposure pathway begins with water intrusion into the drain tank cell or the drain tanks themselves. Building 7503 was originally constructed in the early 1950s for use by the aircraft reactor project, and was modified several times as it was adapted to new uses. In 1957, construction of an Aircraft Reactor Test reactor was stopped as part of the downscaling of the overall aircraft reactor program. In the intervening years until construction of the MSRE began, the building was largely abandoned. At that time, it contained negligible quantities of radioactive material. The present reactor cell existed, but the drain tank cell had yet to be constructed. The basic system of french drains around the reactor cell and the sump and pumps southeast of the reactor cells was in place. Thus, groundwater at the site has been suppressed by pumping for about 40 years. During this intervening period, a failure of the sump pumps went undetected for several weeks. Groundwater rose to an elevation about chest high in the sump room (personal communication from T. C. Morelock to F. J. Peretz, Oak Ridge National Laboratory, July 24, 1996). This water level correlates to an elevation of 823 ft above sea level, or approximately the elevation of the large opening between the reactor and drain tank cells as shown in Fig. 1.17. Other reviews of water level in the area indicate that a likely undisturbed year-round average groundwater elevation would be about 835 ft above sea level (personal communication from P. Howell to F. J. Peretz, Oak Ridge National Laboratory, July 24, 1996). Even at 823 ft, the fuel and flush drain tanks are totally submerged, as is much of the salt and off-gas system piping above the tanks. At present, these components are well protected from groundwater because of the operation of the sump pumps and the physical barriers provided by the concrete cell walls, the stainless steel liner, and the integrity of the tanks and piping themselves.

In the long term, however, it cannot be assumed that pumping will continue, and eventually the barriers can fail. The failure need not be to the cell walls and liner directly, but could be a line that penetrated the cells below the water level. It is very possible that the solidified salt in the drain tanks has fractured as it cooled. This provides a mechanism for water entry into the salt itself, once water enters the tank interior. A simple calculation has shown that if a 2% void in the salt is filled with water, a k_{eff} of 1.06 is obtained (Crume 1994). A criticality in a fuel salt drain tank then leads to exposure pathways ranging from direct exposure to radiation to the generation and dispersal of gaseous fission products.

This mechanism is absolutely prevented when the dominant fissionable isotope, ^{233}U , decays away with a 1.6×10^5 year half-life. Although the barriers to water intrusion are very effective in the short term, reliance on such barriers for over a hundred thousand years is not credible.

Other secondary pathways have also been identified. These include the gradual dissolution of the salt once groundwater enters the drain tanks, and transport of a range of contaminants to nearby receptors. These pathways are generally slow, chronic processes, and pose a lesser risk to the potential receptor than the gas release or criticality scenarios.

1.5 OUTLINE OF THE ALTERNATIVES EVALUATION PROCESS

The remainder of this report directly addresses the identification and evaluation of alternatives for the disposition of the MSRE fuel and flush salts. In Chap. 2, potential end points for the key contaminants in the salt are identified, and the key factors that address the potential and requirements for placing the MSRE material in each end point are discussed. In Chap. 3, the technologies available for removing the salt from the tanks, for separating uranium from the other key contaminants, and for stabilizing materials as waste or product are identified and discussed. In Chap. 4, the removal, separations, and stabilization technologies are used to develop real scenarios, in many cases using existing facilities for performing the necessary operations to place the key contaminants in the identified end points. Of these scenarios, a representative sampling is identified as the list of alternatives for evaluation. In Chap. 5, an evaluation matrix is prepared for these alternatives, leading to a set of recommendations. Chap. 6 identifies the key uncertainties that could affect these evaluations, and the activities that are recommended to resolve the uncertainties.

The overall logic for identifying and evaluating alternatives is shown in Fig. 1.18. The evaluation begins with the salt in its present conditions, assuming no other actions are taken to mitigate the transport of the key contaminants to potential receptors. The present condition of the fuel and flush salts is evaluated in the context of the baseline risk established in the previous section. Because unacceptable consequences result from a "no action" alternative, this condition is not selected as the ultimate end point, and further evaluation is necessary.

The next step evaluates permanent storage in the drain tanks, with additional features in place to prevent the transport of key contaminants. Because the criticality issue continues for hundreds of thousands of years the alternative of long-term storage is deemed unacceptable and the evaluation proceeds on the basis of the removal of the salts.

Once removed, the salts are evaluated against the requirements for disposal or reuse against the full set of potential end points, as shown in Fig. 1.19. If the salt in its present condition cannot meet requirements for any of these end points, further activities are taken. In the logic depicted in Fig. 1.18, the next step is to consider separating the fissile and long-lived actinide activity hazards from the rest of the salt. This results in two streams, each of which is again evaluated against the requirements of the end points. If the requirements are not satisfied, further stabilization steps are considered. Once material meets requirements for disposal, the process stops. If no disposal path based on an accepted end point is identified, the result is long-term interim storage of a unique waste form.

In the evaluation matrix, the identified alternatives are evaluated against the seven CERCLA evaluation criteria. In addition, two other criteria are used. Because the requirements for many of the potential end points, such as the federal repository, are either not fully developed or are subject to change as a result of external factors, the alternatives are evaluated in terms of the ease in which a waste form

Fig. 1.18. Logic diagram of the alternatives identification process.

Fig. 1.19. Expanded logic of the disposal evaluation block.

or product specification can be changed to address the potential new requirement. Adaptability to changing requirements is added as an evaluation criteria to address this issue. Second, there are objectives for the fuel salt disposition task that are not necessarily addressed by the CERCLA process. These include a commitment to fulfill the DNFSB 94-1 commitment that the salt will be removed and the uranium will be placed in storage as an oxide, and a preference to remove the salts (or clearly establish a permanent disposition at the site) so that the final decommissioning of the MSRE systems in Building 7503 can proceed. Consistency with programmatic objectives is added as an evaluation criteria to address this issue. The full set of criteria used, beginning with the seven CERCLA criteria, is:

- Overall protection of human health and the environment
- Compliance with applicable or relevant and appropriate requirements
- Long-term effectiveness and permanence
- Reduction of toxicity, mobility, or volume through treatment
- Short-term effectiveness
- Implementability
- Cost
- Adaptability to changes in system requirements
- Compatibility with programmatic objectives

The primary evaluation of alternatives is performed using scenarios judged to be preferred, or at least representative, to achieve the desired end point. Once a recommendation is made, the selection of scenario for that alternative is reviewed in more detail. Again, all credible scenarios that achieve the recommended end point are listed in an evaluation matrix, and an evaluation at this second-tier level is conducted to refine the recommendation. This matrix again uses the CERCLA criteria, with any additional evaluation criteria judged appropriate added to the matrix.

2. POTENTIAL END POINTS

2.1 MSRE DRAIN TANK CELL

The most obvious potential end point for the MSRE fuel and flush salts is to remain stored in the drain tanks in the drain tank cell until all radionuclides have decayed to innocuous levels. The drain tanks and the drain tank cell have been described earlier. Further modifications could include additional sealing of penetrations, the cutting and capping of all off-gas lines, and sealing the penetration between the reactor and drain tank cells. The drain tank cell (or even the tanks themselves) could be filled with grout or some other material. Neutron absorbers could be placed in the tanks, on top of the salt, or around the tanks in the drain tank cell. Likewise, the salt could be stored in its present condition or it could be removed, treated in a number of ways, and returned to the tanks.

The drain tank cell, a heavily reinforced concrete structure with a stainless steel containment barrier, is a substantial structure and is located below grade. It is, however, at a lower elevation than the natural water table. It is located at a key intersection in the Melton Valley portion of ORNL, and part of an attractive site for future utilization. As part of the ORNL site, it is a controlled industrial site. The MSRE site is near a number of other radioactive waste facilities, including solid waste burial sites, liquid waste seepage pits, and the hydrofracture waste disposal facilities. The permanent disposal of radioactive materials in at least some of these facilities in Melton Valley is assured.

There is presently no defined regulatory basis for permanent disposal of the salts in the MSRE drain tank cell. This issue would have to be addressed in the Federal Facilities Agreement site treatment plan, and would have to be agreed to by TDEC and EPA Region IV. Disposal of materials classified as transuranic waste (transuranic activities greater than 100 nCi/g) in shallow land facilities may be prohibited by DOE Orders.

If permanent disposal in the drain tank cell were to be allowed at all, the requirements for disposal would likely be performance based. A detailed risk assessment would be performed to demonstrate that the risks to human health and the environment near the MSRE site would be acceptably small.

2.2 REUSE

Reuse of the salt or components from the salt can be described in a number of ways. The entire mass of salt may have reuse potential in another molten salt reactor or as a target or blanket material in a neutron-producing accelerator system. In some neutron-producing accelerators, the target incorporates a subcritical assembly, making it similar to a reactor core. Salt may be useful for an actual pilot or production facility, or may be used in the research and development activities surrounding the development of a reactor or accelerator project. The latter includes research into the separation of fuel, target, or other radioactive materials from a reactor or accelerator system. Other reuse end points could apply to the fissile ^{233}U separated from the salt, or to all or components of the carrier salt after separations. The lithium in the salt is isotopically pure ^7Li .

In some cases, the key contaminants in the salt may be accepted in the reuse option. In others, the contaminants must be removed first, and a nonradioactive or otherwise separated material would be transferred to the new user. In the case of the latter, another end point must be found for the contaminants separated from the salt before its transfer.

The attractiveness of the reuse end point is a matter of whether or not a credible use option exists. Although no significant molten salt reactor development activities have been identified, an active program to develop accelerator-driven neutron sources for transmutation of plutonium or other materials in nuclear waste is underway at Los Alamos National Laboratory. This program is currently funded at a relatively low level, but does support laboratory work for the design and development of pilot and production level facilities. Recent contacts have been established with Los Alamos personnel (Toth 1996). These contacts have led to a request by the Director of the Los Alamos Neutron Scattering Center and Energy Research Programs to explore the details of a transfer of salts from the MSRE to Los Alamos (Brown 1996). The most immediate interest is in the nonradioactive coolant salt. Requirements for storage, handling, and the ultimate use of the flush and fuel salts will also be explored. Storage and use of these salts may require a higher level of funding than is presently available. Even in the near term, however, the transfer of small quantities of flush or fuel salt may be useful for the laboratory development of salt processing systems.

No programs to develop reactors that use ^{233}U as fuel are active in the United States today. Use in a solid-fuel reactor (traditional reactor designs that use fuel rods or plates) requires fuel fabrication facilities that are designed to handle the radiation associated with the uranium isotopes present. Uranium with a high ^{232}U content is particularly unlikely to be desirable as a reactor fuel.

In general, the individual components of the salt do not appear to be particularly valuable. A possible exception is high-purity ^7Li . Other systems, including tritium production systems, have required significant quantities of ^6Li . The residues from ^6Li processing could provide a significant source of ^7Li , although the isotopic purity of this material has not been checked. As chemicals, the individual components of the salt are readily and inexpensively available from commercial sources.

From a regulatory standpoint, it is more desirable to reuse an existing contaminated material than place it in a disposal facility and contaminate another material. Specific regulations for the handling and transportation of radioactive materials would have to be met in the course of transferring salt or components from the salt to a new user.

Physical requirements for the material to be transferred would be established on a case-by-case basis, balancing economics against the needs of the new user. Material requirements could include some level of decontamination, chemical purity, and packaging.

2.3 WASTE ISOLATION PILOT PLANT

2.3.1 General Description

The Waste Isolation Pilot Plant (WIPP) has been authorized, designed and constructed to provide for the safe disposal of defense-related transuranic waste, including waste generated during the cleanup of nuclear weapons production facilities. It is part of an overall transuranic waste program that provides an integrated management system from generation through transportation and disposal. Disposal of commercial, high-level waste, or spent nuclear fuel at WIPP is not allowed (DOE Carlsbad Area Office 1995; DOE/CAO 95-1095 1995).

WIPP is located in southeastern New Mexico, 26 miles east of Carlsbad, New Mexico (Fig. 2.1). Surface facilities include a waste handling building, designed for receiving and inspecting waste containers and preparing the containers for transfer underground. The disposal areas are excavated into the 25 million year old Salado bedded salt formation 2,150 feet below the earth's surface (Fig. 2.2).

Fig. 2.1. Location of the Waste Isolation Pilot Plant, indicating transportation routes from major DOE sites.

Fig. 2.2. Geologic formations at the Waste Isolation Pilot Plant.

The waste disposal area within WIPP consists of eight panels, each containing seven rooms between access drifts. Waste is classified into contact-handled transuranic (CH-TRU) and remote-handled transuranic (RH-TRU), depending on whether the dose at the surface of the waste package exceeds 200 mrem/h. The RH-TRU wastes will be emplaced in a manner different from that for the CH-TRU wastes because of packaging, shielding, and loading requirements; operational equipment; and structural considerations. The disposal configuration of the CH-TRU waste inventory calls for emplacement of the waste packages in disposal rooms that measure 33 ft wide, 13 ft high, and 300 ft long (Fig. 2.3). The configuration for RH-TRU disposal provides for emplacement into the walls of the disposal rooms in horizontal boreholes. These boreholes will be drilled 4 feet from the floor on 8-foot centers. The CH-TRU waste inventory will be emplaced in the disposal rooms following completion of all RH-TRU waste disposal activities in that room. A total of ~7,955 RH-TRU waste boreholes will be provided in WIPP.

The CH-TRU waste packaging will include 55-gallon drums, standard waste boxes, and ten drum overpacks. The standard waste box is an oblong steel box that is 37 in. high, 54.25 in. wide, and 71 in. long. The ten drum overpack is a welded-steel cylinder 74 in. in diameter and 74 in. high. CH-TRU waste containers will be transported and received in TRUPACT-II shipping containers. These containers are eight feet in diameter and 10 feet high, and are provided with inner and outer stainless steel containment vessels. They satisfy U.S. Department of Transportation standards and are certified by the Nuclear Regulatory Commission. Conventional diesel tractors will pull trailers designed to transport as many as three TRUPACT-II containers.

RH-TRU wastes will be received at WIPP in Nuclear Regulatory Commission (NRC)-certified type B shipping containers. One canister, which holds ~3 55-gallon drum equivalents of waste, will be placed into each borehole. Each RH-TRU canister is made of 0.25-inch-thick carbon steel, is 121 in. long and 26 in. in diameter. A general depiction of the RH-TRU canister is given in Fig. 2.4. A shield plug will be inserted into the borehole after the canister is emplaced to protect workers from radiation. The RH-TRU canisters are to be transported in the RH-TRU 72-B shipping cask.

All waste containers, both CH-TRU and RH-TRU, will be vented to prevent the accumulation of gas in the container.

Revision 5 of the WIPP Waste Acceptance Criteria (DOE/WIPP-069 1996) has recently been issued. The purpose of the document is to provide transuranic waste generator and storage sites with the minimum requirements transuranic waste must meet before transport to and disposal at the WIPP. Revision 5 combines in a single document the criteria from several sources, including the WIPP Safety Analysis Report, the TRUPACT-II Safety Analysis Report for Packaging, the Resource Conservation and Recovery Act Permit Application, the WIPP No Migration Variance Petition, and the WIPP Land Withdrawal Act.

The WIPP Transuranic Waste Baseline Inventory Report (WTWBIR) data gives inventory quantities and waste material parameters for TRU waste. These data, as well as the radionuclide inventory, are supplied by the DOE waste generator/storage sites. Summaries of the radionuclide and non-radionuclide inventories obtained from the WTWBIR will be used in the WIPP performance assessment process.

Generator/storage sites' anticipated remote-handled waste inventories are likely to fill the WIPP remote-handled waste capacity of 250,000 cubic feet. Most of the stored remote-handled transuranic waste will come from ORNL. Total allowed repository capacity is 6.2 million cubic feet.

Not to Scale

Fig. 2.3. Arrangement of the remote handled transuranic waste disposal facilities at WIPP.

Fig. 2.4. Dimensions of a remote handled transuranic waste canister.

All transuranic waste destined for the WIPP will be certified for disposal. The generator sites will make sure that all transuranic waste meets waste acceptance criteria before being shipped to the WIPP site. The WIPP will oversee this certification process to assure that generator site certifications are being carried out to acceptable standards.

After the facility has reached its capacity, the underground openings will be backfilled with salt, the surface facilities will be removed, and seals will be installed in drifts and shafts. The plastic, self-healing nature of the salt formation will also contribute to the sealing process.

WIPP is now entering a waste handling demonstration mode in preparation for disposal operations. In October 1997, after completing all activities in the WIPP Disposal Decision Plan, including receiving all necessary permits and certifications, the Secretary of Energy is expected to notify Congress of the decision to operate the WIPP as a disposal facility. After a mandatory six-month waiting period, the first container of transuranic waste is scheduled to arrive at the site in April 1998. Initial operations will be with CH-TRU only. RH-TRU operations are to begin in fiscal year 2002.

2.3.2 Regulatory Basis

Construction of WIPP was originally authorized by the *U.S. Department of Energy National Security and Military Applications of Nuclear Energy Authorization Act of 1980* (Pub. L. 96-164, 93 Stat. 1259). This act defines the mission of WIPP as a facility for the disposal of defense-related transuranic waste. More recently, the *WIPP Land Withdrawal Act* (Pub. L. 102-579, 106 Stat. 4777) provides for the transfer of the land on which WIPP is constructed to the Department of Energy, and outlines the activities required for bringing WIPP into operation. As a result of this legislation, various agencies are given certain responsibilities for promulgating regulations, preparing and reviewing documents, and certifying compliance with regulations.

The DOE will complete construction, evaluate readiness, and bring WIPP into operation under its system of Orders and Price-Anderson legislation. DOE will prepare a Supplemental Environmental Impact Statement (EIS) for Disposal Operations before the declaration that WIPP is ready to operate. An Implementation Plan for this supplemental EIS was issued in May 1996. The DOE will also maintain and implement a Disposal Decision Plan, and the Secretary of Energy will notify Congress that WIPP is ready to operate when all actions in that plan have been completed and all certificates of compliance have been obtained. There is a mandatory 180 day waiting period following this notification before waste disposal operations can begin.

The EPA has two major roles in the certification of WIPP. EPA must issue a No-Migration Determination to allow the disposal of mixed radioactive and hazardous transuranic waste at WIPP. This will be issued in response to a No-Migration Variance Petition that has just been submitted to EPA by DOE/CAO in July. The second role held by EPA is to define the specific criteria to be used for demonstration of WIPP compliance with the technical standards for radioactive waste disposal provided in the *Code of Federal Regulations* (40 CFR 191), and to accept a Final Compliance Certification Application that will be submitted by DOE. The EPA recently finalized the specific criteria for the WIPP compliance demonstration. The final disposal criteria, promulgated as 40 CFR Part 194, was approved by the EPA Administrator on February 1, 1996. A companion document, referred to as the Compliance Application Guidance, will further interpret the final criteria. DOE expects to submit the Compliance Certification Application in October, 1996. Completing the necessary activities to apply for compliance certification is a substantial task, but DOE/CAO intends to meet the schedule.

The New Mexico Environment Department is responsible for issuing a RCRA Part B permit for operation of WIPP as a mixed-hazardous waste disposal facility. DOE submitted a permit application to New Mexico in May 1995, and has recently responded to formal comments on it. The Disposal Decision Plan calls for the permit to be issued in August 1996.

The NRC issues licenses for transportation of waste to WIPP. Requirements for transportation are reflected in Revision 5 of the waste acceptance criteria. The NRC recertifies the transportation containers on a regular basis. The TRUPACT-II was recertified in August 1994. The RH-TRU 72-B cask will be certified when WIPP is closer to operation with RH-TRU waste.

The Land Withdrawal Act specifies a number of other required activities before WIPP can open. These include completion of the RH-TRU study (DOE/CAO 95-1095 1995), a review by the National Academy of Sciences, and various notifications of Congress, states, and Indian tribes.

2.3.3 Disposal of MSRE Salts in WIPP

WIPP is an attractive end point for the key contaminants in the MSRE salts for a number of reasons. It is the only repository with a reasonable probability of opening in a time frame consistent with the fuel salt disposition task schedule. As a repository, it provides for true ultimate disposition of the salt contaminants. The operating mode, waste package, and waste acceptance criteria are defined. Confinement of radionuclides is provided by the repository salt matrix, and extensive processing of the MSRE salt may not be required.

A proposed package for the fuel and flush salt residues is depicted in Fig. 2.5. An inner Hastelloy-N can is filled with molten salt. This can is constructed of 0.5 in. thick walls to provide an adequate corrosion allowance should uranium be separated from the salt by fluorination in the can. The can is then inserted into a shielded container with the approximate outer dimensions of a 55 gallon drum. This container provides two inches of steel in each direction as a radiation shield. There are a total of 24 cans each of fuel and flush salt, packaged three to an RH-TRU canister as shown in Fig. 2.6. Thus, there are 8 RH-TRU canisters for the fuel salt, and 8 for the flush salt. Each salt can is filled with salt to ~75% of its internal volume. The rest of the volume (at least, in the fuel salt packages) accommodates a soda-lime getter package. The can and shield structure will be vented through the getter and HEPA filters, as required by the WIPP packaging requirements.

Uranium will be separated from the fuel salt to remain within the WIPP limit for fissile material. This will also greatly reduce the long-term radionuclide inventory in the salt by eliminating the ^{232}U and ^{233}U decay chains. Table 2.1 shows the total inventory of radionuclides in the salt in 200, 500, and 1000 years (DeVore 1996a). Separation of the uranium affects the radionuclide inventory in two ways. It speeds the decay of the ^{232}U chain by removing the 72 year half-life ^{232}U parent, leaving the chain to decay with the 1.9 year half-life of ^{228}Th . It also prevents the grow-in of the ^{233}U daughter chain. It is the growth of that chain that causes the radionuclide inventory to begin to grow between 500 and 1000 years in the case where uranium is left with the salt.

Fig. 2.5. Proposed shielded container for MSRE salt.

Fig. 2.6. Depiction of three MSRE salt packages in an RH-TRU waste canister.

Table 2.1. Radionuclide inventory in all of the fuel and flush salt sent to the repository (Ci)

Years after discharge	Inventory in fluorinated salt ^a	Inventory in salt containing all uranium
200 years	355	879
500 years	80	518
1000 years	68	603

^aBased on residual uranium concentration of 20 ppm in both fuel and flush salt

Radiation dose estimates were also made for both the fuel and flush salt (DeVore 1996b), based on the geometry of Fig. 2.5. These estimates are shown in Table 2.2.

Table 2.2. Dose rates at side surface of postulated fuel and flush salt containers

	Shielded	Unshielded ^a
Fuel salt residue	10 R/hr	270 R/hr
Flush salt residue	0.36 R/hr	4.5 R/hr

^aMeasured at the outer surface of the outer container, with a 2 in. gap where the shielding would have been

For the purposes of comparing this package to the WIPP waste acceptance criteria, it is assumed that the uranium will be removed by fluorination of molten salt, as was done at the MSRE in 1968. The residual levels of uranium were 26 ppm in the fuel salt and 7 ppm in the flush salt. Fissile and other radionuclides that would be present in the fuel and flush salt residues were tabulated, and the appropriate comparisons to the quantitative limits expressed in Revision 5 of the WIPP waste acceptance criteria are shown in Table 2.3. It is seen that in all cases, the MSRE salt residues fall within the limits of the waste acceptance criteria. It is also seen that both salt residues clearly exceed the limits for defining material as transuranic waste.

Table 2.3. Comparison of fuel and flush salt parameters in a remote-handled transuranic canister to Waste Isolation Pilot Plant (WIPP) waste acceptance criteria^a

	WIPP limit	Fuel salt	Flush salt
Volume of salt in canister		0.235 m ³	0.24 m ³
Mass of salt in canister		581 kg	533 kg
Specific activity ^b	23 Ci/L	13.4 Ci/L	0.22 Ci/L
²³⁹ Pu equivalent activity	1000 PE-Ci	36 PE-Ci	0.05 PE-Ci
²³⁹ Pu fissile gram equivalents ^c	600 g package 325 g cask	95 g	4 g
Surface dose rate ^d	100 rem/hr	10 R/hr	0.36 R/hr
(no more than 5% at higher dose)	1000 rem/hr		
Thermal power ^e	300 watts	< 14.2 watts	< 0.25 watts
Transuranic content	> 100 nCi/g	61,900 nCi/g	1,240 nCi/g

^aAssumes the fuel salt is placed in eight RH-TRU canisters, each containing three containers.

^bAssumes 98.3% of all activity is in the fuel salt (ratio given in ORNL/TM-13142 for fission products), decayed to December 1999.

^cBased on the sum of ²³³U, ²³⁵U, and ²³⁹Pu inventories in fluorinated salt.

^dCalculations performed at contact with the side of a salt can with 2 in. of steel for shielding. Unshielded surface doses are 270 R/hr for the fuel salt and 4.5 R/hr for the flush salt.

^eThermal power not reduced to account for uranium migration or fluorination.

The long-term impact of this material on the overall performance of WIPP would seem to be trivial. There are a total of 16 RH-TRU containers (assuming that shielded flush salt is not regarded as contact-handled waste). The total radionuclide inventory after 500 years (a time for which the substantial containers in which the salt is packaged can be assumed to maintain integrity) is only 80 Ci, and the chemical form of the waste is that of a halide salt, similar to the material of which the repository is constructed. Additional work is required to ensure that the addition of fluorides does not in some way significantly change assumptions for container lifetimes in the repositories. The long lifetime that should be achieved by the MSRE containers, constructed of materials compatible with the fluoride salt, does make it likely that fluorides would not be released until other containers are assumed to have lost their integrity.

The issues that do exist with disposal of the MSRE salt residues are programmatic, not technical. The WIPP Land Withdrawal Act, and the earlier legislation authorizing construction of WIPP, designate WIPP for the disposal of defense transuranic waste.

The first major issue is whether the MSRE salt residues are transuranic waste, or if they are spent nuclear fuel or high level waste. Some definitions of these three waste classifications are provided as Table 2.4. Sec. 12 of the WIPP Land Withdrawal Act states:

The Secretary shall not transport high-level radioactive waste or spent nuclear fuel to WIPP or emplace or dispose of such waste or fuel at WIPP.

Table 2.4. Definitions of waste classifications

High Level Waste Definitions

DOE Order 5820.2A, Attachment 2, Definition #18: The highly radioactive waste material that results from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid waste that contains a combination of transuranic waste and fission products in concentrations requiring permanent isolation.

NRC 10 CFR 60.2: *High-level radioactive waste or HLW* means: (1) Irradiated reactor fuel, (2) liquid wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuel, and (3) solids into which such liquid wastes have been converted.

NRC 10 CFR 60.2: *Isolation* means inhibiting the transport of radioactive material so that amounts and concentrations of this material entering the accessible environment will be kept within prescribed limits.

NRC 10 CFR 60.2: *Permanent closure* means final backfilling of the underground facility and the sealing of shafts and boreholes.

EPA, 40 CFR 191.02(h): High-level radioactive waste, as used in this part, means high-level radioactive waste as defined in the Nuclear Waste Policy Act of 1982 (Pub. L. 97-425)

Nuclear Waste Policy Act of 1982 (Pub. L. 97-425), Section 2, (12): The term high-level radioactive waste means (A) the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations, and (B) other highly radioactive material that the Commission, consistent with existing law, determines by rule to require permanent isolation.

Department of Energy Spent Nuclear Fuel Programmatic Environmental Impact Statement Implementation Plan: High-Level Waste - 1) Irradiated reactor fuel, 2) liquid waste resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated waste from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuel, and 3) solids into which such liquid wastes have been converted.

Spent Nuclear Fuel

DOE Order 5660.1, Definition (4.g): Irradiated nuclear material that contains fission products, requires shielded storage and handling facilities, and is in an unusable form.

DOE Order 5820.2A, Attachment 2, Definition #33: Fuel that has been withdrawn from a nuclear reactor following irradiation, but that has not been reprocessed to remove its constituent elements.

NRC, 10 CFR 72.3: *Spent Nuclear Fuel* or *Spent Fuel* means fuel that has been withdrawn from a nuclear reactor following irradiation, has undergone at least one year's decay since being used as a source of energy in a power reactor, and has not been chemically separated into its constituent elements

by reprocessing. Spent fuel includes the special nuclear material, byproduct material, source material, and other radioactive materials associated with fuel assemblies.

EPA, 40 CFR 191.02 (g): Spent nuclear fuel means fuel that has been withdrawn from a nuclear reactor, the constituent elements of which have not been separated by reprocessing.

Table 2.4 (continued)

Nuclear Waste Policy Act of 1982 (Pub. L. 97-425), Section 2, (23): The term *spent nuclear fuel* means fuel that has been withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated by reprocessing.

Department of Energy Spent Nuclear Fuel Programmatic Environmental Impact Statement Implementation Plan: *Spent Nuclear Fuel (SNF)* Material used as the fuel for a nuclear reactor that has undergone nuclear fission, including material such as leftover unreacted fuel, fission products, transuranic elements, and various fuel assembly hardware. Spent fuel can be reprocessed to recycle the unused portion of the fuel and to separate the other components.

Transuranic Radionuclides or Waste

DOE Order 5820.2A, Attachment 2, Definition #38: *Transuranium Radionuclide*. Any radionuclide having an atomic number greater than 92.

DOE Order 5820.2A, Attachment 2, Definition #38: *Transuranic Waste*. Without regard to source or form, waste that is contaminated with alpha-emitting transuranium radionuclides with half-lives greater than 20 years and concentrations greater than 100 nCi/g at the time of assay. Heads of Field Elements can determine that other alpha contaminated wastes, peculiar to a specific site, must be managed as transuranic waste.

EPA, 40 CFR 191.02 (I): *Transuranic radioactive waste*, as used in this part, means waste containing more than 100 nanocuries of alpha-emitting transuranic isotopes, with half-lives greater than twenty years, per gram of waste, except for: (1) High-level radioactive wastes; (2) wastes that the Department has determined, with the concurrence of the Administrator, do not need the degree of isolation required by this part; or (3) wastes that the Commission has approved for disposal on a case-by-case basis in accordance with 10 CFR Part 61.

Sect. 2(12) of the Land Withdrawal Act provides the following definition of high-level radioactive waste:

The term "high-level radioactive waste" has the meaning given such term in section 2(12) of the Nuclear Waste Policy Act of 1982 (42 U.S.C. 10101(12)).

The Nuclear Waste Policy Act of 1982 (42 U.S.C. 9701) defines high-level waste:

The term "high-level radioactive waste" means (A) the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations; and (B) other highly radioactive material that the Commission, consistent with existing law, determines by rule to require permanent isolation.

The MSRE fuel and flush salts are presently identified in the DOE Integrated Spent Nuclear Fuel Database, and the MSRE fuel salt is briefly addressed in the Programmatic Spent Nuclear Fuel Management and Idaho National Engineering Laboratory Environmental Restoration and Waste Management Programs EIS (DOE 1995). Separation of uranium from the salts, although not for the purpose of reuse, might be construed as reprocessing. The term "highly radioactive material" is not

quantitatively defined. The dose rates at the surface of an unshielded container (as shown in Table 2.2) are not inconsequential. However, the activity concentration in the fuel salt residue is 13 Ci/L, far less than in the reference DWPF borosilicate glass waste (Baxter 1983). The Savannah River waste contains 177,000 Ci in 22.1 ft³ (205 L), or about 860 Ci/L. The radiation level at the surface of a reference Savannah River waste canister is 5500 R/h. Although not presented as a threshold for high-level waste, the Land Withdrawal Act does place a quantitative limit of 23 Ci/L for waste to be emplaced in WIPP.

A draft recommendation on distinguishing RH-TRU from high level waste (Watkins 1996) was recently presented to the National TRU Steering Committee. This recommendation proposes two decision points. The first is whether the waste is irradiated fuel elements, or reprocessed, or liquid or solid wastes resulting from reprocessing of, irradiated fuel elements. The draft guidance recommends classification of these wastes as high level waste. The second decision point is whether samples of fuel elements were irradiated only for R&D purposes and not to produce power. If so, it is recommended that they be considered for disposal in WIPP. The recommendation goes on to state that the document should not be interpreted that fuel used to "power" test reactors be clarified as RH-TRU, but rather be classified and managed as spent nuclear fuel.

The second issue is whether the MSRE salt residues are defense related, or commercial. Although an outgrowth of defense programs to develop molten salt aircraft reactors, the MSRE was research performed by the Atomic Energy Commission directed at the development of a commercial reactor. MSRE itself was in no way a commercial facility, but a government research facility. Definitions of defense that have included all research activities at DOE sites that perform a defense mission have been proposed. A recent memorandum from the DOE General Council (Nordhaus 1996) would narrow the definition of defense dramatically. The general council recommendation is to interpret defense as only wastes derived from the manufacture of nuclear weapons and operation of naval reactors, and associated activities such as the research in weapons laboratories. Wastes generated by DOE's environmental management program in its cleanup and management of weapons production waste is also construed as acceptable for disposal at WIPP.

Before the MSRE salt residues can be disposed of at WIPP, these issues must be resolved. The salt residues appear to meet all quantitative requirements for disposal at WIPP, but may clash with policies, including those expressed in the Land Withdrawal Act. It may be necessary to obtain a favorable legal finding, or even await future legislative activity, before the MSRE salts can be accepted at WIPP.

Aside from resolution of policy issues, other activities will be necessary before disposal of MSRE salt residues in WIPP can be approved. As yet, the actual certification process has not been initiated for the MSRE salt residues. The MSRE salts do not appear in the WIPP Transuranic Waste Baseline Inventory Report. These activities will be initiated if it is determined that there is a reasonable chance that the MSRE salts could be accepted in WIPP.

2.4 FEDERAL REPOSITORY

2.4.1 General Description

The Nuclear Waste Policy Act of 1982 (42 U.S.C. 9701), along with other legislation, authorizes activities leading up to the siting, construction, and operation of a geologic repository for the disposal of high-level radioactive waste and spent nuclear fuel. The federal repository is to be operated by the Department of Energy, under a license issued by the Nuclear Regulatory Commission that ensures that standards established by the EPA, with the guidance of the National Academy of Sciences, are met. The

Nuclear Waste Policy Act establishes a Nuclear Waste Fund, with payments made by generators and owners of spent nuclear fuel and high-level wastes to fund the repository and associated transportation and waste acceptance programs. A presidential decision in 1985 directed that the repository also be used for the disposal of radioactive wastes resulting from atomic energy defense activities. A General Fund appropriation is made to offset the costs associated with the disposal of defense-related wastes. Three sites were nominated out of an initial evaluation of 9 sites; this evaluation has currently been narrowed by law to the Yucca Mountain site in southern Nevada, about 66 miles northwest of Las Vegas and adjacent to the Nevada Test Site. The Yucca Mountain site has not been selected as the repository site; it is only the focus of an intense characterization activity. The characterization activities are part of an overall program for the management of such wastes managed by the DOE Office of Civilian Radioactive Waste Management.

For the purposes of demonstrating that the Yucca Mountain site is capable of supporting a repository, a conceptual design of repository facilities is being proposed. An overall depiction of that design is shown in Fig. 2.7. A ramp extends down and into the mountain from a north portal, passes through the waste emplacement zone, and circles back to a south portal. Upper and lower waste emplacement blocks are accessed from that tunnel. As part of the characterization activities now underway, the tunnel is being bored from the north portal into the waste emplacement areas. As of March 1996, over 2.5 miles of tunnel had been drilled, and various alcoves are being completed and fitted out with experiment equipment. Completion of a thermal testing alcove, that will be fitted out with experiments that simulate waste-rock interactions with wastes generating significant heat, and an alcove that accesses the Ghost Dance Fault, allowing studies as to how that geologic structure may influence water movement, is expected to be completed this year.

The budget request for 1996 was not fully provided (\$400 million was provided as opposed to a requested \$630 million and a 1995 level of \$512 million. Of the funds provided, \$85 million was reserved for development of an interim storage facility that would begin accepting spent fuel from utilities, when such a facility is authorized. Since that facility has not yet been authorized, the effective funding provided in 1996 is \$315 million. As a result, a new program plan is being prepared, either changing the scope or date of earlier commitments. The plan is now to produce a viability assessment of the Yucca Mountain site in 1998, as opposed to a full characterization report. Contingent on approval of a more streamlined licensing process, an application to the NRC for construction permit in 2002 may still be possible. The goal is to begin emplacement of nuclear waste in the repository in 2010.

Development of a multi-purpose canister for the transport, storage, and disposal of spent fuel elements from commercial reactors had been underway but has been affected by the budget restrictions. The Navy is supporting limited development of the concept for transportation of naval fuel to Idaho National Engineering Laboratory (INEL).

A notice of intent to begin preparing an EIS for a federal repository at the Yucca Mountain site was issued in 1995. This work, too, has stopped because of a lack of funding.

2.4.2 Regulatory Basis

The regulatory basis for the activities to develop a federal repository is provided by the Nuclear Waste Policy Act of 1982, as amended. Major amendments, focusing the characterization effort on only the Yucca Mountain site, were enacted in 1987. Further amendments are before Congress now. The proposed amendments include direction for the immediate construction of spent-fuel interim storage facility so that DOE can begin to accept fuel from contributors to the Nuclear Waste Fund in 1998. If

Fig. 2.7. Depiction of the federal waste repository under consideration at the Yucca Mountain site.

enacted, this direction may distract attention from direct progress on the Yucca Mountain characterization and subsequent repository design and licensing activities.

In 1992, the Comprehensive National Policy Act specified that unique standards were to be established for the protection of public health and safety from releases of radioactive materials stored or disposed of in the repository at the Yucca Mountain site. The standards are to be the only such standards applicable to the Yucca Mountain site; notwithstanding other standards authorized by the Nuclear Waste Policy Act or the Atomic Energy Act. Within 90 days of enactment, the EPA was to contract with the National Academy of Sciences to conduct a study to provide findings and recommendations on reasonable standards for protection of the public health and safety. This study was issued in final form in 1995 (Anon. 1995).

Within a year of receiving the recommendations of the National Academy of Sciences, the EPA is to promulgate public health and safety standards for protection of the public from releases from radioactive materials stored or disposed of in the repository at the Yucca Mountain site. These standards are to be the only such standards applicable to the Yucca Mountain site.

Within a year of when the EPA promulgates its standards, the Nuclear Regulatory Commission is to modify its technical requirements and criteria as given in 10 CFR 60 to be consistent with the EPA standards.

A number of review boards are mandated by the legislation guiding the development of the repository. Among these is the Nuclear Waste Technical Review Board, with membership nominated by the National Academy of Sciences.

The Nuclear Waste Policy Act prohibits the emplacement of spent fuel containing more than 70,000 metric tons of heavy metal or an equivalent quantity of high-level waste resulting from the reprocessing of such a quantity of spent fuel until a second repository enters operation.

2.4.3 Disposal of MSRE Material in the Federal Repository

The federal repository provides for the ultimate disposal of spent fuel and high-level waste. If the MSRE salts, salt residues, or material separated from the salts are defined as spent fuel or high-level waste, the federal repository is the only proposed facility that can ultimately accept the wastes.

Although characterization of the Yucca Mountain site is well underway, selection of that or any other site for the repository is in the future, and operation of a federal repository is even further in the future. Program plans call for operation of the repository in 2010 at the earliest. The approach to setting standards and licensing the repository is complex, involving the DOE, EPA, NRC, the National Academy of Sciences, and a number of other advisory boards. The process is expensive, and it is difficult for the government to fund it. Issues such as the immediate construction of an interim spent fuel storage facility can further distract from progress on the repository.

Two other issues cloud the likelihood of MSRE wastes entering the initial federal repository. As noted, the capacity of the initial repository has been limited by law until a second repository opens. Wastes in that amount have already been identified; in a sense the initial repository is already fully subscribed. Second, the repository is funded by commercial utilities and contributions from the DOE defense program. Again, the MSRE wastes are neither the result of a commercial activity or, under the strictest definitions, the result of defense activities.

Standards developed to date for the repository address the overall performance of the repository. To date, no waste form has been licensed or qualified for disposal in the federal repository, although a large body of knowledge has been accumulated on borosilicate glass, which is the leading candidate waste form for high-level waste and is being produced at DWPF and the West Valley Demonstration site.

Repository performance assessments performed to date consider retention of radionuclides in the waste form itself (unlike the WIPP performance assessment, which is based on the characteristics of the host salt to seal the waste into a dry environment). Thus, the salts in their present form, which is slightly soluble, are not likely to be acceptable in the federal repository. High-level waste is managed at only a few large sites, including Savannah River, West Valley, Hanford, and INEL. ORNL does not have any waste classified as high-level waste, or any facilities for handling such waste. Such facilities are generally expensive. Qualification of a waste form for disposal in the repository is also expensive. It may be that the only credible path to the repository would be to, in some way, incorporate the MSRE material into one of the waste forms produced by a site with a significant high-level waste program.

2.5 FISSILE MATERIALS DISPOSITION PROGRAM

The fissile materials disposition program has been formed to address the disposition of fissile materials that are no longer needed for their mission, especially materials stockpiled for weapons systems that will not be produced or material from weapons systems that are being dismantled with the cessation of the nuclear arms race between the United States and the former Soviet Union. The primary focus of this program is the disposition of excess plutonium. However, the disposition of highly enriched uranium, including the relatively small (compared to the more common ^{235}U or ^{239}Pu isotopes) amount of ^{233}U that has been accumulated, is also being addressed by the materials disposition program.

Currently, the bulk of the U.S. inventory of ^{233}U is stored at ORNL and at INEL. The material stored at ORNL is mostly in the form of oxides, whereas most of the ^{233}U inventory at INEL is in the form of fuel elements. The ^{233}U stored at ORNL is kept in the Radiochemical Development Facility (Building 3019), shown in Fig. 2.8. About 500 kg of ^{233}U is in storage, mostly as U_3O_8 or other oxides. A significant fraction of this is the result of the Consolidated Edison Uranium Solidification Project (CEUSP), which thermally converted a uranium nitrate solution to oxide. The CEUSP ^{233}U has a similar ^{232}U content to the MSRE uranium. The remainder of the ^{233}U has a low ^{232}U content. It was used in the Light Water Breeder Reactor prototype core installed in the Shippingport reactor.

The uranium oxide is placed in welded canisters that are 3.5 in. outside diameter and 24.25 in. long. The canisters are then placed in a can that is 3.625 in. outside diameter and 24.75 in. long. The canisters, in their protective cans, are stored in wells, many of which are drilled into the concrete walls between the cells of the RDF as shown in Fig. 2.9. Additional storage wells remain available for future use.

There is presently no use identified for the CEUSP ^{233}U inventories in storage. As yet, they have not been formally declared surplus. The low ^{232}U material may have a use as a source of ^{230}Th for medical applications. The inventories are presently managed by DOE Defense Programs. The DOE Materials Disposition Program has requested a program plan from ORNL for the disposition of the ^{233}U inventories. This has resulted in the investigation of disposition alternatives in many ways similar to this study (Kocher N.d.). Disposition options that have been identified include incorporation into a glass matrix (possibly by blending into the DWPF feed stream) with ultimate disposal in WIPP or the federal repository. Fission or transmutation in a reactor or accelerator are other options, although the cost is difficult to justify for the relatively low overall inventory of ^{233}U .

Fig. 2.8. Site plan for the Radiochemical Development Facility (Building 3019) at ORNL.

Fig. 2.9. Storage wells for ^{233}U between cells II and III of the ORNL Radiochemical Development Facility.

Uranium will be collected from the MSRE off-gas system and auxiliary charcoal bed before the removal of the fuel and flush salts. The uranium in the off-gas system is collected as UF_6 , and retained initially on NaF traps. A request has been made to allow the temporary storage of these traps in Building 3019. This request has led to a request by Defense Programs to transfer Building 3019 and its entire inventory to the Environmental Management Program for eventual stabilization and long-term storage (Reis N.d.). This would result in declaring the ^{233}U inventory surplus.

As part of the request to use Building 3019 for temporary storage, a commitment has been made to convert the UF_6 that is chemisorbed on the NaF traps to U_3O_8 within three years of being placed in storage. Thus, the MSRE project is planning a facility to convert UF_6 to U_3O_8 . This conversion facility will be available to the fuel salt disposition task by the time the salts are removed.

As noted earlier, separation of the uranium from the salt results in a salt residue that can meet the quantitative requirements of the WIPP waste acceptance criteria. It reduces the long-term radionuclide inventory (after a thousand years) in the residues to the tens of curies. It also precludes the generation of UF_6 , and the potential migration of uranium, in the near term while the fission product inventory is still relatively high.

Separating the uranium from the salt, converting it to oxide, and placing it in storage in the RDF means that the MSRE uranium will no longer be a unique waste form. Funding that will define the disposition of the existing ^{233}U inventories will address disposition of the MSRE inventory as well.

Separation and disposition of the MSRE uranium separately can also serve the long term management strategy. The ^{233}U in the MSRE salts represents most of the long-term radiological hazard, as seen in Fig. 1.14. The growth of the radionuclide inventory after a few hundred years, up to about 600 Ci in 1000 years, is due to the ingrowth of daughter isotopes of ^{233}U and its immediate daughter product, ^{229}Th . The activity of this chain peaks at well over a thousand curies, and does not begin to fall off until about 50,000 years. At these time frames, package containers have likely deteriorated. Separation of this material from the bulk of the salt and conversion into a stable oxide results in a material more compatible with the very stable waste forms, such as borosilicate glass, proposed for the federal repository.

Likewise, as the large inventory of fission products decays, the external radiation dose from the waste falls off. Placing the entire inventory of the salts (whether as a salt or as an alternate waste form) in a repository creates a deposit of enriched uranium that could be mined. If the uranium is separated by fluorination, it is collected as UF_6 , a vapor. At this stage, it could readily be blended with depleted UF_6 to reduce the enrichment with isotopic mixing (as opposed to particulate mixing). This downblended UF_6 would then be converted to an oxide (and, if desired, incorporated into glass) in a truly proliferation-resistant form.

2.6 LOW-LEVEL WASTE STORAGE FACILITIES

Low-level radioactive waste is generally stored or disposed of in near-surface facilities. ORNL stores low-level waste on pads, in tumulus structures, and in storage wells, depending on the source and radioactivity of the material. Historically, ORNL has operated a number of shallow land burial sites for the disposal of low-level waste. Other DOE sites have similar storage and disposal facilities.

Commercial shallow land disposal sites include the Envirocare site in Utah (which only handles low activity material), the Barnwell site in South Carolina, and others. An effort has been underway for a number of years to establish state compacts that would site low-level waste facilities, restricting the use

of the facility to states in the compact. This process has been controversial, and has generally not led to the opening of new facilities.

DOE Order 5820.2A provides the following definition of low-level radioactive waste:

Waste that contains radioactivity and is not classified as high-level waste, transuranic waste, or spent nuclear fuel, or 11e(2) byproduct material as defined by this Order. Test specimens of fissionable material irradiated for research and development only, and not for the production of power or plutonium, may be classified as low-level waste, provided the concentration of transuranic is less than 100 nCi/g.

DOE Order 5820.2A defines transuranic waste as:

Without regard to source or form, waste that is contaminated with alpha-emitting transuranium radionuclides with half-lives greater than 20 years and concentrations greater than 100 nCi/g at the time of assay. Heads of Field Elements can determine that other alpha contaminated waste, peculiar to a specific site, must be managed as transuranic waste.

Since both the fuel and flush salts contain transuranics in concentrations above 100 nCi/g, neither can be considered as low-level waste by characteristic.

A classification system for low-level waste has been promulgated by the NRC in 10 CFR 61. The highest class of waste considered generally acceptable for disposal in near-surface facilities is called Class C. Limits on Class C waste given in 10 CFR 61.55 state that the concentration of alpha-emitting transuranic nuclides with half life greater than 5 years must be less than 100 nCi/g, and that the concentration of ^{137}Cs must not exceed 4600 Ci/m³. Again, both the fuel and flush salts contain transuranics in concentrations above 100 nCi /g. The fuel salt contains 5505 Ci of ^{137}Cs in 1.88 m³, or 2,930 Ci/m³. This major source of external radiation does not exceed the amount allowed in Class C low-level waste; however, when the 6557 Ci of ^{90}Sr is considered against the limit of 7000 Ci/m³, the sum of the fission product concentrations in the fuel salt is 113% of the limit for Class C waste (based on decay to the year 2000). The flush salt contains 95 Ci in 1.92 m³, or 49 Ci/m³ of ^{137}Cs , and 113 Ci, or 59 Ci/m³ of ^{90}Sr . The fission product concentration alone does not preclude classification of the flush salt as a Class C low-level waste.

Since the salts, as-is or without uranium, are clearly classified as transuranic waste and not low-level waste, disposal of the existing salts as low-level waste is not an option. However, process residues may be evaluated for disposal as low-level waste. It may be necessary that the NRC determines these residues to be "incidental wastes" to avoid other classifications based on origin.

2.7 INTERIM STORAGE

Unlike the previous options in this chapter, interim storage does not provide for the ultimate disposition of the key contaminants in the MSRE fuel and flush salts. Instead, it provides for the safe storage of the material until another disposition option becomes available. In the extreme (or, for certain short-lived isotopes), storage until radionuclides have decayed can become a strategy toward disposition.

Because interim storage does not place the MSRE materials in a facility for which a performance assessment has been used to demonstrate that risks to the public and the environment are acceptable, and because there are no formal acceptance criteria for material held in interim storage, an assessment of the hazards associated with storage must be made for each individual case to ensure protection of workers, the public, and the environment.

Interim storage could take place at ORNL or at another site that processes the salts or materials from the salts. If stored at ORNL, the MSRE material would likely be stored as salt. This is currently the case in the drain tanks in the MSRE drain tank cell.

Hazards associated with the storage of solid salt include the potential for criticality due to uranium in the salt, direct radiation from radionuclides in the salt, the consequences of the potential migration of uranium, uranium daughters, and fluorine as a result of radiolysis, and the consequence of the migration of radionuclides and beryllium as a result of other mechanisms. Uranium that migrates as radiolytic gas could result in a criticality hazard in another location, such as currently exists in the auxiliary charcoal bed. Dispersal of radionuclides as a radiolytic gas can lead to dose commitments as a result of inhalation. Water can provide a pathway for the transport of radionuclides and beryllium to potential receptors. These issues are discussed for the present storage of the salt in the streamlined risk assessment.

Several of the activities proposed as steps in the disposition process can also result in the interim storage of material that poses less risk to workers, the public, and the environment. Separation of uranium from the salt and conversion of that uranium into a stable oxide eliminates the potential for transmission of uranium and uranium decay daughters as a radiolytic gas. Separation of the fission products from the salt, especially cesium, eliminates most of the gamma energy that produces radiolytic gas. If both cesium and the uranium decay chains are eliminated, radiolytic gas production is likely to essentially cease.

Storage of salt at ORNL can take place in the drain tanks, or in a number of other facilities. If fluorinated salt is classified as transuranic waste, it could be stored in the remote-handled transuranic waste facilities at ORNL. Even if not classified as such, a decision could be made to manage it along with RH-TRU waste. Salt placed in storage must, of course, be placed in appropriate containers that are clearly and properly labeled. The salt in its present form is not construed to be a RCRA waste (Nix 1992a,b; Skipper 1992). If materials from the salt are to be stored in other physical forms, it must be determined whether that form is a listed or characteristic RCRA waste.

The programmatic EIS for DOE spent fuel (DOE 1995) identifies regionalization by fuel type as the preferred alternative. Fuel type is classified into aluminum-clad fuel, and other fuel. Aluminum-clad fuel is to be managed at the Savannah River Site. Other DOE spent fuel is to be managed at INEL, except for N-reactor fuel which is to be managed at the Hanford site. Since the MSRE salts are obviously not clad with aluminum, the programmatic EIS designates management at INEL. A study was performed by INEL to determine what storage options would exist for the MSRE fuel and flush salts (Denney 1996).

Shipments of spent fuel to the State of Idaho have been the subject of extensive litigation, resulting in a settlement agreement (Settlement agreement N.d.) that places strict limitations on such transfers. The principal conclusions drawn in the INEL study are that (1) the MSRE spent fuel is projected to be shipped to INEL for storage; (2) all spent nuclear fuel stored at INEL, including MSRE spent fuel if received at INEL, must be removed to a location outside the State of Idaho by January 1, 2035. If materials from the salt are treated or reprocessed at INEL, the resulting high-level waste must be ready

for shipping by January 1, 2035; and (3) acceptance at INEL is contingent upon the availability or prior construction and preparation of appropriate facilities for receiving the materials.

A special concern was expressed relative to the flush salt. This salt is currently listed in the DOE national spent fuel database. However, only the fuel salt is mentioned in the programmatic EIS. If a classification other than spent fuel is determined by the Idaho regulators during the permitting process, there would be no legal mandate for INEL to accept them for reasons other than treatment.

The INEL study includes a survey of existing and proposed facilities in which the salts could be stored. Facilities considered include the CPP-749 underground fuel storage vaults, the CPP-651 Unirradiated Fuel Storage Facility, the CPP-603 Irradiated Fuel Storage Facility, the Intermediate Level TRU Storage Facility at the Radioactive Waste Management Complex, and a proposed aboveground dry storage vault facility based on commercially available dry spent fuel storage casks such as the NUHOMS system. Of these, the proposed dry cask facility is identified as the most credible storage location. The study notes that stabilization of the fuel salt with a getter or by some other processing will be necessary before transferring the salt to INEL. It also identifies the need for further studies to determine shielding, criticality safety, and handling requirements, and observes that adequate funding should be identified for the interim storage as well as for the final disposition of the salts.

Interim storage of material in the salts could also take place at other DOE sites as a result of processing in a facility located at that site. Examples would be if the salt were incorporated into glass in the DWPF and the glass were placed in interim storage at Savannah River, if the salts were calcined and stored in the calcine bins at INEL, or processed by electrorefining and stored with similar wastes at Argonne National Laboratory-West (ANL-W). Again, time restrictions on storage in Idaho after processing are established by the settlement agreement. Interstate agreements may also be needed for storage in other states.

3. TECHNOLOGIES

3.1 REMOVAL TECHNOLOGIES

3.1.1 Features of the Drain Tanks

As described in the beginning of this report, the solidified salt is now stored in three tanks (two containing fuel salt and one containing flush salt) located in the drain tank cell, at the lowest location in the MSRE building with the exception of the building sump. The tanks are constructed of ½ in. thick Hastelloy-N, and are suspended from above in a furnace assembly. A computer model of the drain tank system has been assembled, and is depicted in Figs. 3.1 and 3.2. The first figure shows some of the details of the fuel and flush salt drain tank, furnace, and support assemblies. The main difference between the two tanks is the cooling system that is provided for the fuel salt drain tanks. This system includes 32 thimbles that penetrate the head of the drain tank (along with one additional instrumentation thimble), into which an array of bayonet tubes attached to a steam dome was inserted. The thimbles are constructed of 1½ in. Schedule 40 pipe, which typically has a wall thickness of 0.145 in. The tanks hang from a support ring, which in turn is suspended from weigh cells attached to a system of supports. Each tank has a 3 in. access flange at the top. In the case of the fuel salt drain tanks, this flange is on top of a section of pipe that extends through an opening in the steam dome. Thus, the flange can be accessed without removing the steam dome and bayonet assembly. However, that assembly is itself designed so that it can readily be removed.

The arrangement of the three tanks in the drain tank cell is depicted in Fig. 3.2. The flush salt tank is located closest to the reactor cell. Both bottom shield blocks, resting on support beams, and upper shield blocks, spanning the cell walls, are shown in the figure. The cell is lined with stainless steel, and a stainless steel pan between the two layers of shield blocks completes the sealed containment boundary. A maintenance shield used to access the cells was described at the beginning of this report (Blumberg and Hise 1968).

In addition to the mechanical model, a thermal model of the tanks has been developed.* This model has been used to replicate the steady-state temperatures measured on the tank walls and in the instrument thimble, and to track the temperature profile associated with an annealing procedure. These models are now available as design aids to develop hardware and processes for salt removal.

3.1.2 Removal as Molten Salt

3.1.2.1 Chemistry issues

During the period of time (from 1971–present), fission product radiolysis of the solid fuel has generated fluorine through a process represented in simplified fashion (for the major components) as

*DAC-EA-020794-A019 N.d. *Thermal Analyses of MSRE Fuel Drain Tanks*, in preparation.

Fig. 3.1. Components of the fuel and flush tank system.

Fig. 3.2. Arrangement of the fuel and flush tanks in the drain tank cell, including cell shielding blocks.

In addition, fluorine atoms have apparently reacted with and oxidized the UF_4 fuel component:

In spite of the annual annealing procedure which was conducted from 1970 to 1989 and which was intended to reverse the above radiolytically-induced reactions, significant amounts of UF_6 and F_2 have left the salt. The net result of this migration of oxidized species from the fuel salt is that the salt itself is left in a highly reduced state with a large potential for further reaction in a melt, equivalent in magnitude to the loss of oxidized material. It has been estimated that at least 115 mol of fluorine was generated by radiolysis and removed from the solid (Williams et al. 1996). This represents a net 230 equiv of reductant present in the form of isolated metal sites (Li° and Be°). The present reducing potential of the stored salt is latent in the solid form, but once the salt is melted the reducing potential of these sites can be realized, and the metal species will react according to their redox potentials, $\text{Li} > \text{Be} > \text{U} \sim \text{Zr}$, as shown in Fig. 3.3 (Williams et al. N.d.). This figure is based on extensive compilation of Baes (1969), and represents the best thermodynamic information available on these salt mixtures. Concentration effects are accounted for by the Nernst equation and do not include any corrections for solution phase nonideality at high concentrations. Only elements present in significant quantities (Li, Be, Zr, and U) are considered. The following reactions are a consequence of this reduction series:

Predictions of the equilibrium state of the reduced fuel salt when it is melted can be made based upon the values of Fig. 3.3 and our best estimate of the reduced condition of the fuel salt (~230 equivalents of Li°). There is sufficient reductant to convert all of the uranium to U(III) and some fraction of the zirconium and uranium to the metal. If the thermodynamic data in Fig. 3.3 were fully representative of the system, it would indicate the formation of zirconium metal, with uranium remaining as UF_3 . However, the projected reduction potentials of uranium and zirconium are very close, and small errors in estimates, or the effects of previously unknown species or interactions could act to increase the probability of forming uranium metal. The presence of strong reducing sites can be envisioned as a large reduction overpotential that is capable of driving a number of reduction reactions even though they are not favored in the eventual equilibrium distribution. The potential for wall interactions must also be taken into account (Baes 1969).

The consequences of a high ratio of UF_3/UF_4 are also being investigated (Baes 1969). These include the potential to plate out uranium and zirconium on the metal walls of the drain tank or the thimbles, and the possibility of forming a high melting heel. During the 1960s, a series of experiments were performed at the Materials Test Reactor (MTR) at INEL to study interactions between molten salt and the metal alloys and graphite materials proposed for construction of the MSRE. It was during this sequence of experiments that the formation of radiolytic fluorine was discovered. In 1963, a test capsule referred to as MTR-47-5, capsule 36, was irradiated to a fluorine removal of about 2.1%. (This compares to a

Notes:

Potentials referenced to HF/H₂ in 0.67 LiF - 0.33 BeF₂.

All values are for standard electrode potential except for U(IV)/U and Zr(IV)/Zr. These values are corrected by the Nernst equation.

Source:

Baes, C. F., "The Chemistry and Thermodynamics of Molten Salt Reactor Fuels," *Nucl. Metal.* 15, 617-44 (1969)

Fig. 3.3. Reduction potentials for metals of interest in the MSRE drain tanks.

fluorine removal of at least 0.13% in the MSRE salts today, with higher removal possible if additional deposits of solid UF_6 exist beyond those that have already been identified.) After irradiation, cooling, and measurement of the gaseous product from radiolysis, a melt-out recovery of the contents of capsule 35 was conducted to help establish the chemical condition of the radiolyzed salt. This operation was first performed on an unirradiated test capsule and worked flawlessly. However, when the contents of capsule 36 were heated and removed, only about half the salt was removed and the recovered fraction exhibited a 34% reduction in uranium concentration and a 50% reduction in the expected reducing power. It was concluded that substantial reduction of uranium (and possibly other species) must have occurred before the removal operation, and that this reduction produced a high-melting heel that would not drain. It was also noted that the pale green color of the salt drained from capsule 36 indicated that most of the uranium in the melted fraction was present as UF_4 . Unfortunately, no analysis of the high melting heel was reported.

In the earlier days of the development of molten salt reactors for the Aircraft Nuclear Propulsion Program, the use of NaF-ZrF_4 mixtures and various alkali metal fluorides (including LiF-NaF-KF , or FLINAK) was explored as a solvent for UF_4 . During flow-loop corrosion experiments various reductants (usually ZrH_2) were added to the salt to suppress the redox potential for corrosion of chromium in the Inconel piping. These additions were effective in preventing corrosion of chromium, but they also caused reduction of dissolved Zr(IV) and U(IV) to the metal. The addition of ZrH_2 to $\text{NaF-ZrF}_4\text{-UF}_4$ (56-46-4 mol %) caused two distinct changes: (a) loss of uranium from the salt during reductant addition in the 700°C (1292°F) makeup vessel, and (b) deposition of metallic zirconium (and perhaps some uranium) on the inner wall of the Inconel flow loop. Reduced alkali metal fluorides of various strengths were prepared by controlling the concentration of trivalent uranium during the salt production process. During circulation salts with more than 2% of the uranium as U(III) a metallic deposit was formed that was judged to be uranium by its metallographic appearance. Although these tests were not performed with the same salt mixture as was used at MSRE, they do demonstrate that the removal of uranium from reduced salt onto metal walls is an issue that must be addressed before the MSRE fuel salt is again melted.

Recently, laboratory tests of salt samples have confirmed that the melting of irradiated salts is very different from that of unirradiated salts. The former produces a metallic-like precipitate whereas the latter melts uniformly to a homogeneous, clear light-green liquid. Further confirmatory tests to characterize these precipitates from the irradiated salts are in progress.

3.1.2.2 Melting without chemistry adjustment

It would be a simple matter to melt the salts in the drain tanks were chemistry adjustment not required. As of the end of the annealing operations in 1989, all of the heaters in the drain tank furnaces appeared to be operating properly. All power and control systems for the heaters have been maintained intact, and (with the exception of the heaters themselves) are easily accessed for inspection or replacement. Even the heaters inside the tank furnaces were designed for remote replacement. Thus, the salts could be melted by simply turning on the heaters.

The issue with turning on the heaters is prevention of the potential consequences discussed in the previous section. These include the formation of phases which do not melt at the desired temperature, and the separation of metallic uranium from the salt (although a criticality as a result of precipitation of uranium metal from salt is unlikely). If the uranium plates out on the tank walls then it is not removed from the tank, and a more difficult process for removing the uranium from the tank walls could be required.

It is possible that the consequences of melting the salt in a reduced condition are reversible. If the salts were first melted, and then sparged with an appropriate oxidant (e.g., HF or F₂), the salts might be returned to their original equilibrium. A rigorous demonstration of this procedure with truly representative surrogate salt (and possibly with a sample of actual MSRE fuel salt) would be essential before this strategy could be implemented. Without unequivocal results from such experiments, this approach is not recommended.

3.1.2.3 Adjusting the redox potential before melting

The consequences of melting a reduced fuel salt could be avoided if the redox potential of the salt could be adjusted in the solid phase, before melting. This could take place by exposing solid salt to fluorine or HF at ambient temperatures. Since gas analysis indicates that there is 50% fluorine in the off-gas system at the present time, this would appear to be the present condition of the salt, and under this condition fluorine migrates away from the salt. The salt could be exposed to oxidant at elevated temperatures. Fluorine would create more corrosive conditions in the tanks than HF/H₂. The oxidant could be carried in an inert diluent gas, such as argon, to achieve a nonexplosive mixture.

For this approach to be relied upon, it must be demonstrated that the fluorine diffuses through the solid salt matrix and reaches all of the active metal sites. It must also be demonstrated that the back reaction to the metal fluoride actually goes to completion at the chosen temperature. Previous studies into these reactions sought to establish the temperature at which the recombination back-reaction just counterbalances the generation of fluorine by radiolysis. This is the inhibition temperature. Recombination of fluorine with reduced metal sites was measured by noting the rate of fluorine pressure loss over reduced fuel at various temperatures. Comparison of this back-reaction rate with the radiolysis rate gave reasonably good predictions of the inhibition temperature, at about 150°C (302°F). These predictions agreed with the observations made during and after in-pile irradiation of fuel, in which only moderate heating of the fuel [to above 100°C (212°F)] was required to suppress fluorine evolution.

The primary importance of recombination in the context of melting the salt is in assuring that the radiation damage accumulated in the reduced fuel salt is completely annealed. The ability to inhibit further fluorine evolution by heating is well established. The general issue of annealing radiolytic damage encompasses more variables than inhibition predictions and requires a more thorough understanding of governing phenomena. All of the previous studies using radiolyzed salt have measured recombination rates only during the earliest stages of annealing.

An obvious source of concern with present models of annealing is the fact that, despite the conduct of the annual annealing procedure, the migration of fluorine and uranium from the fuel salt did occur. Once the reactive gas is removed from the off-gas system, simple experiments to heat the salt (even slightly) and observe evolved gas may shed additional light on gas diffusion mechanisms. Heating the salt with a controlled amount of fluorine (possibly as HF) in the cover gas might add a measurable amount of oxidant to the salt, aiding in the development of a more effective solid phase annealing procedure. Even if it is only limited in its effectiveness, implementation of a solid phase annealing procedure while taking the salt to near its melting temperature, followed by additional adjustment of redox potential in the liquid phase, may reduce the risks of unacceptable consequences during melting.

3.1.2.4 Adjusting the redox potential while melting

Unlike adjustments to the salt redox potential in the solid phase, there is abundant experience with adjusting the potential in the liquid phase. Such adjustments were made routinely during preparation of the MSRE salts and throughout the salt operating phase. A common technique to add oxidant to the salt

is to sparge the molten salt with an HF/H₂ gas stream. To implement this approach, adequate assurance must be provided that undesirable consequences do not occur as the salt begins to melt before the redox potential has been adjusted.

An approach to melting the salt while at the same time adjusting the redox potential is depicted in Fig. 3.4 (Toth and Williams 1996). The process uses a central heating system to melt a small controlled pool of salt at the top center of the salt mass. A HF/H₂ gas stream would be sparged into the melt to continuously adjust the chemistry through the reaction:

This manner of adjustment of the fluoride salt redox state is based on proven chemistry. Any small amount of precipitate would settle to the bottom of the pool at the liquid/solid interface and would be subject to sparge gas contact without contacting anything but additional salt. The redox chemistry of the molten pool would be continuously monitored by analyzing the exit HF/H₂ ratio and comparing it with the entering gas stream. When the ratio in the exiting stream was equivalent to that entering, the molten pool redox chemistry would be satisfactorily corrected and any reducing precipitate would be redissolved in the molten pool. Additional heat could then be supplied through the central heater, causing an increase in the molten pool. The previous pool salt volume would serve as a buffer to equilibrate with the newly melted salt and less severe inhomogeneities would result. Further sparging of the HF/H₂ mixture would adjust the new pool volume to the desired redox state before the addition of more heat to the system. This process would be continued until all of the salt in the drain tank was molten. Some heat can be supplied to the overall system through the external heaters to raise the salt to a subliquidus temperature and thus lessen the heat requirements of the central heater. It is calculated that it would take ~5 days to adjust the fluoride deficiency in one drain tank with a 4% H₂ in argon (non-explosive mixture) containing 4% HF flowing at 10 L/min.

This approach to melting the salt would require additional heating and sparging equipment, but it can be integrated into the existing maintenance system that has been used to access the drain tanks in the past (Fig. 1.8). It is likely that heater elements and a sparge line can be designed to enter the central flange on top of the tanks. A new interface fixture between the existing maintenance shield and the drain tanks would be designed and procured. A potential heater system, based on the development of a rock melter at Los Alamos National Laboratory, has been identified (Jensen 1995). Other commercial heater systems may also be applicable.

3.1.2.5 Withdrawal of the molten salt

Once the salt is safely melted, and the desired redox potential has been re-established, transferring the salt out of the tanks should not pose any major difficulties. Two basic alternatives exist. The first is to transfer the salt out from the drain tank cell into the fuel storage tank in the fuel processing cell, as has been done several times in the past. This requires pressurizing the drain tanks with helium. The integrity of seals provided by freeze valves and salt line plugs would have to be verified before this operation. Some indication of the condition of these components may be obtained when the off-gas system is evacuated by the reactive gas removal system. The condition of the salt lines themselves and the fuel storage tanks would also be assessed. The drain tanks are thick-walled, and not been exposed to corrosive gases at molten salt temperatures. Exposure to fluorine at the annealing temperature is not likely to have challenged the integrity of the drain tanks. However, the fuel storage tank was exposed to fluorine at molten salt temperatures when the uranium was removed from the fuel and flush salts in 1968.

- 1) Heat supplied by external heaters to bring salt up to a subliquidus hot state.
- 2) Rock Melter supplies extra heat in specific region to cause localized melting.
- 3) Heat from Rock Melter increased as HF/H₂ sparge is continued.

Fig. 3.4. Diagram of process to melt a pool salt with an internal heater while restoring the fluorine balance with a HF/H₂ sparge.

The salt could be transferred to the fuel processing cell for separation of uranium, or just as a step in removing the salt. A line extends from the fuel processing cell to the spare cell. In early facility drawings this line was indicated for the removal of salt; it was in fact used to transfer salt to the distillation experiment and remains connected to that experiment. The line could be cut and diverted to a salt canning station in the spare cell.

Alternately, the molten salt could be lifted directly out of the drain tanks into a cask set up over the drain tank cell. This could be done by pressurizing the tank, or by lifting it with a vacuum. Depending on the equipment arrangements, multiple vacuum lifts could be required. Again, the general arrangement for this operation would be similar to that depicted in Fig 1.8.

Withdrawal of molten salt from the tanks does not appear to present any fundamental challenges similar to the challenge of safely and effectively melting reduced salt in the first place.

3.1.3 Removal as Solid Salt

As an alternative to removing the salt as a liquid, various approaches to removing solid salt were investigated. Three representative approaches were identified (Kring and Richards N.d.). These, involving a minor intrusion into the tank, a major intrusion into the tank, and removal of the tank and salt as a unit, are described in the following sections.

3.1.3.1 Removal with minor tank intrusion

The removal of the salt through an opening in the top of the tank made by cutting out the 3 in. flange represents the least radical intrusion into the tank. It involves deploying hardware through the cell shield plug penetration into the opening. This approach would require removal of the steam dome and bayonets, and the thermal insulation on top of the tanks. It also requires the adaptation or development of presently available hardware and end effectors. The thimbles in the tank interior would be a serious obstacle to total mechanical removal of the salt. Any attempt to go through a small opening in the top of the tank is complicated by the fact that equipment must be small enough to deploy and then be navigated around the thimbles and other tank internal hardware. Options for removal included mechanical devices such as augers, impact chisels, chipping hammers, needle scalers or water blasters to break up the salt and then vacuum or scoop the material out of the tank. A CO₂ blaster that would dislodge or break up the salt with simpler mechanical hardware was eventually selected as the desired option to pursue.

The minor tank intrusion sequence is illustrated in Figs. 3.5 and 3.6. These figures identify the equipment and facility modifications necessary for the operation. The operation of the CO₂/vacuum ablation wand will require the installation of a remote salt collection system consisting of a recirculating loop of air provided by a vacuum suction nozzle, cyclone separator, bag filter, vacuum blower, and return air piping loop to the tank interior through a primary containment extension. Collected salt will be dispensed into appropriate containers and stored in the drain tank cell.

Two approaches are shown for deployment of the CO₂/vacuum wand. A manipulator-actuated approach is shown in Fig. 3.5, and a stand-alone assembly is depicted in Fig. 3.6. The manipulator-actuated wand nozzle is positioned to direct a stream of high velocity solid CO₂ pellets the size of a pencil lead to impinge onto the salt. The salt is abraded off into particles to be swept into the vacuum annulus of the nozzle and transferred to the cyclone separator. The salt particles are collected in containers located in the drain tank cell. The wand (Fig. 3.7) is attached to a tank primary containment extension that prevents distribution of salt dust throughout the drain tank cell. The wand is spherically

Fig. 3.5. Depiction of the hardware needed to mechanically remove the salt using a CO₂ blaster mounted to an overhead manipulator system.

Fig. 3.6. Depiction of the hardware needed to mechanically remove the salt using a CO₂ blaster mounted directly onto the drain tank.

Fig. 3.7. Depiction of the wand and nozzle for the CO₂ ablation process.

mounted, providing both vertical roll and pitch, allowing the nozzle to target the space between the thimbles. Viewing equipment will be inserted into the tank to observe the process.

The stand-alone option (Fig. 3.6) is more complex but has no dependence on the pendulum characteristics of the telescopic mast manipulator. In both cases, an initial excavation of the salt down and out of the thimble radius may be required to provide access for wand installation and to decrease the overall time required for salt removal.

The rate of removal of the fuel salt using the CO₂ ablation technique is not known. A development program would be required to prove the technique in general and to demonstrate the needed dexterity to position the nozzle between and around the thimbles.

The installation will require removal of the existing 3-in. nozzle on top of the drain tank and replacing it with an 8-in.-diam. tank containment extension for mounting the wand. As a result, remote cutting and possibly remote welding will be needed to prepare the equipment. This, in turn, may require a special cell membrane extension and a glovebox-type secondary containment to operate and install the cutting and welding systems.

3.1.3.2 Removal with major tank intrusion

Removal of the salt after cutting off the top of the tank represents the most radical intrusion into the tank. This approach involves the greatest number of remote activities of all the mechanical removal options. Its single advantage is the exposure of the salt bed, free of obstructions for salt mining operations. This approach involves deploying hardware through the access shield plug penetration into the opening. It requires removal of the steam dome and bayonet assemblies, as well as the thermal insulation on top of the tanks. An extension of the tank shielding would also have to be built. Remote cutting tools, based either on core drills or a plasma torch, would be used to remove the thimbles and/or the upper dished head. Options for obtaining access to the tank would be to individually separate and extract the thimbles or to separate the thimbles from the salt while still attached to the tank head. The extraction of thimbles from the salt is complicated by the bond between the salt and the thimble surface. If this bond proves to be weak, rotary or impact shearing techniques may prove adequate to free the thimble. Applying heat to the thimble may serve to weaken the bond. At worst, the thimble could be drilled out with the salt. After the top of the tank is removed various tools could be used to remove the salt. Adaptation of commercially available tooling would be preferred over the development of new types of tooling. These operation are depicted in Figs. 3.8 and 3.9.

Figure 3.8 shows the salt being removed using a dedicated salt milling/vacuum device mounted on the tank, and positioned by a general-purpose polar fixture. The system consists of a radial arm, rotary mast milling head and vacuum auger that provides for the vertical, radial, and rotary motions of the auger, and a salt collection system. The latter includes a nozzle, a cyclone separator, a bag filter, a vacuum blower, and a return line to the tank. Viewing, handling and maintenance of the equipment is provided with a remote manipulator mounted on a telescoping mast crane located in an extension of the secondary containment above the cell.

After most of the salt has been removed, a final cleanup system will be needed to remove salt crust from the tank interior. Equipment for this purpose could include a CO₂ blaster, a needle descender, or a rotary descender. Vacuum transfer of the salt would be accomplished separately or using a vacuum system integrated into the tools. A development program would be required for all of the tooling described in this section.

Fig. 3.8. Depiction of a system to mechanically remove the salt from the tanks using a vacuum auger.

Fig. 3.9. Depiction of a system to withdraw the cooling thimbles from a fuel salt drain tank.

3.1.3.3 Removal of salt and tank as a unit

The tanks, with the solid salt in them, could be removed as a unit and transferred to some other processing facility for removal of the salt, or they could be lifted into an extension of the drain tank cell to enable mechanical access to the tank interior with shorter tooling. In either case, a basic set of activities is required. In the case of a transfer, the tank is lifted into a cask (Figs. 3.10 and 3.11). In the case where the tank is lifted to perform additional mechanical operations, the tank would be lifted into a cell extension provided with shielding windows and manipulator systems.

To remove the tanks, all instrumentation and heater lines would have to be disconnected or cut. The steam dome and bayonet assemblies would be freed from the water and condensate lines and the tank supports, and would be withdrawn through the maintenance shield into plastic bags or similar enclosures to prevent the spread of contamination. Salt and off-gas lines to the tanks would be cut and plugged. A special, bottom-loaded shielded cask would be procured. A structure would be erected on top of the drain tank cell (presumably at the high bay elevation) on which the cask would be set. This structure would complete the shielding around the cask. A contamination control barrier would be erected around the path that the tank travels as it is lifted into the cask. A lifting fixture would be attached to the tank, and the tank would be lifted using a hoist that is integrated into the top of the cask. Once in the cask, the tank would be placed on a jig to provide support for the tank. The cask bottom shield would then be closed and the cask can be moved from the drain tank cell. Provisions would have to be included in the design of the cask system to control reactive gases from the irradiated salt in the tank.

Once in the cask, the tank could be moved within the ORNL site, or it could be loaded into a cask approved for transport over the road. At present, no existing, licensed cask has been identified. A loading pit, would have to be identified for the transfer, and tank supports would have to be integrated into the transportation cask. It is unlikely that the cask depicted in Fig. 3.11 could be licensed for transportation over public roads; even if so, the cost of obtaining such a license would be high.

3.1.4 Removal with a Liquid Solvent/Carrier

3.1.4.1 Dissolution

The most obvious, common solvent for the MSRE fuel and flush salts is water, or water with various acidic or basic additives. Because uranium generally precipitates out of basic solutions, acids were the focus of this evaluation.

A set of simple dissolution experiments were carried out to establish the solubility of the MSRE fuel and flush salts (personal communication, L. M. Toth, September 6, 1995). The results of these tests are shown in Table 3.1.

Table 3.1. Solubility of components in MSRE fuel salt
in various solvents (g/L at 25°C)

Solvent medium	LiF	BeF ₂	ZrF ₄
H ₂ O	5.6	2.7	25
4 M HF	2.9	5.0	10
4 M HF + 2 M HNO ₃	3.3	2.5	4.2

Fig. 3.10. Depiction of the general arrangement of equipment and shielding needed to remove a fuel drain tank and salt as a unit and transport it to another location.

Fig. 3.11. Depiction of a cask system that could be used to remove a fuel drain tank and salt as a unit and transport it to another location.

At these low solubilities, it would require more than 500 m³ of water to dissolve the salt, resulting in a volume increase of more than 250 times. The salt did not dissolve readily. The salt was broken up to increase the surface contact with the solvent, and was agitated.

These experiments indicated some of the difficulties that would be encountered with salt dissolution, based on typical aqueous solvents. Further complications result from the need to maintain criticality safety. Simple models show that if the salts have a void fraction of 2%, and that void is filled with water, a nuclear criticality is likely. Thus, any solvent may need to incorporate a neutron poison. It might be necessary to drill a core through the salt, add a measured amount of water, and withdraw the water from the bottom of the tank before more can be added. If the water is taken up in the salt matrix (either incorporated into the salt itself or trapped in cracks and fissures in the salt monolith), this procedure may not work. A need to draw water from the bottom of the salt, using a core drill, incorporates some of the concepts of mechanical removal into this approach.

3.1.4.2 Suspension in a slurry

An approach to transport the salt with a smaller amount of solvent would be to break up the salt and transport it as a slurry. In a sense, this is the same concept as breaking up the salt with a CO₂ blaster and vacuuming up the broken particles, except that a liquid medium is used instead of the first solid, then gaseous, CO₂ medium. Thus, this approach has in essence been covered in Sect. 3.1.3.1, and is not addressed further here.

3.1.5 Screening of Removal Technologies

The technologies identified for removal of the salt include approaches for removal as molten salt, mechanical removal of the salts from the tanks, removal of the salt as an aqueous solution or slurry, and removal of the salt and tanks as a unit. Of these, removal as molten salt is the most straightforward and requires the least additional equipment. It is likely to be far less expensive than other options. But chemistry issues associated with excess reductant now present in the solid salt as a result of the migration of F₂ and UF₆ from the tanks must be resolved before the tanks are melted. Techniques for melting the salt while safely adjusting the chemistry have been proposed, and an experimental program to verify these techniques has begun. Removal as molten salt, with properly adjusted redox potential, interfaces well with useful technologies for separation of uranium and other materials from molten salt.

Removal of the salt by mechanical means or as a solution or slurry is more expensive, entails the development of more and complex equipment, and is likely to incur more cost and risk of the spread of contamination. Removal using the CO₂ blaster appears to be the most practical of these, and could be a viable backup to removal as a molten salt. Aqueous removal techniques are hindered by the very low solubility of the salt, and by the potential for a nuclear criticality if water moderator is introduced directly into the salt matrix. Removal of the tanks filled with solid salt is possible, although the cask and tooling needed for this operation would be expensive. To date, a destination that could accept and further process the salt and tank as a unit has not been identified.

3.2 SEPARATION TECHNOLOGIES

3.2.1 Fluoride Volatility

Fluoride volatility is a technology developed to separate uranium and other materials from fluoride salt solutions. As such, it has been applied to molten salt reactor fuels throughout the development of such reactors. Uranium was separated from carrier salt used in both the MSRE and its predecessor, the Aircraft Reactor Experiment. The operating experience with the MSRE salts is well documented (Lindauer 1969), and an overall review of the technology has recently been completed (Advanced Integrated Management Services 1996).

The flowsheet used to separate uranium from the MSRE is shown in Fig. 3.12. Salt was transferred from the drain tanks to the fuel storage tank in the adjacent fuel processing cell. This tank resembles one of the drain tanks in many ways, including the overall configuration of being hung in a furnace on a support ring that in turn rests on weigh cells. The tank is slightly larger than the drain tanks, so that the entire inventory of fuel or flush salt can be fluorinated in one batch, with sufficient freeboard in the tank to minimize salt carryover in the outlet gas. The outlet gas then passes through a high-temperature [399°C (750°F)] NaF trap located near the floor of the fuel processing cell. Volatile fission products were collected on this trap, but at this temperature uranium passed through. Uranium was then collected on a set of NaF traps located in a cubicle in the high bay. Excess fluorine was then reacted with KOH in a liquid caustic scrubber, and the outlet from the scrubber passed through a mist filter, a soda lime trap, several stages of charcoal, and a HEPA filter before being discharged to the MSRE ventilation system.

The salt was transferred at a relatively high temperature, and was then cooled to within 10°C (50°F) of the liquidus temperature to minimize corrosion and fission product volatilization during fluorination. The sample line was purged with helium to prevent condensation of UF_6 at the cold upper end. The salt was sparged with either pure fluorine or a fluorine-helium mixture at a relatively high flow rate (~ 40 L/min) to convert the UF_4 to UF_5 . Fluorine utilization was high during this period. When all the UF_4 had been converted to UF_5 , UF_6 began to form and volatilize, as indicated by a temperature rise in the first absorber and a rise on the inlet flowmeter. When this occurred, the fluorine flow was reduced to 15 or 25 L/min to increase the absorber residence time for more efficient absorption and to increase the fluorine utilization.

The gas leaving the fuel storage tank consisted of UF_6 , excess fluorine, helium, MoF_6 and some CrF_4 or CrF_5 from corrosion, IF_7 , and the fluorides of some other fission products such as tellurium, niobium, ruthenium, and antimony. The gas passed through the 399°C (750°F) trap where the chromium and most fission products were absorbed. A small fluorine flow was introduced upstream of this bed to ensure an excess of fluorine and to prevent any nonvolatile UF_6 from forming and remaining on the heated NaF in the event that the fluorine utilization was near 100%. Although the fluorine utilization was not high enough to require this additional fluorine stream, a small flow was maintained to prevent diffusion and condensation of UF_6 in the line.

The gas stream then left the shielded cell and passed through five NaF absorbers in a sealed cubicle in the operating area. These absorbers were heated to $93\text{--}121^{\circ}\text{C}$ ($200\text{--}250^{\circ}\text{F}$) to increase the reaction rate and to minimize MoF_6 adsorption. The UF_6 piping was heated to at least 60°C (140°F) to prevent condensation of UF_6 . As the UF_6 began to load on a given absorber and the temperature started to rise, the cooling air was turned on that particular absorber to limit the temperature to a maximum of 177°C (350°F). High temperature reduced the uranium loading by promoting surface absorption and reducing penetration of the UF_6 to the inside of the pellets. The final absorber was operated below 121°C .

Fig. 3.12. Flowsheet of the MSRE salt processing system.

(250°F), where the partial pressure of UF_6 over the $\text{UF}_6\cdot\text{NaF}$ complex allowed only a negligible amount of uranium to reach the caustic scrubber.

If the gas stream leaving the absorbers contained greater than 50% fluorine, it was diluted with helium before reaching the caustic scrubber. This allowed a smooth reaction in the scrubber without the production of a flame or pressure oscillations. The caustic scrubber was charged with 1300 L of 2 M KOH—0.33 M KI containing 0.2 M $\text{K}_2\text{B}_4\text{O}_7$, which was added as a soluble neutron poison. The reaction that occurred in the scrubber is

The scrubber solution was replaced before one-half of the KOH had been consumed, as determined by fluorine flow and calculated utilization, because dip tube corrosion was increased when the OH^- concentration was less than 1 M. Besides fluorine, most of the molybdenum and iodine were removed in the scrubber.

The high-surface-area mist filter located downstream of the scrubber removed any particulate matter from the scrubber. The soda-lime trap provided a means for detecting fluorine and a means for removing traces of fluorine from the scrubber off-gas before it reached the charcoal absorbers. Activated impregnated charcoal traps sorbed any iodine that was not removed in the caustic scrubber. The gas leaving the charcoal traps consisted of only helium and oxygen that was produced in the caustic scrubber. This gas flowed through a flame arrester and then through an absolute filter before being routed to the cell exhaust.

The flush salt was fluorinated and the uranium was trapped in a single set of NaF absorbers. After 5 h of fluorine sparging the flush salt contained 24 ppm uranium. The salt was sparged for an additional 1 h and 49 min at which time the uranium concentration was 7 ppm. A total of 6.5 kg of uranium was recovered from the flush salt. The average fluorine utilization was 7.7% during fluorination of the flush salt.

Fuel salt was fluorinated in a single batch, and the uranium was trapped in six sets of fluorine absorbers. Between runs, the fluorine trailers were changed and the caustic scrubber was recharged. Approximately 7.5 h of fluorination at about 40 L/min was required for conversion of UF_4 to UF_5 before UF_6 evolution was observed. After UF_6 evolution began, the fluorine utilization remained steady at about 30% for ~33 h of fluorine sparging at a rate of about 19 L/min for an average fluorination rate of about 6 to 7 kg/h. During the last 6 h of fluorination, the fluorine utilization decreased from about 30% to near zero as the uranium concentration in the salt decreased to 26 ppm. A total of ~45 h of fluorination time was required to fluorinate 216 kg of uranium from the salt. The overall fluorine utilization was 39% during fluorination of the fuel salt. Identifiable uranium losses were less than 0.1%. The recovered uranium was decontaminated from fission products by gross gamma and gross beta decontamination factors of 8.6×10^8 and 1.2×10^9 , respectively.

Use of this existing equipment is being evaluated for separation of the ^{233}U now present in the fuel and flush salts (DeVore N.d.). Certain changes would be required to accommodate highly enriched material (the original charge was about 30% ^{235}U). The off-gas system would need to be evaluated in terms of providing effective retention of ^{232}U decay products, including radon. The fission product inventory is now much less significant, and use of the hot NaF trap ahead of the uranium absorbers may not be necessary. Because of the radiation associated with ^{232}U daughters, including ^{208}Tl , shielded (and critically safe) absorbers would be required. Instrumentation would have to be upgraded, and the physical integrity of all components would have to be verified. This includes the integrity of equipment in the

drain tank cell, to ensure that the drain tanks can be safely pressurized to transfer salt to the fuel processing cell.

If the existing salt processing cannot be reused (at least, in its entirety), several other options exist. The salt could be immediately withdrawn into the containers that have been described earlier and moved into a shielded location for fluorination. The gas outlet from the container would pass through the new shielded absorbers and into the off-gas system. The existing caustic scrubber and the rest of the existing off-gas system might be used in conjunction with the new trapping station and fluorination system. This alternative would be well-suited to a salt removal approach in which molten salt is withdrawn directly from the drain tanks. It avoids the need to certify all of the drain tank off-gas and salt piping systems for pressurization of the salt, and avoids use of the fuel storage tank. This tank was subjected to significant corrosion during the 1968 fluorination operation.

The fluorination process was also evaluated for separation of plutonium from the salt (Advanced Integrated Management Services 1996). Results from laboratory and pilot plant studies indicate that plutonium is more difficult to fluorinate than uranium and very little volatilization of plutonium occurs until most of the uranium is removed. Long fluorination times may be required to significantly reduce the plutonium concentration. This also increases the total amount of corrosion experienced by the fluorination vessel. Plutonium is also thermally unstable at elevated temperatures and a high fluorine to PuF_6 ratio is necessary to prevent decomposition. If the plutonium is removed by fluorination, it is likely that some decomposition will occur that will result in deposition of PuF_4 in process piping and vessels. Thus, the fluorination process is not recommended for separation of plutonium from the salts.

3.2.2 Electrometallurgical Separation

The electrochemical process for treatment of MSRE fuel and flush salts is being developed and demonstrated (with simulated MSRE fuel salt to which representative fission products have been added) by Argonne National Laboratory (Laidler 1996a,b). The purpose of the electrochemical treatment is the extraction of actinides and fission products from the fuel/flush salt, concentrating the radioactive constituents in minimal-volume high-level waste forms and leaving a large volume fluoride salt residue containing only trace amounts of radioactivity. The process is carried out in a very compact system, with the present concept for fuel/flush salt treatment involving 30-L batches of salt (a slightly smaller quantity than the salt container described in earlier sections, which divides each of the fuel and flush salts into 24 containers with about 80 L of salt in each). Electrochemical treatment is conducted in an inert atmosphere glovebox, about 25 ft long by 8 ft wide by 14 ft high (Fig. 3.13), which can be installed in an existing hot cell or be enclosed with temporary shielding. With the envisioned 30-L batch size, the shielding requirements are about 6 in. of lead.

The process is described in a series of steps, as shown in Fig. 3.14. The materials that result from this process, along with a possible disposition, is indicated on Table 3.2. The quantities indicated are for the entire batch of fuel salt, roughly 2000 L. The process is carried out in 30 L batches, or about 65 batches. Each batch would be in process for one week. The processing approach is to displace the radioactive cations in the MSRE salt with nonradioactive alkali metal (either Li or Na) cations.

In step A of the process, zirconium would be removed from the salt and replaced with lithium. *Product 1* of the process is zirconium metal dendrites, plus metals that are more noble than zirconium. The zirconium is a component of the original fuel salt; the other metals would come from any noble metal fluorides that were present in the feed salt and the metal daughters from the decay of ^{228}Th that are more noble than zirconium. This stream is initially strongly radioactive, but since most of the activity

Fig. 3.13. Overall dimensions for a shielded inert atmosphere enclosure to house the Argonne electrorefiner.

Fig. 3.14. Diagram of the processing steps used to electrometallurgically separate radioactive components from the fuel salt.

Table 3.2. Process steps and products for electrochemical treatment of MSRE fuel salt

<i>Step</i>	<i>Product</i>	<i>Volume^a</i>	<i>Composition</i>	<i>Mass^a</i>	<i>Disposition</i>
A	Fission product metal waste	70 liters	- NM fission products and Th daughters .. (Mo, Ru, Pd, Cd, Rh, Tc, Se, Sb, Nb, Zr, Po, Bi, Pb, Tl) - Zirconium metal from fuel salt	6kg 455 kg	HLW; combine with metal waste from treatment of EBR-II spent fuel
B ^b	(In-Process) Bismuth ingot	n/a	- Bismuth ingot containing: - uranium - transuranic elements - rare earth fission products	37 kg 0.4 kg (trace)	In-process material; sent to Step B-1
B-1 ^b	High-purity uranium ingot	2 liters	- ²³³ U and trace amounts of ²³² U	37 kg	Return to ORNL ²³³ U repository
	Chloride salt waste	1.4 liters	- Transuranic elements	0.4 kg	HLW; incorporate in EBR-II ceramic waste form
C	Bismuth ingot	104 liters	- Rare earth fission products, Cs-Ba, Th, Th daughters - Transuranic elements - Bismuth (non-radioactive)	6 kg 0.4 kg 1000 kg	Interim storage for decay of ²²⁸ Th; final conversion to HLW disposal form as glass-ceramic
D	Metal waste ingot	100 liters	- Sr/Y fission products - Metal ingot	< 4 kg 600 kg	HLW; combine with metal waste from treatment of EBR-II spent fuel
	Fluoride salt residue	2075 liters	- LiF/BeF ₂	4300 kg	LLW; possible conversion to fluorapatite before disposal

^a Based on treatment of 2,000 liters of MSRE fuel salt

^b If uranium is initially removed by fluoride volatility process, these steps are omitted

is from ^{208}Tl it will decay away in a week. This metal waste could be made part of the metal waste form generated by the electrochemical treatment of EBR-II fuel at ANL-W.

In step B, uranium is removed from the salt by electrochemical titration with lithium into a liquid bismuth cathode. the use of bismuth in the cathode provides the means for removal of the active metals from the salt, yet leaving the active metal Be in the salt as a salt constituent BeF_2 . While removing all of the uranium into the cathode we would remove about half of the plutonium and a trace of the rare earths.

To make a high-purity uranium from this bismuth metal cathode, it is made into the anode of a second cell (which uses LiCl-KCl as the electrolyte). High purity uranium metal (*product 2*) is produced at the cathode of this second cell. This metal could be sent directly to the ORNL RDF for storage, or could be converted to oxide for storage. There is no physical connection between the fluoride and chloride cells. Plutonium and the rare earths accumulate in the chloride cell electrolyte, as they do in processing the EBR-II fuel at ANL-W. The salt left over at the end of the campaign is thus a candidate for further treatment at the EBR-II facility. The total quantity of chloride salt is at most 60 L, or less than half the salt charge at the ANL-W facility. At the completion of the MSRE campaign the process crucible from the chloride cell would be sealed and shipped to ANL-W, forming *product 3* of the process.

If uranium were separated by fluoride volatility before placing the salt in the fluoride electrorefiner, the second chloride electrorefiner would not be required. There would only be one extraction into bismuth, represented by the following step.

In step C, the remainder of the plutonium, rare earth fission products, the $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$, and the thorium (including daughters of ^{228}Th decay) are removed from the salt into a bismuth cathode. This forms *product 4* of the process. It is recommended that this metal product be held in interim storage until the ^{228}Th decays, with a 1.9 year half-life. A number of options are available for the ultimate disposal of this waste: (1) qualify the bismuth metal waste directly as a waste form, (2) since Bi is "glass forming," the entire waste could be added to a glass melter, or (3) the bismuth could be electrorefined to separate the rare earths and cesium from the bismuth, leaving a chloride waste salt that might be disposed of at ANL-W.

In step D, the strontium (including ^{90}Sr) would be electrorefined out of the salt. This will require the development of nitride- or oxide-enhanced technique for the extraction of the strontium at the cathode, since this ordinarily does not happen. The strontium waste form, *product 5*, is a small bed of nitride or oxide solids trapped within the cathode metal ingot. Candidate metals for this cathode are bismuth, cadmium, lead, antimony, or alloys of these metals. Since ^{90}Sr has a half-life of 28 years it could be placed into storage for 150 to 200 years for decay.

Finally, *product 6* is the basic matrix salt LiF-BeF_2 (or NaF-LiF-BeF_2) stripped of actinides, transuranics, and fission products. The salt volume is essentially unchanged from that initially fed into the process. This residue might be disposed of as low-level radioactive waste.

The mechanical handling steps are depicted in Figs. 3.15 through 3.17. Figure 3.15 shows the crucible handling steps, including bringing the salt can in through the transfer lock, operating the electrorefiner with the crucible in place, and removing the crucible after processing of that batch of salt is completed. The second step depicts handling of the solid cathode used for zirconium removal. Activities shown include steps used to separate salt from the metal product, including processing with a mandrel stripper and a spinning operation. The product receiver is shown leaving through the transfer

Fig. 3.15. Depiction of the crucible handling activities for the Argonne electrorefiner.

Fig. 3.16. Depiction of the solid cathode handling activities for the Argonne electrorefiner.

Fig. 3.17. Depiction of the bismuth electrode preparation and salt cleaning from the pounder cathode steps activities for the Argonne electrorefiner.

lock. Figure 3.17 depicts the handling steps for the liquid metal pounder cathode. An ingot preparation furnace is shown. During operation, the pounder mechanism agitates the metal-salt interface to "pound" the cathode deposit into the metal, ensuring that it goes into the metal solution instead of depositing on the cathode surface. After operation, the metal cathode is cooled and the solidified bismuth ingot is removed.

The electrorefining process is well-matched to a starting point of a halide salt containing uranium, actinides and transuranics, and fission products (in the EBR-II process, mechanical segmenting and dissolution activities are needed to get the fuel into the chloride salt). It produces a good-quality uranium product and, with the addition of the nitride- or oxide-enhanced strontium removal step, decontaminates the salt matrix sufficiently to dispose of it as low-level waste. However, the other product streams are not readily disposed of at ORNL. These include the zirconium metal waste, a chloride salt contaminated with plutonium and other radioactive materials, a waste form that incorporates plutonium and other materials in a bismuth ingot, and a metal waste incorporating the ^{90}Sr . If the uranium is removed by fluoride volatility before electrorefining, the second chloride electrorefiner is not needed. If the uranium could be disposed of with the other materials in the bismuth, the chloride electrorefiner is again eliminated. Storage of the salt with ^{90}Sr until the strontium decays could be considered, eventually resulting in a proposed low-level waste form. This would reduce the waste products to the zirconium metal waste (a material that must be removed before other materials are removed from the salt) and the wastes encapsulated in bismuth.

Ensuring the disposal of the bismuth product is a key to evaluating this technology. If the waste were qualified for direct disposal, this would make electrorefining a more attractive technology. Likewise, if a bismuth glass were qualified, the process would be attractive. If the full process were to be implemented, it would be useful to implement it at ANL-W, and directly interface with the EBR-II electrorefiner. The full strategy described above relies on several types of material being transferred to Idaho in any case. Issues with waste qualification were identified in a recent National Academy of Sciences review of the electrorefiner process (Committee 1995).

Costs of constructing an electrorefiner at ORNL are not thought to be very high (a few tens of millions), but the costs of the inert atmosphere facility are not included. At present, an appropriate facility at ORNL has not been identified.

3.2.3 Vacuum Distillation of Salt

Low-pressure distillation was studied as a method for separation and recovery of LiF and BeF_2 from less volatile rare earth fission products in the Molten Salt Breeder Reactor (MSBR) program. Removal of the rare earths was desirable in order to achieve a high breeding ratio in the MSBR. It was not considered economical to discard the salt to remove rare earth fission products in the MSBR. Investigations into low-pressure distillation included the operation of a test still using both nonradioactive salt and fluorinated MSRE fuel salt (Hightower et al. N.d.; Advanced Integrated Management Services 1996). This experiment, located in the spare cell adjacent to the fuel processing cell, is shown in Fig. 3.18.

Low pressure molecular distillation used for volatilization of the molten salt is considerably different from conventional distillation systems in which bubbles of vapor occur in the bulk of the liquid. In molecular distillation, vaporization occurs from the quiescent liquid surface and the vaporizing component is transferred to the surface by diffusion or convective mixing. Evaporation rate is proportional to the surface area exposed. Molecular distillation requires large vapor handling areas with the condenser located within a few mean free path lengths of the evaporating surface. These requirements

Fig. 3.18. Simplified flow diagram of the MSRE distillation experiment.

make scale up or the design of multi-stage units difficult. Data from operation of the single-stage unit using MSRE type salt indicated that distillation rates on the order of 1.5 ft³ of salt per day per square foot of vaporization surface can be achieved. Operating experience with the MSRE still (0.52 ft² evaporating surface area) included 6 test runs with nonradioactive MSRE-type salt for a total operating time of ~293 h during which time about 185 L of salt was distilled. In the test with radioactive salt from the MSRE (in the same still) ~12 L of salt was distilled in 23 h of operation. Operating difficulties during the period with nonradioactive salt included plugged off-gas lines due to ZrF₄ deposits and plugged feed lines due to metal deposits. The vaporization rate may have been reduced by concentration polarization and droplet entrainment in the vapor may have occurred. The corrosion rate of the vessel appeared to have been acceptably low.

Single state low-pressure distillation of the MSRE fuel and flush salt will likely produce an overhead product containing most of the salt and volatile fission products (mostly cesium fluoride) and a bottom product containing salt with a higher LiF content than the original salt (possibly 3% to 5% of the original salt volume), that contains most of the uranium, plutonium, and major fission products other than cesium. Based on the work done for the MSRE off-gas uranium, the uranium from the distillation will require considerably more processing before it is suitable for long-term storage. It is not clear that the storage capability of the overhead product (possibly containing 95% of the salt) has been significantly improved (other than from removal of the uranium and plutonium) since it still contains cesium, is highly radioactive, and contains a high concentration of fluorides. Removal of enough of the uranium, plutonium and americium from the overhead product could lead to the larger quantity of salt being classified other than transuranic waste.

While distillation rates and corrosion data from the short term engineering scale distillation tests indicate that distillation of the quantities of fuel and flush salt to be processed is probably feasible, it is expected that the processing rate would be slow and considerable design and development work would still be required.

In summary, low pressure distillation might provide a technology that concentrates uranium, plutonium, strontium and other radioactive materials in a small quantity of salt, while leaving the cesium and other radioactive materials in the larger quantity of salt. It is not clear that this technology, by itself, accomplishes significant gains toward disposing of the fuel or flush salts.

3.2.4 Other Uranium Separation Technologies

A number of other alternatives for separating uranium from the salt have been identified and briefly evaluated (Advanced Integrated Management Services 1996). None of these was found to offer any advantages over the technologies already described.

3.2.4.1 Precipitation of uranium from molten salt

Conversion of the uranium into a compound that is insoluble in the fuel salt could allow separation of the uranium as a solid. Various strategies to precipitate uranium were identified. No insoluble fluoride was identified. Several strategies were identified that might convert uranium in the salt to an oxide. However, removal of the insoluble oxides from the salt poses several practical difficulties. This technique was considered speculative with major uncertainties and doubtful performance.

3.2.4.2 Reduction of uranium in molten salt to metal

A reducing metal, such as lithium or calcium, might be added to give a complete reduction of uranium fluorides to uranium metal which would then be separated from the fuel salt. A number of serious concerns, including the potential for a nuclear criticality and the development of practical methods to collect the uranium product, were identified. Again, this technique is not recommended.

3.2.4.3 Dissolution and separation by solvent extraction

Several options were identified that would separate uranium using an aqueous process. For all of these, the low solubility of the salt in aqueous solvents (Table 3.1, Sect. 3.1.4) results in a much larger aqueous solution, without an established basis that all components of the salt go into solution. To separate the uranium by solvent extraction, several feed adjustments would be required. These include the addition of aluminum nitrate to complex the fluoride, addition of an oxidant to put the uranium and plutonium in the (VI) valence state necessary for extraction, and other additives to achieve the required salting strengths and to minimize corrosion.

While solvent extraction has been used for a wide variety of conditions, a development program would be required to establish the specific operating parameters for this system. There is no known operating solvent extraction system that could simply be adapted to process the salt solutions. Therefore, a relatively large, complex (and expensive) system would have to be built.

3.2.4.4 Dissolution and separation by ion exchange

After complete dissolution of the MSRE fuel salt (with the difficulties addressed previously), an ion exchange process might be the most efficient and practical separation procedure for uranium and perhaps plutonium. Feed adjustments would be required to give the optimum conditions for metal separations. These are likely to include oxidation of all uranium to the U(VI) valence, adjustment of pH without precipitation of U, Zr, or Be compounds, and possibly the addition of $(\text{NH}_4)_2\text{SO}_4$ or other salts to give anionic complexes of UO_2 .

The ion exchange separation would probably be a batch operation with preferential removal of uranium and perhaps plutonium. The preferential removal of the main salt components (Zr, Be, and Li) leaving uranium in solution would require excessive volumes of ion exchange resin.

Ion exchange separation of uranium is likely to produce a concentrated uranium solution product. Impurities in the product are not significant if it is for the purpose of disposing the uranium. Losses of uranium to the larger volume of solution waste are only important if they affect prospects for disposal of this material. The used ion exchange resin itself might retain enough uranium or fission product activity to require disposal as a radioactive waste.

An ion exchange separation of plutonium is also likely to be effective and practical. But the conditions for plutonium separation probably differ from those for uranium. Thus, separation of both uranium and plutonium would probably require two feed adjustments and two ion exchange treatments.

3.2.4.5 Dissolution and separation by precipitation

The precipitation of uranium from the other materials in the MSRE salts has much different requirements than those that commonly apply. The principal requirement is separation from beryllium, lithium and zirconium salts in solution. Requirements for product purity and recovery percentage are less

restrictive for waste disposal than for the production of fuel. Impurities in the uranium precipitate are of little importance up to the point where they result in significantly larger amounts of waste solids for disposal. Losses of uranium to the waste solution are only important when they affect the prospects for disposal of that solution.

The peroxide precipitation of uranium as $\text{UO}_4 \cdot \text{H}_2\text{O}$ solids is more selective for uranium than the more commonly used ammonium diuranate or ammonium uranyl carbonate precipitations. The solubility of uranium oxalate is probably too high to give an acceptable recovery of uranium by oxalate precipitation. The separation from zirconium is probably the poorest and the controlling separation. The separation factors would have to be determined by experimental tests. After the salt was in solution, the pH should be adjusted upward to near 2, or as high as possible without precipitation of zirconium. After addition of peroxide and perhaps additional pH adjustment the solids and solution should be separated and analyzed. The uranium content of the solids and of the solution would be the critical results. Good yields and separations from impurities have been demonstrated but for significantly different solutions than would result from dissolving the MSRE salts.

3.2.4.6 Preferential dissolution of uranium from pulverized solid salt

The solubility of U(VI) as UO_2F_2 is high compared to the solubilities of lithium, beryllium and zirconium fluorides. The concentration of uranium is much lower than that of the three major components. Therefore, a small volume of equilibrium solution could dissolve a high fraction of the uranium with only very small fractions of the other salts.

Leaching of a soluble component from solids is a physical process dependent on the fineness of the solids and other conditions. Empirical, experimental information is required. If mechanical removal of solid salt is selected, then the usefulness of performing these tests should be considered. Leaching has no application if the salts are dissolved. Fluoride volatility is preferable for separation of uranium from molten salt.

Some MSRE studies were made to measure the aqueous solution concentration after fluoride salt powders were stirred in water. The solution concentrations showed higher U/Li and U/Be ratios than those in the salt. Oxidation of U(IV) to U(VI) would greatly increase the solubility of uranium.

The preferential leaching of uranium would give a UO_2F_2 and HF solution saturated with the other fluoride salts. Additional processing would be necessary to give uranium solids acceptable for storage. After the solution concentrations are determined by experimental studies of leaching, procedures for conversion to uranium solids could be selected and tested. Precipitation of $\text{UO}_4 \cdot \text{H}_2\text{O}$ and calcination to U_3O_8 would probably be satisfactory.

3.2.5 Screening of Processing Technologies

Fluorination is a technology for separating uranium from molten salt that has been used successfully in MSRE in 1968, is simple, and interfaces well with facilities that will have been constructed for the conversion of the UF_6 present in the MSRE off-gas system to U_3O_8 for stable, long-term storage and transfer to the fissile materials disposition program.

Electrorefining is a technology that can separate uranium, transuranics and actinides, and fission products from the salt matrix. An electrorefiner based on simulated MSRE fluoride salt is now being demonstrated at Argonne National Laboratory. This technology produces a range of product streams, and achieves both uranium separation and stabilization waste forms containing transuranics, actinides,

and fission products. Disposition of some of the waste products may require additional processing, combination of wastes from similar processes, or a waste qualification process.

Other separations technologies have been identified, but either require large, expensive facilities for implementation or are technologically immature. None of the other technologies appear to offer important features not offered by fluorination or electrorefining.

3.3 STABILIZATION TECHNOLOGIES

3.3.1 Stabilization of Fluoride Salt with a Getter

As discussed in Sect. 1.2.4, irradiation of solid salt liberates fluorine from the salt matrix. At elevated temperatures, the fluorine radicals produced back-react with the metal sites left behind, restoring the fundamental salt chemistry. However, at room temperature the fluorine radicals combine to form fluorine molecules, which diffuse through the salt and are released as fluorine gas. In addition, the fluorine released by radiolysis appears to oxidize uranium in the salt matrix, producing UF_6 . This, too, diffuses out of the salt matrix. Preliminary experiments have suggested that fluorine is liberated from the salt matrix by beta and gamma, not alpha, radiation. Production rates have been quantified under a number of conditions, and projected future fluorine production is plotted in Fig. 1.16.

Generation of these reactive gases and their migration have led to the most important issues now faced by the MSRE Remediation Project.

Any package that contains fluoride salt that is exposed to a significant flux of beta-gamma radiation will require measures to control the evolution of fluorine and UF_6 . Reacting the gases with an appropriate chemical (referred to as gettering) is the simplest approach to controlling this phenomenon. This technique could be applied to control the production of both F_2 and UF_6 , or it could be applied to salt from which the uranium has been removed, in which case only fluorine is the issue. Since technologies are available for the separation of uranium from fluoride salt, and since the consequences of transport of uranium out of the salt matrix are potentially severe, gettering is considered a more appropriate technique for controlling fluorine only, except in cases where gas control may be required for a relatively short time. If needed, a sodium fluoride trapping system can be used to control UF_6 evolution. The reactive gas removal system now being brought into operation is an implementation of this technique, and the trapping of UF_6 on NaF will not be discussed further.

If the uranium is separated from the salt, and the salt residue is proposed as a waste form, a getter might be placed into the salt package. As seen in Fig. 1.16, the production of fluorine falls off as the sources of beta and gamma radiation in the salt decay away. Thus, the amount of getter needed for the fuel salt waste is that needed to ensure that ~200 moles of fluorine are reacted.

A getter can be used in two ways. A package of chemical can be placed in the container but as a discrete unit adjacent to the salt. In this case, fluorine is allowed to diffuse out of the salt matrix, travel to the getter, and react with the chemical in the getter. If the package is vented, it should be designed so that any gas leaving the package passes through the getter. Alternately, a material could be integrated into the salt matrix itself. In this case, the fluorine reacts with the getter before it diffuses out of the salt. As irradiation of the salt proceeds, isolated metal sites are formed at the locations where fluorine has been liberated. Eventually, these sites begin to serve as a getter. Experiments have demonstrated a "damage limit," at which point sufficient metal sites exist that fluorine gas evolution stops. This limit is reported to be about 2% fluorine loss. The loss of fluorine from the MSRE fuel salt is estimated to be

about an order of magnitude lower than this, and thus the damage limit will not be reached before the source decays away.

A very preliminary review of getter materials has been performed (personal communication, D. F. Williams, July 25, 1996). The initial, conservative recommendation is that the use of a simple overpack of reactive solids would involve a reasonably straightforward laboratory demonstration. The number of equivalents necessary can be predicted by simple stoichiometry. An initial proposal should recommend the use of proven fluorine getters such as soda-lime or alumina, even though active metals like aluminum or titanium sponge may have better performance. These other materials may be considered after some preliminary effectiveness tests have been performed, and the potential reactions with containers, other components of the gas, and the salt have been considered. Until performance tests are available, a stoichiometric excess (such as 200% of that required) will be assumed. A getter in an overpack should be separated by some distance from the salt in order to minimize the potential for re-radiolysis of the fluoride salt in the overpack.

The reactions that take place using soda-lime (5-20wt% NaOH, 6-18wt% water, balance CaO) are

and the reaction for alumina is

The gettering of the salt in a more intimate manner, either by alteration of the salt chemistry on microscopic scale, or by blending of a second phase into the salt, is a far more challenging goal and requires additional development. It does, however, eliminate all issues associated with separation of salt and getter material or the interaction of materials with fluorine between salt and getter. Introduction of reducing sites into the salt might be accomplished by adding a soluble transition metal salt that has a stable lower oxidation state [e.g., Ce(III/IV)], by electrochemical means, or by addition of a second phase which is well distributed in the salt.

If soda-lime (assumed to be 10% NaOH, 10% H₂O, and 80% CaO) were used in conjunction with the packages described earlier in this report, if only the CaO were considered in the calculation, and if twice the amount of CaO were provided as is necessary to react with the fluorine, then about 28 kg of soda lime would be required for all of the fuel salt. Each of the 24 packages would contain a little over 1 kg of soda lime. Such a package will occupy a few liters of space, consistent with the volume of the package not occupied by salt (about 25%, or about 20 L).

3.3.2 Conversion of Fluoride Salt to Oxide Using the INEL New Waste Calcining Facility

An alternate approach to stabilizing the fluoride salts is to convert the material from a fluoride to an oxide. An existing technology that could be applied is calcining, such as is performed at the INEL New Waste Calcining Facility. This facility uses a kerosene-fired spray calciner to solidify waste solutions from the tank farm at the Idaho Chemical Processing Plant (ICPP). A general flowsheet of the INEL calciner is shown in Fig. 3.19. Wastes are transported from the waste tanks, excess water is evaporated off, and the feed is injected into the calciner which operates at 500°C (932°F). The calcine particles accumulate in a fluidized bed, and are drawn off at the bottom and pneumatically transported to the calcine storage bins. The off-gas (containing nitrogen oxides) is led to a cyclone to separate any

Fig. 3.19. Diagram of the overall operation of the INEL New Waste Calcining Facility.

entrained calcine particles. It then goes to a series of off-gas treatment steps before being released to the stack.

The feed to the calciner is an aqueous nitrate salt solution. The primary reactions taking place during calcination of typical INEL feed are (1) the decomposition of nitric acid; (2) the evaporation of water; (3) the conversion of the aluminum and stainless steel nitrates to the metal oxides; (4) the conversion of zirconium fluoride to zirconium oxide, and (5) the formation of zirconium fluoride (personal communication, P. A. Ostby, July 15, 1996). The fission product elements are converted to oxides if the nitrate is unstable at the calcination temperature. Cesium and strontium probably remain predominantly as nitrates, as does sodium nitrate and possibly calcium nitrate if it is present in excess of the amount that reacts with the fluoride in the feed. The simplified chemical reactions taking place in the calcination process are as follows:

To prevent corrosion of the stainless steel off-gas equipment during calcination of fluoride-bearing waste, calcium is added (as calcium nitrate) before calcination to retain the fluoride in the calcined solids. The calcium reacts with fluoride in the feed solution to form a gelatinous precipitate of calcium fluorozirconate (CaZrF_6). This gelatinous precipitate remains suspended in the feed solution and during calcination at 500°C (932°F) reacts to form calcium fluoride, according to the reaction:

The calcium fluoride is thermally stable at the calcination temperature of 500°C (932°F).

Calcination of the sodium-bearing waste, which contains up to 2 M sodium nitrate, is difficult because the solid sodium nitrate, which is molten at 500°C (932°F), causes agglomerates to form in the fluidized bed of the calciner. To prevent agglomeration, sodium-bearing waste is blended during calcination with zirconium fluoride waste to form cryolite (NaAlF_6). The resulting calcine is thermally stable at the calcination temperature.

Typical product resulting from calcination consists of granular particles that are nearly spherical. The particle diameter of the product from the bed is generally in the range of 0.2 to 0.6 mm, but the diameter may vary from about 0.1 to 1.5 mm. It is free-flowing and readily transported pneumatically through pipelines. Most of the particles that leave the calciner vessel in the off-gas are removed by the primary cyclone and routed to the storage bins along with the calciner bed material.

It is probably feasible to dissolve the MSRE fuel salt in an aqueous nitrate solution (with the difficulties discussed in Sect. 3.1.4) and blend the MSRE salt solution into feed to the INEL calciner (Denney N.d.). The corrosivity of the MSRE salt is not significantly different from that of other streams that can be handled (and have been handled) by the New Waste Calcining Facility. In particular, the beryllium content is no more troublesome than the cadmium content of other wastes. If the uranium is still present in the salt, the salts will be fed into the input stream of the calciner gradually, with full regard for criticality issues. The resulting calcine would be stored in an existing facility instead of a new one yet to be built. The calcine resulting from the calcination process switches the fluorine content of the MSRE salt to CaF_2 , with sufficient calcium added to the mix to retain the fluorine. All of the fluorine that enters with the MSRE salt solution remains in the calcine. The product would be blended with the calcine already in storage at INEL. This option appears to be technically feasible, and makes use of an existing facility. It would require the restart or construction of a salt dissolver, and provision of adequate piping from these to the calciner feed.

The chemistry of calcining the MSRE salts should be reviewed to ensure that no operational difficulties, such as those discussed for the sodium-bearing wastes, are encountered. In the case of sodium-bearing wastes, the addition of zirconium provides a solution to operational difficulties in the calciner. It is not known whether lithium behaves similarly to sodium in the calciner feed. Both lithium and zirconium would be present in the MSRE feed (lithium in higher concentration than zirconium).

3.3.3 Conversion of Fluoride Salt to Borosilicate Glass

3.3.3.1 General approach to vitrification

Vitrification involves combining a liquid, solid or slurry waste material with a glass-forming frit (typically SiO_2 , B_2O_3 , and Na_2O) at moderate-to-high temperatures [$1050\text{--}1200^\circ\text{C}$ ($1922\text{--}2192^\circ\text{F}$)] to produce a glass. The glass is then poured into a container and solidified. A typical high-level waste glass container is depicted in Fig. 3.20. Borosilicate glass is the only waste form for which Preliminary Waste Acceptance Specifications for disposal in the federal repository exist.

A borosilicate glass process has been used in France by COGEMA to immobilize high-level waste slurries for a number of years. Vitrification plants have recently started up at the Savannah River and West Valley sites. A proposal has been developed for the construction of a vitrification facility at INEL. Bids are being evaluated for the demonstration of high-level waste management at the Hanford site, which could include vitrification. Use of the existing vitrification facilities, and the proposed INEL facility (which could immobilize calcine produced at INEL) are discussed in the following sections.

3.3.3.2 Conversion of fluoride salt to borosilicate glass using the Savannah River Defense Waste Processing Facility

Weapons material production at the Savannah River Site (SRS) has produced unusable byproducts such as intensely radioactive waste. The high-level radioactive waste, about 35 million gallons, is stored in waste tanks on site. The S-area DWPF will bond the radioactive elements in borosilicate glass, a stable storage form (WSRC-RP-94-396 N.d.).

Figure 3.21 shows a schematic diagram of the process to immobilize high level waste stored at SRS. The DWPF sludge feed slurry is considered to be well-mixed because of the extended sludge processing in the tank farm.

Fig. 3.20. A typical borosilicate glass high level waste package.

Fig. 3.21. Diagram of the overall operations performed at the Savannah River Defense Waste Processing Facility.

Waste salt solution is processed in the in-tank precipitation process to remove ^{137}Cs and to adsorb strontium on monosodium titanate. Soluble uranium and plutonium are also adsorbed on monosodium titanate. The tetraphenylborate slurry containing potassium and cesium tetraphenylborate precipitates and monosodium titanate with adsorbed strontium, uranium, and plutonium is then washed in the DWPF late wash facility before it is sent to the DWPF salt processing cell.

In the salt processing cell, the precipitate slurry is first stored in the precipitate reactor feed tank and then processed in the precipitate reactor. In the precipitate reactor, tetraphenylborate is destroyed by acid hydrolysis reactions to produce benzene and an aqueous phase containing radionuclides.

The sludge feed is slurried, washed, and filtered several times in Tanks 40, 42, and 51 and becomes homogenized during extended sludge processing operation. Alkaline sludge feed is then transferred from the tank farm to the sludge receipt and adjustment tank in the DWPF chemical processing cell. The sludge slurry is treated with nitric acid in the sludge receipt and adjustment tank to control the rheological properties of the sludge slurry, primarily nitrites, carbonates, and soluble hydroxides.

The precipitate hydrolysis aqueous product is combined with the sludge slurry and the borosilicate glass frit in the DWPF chemical processing cell to produce melter feed. The high level radioactive waste is finally immobilized in a glass matrix contained in sealed stainless steel canisters.

To summarize the overall DWPF process operation, there are two high-level waste feed streams from the tank farm delivered to the S-area DWPF. The precipitate feed slurry is processed in the salt processing cell to produce the precipitate hydrolysis aqueous product for subsequent sludge receipt and adjustment tank and melter operations. The sludge slurry is processed in the sludge receipt and adjustment tank, and combined with the precipitate hydrolysis aqueous product. The amount of precipitate hydrolysis aqueous product, or more correctly the amount of soluble and insoluble solids in the product, is half of the sludge solids. All of the waste slurry feeds are combined in the slurry mix evaporator with the glass forming frit. The melter immobilizes all of the waste feeds in a waste borosilicate form.

It has been proposed that the MSRE salts be dissolved and blended into the feed to the DWPF. The acceptability determination for DWPF process control (Brown and Postles N.d.) limits the fluoride content in the DWPF feed to 1 g NaF per 100 g glass. Assuming this limit is based on the effect the fluoride has on the process, a molar conversion was performed to define the rate at which the MSRE salt fluorides could be bled into the DWPF feed stream, and the number of glass canisters in which that the MSRE material would be spread. These calculations (personal communication, A. Dubbs, July 30, 1996), based on information supplied by Savannah River personnel (personal communication from T. Gutman to A. Dubbs, July 17, 1996), indicate that the MSRE fuel and flush salt each would be distributed through at least 500 waste canisters. If there is already a significant fluoride content in the Savannah River feed, this number would increase. Thus, the MSRE blending operation would require at least 25% of the total DWPF operating campaign to immobilize the contents of the SRS tank farm.

The feed to the DWPF would be an acidic solution. Again, this would require either converting existing equipment in the Savannah River canyons to this purpose or constructing a new dissolver. Waste form performance is an empirical art, and test melts would have to be evaluated to ensure that an acceptable waste form results from the proposed blend. No technical reasons have been identified to date that rule out encapsulation of the MSRE salts in the DWPF, but it does not appear to be a short-term operation to be conducted at minimal cost.

Other approaches to vitrifying materials in the DWPF or a similar facility have been proposed by Savannah River personnel. These include preparing melts of higher concentration material that is then placed inside a standard canister, and surrounded with standard melt. Development of these techniques is still at an early stage.

3.3.3.3 Conversion of fluoride salt or calcine to borosilicate glass using the proposed INEL Waste Immobilization Facility

The INEL has been converting liquid high-level wastes to calcine for a number of years. However, the calcine is considered to be a material suitable for interim storage but not for disposal in the federal repository. Thus, a proposal has been developed for a waste immobilization facility to convert the calcine (and any liquid waste that would remain in the tanks) into a waste form that would be accepted in the repository (Denney N.d.). Borosilicate glass and glass ceramics formed in a hot isostatic press are the candidate waste forms. This discussion focusses on the borosilicate glass waste form. The INEL waste immobilization facility has not yet been approved. However, the settlement agreement stipulates that high-level wastes leave Idaho by 2035 (Settlement agreement N.d.). Design of the waste immobilization facility is expected to begin around the year 2010.

The overall steps of the proposed waste immobilization facility are shown on Fig. 3.22. The first phase of the project would address any wastes that remain in the liquid waste storage tanks, and later would treat dissolved calcine. The proposal treats the waste liquid in a number of stages to concentrate actinides and fission products for immobilization in the vitrification facility. The low activity liquid waste that remains would be solidified with grout and would ultimately be disposed of as low-level radioactive waste. Actinides would be separated from the liquid waste using the TRUEX continuous counter-current solvent extraction process. A set of centrifugal contactors will be used to remove an aqueous concentrated actinide product and to send the raffinate to the next process step. The second process step is based on a similar solvent extraction system, using a crown ether (such as 18-crown-6) to remove strontium. Again, the product is a concentrated aqueous stream, and aqueous raffinate is sent to the next process step. The final process step is the removal of ^{137}Cs by ion exchange. Either spent resin or an eluant solution becomes the final high-level waste stream, and the effluent is sent to the grouting facility. The concentrated aqueous actinide and strontium wastes and the concentrated cesium wastes from the ion exchange process are then recombined and become the feed for the vitrification facility.

The second phase of the project will be the construction of the vitrification facility and a calcine dissolver. Dissolved calcine will be sent through the separations process described above. The vitrification flowsheet is shown in Fig. 3.23. For a liquid feed, the waste solution would be sampled and analyzed, and based on the analytical results, a suitable frit would be selected. The liquid would be dried in a rotary calciner or blended directly with frit and introduced to the glass melter as a slurry. If calcine were to be vitrified directly, it would be mixed with glass frit in the required proportions and fed to the glass melter. Typical calcine waste loadings in the glass vary from 25 to 33 wt% depending on the type of calcine to be vitrified.

The glass melter would typically be operated at a temperature between 1050–1200°C (1922–2192°F). Molten glass produced in the melter would be poured into canisters, sealed, and transported to an interim storage facility before final disposal. The melter off-gas consisting of hazardous (Hg and Cd) and radioactive (Cs, Tc, and Ru) materials would be treated in an off-gas treatment facility and recycled to the melter as needed before stack discharge.

Fig. 3.22. Diagram of the overall operations that would be performed at the proposed INEL waste immobilization facility.

Fig. 3.23. Diagram of the overall operations that would be performed at the proposed INEL vitrification facility.

This process is similar to those implemented at Savannah River, West Valley, and by COGEMA in France. Many features of these facilities are expected to be directly applicable to the vitrification of INEL wastes, reducing the amount of research and development needed to implement the INEL process. Nonradioactive, pilot scale tests of joule-heated ceramic glass melters completed at the ICPP on simulated waste have proved the initial feasibility of the calcine vitrification flowsheet.

It is expected that the MSRE salts could be vitrified in this proposed facility. The MSRE material could be fed as a component of the INEL calcine, or it could possibly be fed directly as a solid or acidic solution. Because of the preliminary nature of the description of the INEL facility, no details on the requirements for accommodating the MSRE materials are available.

3.3.3.4 Conversion of fluoride salt to borosilicate glass using the West Valley Demonstration Project Vitrification Facility

A vitrification facility, in many ways similar to the Savannah River DWPF, has recently begun operation at West Valley, New York, to immobilize wastes remaining from the operation of a commercial reprocessing facility in borosilicate glass. It is assumed that the operation of that facility is limited to the wastes already present at the West Valley site, and use of this particular facility has not been explored. The general technical issues identified with the use of the DWPF would likely apply to the West Valley facility as well. The waste volume in which to dilute the MSRE material would be less, and the facility would be even less able to adapt to an unusual inlet stream.

3.3.4 Other Salt Conversion Processes

3.3.4.1 Oxidation and conversion of fluoride salt to glass using the Glass Material Oxidation and Dissolution System (GMODS)

The GMODS process has been developed to vitrify a wide variety of materials that do not exist in the oxide form. Existing vitrification processes convert only oxides or oxide-like materials to glass. GMODS has been developed to directly convert oxides, metals, ceramics, organics, halogens, and amorphous solids to glass. This can allow the conversion of complex waste mixtures, including filters, process wastes, laboratory wastes, etc.) to glass without pre-processing. GMODS has also been considered for the direct conversion of halogenated materials (initially chlorides, but recently the MSRE fluorides) to glass (Forsberg and Beahm 1996).

The GMODS process converts the feed materials to the glass form inside the melter. The process can operate in batch mode (as shown in Fig. 3.24), or in continuous mode. This discussion describes the batch process. The process begins with a glass melter filled with molten, lead-borate dissolution glass. Oxides dissolve in glass, but metals and organics do not. The GMODS process uses lead oxide (PbO) in the molten glass to oxidize metals to metal oxides and organics to carbon oxides. The resultant metal oxides dissolve into the glass. The carbon oxides exit the melter as gasses. The lead metal reaction product separates from the glass and forms a separate layer at the bottom of the melter. The boron oxide (B_2O_3) in the melt assures rapid dissolution into the glass of any protective oxide layers on metal wastes.

After dissolution of the waste, silicon oxide and other additives are added to the glass to produce a high-quality product glass. Excess PbO is removed from the glass by adding carbon, which converts the PbO to lead metal and carbon dioxide (CO_2). The final glass may have some or no PbO depending on the desired product glass. The product glass is poured from the melter into the waste packages. To generate the next batch of dissolution glass, boron oxide is added to the melter and the lead metal is oxidized to PbO with oxygen.

Fig. 3.24. Process steps for batch processing using the glass materials oxidation and dissolution system.

GMODS can convert halogen-containing materials to glass, a process which creates a separate nonradioactive sodium halogen waste stream. Halogens, such as fluorides, usually make poor-quality glasses. In the GMODS dissolution glass, fluorides in the waste produce lead fluoride (PbF_2), which is volatile at glass melter temperatures and exists to an aqueous sodium hydroxide (NaOH) scrubber. In the scrubber, the PbF_2 will react with the NaOH to yield insoluble lead hydroxide [$\text{Pb}(\text{OH})_2$] and soluble NaF . The insoluble [$\text{Pb}(\text{OH})_2$] is recycled back to the melter, where it decomposes to PbO and steam. The aqueous NaF stream is cleaned and discharged as a chemical waste.

Because of the corrosive characteristics of the initial dissolution glass, GMODS requires a cold-wall melter in which cooling jackets in the walls produce a "skull" of solidified material that protects the walls from the contents of the melter. The melters can be heated by fossil, induction, plasma arc, or electron-beam systems. Such systems are currently used to melt high-temperature materials (e.g., titanium and superalloys) and to produce specialty glasses.

The basic GMODS process creates a lead borate fusion melt. From that melt a borosilicate glass can be produced. Alternatively, the lead oxide could be removed from the melt by adding carbon, producing a borate fusion melt. This material could then serve as a feed to a standard borosilicate glass melter, such as DWPF.

Tests performed to date have demonstrated the dissolution of UO_2 , ZrO_2 , Al_2O_3 , Ce_2O_3 , MgO , and other oxides. Oxidation-dissolution tests demonstrated the oxidation of uranium, cerium, zircalloy-2, aluminum, stainless steel, and other metals. Oxidation-dissolution tests have also demonstrated the oxidation of carbon and graphite, with production of CO_2 . The other process steps (adding glass frit, removing lead from the glass, and oxidizing lead back to PbO) have been investigated in the laboratory. The reactions necessary to convert the materials in the MSRE salts have been reviewed using literature data, but have not been verified in the laboratory.

To move forward with application of GMODS to the MSRE salts, small laboratory tests are needed with lithium fluoride and beryllium fluoride to experimentally confirm the thermodynamic analysis of the behavior of fuel salts in the GMODS process. Discussions should be held with DWPF personnel on the option of feeding a GMODS product into the DWPF. Design and construction of a GMODS facility might then proceed. It is possible that a number of potential users can jointly fund the further development of a pilot-scale GMODS facility.

3.3.4.2 Conversion of fluoride salt to mineral phosphate or phosphate glass

An alternate proposal for conversion of the MSRE fluoride salts involves the production of a mineral phosphate or phosphate glass waste form by reacting the salts with boron phosphate (personal communication, C. Baumberger and D. Beach, May 16, 1995).

This proposal is based on the reaction of boron phosphate (BPO_4) with the molten (or granulated solid) salt mixture to remove the fluoride ions from the system and to generate highly stable metal phosphates. The basic reactions are shown below for the major constituents of the salt:

The driving force for these reactions is the formation of boron trifluoride (the bond dissociation energy of BF_3 is 145 kcal/mole, indicating a very strong boron/fluorine bond) which is evolved as a gas, further driving the reaction to completion. The reaction could be carried out on the cold, solid salt, should some method of removing the salt from the vessels as a solid be used, or the reaction could be carried out on the molten salt removed from the vessels. The boron trifluoride would be collected, hydrolyzed, and disposed of as very low-level waste. Because the process uses solid-solid (in the case of solid salt) or solid-liquid (in the case of molten salt) reactions, no solvent would be required, minimizing any waste disposal problems. It may not be necessary to remove the uranium as it too would be converted to a highly stable phosphate complex, but it might be necessary to dilute the phosphate products in a glass to remain under limits for fissile material concentration or mass in a waste package. If the uranium were removed by fluorination, this would not be an issue.

The lanthanum orthophosphates are analogs of the mineral monazite. This mineral is exceedingly stable, does not readily leach, and is resistant to alpha-particle damage in naturally occurring thorium- and uranium-containing materials. In addition, a study of the use of phosphate glasses as an alternative to borosilicate glasses shown superior resistance to leaching. Lithium orthophosphate *per se* is one of the least soluble salts of lithium.

To advance this proposal, experiments are needed to obtain the identify of the phosphates and the kinetics of the reaction of boron phosphate with a laboratory mixture of the fluoride salts present in the MSRE. While the individual reactions have been shown in initial tests to proceed to completion at temperatures above 1000°C (1832°F), it is necessary to determine if double or triple phosphates may form, and it is desirable to obtain information on the kinetics of the reaction with mixtures of salts. There is a belief that the reaction in molten salt may proceed considerably faster than the solid-state reactions of the initial tests. This is due to the fact that reactions in the solid-state often require high temperature and/or prolonged reaction times because of the slow diffusion of reactive species in the solid state. The reaction in molten salt should not suffer this problem.

This development program would provide engineering data for the design of a conversion system. It would also make recommendations on the materials of construction, optimum temperatures, and method of introduction of the reactants.

3.3.5 Conversion of Uranium to U_3O_8

3.3.5.1 Conversion of UF_6 to U_3O_8

Conversion of UF_6 to U_3O_8 is being addressed by the MSRE Remediation Project as part of the campaign to place the uranium now present in the off-gas system into safe storage in the ORNL RDF. Initially, the uranium will be stored as UF_6 trapped on NaF. A commitment has been made to convert this material to oxide within three years of being placed in temporary storage on NaF. A study into alternative flowsheets for conversion of UF_6 to oxide has been performed (Advanced Integrated Management Services 1995). This report will only summarize a likely selection from that study, and will not attempt to address all of the options considered.

The flowsheet for one of the conversion processes recommended to convert the uranium collected from the off-gas system is shown in Fig. 3.25 (Sherrill 1995). The uranium enters the process chemisorbed on a NaF trap. The UF_6 is volatilized by heating the NaF in the presence of a fluorine gas stream. The fluorine, fed as a 5% mixture with helium, maintains the uranium as UF_6 as it passes to a cold trap. Solid UF_6 is condensed out of the outlet gas from the NaF in a cold trap. The other gasses then pass through a NaF trap for the removal of any uranium carried over from the cold trap, and an activated

Fig. 3.25. Proposed overall flowsheet for the conversion of UF_6 to oxide.

alumina trap to remove the excess fluorine. The inert gas stream is then discharged into the process off-gas system.

The UF_6 is then hydrolyzed to UO_2F_2 with water in the cold trap, and flushed over to the precipitation and calcination furnace vessel. Uranium is precipitated either as ammonium diuranate by the addition of ammonia, or as a peroxide. The solids in the vessel are then washed with water, and then heated to drive off excess water. They are then thermally calcined at temperatures ranging from about 575°C to 800°C (1067 to 1472°F).

The resulting oxide is removed for analysis and packaging, and is sealed in a storage container that conforms to the design of the ORNL RDF handling systems.

3.3.5.2 Conversion of uranium metal to U_3O_8

An alternative to fluorination, electrorefining, can produce a metal uranium product. Uranium is a reactive metal. If this material is to be placed in storage in the ORNL RDF along with the rest of the ^{233}U inventory, it is preferred that it be converted to a stable oxide.

Specific flowsheets for the conversion of uranium metal to oxide have not been addressed to date as part of this effort. If the electrorefining approach is selected, with the transfer of uranium to the ORNL RDF as oxide, a flowsheet for this conversion process will be identified. Uranium conversion processes have generally been studied by the nuclear fuel and weapons industries, and identification of a flowsheet for this conversion is not considered to pose a risk to the implementation of the electrorefining alternative.

3.3.6 Screening of Stabilization Technologies

Even with the separation of uranium, further stabilization of the salt is necessary to prevent the release of fluorine produced by radiolysis of solid salt. The simplest approach is to react fluorine with a getter, such as soda lime, as it forms in the vapor space above the salt. This provides a waste form that can meet the acceptance criteria for WIPP. It may not, however, be certified as a waste form for the federal repository, which relies more strongly on the performance of the waste matrix to achieve its repository performance goals. Packaging the salt with a getter does not preclude the possibility of further processing into an alternate waste form at a later time.

The electrorefining technology discussed in the previous section can function as a stabilization technology as well as a separations technology. As proposed by Argonne National Laboratory, the electrorefining technology produces a zirconium/noble metal waste, a waste consisting of actinides and fission products encapsulated in metallic bismuth, a metallic uranium product, a metallic waste encapsulating the ^{90}Sr fission product, and a chloride waste salt contaminated with plutonium and other radionuclides. The disposal of the zirconium metal waste and the chloride salt is linked to waste management activities associated with the processing of EBR-II wastes at ANL-W. This technology is currently being demonstrated with simulated MSRE fuel salt at Argonne National Laboratory-East. It requires a moderate-sized facility that might be installed in an inert atmosphere enclosure in an existing facility. Qualification of the bismuth metal waste form has not yet taken place. If the electrorefining technology were used only in a sequence that removes the zirconium metal waste, all actinides, transuranics, and most of the fission products in the bismuth waste form, and leaves the ^{90}Sr in the salt for decay, a simpler process results. The metal waste form from this process might be further stabilized in a vitrification facility.

Vitrification of the salts, or the key radionuclides in the salt, produces the borosilicate glass waste form that has been deemed acceptable for disposal in the federal repository. Vitrification of the salt is technically challenging because of the high fluoride content. A test program of glass containing higher fluoride concentrations may be necessary to evaluate the resulting waste product.

The fluoride salts may be converted to oxides by calcining at high temperature. The chemistry of calcining may need to be demonstrated for the materials present in the MSRE salts. The calcine stored at INEL is not considered a permanent waste form. Calcine may produce a stable, although water-soluble, solid for interim storage. Dissolved calcine may later serve as a feed for vitrification.

Other salt stabilization technologies, such as conversion to phosphate-based waste forms or conversion in a glass material oxidation and dissolution system are interesting but are not technically mature at this time, and no actual conversion facilities exist.

Technologies to convert uranium to oxide for storage in the ORNL RDF are generally well understood. A facility to convert UF_6 to U_3O_8 is expected to be available by the time the salts can be removed from the drain tanks.

3.4 PACKAGING AND TRANSPORTATION

3.4.1 Salt Packaging and Transportation

A proposed container for salt removed from the drain tanks is shown in Fig. 2.5. This container is consistent with packaging defined in the WIPP waste acceptance criteria, and presumably could be transported in the 72-B cask. The dose at the surface of the salt container, with two inches of steel as a shield, would be about 10 R/h (Table 2.2). Without the internal shielding, the surface dose would be about 270 R/h. Although the weights and shielding requirements were not defined, it is presumed that these doses are consistent with use of the 72-B cask.

If fluoride salt containing the gamma source from cesium or the ^{232}U daughter chain is to be transported, evolution of radiolytic fluorine must be controlled. A getter, such as soda-lime, is proposed for this purpose. The containers can be vented through the getter and a HEPA filter, if necessary. The licensability of such a transportation package needs to be reviewed. The amount of fluorine expected can be calculated and verified in the laboratory; thus the amount of getter required can be clearly established.

The use of the 72-B cask is part of an overall transportation system being developed to ship wastes from a number of DOE sites to WIPP, including the shipment of RH-TRU from ORNL to WIPP. The WIPP transportation program has identified proposed shipment routes, and has been interacting with the states through which wastes pass. The technology could be used to transfer salt to other DOE sites (e.g., Savannah River or INEL/ANL-W). Definition of transportation routes and coordination of the sites may begin with the review of other shipments of radioactive materials between those sites.

Transportation, particularly arrangements between states for acceptance of waste shipments, could significantly affect the implementability of several options. Shipping packages or casks will be needed to implement any of the ultimate disposition strategies. The actual status of the 72-B cask, or other containers and casks that might be used to ship salt or salt components, has not yet been explored.

3.4.2 Uranium Packaging

Uranium storage as an oxide at the ORNL RDF is practiced today. A container that was developed for the storage of oxide produced by CEUSP is readily adaptable for use by the MSRE project, and is being implemented in the planning and design of the facility that will convert uranium withdrawn from the MSRE off-gas system to oxide. Traps and shielded carriers have been designed and fabricated for the transfer of UF_6 on NaF within ORNL as part of the reactive gas removal activity. Packaging and transportation of uranium that might be separated at other sites, or that might be in other physical forms, will be addressed if it becomes clear that such a strategy is desirable.

3.4.3 Packaging and Transportation of Other Waste Forms

Most of the facilities that are vitrifying high-level waste are placing the waste glass in containers of similar dimensions, as depicted in Fig. 3.20. A transportation system will be developed for shipments of waste glass from the major sites producing such material to the federal repository. This system would address the MSRE requirements if a glass waste form is produced.

Other wastes could be produced by processes such as electrowinning. The wastes produced by the electrowinner are generally stable and physically small. It may be possible to transport those wastes in existing casks used to transport radioisotopes.

Further definition of packaging and transportation requirements for these processes will be developed if the associated alternative is pursued further.

3.4.4 Licensing, Regulatory, and Other Issues

Specific activities to address the licensing of shipments of MSRE materials have not yet been initiated. Licensed casks will be needed for transportation on public roads. Interfaces with the destination state, and other states through which materials pass, will be established once the content of specific shipments is identified. Of course, concurrence by the receiving state will address the overall activities to be conducted within that state's boundaries as well as the transportation issues themselves.

4. IDENTIFICATION OF ALTERNATIVES

The alternative identification process described in Sect. 1.5 is based on achievement of the end points defined in Sect. 2. Seven principal alternatives are defined here. Some of the defined alternatives address in general a range of treatment options that can be evaluated collectively.

The alternatives that are selected for evaluation are based on the use of existing facilities, or on facilities that are currently being demonstrated with MSRE-type salt. Other, generally similar alternatives could also be proposed. An example would be to develop a glass form that performs adequately with a high fluoride concentration, and construct a vitrification facility at ORNL or another site. In several cases, alternatives might be applied to salt containing the uranium, or to salt from which uranium has been separated. The selection of representative scenarios using existing and planned facilities at the various DOE sites is based on the recommendation of the Programmatic EIS for DOE spent nuclear fuel. In fact, several of the options could be assessed either with or without the presence of the uranium.

The first six alternatives evaluate scenarios for the ultimate disposition of the key contaminants in the MSRE fuel and flush salts. The seventh alternative addresses the case in which a commitment to a specific ultimate disposition schedule cannot be made at this time, and ends with a period of interim storage. A representative interim storage mode is selected for the initial evaluation; this is followed by a review of credible approaches to interim storage.

It is presumed that uranium removal is necessary to meet the WIPP acceptance criteria for ^{239}Pu fissile gram equivalents. The effects of downblending the uranium to reduce the potential for criticality have not been considered at this time.

4.1 PERMANENT DISPOSAL IN THE DRAIN TANKS

Permanent disposal in the drain tanks could take place by leaving the material in its present condition or by performing a number of activities to improve safety and protection of human health and the environment. In order to provide a baseline evaluation of other alternatives, "no action" is evaluated as an alternative. In this alternative, the salts are left in their respective drain tanks with no further actions taken. All facility operations are eventually assumed to cease.

A number of enhancements can be applied to the storage of the salts in the drain tank. The most obvious of these is to monitor and operate the facility (including the sump pumps) and to operate the reactive gas removal system to prevent the further transport of uranium away from the salt. Additional enhancements could include the placement of neutron absorbers in or around the tank, placing a getter in the tank, filling the cell with grout, or even removing the salts, removing uranium and other components, and replacing the salt in the tanks. The enhanced storage alternative evaluated is based on facility operation and operation of the reactive gas removal system. This addresses near-term storage effectively, but breaks down eventually. For the long life of the ^{233}U system, in a location below the natural water table, prevention of criticality by adding material external to the salt is problematic. If the salts are removed for processing, there is no incentive to place them back in the drain tank.

Thus, the alternatives for permanent disposal in the drain tanks are defined as follows:

Alternative 1, No Action. Continue to store the MSRE fuel and flush salt in their respective drain tanks, in their current condition. Assume all facility operations eventually cease.

Alternative 2, Enhanced Storage. Continue to store the MSRE fuel and flush salts in their respective drain tanks, but implement and operate enhancements to control reactive gases, prevent nuclear criticality, and contain radioactive materials.

These alternatives are depicted in Fig. 4.1.

4.2 DISPOSAL OF ALL KEY CONTAMINANTS IN THE FEDERAL REPOSITORY

This approach places all of the significant fissile and radioactive material in the federal repository. It is these materials, and not the chemical carrier salt, that are of importance. Separation of uranium (the bulk of the fissile material) from other material is not absolutely necessary. Since there are existing technologies and facilities that can be considered for implementing this approach, the development of new technologies is not evaluated.

The fuel salt is currently listed on the DOE spent fuel data base, and is referred to in the Programmatic EIS for DOE spent fuel. Because the EIS directs that non-aluminum-clad fuels are to be managed at INEL, the strategy developed by INEL for managing the salt is used to define this alternative. Options include storage of stabilized salt, calcining, and possible vitrification at a later date, before disposal in the national repository. The primary recommendation from INEL is to store as a calcine until a proposed immobilization facility (likely based on vitrification) becomes available. The alternative evaluated is thus defined as follows:

Alternative 3. Dispose of the Salt, Including Uranium, in the Federal Repository. Remove the MSRE fuel and flush salts from their drain tanks. Stabilize the salts as appropriate for shipment. Ship the salts to INEL as spent fuel, in accordance with the Programmatic EIS for DOE spent nuclear fuel. Convert the salt to oxide in the INEL waste calciner. Store the calcine at INEL until the proposed remote-handled immobilization facility becomes available. Vitrify the calcine in the remote-handled immobilization facility. Ship the vitrified waste to the federal repository for ultimate disposal.

Alternative 3 is shown as a flowchart in Fig. 4.2.

Other technologies could also be used to implement this strategy. The salt, with uranium, might be blended into the feed for the Savannah River DWPF. The electrorefining technology developed by Argonne National Laboratory might be applied without the separation of uranium. (In fact, if uranium separation were deleted and an approach to vitrifying metal wastes from the electrorefiner were identified, a significantly more streamlined flowchart for the electrorefiner approach can be generated.) Since these technologies are evaluated for the approaches that do incorporate separation of uranium, they are not re-evaluated as part of this alternative.

Fig. 4.1. Flowcharts for alternative 1, no action, and alternative 2, enhanced storage.

Fig. 4.2. Flowchart for alternative 3, dispose of the salt, including uranium, in the federal repository.

4.3 DISPOSAL OF SEPARATED URANIUM

In assessing the hazards either in the near term, or in the very long term (repository time frames of 10,000 years or later), the hazards posed by ^{232}U and ^{233}U are the major, if not totally dominant (in the repository), fraction of the total hazard. For example, at 10,000 years of decay, the radionuclide inventory in salt residue from which uranium has been separated by fluorination would be about 46 Ci, whereas the radionuclide inventory of the uranium package that had been separated from the salt is about 1,800 Ci. Thus, strategies that separate the uranium from the rest of the materials in the fuel and flush salts are proposed.

Technologies are available that can separate uranium from molten salt as either UF_6 or metal. There are known technologies to convert these materials to oxide, such as U_3O_8 . The MSRE Remediation Project is committed to build a facility to convert the UF_6 removed from the off-gas system to U_3O_8 , and this facility should be available to convert UF_6 removed from the fuel and flush salts as well. This oxide is the preferred form for storage in the designated national ^{233}U repository in the Radiochemical Development Facility (Building 3019) at ORNL. A subset of the DOE Fissile Materials Disposition program will address the disposal of that uranium. Downblending and vitrification is one of the proposals under evaluation. If downblending is part of the strategy of the materials disposition program, it could readily be performed by adding depleted or natural UF_6 to the MSRE $^{233}\text{UF}_6$ fed into the conversion process.

Since the DOE Fissile Materials Disposition program is addressing the disposal of an existing (and much larger) ^{233}U inventory of the same physical and chemical form, there is no incentive to address the disposition of uranium from the MSRE separately. The latter would only incur additional cost to DOE to provide two separate programs for the disposition of the same material. Thus, all alternative strategies that involve separation of uranium are based on conversion to oxide and transfer to the materials disposition program. This is reflected in the definition of alternatives in several of the following sections.

4.4 DISPOSAL OF THE KEY CONTAMINANTS IN THE SALT RESIDUE IN WIPP

The fissile and radioactive materials in the MSRE salts include long-lived transuranic and actinide isotopes that warrant some form of geologic disposal. DOE defense transuranic wastes are to be disposed of in the Waste Isolation Pilot Plant. A review of the quantitative waste acceptance criteria for remote-handled transuranic demonstrates that these criteria can be met by fluorinated fuel salt that has been stabilized with respect to the generation of fluorine. Additional study into the acceptability of gettering and the potential risk associated with fluorine in WIPP are needed, but at this time no need for further processing of the salt is identified. This alternative, charted in Fig. 4.3, is defined as follows:

Alternative 4. Transfer the Uranium to the Materials Disposition Program and Dispose of the Salt Residue in WIPP. Remove the MSRE fuel and flush salts from their drain tanks. Separate the uranium from the salts using fluoride volatility or another process. Convert the UF_6 to U_3O_8 and place the oxide in storage in the ORNL Radiochemical Development Facility (Bldg. 3019). Interface with the uranium materials disposition program through the national ^{233}U repository at the ORNL RDF. Remove the MSRE fuel and flush salts from their drain tanks. Stabilize the salts (by the addition of a chemical getter or by conversion to another waste form). Place the salts in containers and load into an

Fig. 4.3. Flowchart for alternative 4, transfer uranium to the materials disposition program and dispose of the salt residue in WIPP.

RH-TRU canister. Store the salt waste in the ORNL RH-TRU storage facilities until WIPP is available. Ship the RH-TRU canisters to Carlsbad, New Mexico, and place in WIPP for permanent disposal.

The major issue is whether MSRE salt residue, without uranium, can be classified as defense transuranic waste, or if it will be classified as high-level or nondefense waste. The WIPP Land Withdrawal Act prohibits the disposal of high-level waste at WIPP. The classification of the MSRE salt is a programmatic decision.

The waste acceptance criteria for WIPP are not met if the uranium is not removed from the fuel salt. They probably can be met without fluorination of the flush salt. With fluorination in place for the fuel salt, however, fluorination of the flush salt would also be feasible.

4.5 DISPOSAL OF KEY CONTAMINANTS IN SALT RESIDUE IN THE FEDERAL REPOSITORY

If the salt residues are classified as high-level waste, then the federal repository, such as the repository proposed for the site under characterization at Yucca Mountain, would be the ultimate destination.

This section differs from Sect. 4.3 in that it presumes that the uranium is separated from the other radionuclides in the salt. The waste acceptance criteria have not yet been defined for the federal repository. However, borosilicate glass has been extensively studied, and is being produced at Savannah River and West Valley. Borosilicate glass is as close to a standard form for disposal in the repository as exists at the present time.

A number of strategies can be identified for placing the key contaminants in the MSRE salts into borosilicate glass, using existing or proposed facilities. The simplest approach would be to dissolve the salts and blend them into the feed to the Savannah River DWPF. Although this would take place over an extended period of time (possibly more than 25% of the overall DWPF operating campaign), it does appear to be technically possible. The low limit on the fluoride concentration that leads to the long campaign at DWPF is likely to be common to all similar facilities. A proposal has been made to first calcine the MSRE salt solution, then vitrify it at a later date. This option is identified for the case in which the uranium remains with the rest of the materials, and is not addressed again in this category. It could, of course, be implemented with uranium removal, but the basis for transferring material to INEL is the spent fuel EIS; the settlement agreement between Idaho, DOE, and the U.S. Navy could prohibit the acceptance of the MSRE material without the uranium. Fluorination is considered the obvious technology for uranium removal before vitrification.

A different type of technology has been proposed by Argonne National Laboratory, based on an adaptation of the electrorefiner developed for the advanced liquid metal-cooled reactor program. This technology produces a series of metal waste forms, including a metallic uranium product. These wastes are being produced at ANL-W, and activities are underway to define the disposition of the wastes from that program. Because this technology is so different than vitrification, and because the electrorefiner process itself is so readily adapted to fluoride salt processing, it is charted as a second strategy under this section.

Thus, two alternatives are defined. The first, charted in Fig. 4.4, is defined as follows:

Alternative 5a. Transfer the Uranium to the Materials Disposition Program, Vitrify the Salt in DWPF, and Dispose of the Salt Residue in the Federal Repository. Remove the MSRE fuel and flush salts from their drain tanks. Separate the uranium from the salts using fluoride volatility or another process. Convert the UF_6 to U_3O_8 and place the oxide in storage in the ORNL Radiochemical Development Facility. Interface with the uranium materials disposition program through the national ^{233}U repository at the ORNL RDF. Remove the MSRE fuel and flush salts from their drain tanks. Stabilize the salts with a getter for shipment. Ship the salts to Savannah River. Dissolve the salts and bleed into the waste stream being fed into the DWPF, keeping fluorine content within specification. Store the waste in glass logs at Savannah River until the federal repository is available. Ship the vitrified waste to the federal repository for ultimate disposal.

Alternative 5b, charted in Fig. 4.5, is defined as follows:

Alternative 5b. Transfer the Uranium to the Materials Disposition Program, Process the Salt by Electrowinning, and Dispose of the Salt Residue in the Federal Repository. Remove the MSRE fuel and flush salts from their drain tanks. Construct an electrowinner at ORNL. Separate the zirconium and rare earths from the salt by electrowinning and convert into a metal waste form to be managed along with similar wastes at ANL-W. Separate the uranium and other radioactive materials from the salt. Electrowin this material in a chloride salt electrowinner to separate the uranium. Convert the uranium to U_3O_8 and place the oxide in storage in the ORNL RDF. Interface with the uranium materials disposition program through the national ^{233}U repository at the ORNL RDF. Dispose of the chloride salt along with similar wastes generated at ANL-W. Separate the transuranics, actinides, and cesium and place in a bismuth metal waste form. Either qualify this waste for disposal in the federal repository, or develop a vitrification technology for this material. Separate the strontium from the salt and place in long-term storage for decay. Stabilize the salt residue and transfer to a low-level waste storage facility.

4.6 REUSE OF THE SALT

Reuse of the salt is preferable to disposing of one batch of contaminated salt and preparing another with fresh materials. However, the prospects for reuse of the MSRE salts are limited. One prospect that has been identified is a program at Los Alamos National Laboratory to develop high-power accelerator targets that can generate a significant flux of neutrons for transmutation of plutonium or actinides, or other purposes. Thus, this alternative, charted in Fig. 4.6, is defined as:

Alternative 6. Transfer the Uranium to the Materials Disposition Program and Transfer the Salt to Another Program for Reuse. Remove the MSRE fuel and flush salts from their drain tanks. Separate the

Fig. 4.4. Flowchart for alternative 5a, transfer uranium to the materials disposition program and dispose of the salt residue in the federal repository, based on vitrification at the DWPF.

Fig. 4.5. Flowchart for alternative 5b, transfer uranium to the materials disposition program and dispose of the salt residue in the federal repository, based on electrorefining molten fluoride salt.

Fig. 4.6. Flowchart for alternative 6, transfer uranium to the materials disposition program and transfer the salt to another program for reuse.

uranium from the salts using fluoride volatility or another process. Convert the UF_6 to U_3O_8 and place the oxide in storage in the ORNL RDF. Interface with the uranium materials disposition program through the national ^{235}U repository at the ORNL RDF. Remove the MSRE fuel and flush salts from their drain tanks. Stabilize the salts with a getter and transport the salt to Los Alamos for use as a molten salt accelerator target.

Immediate interest at Los Alamos is focused on the largely nonradioactive coolant salt. If the program develops as planned, transfer of the flush or fuel salts is possible.

4.7 INTERIM STORAGE

Ultimate disposition requires the availability of repositories not yet in operation or constructed; consequently interim storage of intermediate or final waste forms will probably be required for most alternatives. Thus it is advisable to evaluate interim storage as an end point for this selection process, even though it will require further activities at a later date.

Implementation of the previous strategies (aside from permanent disposal in the drain tanks) requires the availability of WIPP or the federal repository, as well as the availability of processing facilities at other sites. WIPP has been the subject of a long legal and regulatory struggle to bring it near to operation, and a successful completion of that process still cannot be assured. The federal repository is at a far earlier stage of the process; the Yucca Mountain site is a candidate site undergoing characterization. The INEL strategy involves a vitrification facility that is planned for construction after 2010. Although a demonstration is underway, the Argonne electrorefiner has not been tested or constructed, and linkages with waste disposal at ANL-W are in early stages. Thus, it is possible that a firm commitment to a schedule for the full strategy represented by any of these options cannot be made at this time, and a period of interim storage is required.

Material placed in interim storage should be stable and pose minimal risk to personnel and the environment at the storage site. Given the uncertainties in ultimate disposition, the material should be packaged and stored in a manner acceptable for decades with minimal or no maintenance required. The storage mode should be targeted to at least one ultimate disposition strategy; flexibility in adapting to one of several strategies can be an advantage. At the same time, once the salts are being processed, it is desirable to produce a waste form acceptable for ultimate disposal if at all possible. This eliminates the need for a second processing campaign at a later date.

In general, the logical interim storage modes can be identified by examining the full disposition strategies, and identifying the rational hold points in each strategy. The material that exists at that hold point is then evaluated against criteria for safe interim storage. It should be noted that a strategy that leads to a desirable ultimate disposition may not exhibit an equally desirable opportunity for interim storage.

There are five general modes for interim storage that appear representative. Four of these are associated with alternatives identified earlier. These are fluorination and stabilization of salt with a fluorine getter, electrorefining the MSRE salts, management as spent fuel at INEL and conversion to glass at DWPF. Some of the additional proposals for new forms of processing at ORNL could also lead to safe interim storage; these are collected into a fifth interim storage mode. The five options that result are summarized as:

Alternative 7a, transfer uranium to the materials disposition program, stabilize the salt residue with a fluorine getter, and store at ORNL.

Alternative 7b, transfer uranium to the materials disposition program, convert radioactive materials in the salt into metallic and other waste forms by electrorefining, and store at ANL-W.

Alternative 7c, Calcine the salt, including the uranium, and store the calcine at INEL.

Alternative 7d, transfer uranium to the materials disposition program, incorporate the salt residue in borosilicate glass, and store at Savannah River.

Alternative 7e, transfer uranium to the materials disposition program, construct a salt conversion facility at ORNL, convert the salt residues to glass or phosphate waste forms, and store at ORNL.

Since the first of these is the most readily implemented and the least expensive, it is used in the overall evaluation of alternatives. Alternative 7, diagramed in Fig. 4.7, is thus identified as:

Alternative 7. Transfer the Uranium to the Materials Disposition Program and Place the Salt Residue in Interim Storage. Remove the MSRE fuel and flush salts from their drain tanks. Separate the uranium from the salts by fluoride volatility. Convert the UF_6 to U_3O_8 and place the oxide in storage in the ORNL RDF. Interface with the uranium materials disposition program through the national ^{233}U repository at the ORNL RDF. Remove the MSRE fuel and flush salts from their drain tanks. Stabilize the salts by the addition of a chemical getter. Package the salts in a form compatible with repository containers such as the RH-TRU canister. Store the salt waste in the ORNL waste storage facilities until a permanent disposition mode becomes available.

Fig. 4.7. Flowchart for alternative 7, transfer uranium to the materials disposition program and place the salt residue in interim storage.

5. EVALUATION OF ALTERNATIVES

5.1 EVALUATION MATRIX

Table 5.1 presents the evaluation of the most credible alternatives to each disposition end point against the CERCLA evaluation criteria and two additional programmatic criteria. A qualitative ranking system is used, scoring each alternative as high, medium, or low based on relative comparisons of the alternatives for each criterion. In some cases, specific criteria are not applicable, or the score cannot be assigned without additional information. The scores are based on the particular sequence of activities identified in the previous chapter. In some cases, notes are provided on how alternate implementations of a strategy might affect the scores.

5.2 SCORING RATIONALE FOR EACH CRITERION

5.2.1 Overall Protection of Human Health and the Environment

The baseline risk presented by reactive gas currently generated in the salt and by the potential for criticality should water flood the salt in the drain tanks represents an unacceptable level of protection of human health and the environment. The no action alternative incorporates no features to mitigate the above consequences, and is thus scored as unacceptable against this criterion. In the case of enhanced storage, adequate protection is provided so long as the reactive gas removal system and the building sump pumps remain in operation. Although this provides an adequate level of safety for interim storage, reliance on active systems cannot be assured for the lifetime of the ^{233}U isotope. Thus, even if the consequence of reactive gas generation can be controlled, criticality safety remains an issue. The drain tank cell can be further sealed to guard against water intrusion, and neutron poisons can be placed around the tanks or in the vapor space inside the tank above the salt. However, it cannot be assured that these measures will remain in place for tens of thousands of years. The activities needed to integrate poisons or depleted uranium directly into the salt matrix are the same as would be required to remove the salt, and removal of the salt to a waste storage or disposal facility is a preferred activity. Thus, enhanced storage is also scored as unacceptable against this criterion. Since alternatives 1 and 2 do not provide an acceptable level of protection of human health and the environment, they are rejected outright and are not scored further against the other CERCLA criteria.

Alternatives 3 through 7 are scored in terms of the level of protection provided by the form of material being stored and the final storage location. All of the options that result in the key contaminants being placed in geologic disposal rank high. It is assumed that the fissile materials disposition program will either provide for the reuse of ^{233}U or that it will eventually be placed in geologic disposal. Likewise, it is assumed that the reuse option places the salt in responsible stewardship; for the purposes of the MSRE program, this alternative is also scored as high. In alternative 7, the uranium is separated and the salt is stabilized. However, the salt remains in interim storage in a relatively accessible location, and this alternative does not provide as much protection as the repository alternatives. Therefore, alternative 7 is scored as medium.

5.2.2 Compliance with Applicable or Relevant and Appropriate Requirements

It is assumed that all of the alternatives are executed in a way that complies with all applicable or relevant and appropriate requirements. Thus, all of the options are scored as high.

**Table 5.1. Alternatives evaluation matrix for the Molten Salt Reactor Experiment
Fuel Salt Disposition task**

CERCLA evaluation criteria	Alternative ^a							
	1	2	3	4	5a	5b	6	7
Overall protection of human health and the environment	U	U	H	H	H	H	H	M
Compliance with applicable or relevant and appropriate requirements	x	x	H	H	H	H	H	H
Long-term effectiveness and permanence	x	x	H	H	H	M	na	L
Reduction of toxicity, mobility, or volume through treatment	x	x	H	M	H	H	na	M
Short-term effectiveness	x	x	H	H	H	H	H	H
Implementability	x	x	L	L	L	L	?	H
Cost (scored as affordability)	x	x	L	M	L	L	?	H
<i>Other evaluation criteria:</i>								
Adaptability to changes in system requirements	x	x	H	H	H	M	H	H
Compatibility with programmatic objectives	L	L	H	H	H	H	H	M

^aKey to alternatives:

1. No action.
2. Enhanced storage.
3. Dispose of the salt, including uranium, in the federal repository.
4. Transfer the uranium to the materials disposition program and dispose of the salt residue in WIPP.
- 5a. Transfer the uranium to the materials disposition program and dispose of the salt residue in the federal repository (via DWPF).
- 5b. Transfer the uranium to the materials disposition program and dispose of the salt residue in the federal repository (via electrorefining).
6. Transfer the uranium to the materials disposition program and transfer the salt to another program for reuse.
7. Transfer the uranium to the materials disposition program and place the salt residue in interim storage.

Key to matrix scores:

- L Low
M Medium
H High
U Unacceptable
na Not applicable
x Not scored
? Unknown

However, regulatory and policy issues may affect the implementability of the various alternatives. In particular, compliance with the WIPP Land Withdrawal Act may preclude classification of the salt residues as RH-TRU waste. These considerations are reflected in the scores assigned to implementability.

5.2.3 Long-Term Effectiveness and Permanence

High scores are assigned to those alternatives that place the key contaminants in ultimate geologic disposal or place the uranium under the management of the fissile materials disposition program as an oxide. A low score is assigned to the interim storage alternative. The reuse alternative is not scored against this criterion.

5.2.4 Reduction of Toxicity, Mobility, or Volume Through Treatment

A high score is given to alternative 5a, which results in a well-qualified borosilicate waste form. Although the exact waste form for alternative 3 has not been defined or tested, it too is assumed to be borosilicate glass and is scored high. The waste forms produced by alternative 5b vary, and have not been qualified. Until they are qualified, it is not clear that they represent a final end point. However, because the volume is low, alternative 5b is scored high. Scores of medium are assigned to alternatives that do separate uranium from the salt and that have stabilized salt as an endpoint (alternatives 4 and 7). The reuse alternative is not scored against this criterion.

5.2.5 Short-Term Effectiveness

Alternatives 4 through 7 all remove the salt, separate uranium from the salt, place the uranium in storage as an oxide, and as a minimum place stabilized salt in storage in a dry location. All of these alternatives prevent further migration of uranium, and control any additional radiolytic fluorine. These alternatives are scored as high. Alternative 3 does not remove the uranium from the salt, but presumably converts it to an oxide in the calcination step, and immobilizes it in glass in the final immobilization step. Thus, this alternative is also scored as high.

5.2.6 Implementability

Alternatives 3, 5a, and 5b all rely on the federal repository for spent fuel and high-level waste, which is years away from construction. Alternative 4 relies on WIPP, which although constructed is not yet receiving waste. The classification of salt residues as RH-TRU may not be possible, in light of the WIPP Land Withdrawal Act and associated guidance on distinguishing RH-TRU from HLW. Alternative 3 relies on the future funding and construction of an immobilization (presumably vitrification) facility at INEL. Dissolving and blending the salts directly into the feed to the DWPF requires such a long, gradual bleed that if any difficulties are encountered (such as existing material in the Savannah River waste that further reduces the acceptable feed rate) it may fail on technical grounds. The electrorefining technology itself can probably be implemented, but the trail of activities needed to fully dispose of the wastes produced by the initial electrorefining step is not fully developed. Thus, all four of these alternatives are scored as low in terms of implementability.

Four of the alternatives are ranked low in implementability for different reasons. Consequently, it is difficult to rank the four comparatively. WIPP is further along than the federal repository, and the impediments to implementation of the WIPP option are legal and programmatic. Thus, alternative 4 might stand a better chance than blending directly into an existing borosilicate glass facility. Although the initial calcination step associated with alternative 3 may prove credible (at least for the fuel salt, with transfer to Idaho made under the spent fuel EIS), further processing into a final waste form would be in a facility not yet funded and disposal in a repository not yet sited. Similar issues apply to alternative 5b. Without transfers of waste to Idaho for storage, the alternative cannot be implemented as defined. The settlement agreement between Idaho, DOE, and the Navy may make such transfers difficult.

Alternative 6 relies on a program that can make use of the salts. Programs such as the accelerator-driven transmutation project at Los Alamos are in the planning stage and are not yet funded. The probability of such programs accepting salt is a factor of the maturity of the program and the salt in question. Use of the nonradioactive coolant salt may be relatively likely. Use of the highly radioactive fuel salt may in general be relatively unlikely, although samples may be of use by researchers developing salt cleanup systems. At this time, implementability of alternative 6 is left as a question mark.

Implementability of the interim storage option is, of course, higher. Alternative 7, based on interim storage on the ORNL site, is scored as high. All of the technologies needed to implement this alternative have been practiced at some time or other in the history of the MSRE project, or are common uranium processing technologies. Only the salt chemistry issue poses a technical implementability question, and activities are already underway to bound the potential consequences of this issue and to ensure that appropriate technology is available to safely melt the salt. The main implementability issue is associated with the acceptability of interim storage as an option. It is crucial that this storage option be defined in the context of a credible ultimate disposal strategy.

5.2.7 Cost

This criterion is scored as affordability, so that high is a desirable ranking as in the case of all other criteria.

The relative cost of the alternatives can be evaluated by comparing the number of activities needed to implement the alternatives. In each of alternatives 3 through 7, removal of the salt is necessary. The cost of salt removal is assumed to be an equal baseline cost for each alternative, and removal cost is not a discriminator.

For all scenarios except alternatives 3 and 5b, the uranium is separated by fluorination and converted to oxide. Because fluorination is a simple process (as seen by the relatively small equipment in the present fuel processing cell), and because an oxide conversion facility is already being constructed for the project, this cost is seen as being relatively moderate.

The cost of gettering is assumed to be insignificant. Design of an external getter may be no more difficult than including a chemical filter in series with a HEPA filter in a package vent. If a getter material is integrated into the salt matrix, the cost of gettering (development aside) would likely only be the cost of adding the material to the salt before it is allowed to freeze.

For alternative 7, the only other cost incurred is storage. In the very long haul, storage costs will accrue. But for any near-term cost estimate, the affordability of alternative 7 is high.

For alternative 4, the only other cost incurred is shipment to WIPP. This entails transport in a licensed cask from Oak Ridge to Carlsbad, New Mexico. Because transportation issues can be costly to resolve, this alternative is scored as medium in terms of affordability. If implementation can be based on an existing, licensed WIPP cask and all transportation issues are resolved by the transuranic waste program, the affordability of this alternative might be raised to high.

In the case of alternative 3, fluorination and conversion is not required. However, a fissile material must be shipped from Oak Ridge to Idaho. No existing program is likely to pay the costs for cask licensing or other transportation issues. Thus, the affordability of this alternative would be no higher than medium. But on top of these issues, a dissolver and feed system must be constructed to interface with the calciner facility. This dissolver would need to be shielded and provided with an appropriate off-gas system. An existing facility at the ICPP might be used, but this would incur the cost of restarting an ICPP facility. A new facility could also be constructed for this purpose. The real cost does not end with calcining, although the waste becomes indistinguishable from other INEL waste once it is mixed and sprayed into the calciner. The affordability of this alternative is ranked low.

In a similar way, the alternative to utilize the DWPF begins with all of the activities associated with storing and shipping fluorinated, stabilized salt, and then adds the cost of a dissolver facility and an extended operating campaign. This alternative is also ranked as low in terms of affordability.

The cost of constructing and operating an electrorefiner cover the construction of an inert glovebox, shielding around the glovebox, an appropriate off-gas system, further refining of the uranium product, and disposal of the electrorefiner wastes. Thus, alternative 5b is ranked as low.

Until the specific activities associated with a reuse option are identified, a score is not given for the cost of alternative 6. If implemented, the cost is likely to be relatively low.

5.2.8 Adaptability to Changing Requirements

Because no repository is currently operating and acceptance criteria are still being developed, the ability to adapt to changes in waste form and handling requirements is a valuable attribute. At present, any processing that leads to an alternate waste form begins with salt. Thus, any alternative that ends with stabilized salt likely preserves all processing alternatives that are presently available. Uranium oxide is a common form for both storage and as a feed for other processes. Uranium fluoride is also a common feed to other processes. Thus, alternatives that leave the uranium as oxide or as a fluoride salt preserve a wide range of processing alternatives. Alternatives 4, 7, and probably 6 all result in processing end points consistent with the above, and are scored as high.

Alternatives 3 and 5a result in the salt residue being placed in a borosilicate glass waste form. It is very difficult to remove the materials from this waste form and convert them to another; thus these alternatives might be scored as low. However, it is also very unlikely that the borosilicate glass waste form would not be accepted under any future waste form acceptance criteria. Thus, alternatives 3 and 5a are scored as medium.

Alternative 5b results in a variety of metal waste forms. Further processing flowsheets for these waste forms are limited at this time. The waste forms are not yet qualified for disposal. Thus, this alternative is scored as low. (On the other hand, the technology itself could be modified to fit within other waste management strategies. Since this does not fit within the definition of the baseline strategy, it is not a basis for scoring.)

5.2.9 Compatibility with Programmatic Objectives

Programmatic objectives include meeting the DNFSB goals of removing the salt from the drain tanks and placing the uranium in storage as oxide, and allowing the decommissioning of the MSRE facility to proceed. Achieving an ultimate disposition of the salt, with no further cost incurred for interim storage, is also a programmatic objective.

The repository and reuse alternatives accomplish all these programmatic objectives, and are scored as high. Alternative 7 meets all objectives except eliminating further storage cost for the salt, and is scored as medium. Alternatives 1 through 3 do not result in the separation of uranium from the salt and conversion to oxide, as specified in the DNFSB 94-1 Implementation Plan. Alternative 3 does, presumably, convert the uranium to oxide without separation. It is thus given the same score as alternatives that convert uranium to oxide after separation. Alternatives 1 and 2 do not result in removal of the salt from the drain tanks, as specified in the DNFSB 94-1 Implementation Plan, and as needed to continue with facility decommissioning. These alternatives do not eliminate further storage costs for the salt. Thus, alternatives 1 and 2 are scored as low.

5.3 RECOMMENDATIONS

The reuse alternative (alternative 6) and the geologic disposal alternatives (alternatives 3, 4, 5a and 5b) score the highest, but all have significant implementability issues. Reuse of the MSRE salt is preferable to disposal of MSRE salt and production and contamination of a new batch of salt. In the case of reuse at Los Alamos, transfer of the salts is contingent upon funding for the accelerator-driven transmutation program. Transfer of the nonradioactive coolant salt may occur upon funding for the research phase of the project, and is relatively probable. Samples of fuel or flush salt may also be wanted in the research phase to test salt cleanup systems. Full transfer of the fuel and flush salts involves a more significant investment in storage and cleanup at Los Alamos; availability of such funding is likely contingent on approval of a line-item to design and construct the accelerator. The relative costs of cleaning up and reusing the MSRE salt (if clean salt is required) as opposed to preparing a new batch of salt will also be a factor. In evaluating this tradeoff, the cost savings of not disposing of MSRE salts should be taken into consideration.

Alternatives 4, 5a, and 5b transfer uranium to the fissile materials disposition program in a generally accepted form, and provide for true disposal of the salt residues. Alternative 3 does not separate the uranium, but is presumed to feed it into a vitrification facility as an oxide. Alternatives 5a and 5b, based on disposal in the federal high-level waste repository, cannot be fully implemented until the repository is constructed. Incorporation into the DWPF feed and storage in borosilicate glass at Savannah River might be implemented in this time, resulting in interim storage of a waste form clearly targeted for the repository; this is one of the alternative versions of the interim storage option. Similarly, alternative 3 could produce interim storage first of calcine, later of glass. Disposal at WIPP is more credible in the near future as WIPP has been constructed and is scheduled to begin receiving RH-TRU waste early in the next decade. However, operation of WIPP is still being challenged and acceptance criteria may change as EPA repository performance guidance is interpreted. Furthermore, although the salt residues appear to meet WIPP acceptance criteria by characteristic, the classification of this unique waste form with respect to the definitions in the WIPP Land Withdrawal Act is unclear. Even in the strategy defined here, alternative 5b does not fully define the path to ultimate disposal for all of the waste forms produced.

Thus, none of the alternatives 3, 4, 5a, 5b, and 6 can be fully implemented at this time.

Alternatives 1 and 2 (no action and enhanced storage) do not provide adequate protection of human health and the environment for final disposition, and are thus rejected. Reasonable measures can be implemented to control reactive gases and prevent criticality in the near term, providing safe storage until the disposition activities are implemented. However, enhanced storage does not meet programmatic objectives, and as equipment ages, removal of the salts from the tanks becomes more difficult.

Interim storage of salt residues after the uranium is separated and converted to oxide can be implemented in a number of ways. The result is storage of salt residues in a monitored facility, but the storage mode can be tailored to the most likely ultimate disposition path. Uranium is separated, converted to oxide, and transferred to the fissile materials disposition program. This addresses the most serious near term concern (that of ^{232}U and its daughters), and if ultimate disposal by the materials disposition program is assumed, it also addresses the most serious very-long-term problem (the radionuclide inventory associated with the ^{233}U decay chain). The base path chosen for the alternatives evaluation is storage of fluorinated and stabilized salt residues at ORNL, in a form compatible with ultimate disposition in WIPP. Other versions of this alternative are considered in the next section. The waste form is sufficiently stable that a reasonable level of protection of human health and the

environment is achieved. Generation of UF_6 is no longer possible, and generation of gaseous fluorine is chemically controlled. All programmatic objectives except the elimination of future storage and monitoring costs are met. This alternative can be implemented now with a modest investment in facilities at the MSRE and at the site chosen for conversion of other MSRE uranium.

In the end, all of the options except those that leave the salt in the drain tanks are reasonable. Interim storage does not complete the job, and should be selected only as a temporary measure. The most significant discriminator for all other alternatives is implementability. The following sequence of preferences can be defined:

If reuse of the fuel and/or flush salts is a serious option, then it should be selected.

If *any* of the geologic disposal alternatives prove technically and programmatically implementable, every reasonable effort should be made to implement that alternative. In particular, efforts should be made to resolve the regulatory and programmatic obstacles to disposal in WIPP.

At the present time, only the interim storage option is likely to be implementable. It does provide adequate protection of human health and environment, but at some time an ultimate disposition must be identified to end the cost of perpetual care and monitoring. Storage of fluorinated, stabilized salt can meet the quantitative requirements for disposal at WIPP, or can serve as the feed for any of the other processes evaluated. Thus, interim storage is recommended as being consistent with ultimate disposition and being fully implementable at this time.

5.4 REVIEW OF THE ALTERNATE APPROACHES TO INTERIM STORAGE

Because the previous evaluations were performed in the context of a series of activities that, in most cases, end with geologic disposal, the application of a subset of those actions to provide an interim storage mode was not formally evaluated in the previous matrix. Since that matrix identified interim storage as the only credible alternative for implementation at this time, a brief review of a set of alternatives for interim storage is presented here. Table 5.2 presents an evaluation matrix for interim storage alternatives. These alternatives were defined in Sect. 4.7. Since all of these strategies are for interim storage, many of the CERCLA scores are nearly identical, and the overall scoring tends to be compressed. Because the scores are relative to the other interim storage options, alternative 7a does not necessarily score the same as in the main matrix. Three additional criteria were added to the interim storage evaluation matrix. One evaluates the stability of the material that is placed in interim storage. The second addresses the ease (and thus the long-term cost) with which the material can be stored. The last addresses the adaptability to changes in the ultimate disposition strategy.

All of the options result in stable material in interim storage, and are scored as medium against the overall protection of human health and the environment criterion. Similarly, all will be performed in a manner that fully complies with all applicable, relevant, or appropriate requirements, and are scored high.

None of these options provides for ultimate disposition of the key contaminants, and thus none is scored as high against long-term effectiveness and permanence. The DWPF glass is likely to be

acceptable at any disposal facility, and is thus scored as medium. The immediate products of the electrorefiner and the INEL calcine both require further processing before disposition, and are scored low. If the fluorinated, stabilized salt can be disposed of WIPP, the interim storage option is not needed. If not, the stored material will probably need further processing to fit into any other strategy. Thus, the long-term effectiveness and permanence for alternative 7a is also scored as low. Final definition of the waste forms from a new process cannot be evaluated at this time.

The reduction of toxicity, mobility, or volume through treatment is reasonable for any alternative. Thus, each of the first four alternatives is scored at least medium. Only the borosilicate glass form generated by DWPF has been demonstrated in a rigorous qualification program, and thus alternative 7d is scored as high. Because of the low volume of wastes generated by alternative 7b, it too is scored high. Again, the waste forms from the new processes have not yet been evaluated.

All of the alternatives prevent recurrence of the difficulties that have led to the MSRE Remediation Project. Thus, each is scored high in terms of short-term effectiveness.

The new processes represented by alternative 7e have not yet been developed, and their implementability is scored as low at this time. Moderate investments in studies of these technologies might result in higher scores. Alternative 7a requires only modest activities at the ORNL site, and no significant impediments to implementation are known. Alternative 7b requires the construction of a (moderate) electrorefiner facility and integration with waste management at another site, and alternatives 7c and 7d involve transportation of salt to another state. The implementability of these is ranked as medium. Technical challenges might drive the implementability score for DWPF to low.

The electrorefiner alternative incurs the cost of constructing a moderate processing facility, and possibly the transportation of wastes to ANL-W for common management with wastes generated by processing EBR-II fuel. The affordability of alternative 7b is presently scored as low. Implementation of calcining at INEL or vitrification at Savannah River incur both the costs of transportation to another site and construction of a dissolution and feed facility, and are also scored as low. Alternative 7a incurs the costs of fluorination, using an existing conversion facility to convert to oxide, and storage with a getter. None of these requires a major new facility, and no transportation costs are incurred. The affordability of alternative 7a is ranked as high. Insufficient descriptions of the facilities required to implement the GMODS or phosphate processes exist to score alternative 7e.

The salt can be stabilized with a getter; the package is stable but since radiolysis continues, alternative 7a is scored as medium against stability of waste form. Metal and salt wastes from electrorefining also may need further stabilization, and that waste form is scored as medium. Calcine is presumed to be stable but is soluble and granular; it too is scored as medium. Glass is very stable; alternative 7d is scored as high. Insufficient data exists to score the stability of the new approaches.

Although the salt package defined in this report would appear to be relatively straightforward, such storage is not taking place at ORNL today (MSRE drain tanks excepted). Ease of storage and handling is scored as medium. If the RH-TRU handling facilities at ORNL can be used for the salt, and adapt to the standard RH-TRU configuration, this score might be raised. Likewise, the electrorefiner process produces a host of unusual wastes (none of which, individually, should be difficult to handle) not presently managed at ORNL, and this alternative is scored as medium. The INEL calciner and DWPF glass waste forms are indistinguishable from other wastes generated at those facilities, and both calcine bins and glass storage facilities exist. These are scored as high. Again, handling issues with the novel waste forms are difficult to score at this time. However, no clear difficulties with either GMODS product or the phosphate waste forms are envisioned.

Table 5.2. Evaluation matrix for alternate approaches to alternative 7, transfer uranium to the materials distribution program and place the salt residues in interim storage

CERCLA evaluation criteria	Alternative ^a				
	7a	7b	7c	7d	7e
Overall protection of human health and the environment	M	M	M	M	M
Compliance with applicable or relevant and appropriate requirements	H	H	H	H	H
Long-term effectiveness and permanence	L	L	L	M	?
Reduction of toxicity, mobility, or volume through treatment	M	H	M	H	?
Short-term effectiveness	H	H	H	H	H
Implementability	H	M	M	M	?
Cost (scored as affordability)	H	L	L	L	?
<i>Other evaluation criteria:</i>					
Stability of the waste form	M	M	M	H	?
Ease of storage and handling	M	M	H	H	?
Adaptability to alternate ultimate disposition strategies	H	M	L	H	H ?

***Key to alternatives:**

- 7a. Transfer uranium to the materials disposition program, stabilize the salt residue with a getter, and store at ORNL.
- 7b. Transfer uranium to the materials disposition program, convert radioactive materials in the salt into metallic and ceramic waste forms by electrorefining, and store at ANL-W.
- 7c. Calcine the fuel salt, with uranium, and store at INEL.
- 7d. Transfer uranium to the materials disposition program, incorporate the salt residue in borosilicate glass, and store at Savannah River.
- 7e. Transfer uranium to the materials disposition program, construct a salt conversion facility at ORNL, convert the salt residues to glass or phosphate waste forms, and store at ORNL.

Key to matrix scores:

- L Low
- M Medium
- H High
- ? Unknown

Because interim storage is only selected if a path to ultimate disposition cannot be achieved, it is an obvious advantage for the material stored to be adaptable to several different ultimate disposition strategies. Fluorinated salt is the beginning of most of the processing scenarios, and thus this form is scored high against adaptability. The electrorefiner produces metals and a salt; these waste forms are not unusual materials but they do not appear in most of the ultimate disposition flowsheets. A score of medium is assigned to the electrorefiner wastes. Calcine blended with the INEL waste stream is compatible only with the INEL waste disposition strategy; its adaptability is scored as low. Similarly, the DWPF glass option dedicates the MSRE material to the Savannah River strategy, but since borosilicate glass is considered acceptable at most sites it is scored as high. The GMODS process could produce glass product, or could produce feed material for an existing vitrification process. The phosphate process produces a unique product that may or may not be adaptable to other processing scenarios. Thus, an overall score of high, with an indication of uncertainty, is given to the new technologies.

In the end, implementability and affordability are the major factors that result in a recommendation for alternative 7a. Alternative 7d offers a better, borosilicate glass waste form, but its implementability

score is not high, and its affordability (with a long feed campaign) is likely to be low. The calcine waste form is mainly attractive in terms of creating a waste that is already being managed by the DOE system. Electrorefining creates a variety of relatively simple but unique waste forms, and incurs the cost of constructing a new facility. The novel flowsheets (GMODS or phosphate conversion) might offer advantages over storage of fluorinated, stabilized salt, but further development is needed before this can be demonstrated.

6. IDENTIFICATION OF KEY UNKNOWN, POTENTIAL CONSEQUENCES, AND PATH TO RESOLUTION

6.1 CERCLA PROCESS

This report is being issued to aid in the preparation of a CERCLA feasibility study for an interim remedial action. The CERCLA feasibility study will be followed by a proposed plan, and will eventually lead to a record of decision. It is the CERCLA record of decision that formally commits to a given alternative. It is currently expected that the record of decision will be issued in May, 1998. This report only provides recommendations for use in the CERCLA process.

The CERCLA process therefore leads to an uncertainty in which alternative will actually be selected. It is possible that as the CERCLA process continues, with input from regulators and the public, that new perspectives or even new alternatives will be identified. Therefore, the final record of decision may not reflect the recommendations of this report.

6.2 WASTE CLASSIFICATION

The overall logic of this evaluation is to define the desired end point first, and then to identify credible strategies for arriving at that end point. The transuranic content of the salts indicates that geologic disposal is appropriate, at least for the transuranic isotopes. The WIPP has been constructed and intends to begin operation with contact-handled waste in 1998, and with remote-handled waste around 2002. The federal repository, designated for the disposal of spent fuel and high-level waste, is still in the site characterization phase and will not open until after 2010. Thus, WIPP is an attractive end point for the key contaminants in the salt.

WIPP has been constructed for disposal of defense transuranic waste. The WIPP Land Withdrawal Act prohibits the disposal of high-level waste at WIPP. Fluorinated MSRE salt residues, or other waste forms that can be produced, can meet the quantitative requirements that are presently identified for disposal of RH-TRU at WIPP. If the MSRE waste is classified as spent fuel or high-level waste, however, such disposal would not be allowed. The fission product concentration falls below the quantitative activity concentration limit in the WIPP waste acceptance criteria, and the fission product concentration nearly falls into the range that could be classified as Class C waste under 10 CFR 61 (although the transuranic content greatly exceeds the criteria for near-surface disposal). The total amount of waste is small (8 RH-TRU canisters each of fuel and flush salt residue are projected) and the total radionuclide inventory in the disposal site after 500 years is about 80 Ci. The overall impact on a facility such as WIPP is minimal. If the MSRE waste can be classified based on its characteristics, a transuranic classification appears reasonable. If classified on the basis of history, a more complex processing strategy and a long period of interim storage results. A similar issue is associated with the definition of "defense-related."

Similar waste classification and acceptance issues would be faced by waste forms other than salt from which the uranium has been removed, such as the waste forms produced by the electrorefining technique.

6.3 SALT CHEMISTRY

An improved understanding of several salt chemistry issues is needed to support the methodology for melting the salt, especially the fuel salt. An improved understanding of the performance of getter materials could lead to better strategies for controlling the further production of radiolytic fluorine, including strategies that integrate a getter into the salt matrix to prevent any evolution of fluorine without external controls.

A plan for a series of experiments is being developed to verify the existing knowledge and assumptions of salt behavior. These experiments will

- Establish the significance (or insignificance) of melting highly reduced salt,
- Evaluate the potential for low temperature annealing treatments with F_2 to re-establish salt chemistry,
- Demonstrate an assured gettering strategy,
- Establish confidence in the pool-melt strategy, and
- Continue to strive to identify the mechanism of UF_6 formation.

In addition, a priority will be given in the next fiscal year to activities that will access the drain tank cell, inspect equipment in the cell, and (once the reactive gases have been removed) access a drain tank for inspection of the salt mass. This will provide additional information on the present physical condition of the salt, and will help to assess the condition and operability of equipment that could be used to remove the salt.

6.4 AVAILABILITY OF SUPPORTING FACILITIES

Several of the alternatives presented in this report utilize existing facilities or sites for the storage, processing and disposal of the radionuclide inventory in the salts. The availability and appropriateness of using these facilities would affect the implementation of those strategies. The availability of WIPP or the federal repository is obviously a key issue, both in terms of the facility entering operation and in terms of MSRE waste being allowed into the disposal facility.

Strategies that make use of existing facilities such as the DWPF or the INEL calciner and eventual waste immobilization facility depend on the availability of such facilities. This includes agreements with the sponsor that the MSRE materials can be processed in that facility, and verification that the use is technically acceptable. In some strategies, construction of new facilities (such as the INEL immobilization facility) are assumed; implementation of that strategy is thus contingent on the funding and construction of that facility.

6.5 TRANSPORTATION AND INTERSTATE AGREEMENTS

Transportation of radioactive waste to another state for processing, storage, or disposal is a sensitive issue. States' equity issues may have to be resolved between a host state and the State of Tennessee, or between a host state and the federal government. In some cases, these relationships are highly litigated and controlled by court orders or settlement agreements (such as the Idaho settlement agreement). With other states, these agreements are arrived at on a case-by-case basis. Special purpose casks may be required, involving licensing agencies.

6.6 FUNDING

Implementation of any strategy is contingent upon the availability of funding for the necessary activities. This includes funding for activities performed within the scope of the fuel salt disposition task, as well as funding for key interfacing facilities such as proposed processing or disposal sites.

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