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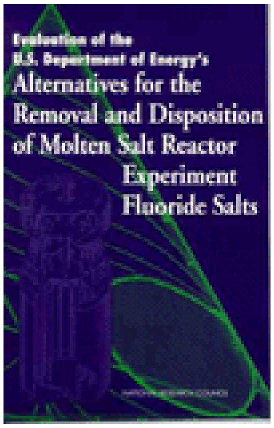

Evaluation of the U.S. Department of Energy's Alternatives for the Removal and Disposition of Molten Salt Reactor Experiment Fluoride Salts

Molten Salt Panel of the Committee on Remediation of Buried and Tank Wastes, National Research Council

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Alternatives for the Removal and Disposition of Molten Salt Reactor Experiment Fluoride Salts

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Board on Radioactive Waste Management
Commission on Geosciences, Environment, and Resources
National Research Council

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NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by the Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Cover: The cover shows a drawing of one of the drain tanks of the Molten Salt Reactor Experiment that contains a solidified mixture of radioactive fluoride salts. The top section, attached to bayonet-like thimbles that penetrate the bottom section, was designed for cooling water to absorb heat from the tank contents. The background shows a ternary phase diagram for the three main ingredients of the fluoride salts—lithium fluoride (LiF), beryllium fluoride (BeF_2), and zirconium fluoride (ZrF_4). The dark green color is the true color of solid uranium tetrafluoride (UF_4), also present in the salts.
Special thanks to Mary Catlin for digitizing the figures from Peretz (1996c) for this artwork.
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Preface

More than 25 years ago, I was a consultant to the group that was designing, building, and operating the Molten Salt Reactor Experiment (MSRE). Now the "mothballed" MSRE presents an environmental hazard that must be remediated soon, and I have been appointed to chair a National Research Council study of the remediation alternatives under consideration. The fluoride salts that were once the reactor fuel and that are now stored in drain tanks have been unstable since the reactor was shut down in 1969. The potential hazards of the toxic, radioactive, and fissionable materials have been extensively reviewed since the early 1970s and are worsening with time.

This report describes the scientific and engineering aspects of feasible remediation plans for the fluoride salt contents of the three drain tanks of the facility. The panel has carefully reviewed the previous studies and the recent technical evaluations of the alternatives proposed by staff at the Oak Ridge National Laboratory (ORNL). The panel was impressed with the information and background knowledge available at ORNL and from other Department of Energy (DOE) sites, including that from retirees who had run the reactor and who had developed the basic fluoride chemistry.

At the present time, DOE has provided funding and personnel to take action on this environmental hazard. Many ORNL staff and now members of the public recognize the high priority of this remediation project. The panel supports the completion of remediation work on this cleanup problem that the present DOE management has inherited and has the opportunity to solve.

JOHN L. MARGRAVE
HOUSTON, TEXAS

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Executive Summary

The Molten Salt Reactor Experiment (MSRE) is a nuclear facility that is no longer operational and now poses a cleanup challenge to the U.S. Department of Energy (DOE). This report comments on several alternative cleanup strategies that are under consideration (Peretz, 1996a,b,c) for remediation of radioactive fluoride salts stored at the site. A brief description of the facility provides a useful context in which to understand its present status and the important issues that affect remediation plans.

THE MSRE FACILITY AND CURRENT REMEDIATION PLANS

The MSRE was built at Oak Ridge National Laboratory (ORNL) in the 1960s to explore the possibility of thermal breeding, using the thorium-232 (^{232}Th) and uranium-233 (^{233}U) fuel cycle. For this experiment, the fissile fuel (initially $^{235}UF_4$ [uranium tetrafluoride], and later $^{233}UF_4$ and $^{239}PuF_4$ [plutonium tetrafluoride]) was dissolved in a molten salt mixture and circulated at 650°C through a metal (Hastelloy N) vessel to achieve a controlled nuclear chain reaction, moderated by graphite rods. This novel nuclear reactor configuration produced a thermal power of 8 MW. However, after the facility was shut down in 1969, no further work was conducted on this reactor or on any similar reactor, except for design studies of a breeder reactor for which a prototype was never built (Weinberg, 1994).

At the time of shutdown, the molten fused salt was drained from the reactor vessel into three metal drain tanks provided as part of the original installation. Two of the drain tanks store the now solidified fluoride salts containing most of the uranium and plutonium fuel. A third "flush" drain tank stores the fluoride salt mixture used to flush the system piping, an operation that imparted to the flush salt a small inventory of radioactive species.

From the 1960s (Peretz, 1996c, p. 1–11; Thoma, 1971, p. 59) it was recognized that radiolysis of the solid fluoride salts produced fluorine, but uranium hexafluoride (UF_6) gas was not observed. Aside from periodic maintenance checks and reheating to submelting temperatures, the facility essentially lay dormant until recent years, when migration away from the drain tanks of both fluorine and UF_6 (representing more than 10 percent of the total uranium) was detected in the system. Without remediation, these gases form continually due to the instability of fluoride salts in the presence of ionizing radiation and increasingly pressurize the system.

The condition of the facility is such that eventual environmental or human exposures to some of the toxic materials in the facility cannot be ruled out (NRC, 1985). Health hazards may arise from radioactive materials such as actinides (especially gaseous UF_6) and fission products and from chemical substances such as hydrogen fluoride (HF) and fluorine (F_2) gases. Accordingly, the facility is now a cleanup priority of DOE. Both the U.S. Environmental Protection Agency (EPA) and the State of Tennessee have regulatory authority over cleanup activities.

One of the cleanup objectives is to reduce the hazard associated with fluoride salts that are now stored in the three unheated drain tanks. These tanks contain 4650 kg (4.65 metric tons, or 5.13 English short tons, where one short ton is 2000 pounds) of solidified fluoride salt that was a fused solution of lithium fluoride (LiF), beryllium fluoride (BeF_2), and zirconium fluoride (ZrF_4). The fuel salt contains approximately 0.7 percent (by weight) radioactive compounds—specifically, uranium fluorides (the compounds UF_3, UF_4, UF_5, and UF_6 are all believed to be present), plutonium tetrafluoride, fission products, and alpha decay products. The flush salt contains much smaller amounts of the same materials.

This cleanup project is at a stage where DOE is assessing several technical approaches to salt removal, conditioning, and processing, as summarized by Peretz (1996c), and is beginning the regulatory approval process. Safe cleanup of the fluoride salts in this one-of-a-kind facility poses unusual challenges.

More than one way to process the salts is possible in principle. One option under consideration is to remelt the salts in the drain tanks where they are now stored, redissolve any radiation-induced precipitates, and transport the fused salt (in liquid form) through the system pipes to an external vessel for further processing. A second option is to extract the uranium content of the fuel salt (through direct fluorination in the drain tanks after partial or complete remelting of the fuel salt, in order to convert the uranium fluorides into volatile UF_6 gas) prior to transport of the melted salt to external storage containers. This option would leave fission products and plutonium fluorides in the residual salt. A third option is to chip or blast away solid pieces of the salt without applying heat to remelt it and then remove the salt as solid particles. In all cases, the radioactive waste would require storage at an approved site, with provision to "getter" any released fluorine and other volatile fluorides.

Which technical approach should be used and why? In order to comply with regulatory requirements, several alternatives must be considered. Relevant EPA Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) criteria include the protection of human health and the environment, compliance with regulatory requirements, effectiveness (in both the long and the short terms), reduction of toxicity, implementability, and cost. The approach that satisfies these criteria most favorably should be the remediation method of choice.

The challenge for project personnel is to select a remediation approach that deals appropriately with all the potential chemical and nuclear problems that could arise in the handling of the fluoride salts. Examples of such concerns are release of UF_6, exothermic chemical reactions of fluorine, and a nuclear criticality excursion due to the quantity of fissile isotopes (e.g., ^{233}U and ^{239}Pu) present in the system.

PURPOSE OF THIS REPORT

The Peretz (1996c) report, published in August, identifies various technical alternatives for the treatment and disposition of the radioactive fluoride salts presently stored in three drain tanks. At the request of DOE, the National Research Council (NRC) has undertaken the present study to review current evaluations of these different cleanup approaches.

Specifically, the panel was asked to review the proposed alternatives for removal, separation, and stabilization of the salts to determine the extent to which

1. appropriate technologies and options have been identified and evaluated,
2. evaluations are sufficiently complete to form a basis for decision making, and
3. potential hazards associated with fuel and flush salt removal have been identified and addressed.

Topics relevant to this determination include nuclear criticality safety, radiolysis, nuclear reactions associated with the radioactive species in the facility, and the chemistry and partitioning of the fluorine salts and fluorinated compounds that exist in various phases and compositions in the facility.

A summary of the findings on these three enumerated issues, posed as responses to questions, is presented below.

SUMMARY OF FINDINGS ON THREE MAJOR ISSUES

To what extent have appropriate technologies and options been identified and evaluated?

The panel finds that the relevant alternatives have been identified. The panel does not find that any important options have been omitted, although some of the information required for a final choice is still to be developed. Nevertheless, with the present state of knowledge, the panel considers that fluorination to extract UF_6 from the salt is the most promising approach for isolation of the uranium. Fluorination has been utilized successfully in the facility in the past. For in-tank fluorination to succeed, major issues need to be resolved, among them the potential for effective redissolution of all the solid phases in the drain tanks and evaluation of the extent of corrosion damage to the tank walls due to the effects of the complex interactions of ionizing radiation and fluorine compounds.

Some alternative approaches exist within this favored technology. These include fluorination within the drain tanks, transfer of the salt to a new fluorination vessel, or use of the existing fluorination vessel in the process cell. Other options are to use alternative fluorinating agents other than F_2, such as bromine pentafluoride (BrF_5), chlorine trifluoride (ClF_3,) dioxygen difiuoride (O_2F_2), krypton difiuoride (KrF_2), or xenon difiuoride (XeF_2).

To what extent are the evaluations sufficiently complete to form a basis for decision making?

The panel finds that the final waste disposal objectives in the proposed (Peretz, 1996c) alternatives 1–6 are presently insufficient to lead to a sound remediation strategy and concludes that interim waste storage (alternative 7) is the only practical approach at present.

Additional information about the system is needed to support decisions about remediation options. The final selection of an approach must be based on additional information about the system and the hazards.

A crucial part of molten salt processing will be the initial melting, which will demonstrate whether the precipitated phases are manageable and the tank confinement is intact. Positive results would show that direct fluorination on a liquid system could proceed.

In Peretz (1996c), the remediation strategy being used by the project is not defined. Each strategy developed for remediation of the drain tank salts should have a primary alternative and one or more backup alternatives to cover the hazard of failure of the primary alternative. A comparative cost estimate should be completed for each case. The decision maker can then optimize the choice of strategies based on probable success, initial costs and risks, and possible ultimate costs.

To what extent have the potential hazards[1] associated with fuel and flush salt removal been adequately identified and addressed?

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[1] The term *hazard* is used here instead of *risk* because the probability of occurrence of the hazard has not been defined. Assessment of a risk can be made only when the likelihood of a hazard scenario has been assessed and applied to the measure of the importance (or size) of the possible consequences. In other words, risk is quantitatively defined as the product of probability of occurrence and consequence of a hazard scenario; in the absence of numerical calculations, one may refer to hazards, not risks. Both concepts (*hazards* and *risks*) are used in this report.

The Peretz (1996c) report contains a baseline hazard section that identifies the present hazards. A preliminary hazards screening has also been made (ORNL, 1995). Evaluation of the possible hazards associated with the various process alternatives awaits the further development of those alternatives.

Once the pertinent assessments of likelihood and magnitude of hazard scenarios are available, present safety standards and risk analysis methodologies, properly applied, can provide adequate delineation of hazards and their potential for becoming risks. In a risk analysis of the MSRE drain tanks, an overly conservative, upper-bound estimate of any particular risk is undesirable if the quantitative results are used to choose among various remediation alternatives, because this approach might then fail to identify the course of action with the least risk. In the absence of more complete data (e.g., realistic probability distribution functions for every uncertain parameter) and for present decisions, the panel believes that estimates of risk that provide the best basis for decision making should be on an expected value basis, bracketed by an uncertainty range.

The panel believes that the probability of an inadvertent criticality hazard during mitigation of the MSRE salt is extremely low and that, even if such an event were to occur, the safety and technical consequences would be minor. However, because the public concern and political consequences could be very large, the panel has addressed the question in some detail.

Regarding radiation hazards, high radiation fields external to the drain tanks necessitate remote operations, with workers outside the shielded drain tank cell except for very brief episodic access. For example, the gamma radiation levels at the surface of the fuel salt tanks due to fission products are approximately 640 roentgens (R) per hour (Williams, 1995), primarily due to the 0.66-MeV (million electron volt) gamma rays from cesium-137.

MAJOR CONCLUSIONS

The panel concludes that cleanup of the MSRE can be accomplished with risks to the public, operations personnel, and the environment that can be well managed to quantitative levels at or below those values that form standard safety guidelines (such as an annual probability of occurrence of 10^{-6}).

Additional information is needed to define and select the most favorable processes for the removal of fissionable materials, the associated removal of the salt, and their interim disposition. However, present information is good enough, and overall safety well enough ensured, to be used as a basis for making the decision to proceed with the overall project.

The responses given above to questions posed in the Statement of Task are generally favorable judgments subject to important cautionary caveats, for example, that some of the specific parameters and procedures required for processing steps are confirmed by further information gathering, testing, and analysis. Examples and suggestions of this kind are contained in the report, particularly in Chapter 8 and Appendix E. These technical options, offered as suggestions for consideration to MSRE project personnel, are secondary to the basic recommendation that MSRE remediation work is ready to proceed, with the fluorination approach the most promising way to remove uranium, given the present state of knowledge. The panel is not chartered to recommend specific parameters or procedures, and these selections are best done by project personnel, as new information is obtained.

What is missing and what could be collected in the first stages of the remediation project are current data on the fuel salts and on the condition of the piping, vent lines, and equipment of the MSRE, which has been shut down since 1969. Final selection of processes and the necessary backup systems will depend on the crucial aforementioned data and on laboratory and engineering developments. Irradiated samples from the period of MSRE operation are available for simulation and mockup of the remediation processes to be used. The project would proceed ideally in stages determined in part by what is learned as the work progresses.

While the drain tanks and their contents were well characterized at reactor shutdown, more than 25 years of radiolysis and corrosion have produced changes in chemistry and may have produced changes in the integrity of components. As a result, the panel recommends a cautious, stepwise approach to all operations.

Fluorination procedures, subject to important caveats and to further information gathered on the system, as noted in this report, appear to be the technical approach most worthy of further consideration. Storage of the separated fissile ^{233}U as the uranium oxide U_3O_8 in an existing ^{233}U storage site at ORNL represents a suitable interim disposition. A stabilized or gettered salt residue after fluorination treatment also is a reasonable form for interim storage at ORNL.

MAJOR RECOMMENDATIONS

The Peretz (1996c) report on remediation alternatives is only a preliminary document related to the CERCLA process. Further analyses and development of specific plans leading to a final decision will occur over the next several years. As new information becomes available on the fuel and flush salts and on the status of the rest of the MSRE system, additional reviews of the major issues may be warranted.

The panel recommends that cleanup strategies for the MSRE project provide one or more sets of workable approaches for the safe removal, processing, and interim storage of fuels and flush salts that take into account the need for alternative and backup strategies. All relevant factors should be considered, including cost, equipment failure, criticality potential, remediation effectiveness and implementability, risk management, uncertainties, trade-offs, and duration of actions. Of equal importance is the need to fully consider possible process perturbations, failures, contingencies, resource requirements, and other factors that may warrant backup support or alternative approaches to offset them.

Plans and work in progress at ORNL are addressing these issues. Sound procedures, such as stepwise processes for the acquisition of information and remediation, are a necessary strategy because not enough is known about the system (e.g., distribution of uranium in the system) to make a fully informed decision at the onset.

Because the final resolution of disposal alternatives may take considerable time, the panel suggests that DOE use a phased decision strategy focusing on interim storage, with the flexibility it provides, rather than trying to make a final disposition alternative determination in the near future. It is premature at this stage to derive treatment alternatives from requirements for ultimate disposition in geologic repositories off-site, because these long-term storage options are not developed sufficiently to define final waste acceptance criteria.[2] It appears that resolution of ultimate (geologic) disposal site criteria and characteristics probably lies beyond the time horizon of the MSRE cleanup project.

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[2] The panel is aware that any processing of the fuel salts may prevent their classification as spent nuclear fuel.

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Introduction

The Molten Salt Reactor Experiment (MSRE) at Oak Ridge National Laboratory (ORNL) was a demonstration of a novel nuclear reactor design. The reactor generated a power of 8 MW from nuclear fission reactions[1] in operations during 1965–1969. Graphite in the MSRE reactor vessel acted as a moderator to slow down (or "moderate") the high-energy neutrons released from fission events, to reduce the neutron kinetic energies to low (or "thermal") values where the fission cross section is much larger than it is at higher neutron kinetic energies. As in any nuclear reactor, the combination of fissile fuel and moderator in the core generated a spatially distributed flow of neutrons, or a neutron flux, which is the number density of neutrons passing through a unit area in a unit time as a function of position in the reactor, time, and neutron energy.

The following features made the MSRE design atypical. The MSRE fuel was in a homogeneous molten fluoride salt medium, rather than in solid nuclear fuel rod assemblies that are used in all commercial nuclear power plants today. The fuel was fissile uranium (first a ^{235}U charge, later ^{233}U) and fissile plutonium (^{239}Pu) contained as the uranium tetrafluoride (UF_4) and plutonium tetrafluoride (PuF_4) salts in a molten salt medium consisting predominantly of lithium, beryllium, and zirconium fluorides (LiF, BeF_2, and ZrF_4), at an operating temperature of approximately 650°C.

Another unusual feature was the lack of a separate coolant in the core design. The reactor vessel contained only the molten salt fuel and the graphite moderator. Heat from the fission reactions elevated the

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[1] To sustain a critical chain reaction in an assembly of fissile material, each nuclear fission event produces, for every thermalized neutron captured, approximately two energetic neutrons (which, with moderation and loss mechanisms, result in approximately one thermalized neutron to participate in a subsequent fission event). Energy is also liberated, on the order of 200 million electron volts (MeV) per fission. The fissile nuclei used in the MSRE were uranium-233 and-235 (^{233}U, ^{235}U) and plutonium-239 (^{239}Pu).

temperature of the fuel salt and was removed by circulating the fuel salt through a heat exchanger external to the reactor core. This design is to be contrasted with that of commercial reactors, which circulate the coolant (water or gas) in the core of solid fuel rods.

Figures 1.1 and 1.2 show the layout of the MSRE. The fuel salts were circulated in a loop containing the reactor vessel, a heat exchanger, and a pump. The coolant salts circulated in a loop consisting of the heat exchanger, a separate pump, and a radiator, from which the heat was dissipated to the air (up a stack) by fans.

The reactor is housed in an isolated concrete building of ORNL inside the Oak Ridge Reservation. The drain tanks and reactor vessel are in a sealed containment system (Peretz, 1996c, p. 1–6) surrounded by concrete walls several feet thick to provide a primary radiation shield between the radioactive materials and the environment (see Figure 1.3). The building provides a secondary containment. The nearest location for exposure to the public is the Bethel Valley Road outside ORNL (Peretz, 1996c, p. 1–36).

The MSRE demonstrated the potential for a thermal neutron breeder design. Introduction of thorium-232 (^{232}Th) in the salt (as a fluoride compound ThF_4) would permit breeding (i.e., generation by nuclear-induced transmutation) of ^{233}U. Absorption of a low-energy (near thermal) neutron by a ^{232}Th nucleus transmutes it to ^{233}Th, which undergoes beta decay to protactinium-233 (^{233}Pa), followed by a second beta decay to produce ^{233}U. Breeding is achieved in a reactor when the rate of production of fuel (^{233}U) is greater than the rate of consumption of fuel by nuclear fission inside the core. The ratio of the rate of production and the rate of consumption defines the breeding ratio.

Although actual experiments with a thorium blanket were not performed, experiments on the MSRE demonstrated the potential for a next-generation design to breed ^{233}U with a breeding ratio greater than one. An on-line chemical processing system could have been installed (in the fuel processing cell shown in Figure 1.2) to extract ^{233}Pa from the salt during operations to enhance the production of ^{233}U. If the ^{233}Pa were left in the core, its absorption of thermal neutrons would reduce both the neutron flux in the core and the breeding of ^{233}U (Nero, 1979). The processing system that was installed was used successfully to recover uranium by fluorination (Peretz, 1996c).

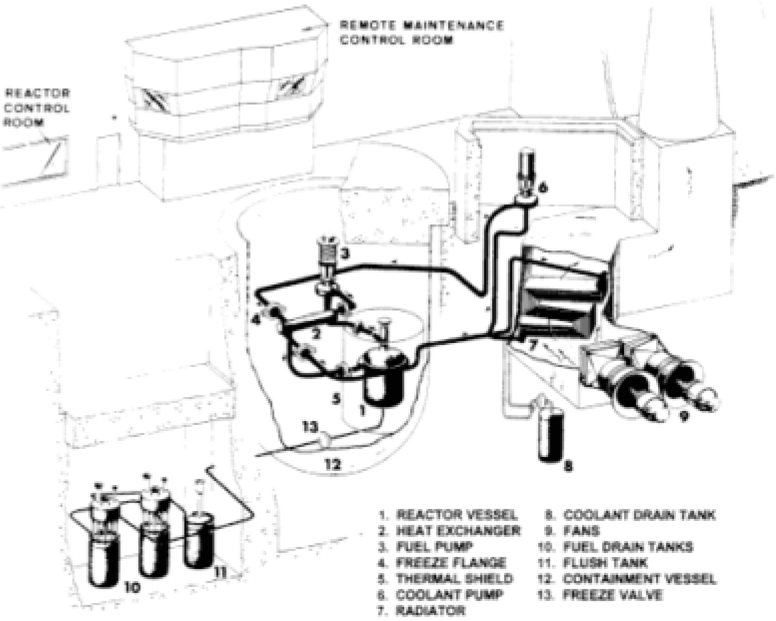

Figure 1.1
Arrangement of the principal components of the MSRE. Source: Modified from Peretz (1996c, Figure 1.1).

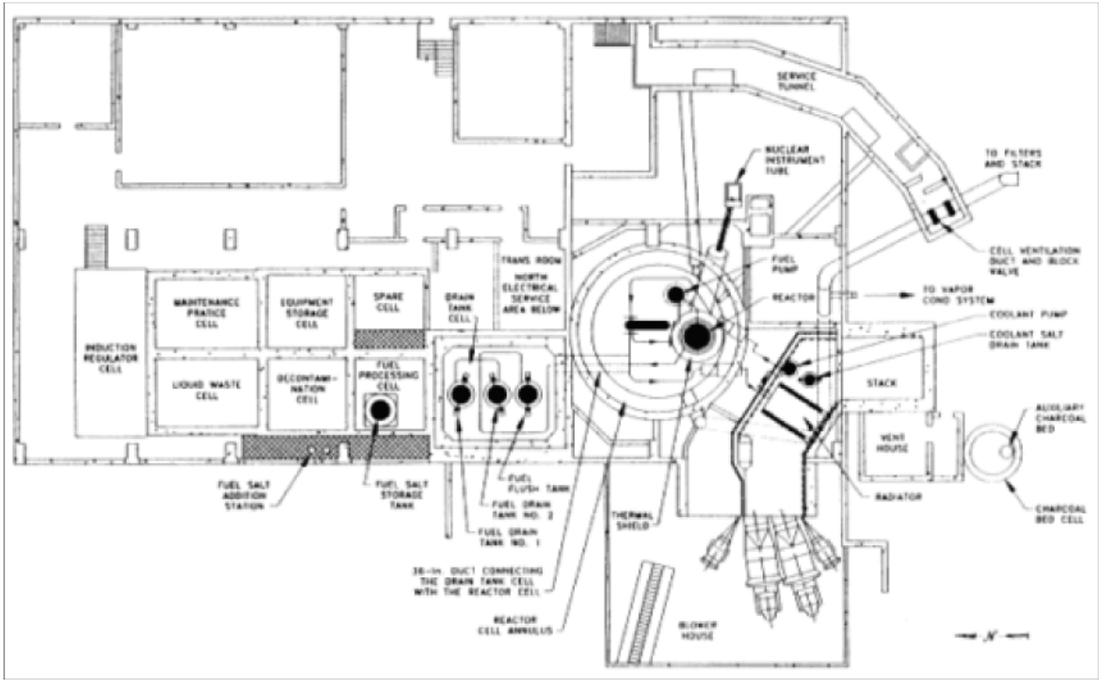

Figure 1.2

Plan of the MSRE facility, showing the fuel processing cell and auxiliary charcoal bed. Source: Peretz (1996c, Figure 1.2).

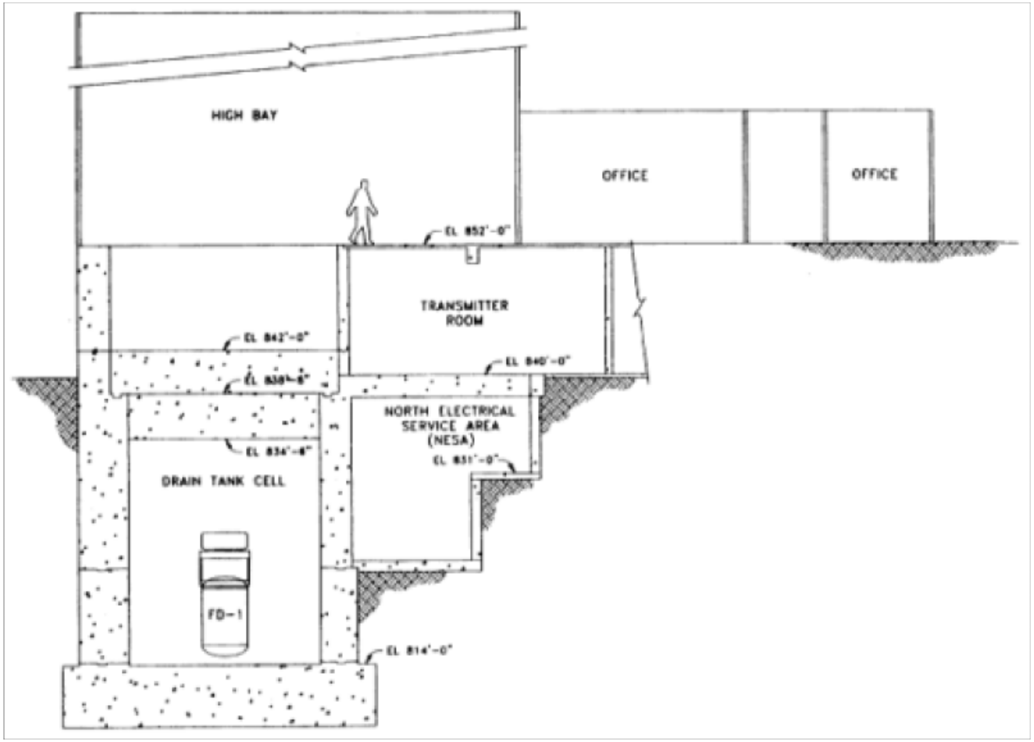

Figure 1.3
Cross section through MSRE drain tank cell and adjacent areas. The elevation (EL) above sea level (in feet and inches) at various locations is shown. Source: Peretz (1996c, Figure 1.4).

A more comprehensive discussion of the reactor can be found in many sources (see, for example, Benedict et al., 1981, p. 10; Knief, 1992, pp. 318–321; Weinberg, 1994, pp. 125–127; Peretz, 1996c, and references therein).

CURRENT STATUS OF THE MSRE

After shutdown in 1969, the molten fluoride fuel salt and a batch of flush salt (used to "flush" the system) were drained into three drain tanks, two fuel salt tanks and one flush salt tank, and were permitted to solidify. The tanks are located in a hermetically sealed (welded shut) enclosure containing both the drain tank cell and the reactor cell (see Figures 1.1-1.4). The major chemical constituents of the salts are lithium, beryllium, and zirconium fluorides; the radioactive species are actinides, their decay products, and fission products.

Radiation emitted from the decay of radioactive species within the salt has interacted with the salt medium to cause radiolytic formation of both F_2 (fluorine) and UF_6 (uranium hexafluoride) gas. These gases have diffused out of the solid salt. This diffusion may have been aided by periodic annealing operations at elevated temperature that were performed in the 1970s and 1980s. Over time, headspace gases in the tanks have migrated into the reactor vent piping and the off-gas vent trap system to the interior of the activated charcoal bed (ACB; see Figure 1.5) through valve openings. In recent years, the migration of UF_6 gas through the system apparently has resulted in the deposition of uranium fluoride solids in the ACB, and such deposits may be present on the interior walls of piping and in the drain tanks. In October 1996, the vent piping was at an overpressure of approximately one atmosphere, due to F_2 and UF_6 gases, with solid plugs of uranium fluoride deposits inferred from pressure differences in piping runs leading from the drain tanks to the ACB at the end of the vent line.

The facility's two immediate hazards—gas buildup and solid uranium fluoride deposits—are being addressed by work in progress at ORNL. A "reactive gas removal" action has been designed to unblock or bypass the plugged piping system and collect the chemically reactive F_2 and UF_6 gases in traps. Pumping initiated in November 1996 has relieved the overpressure in some piping, although nonvolatile plugs have prevented

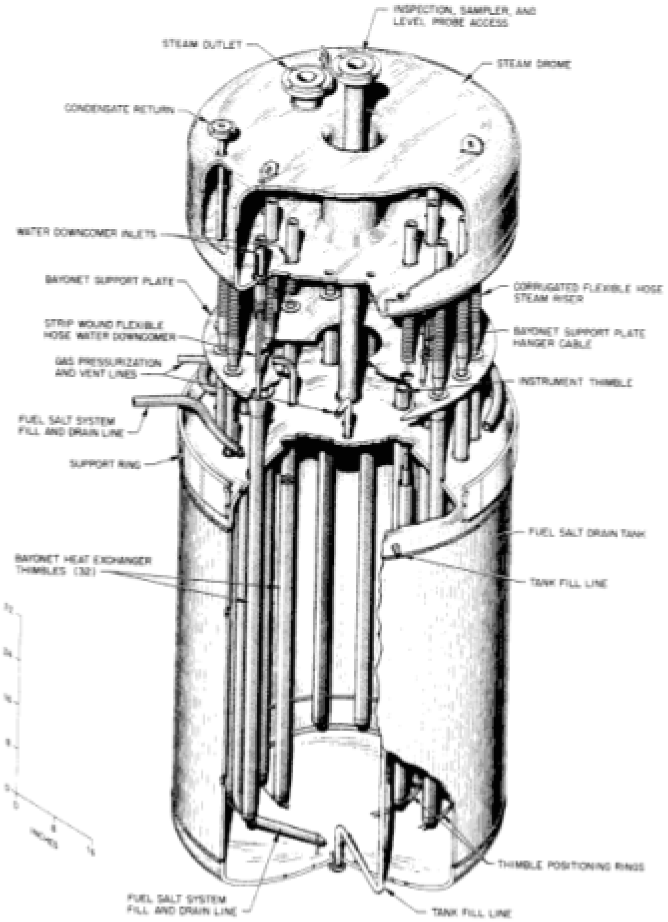

Figure 1.4

Sketch of an MSRE fuel drain tank, made of a nickel alloy (Hastelloy N), showing bayonet thimbles attached to a headspace drome. The flush drain tank lacks the bayonet thimbles. Source: Peretz (1996c, Figure 1.3).

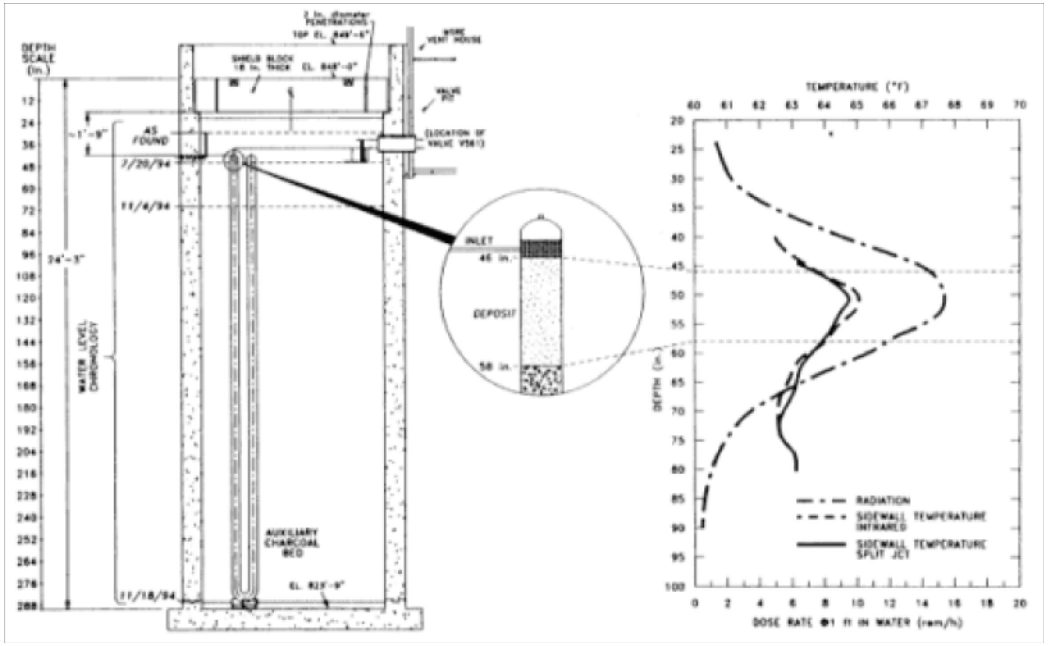

Figure 1.5

Location of the uranium deposit in the auxiliary charcoal bed. The elevation above sea level is shown in places.

Note: EL = elevation; ft = foot; in. = inch; jet = junction; rem = roentgen equivalent man. The expanded view shows the top section of the charcoal bed where 2.6 kg of uranium has been deposited. Source: Peretz (1996c, Figure 1.10).

complete access to all system piping, including that closest to the drain tanks. A robotic vacuuming operation is being designed to extract the uranium deposits and charcoal from the top of the ACB trap.

The uranium fluoride salts in the three drain tanks are a more long-term concern. These fluoride salts are not in a favorable configuration for long-term storage. The salts are unstable due to radiolysis that continues to occur, liberating reactive gases. The fissile materials in the tanks could form a critical configuration if a moderator such as water entered the system. The probability of this happening in the long term must be considered if the salts are to be stored indefinitely in the present location (see Figures 1.1-1.3). In particular, the drain tank cell is capable of being flooded if the hermetic seal is lost because the natural water table is above the tanks (Peretz, 1996c). Waterflooding could occur in the absence of active ground water pumping operations, which are currently practiced. Because a nuclear criticality excursion cannot be ruled out absolutely under these conditions, the salts in the present mode of tank storage pose a long-term hazard, even though it is small.

The Department of Energy (DOE), following the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) regulatory process, is exploring technically feasible operations designed to reduce the hazard posed by the salts in these tanks. A variety of technical alternatives have been identified to date (Peretz, 1996c) for salt removal, separation of uranium, and ultimate disposition of all waste products.

Seven primary alternatives, some with subalternatives, were identified by Peretz (1996c). They are summarized as follows: (1) do nothing, (2) enhance the present storage, (3) treat the salts as spent nuclear fuel awaiting eventual storage in a federal repository, (4) treat the salts as transuranic waste bound for the Waste Isolation Pilot Plant, (5) electrorefine the salts, (6) reuse the salts elsewhere in the DOE complex, and (7) use interim storage at a DOE site. Alternatives 4 through 7 include a possible fluorination step to remove uranium. Chapter 7 lists these alternatives in more detail.

These technical alternatives are also considered in the larger context of a waste management strategy with a view to ultimate disposal options, such as geologic storage in a repository. The strategic conclusion of Peretz (1996c) is that on-site interim storage is the preferred strategy for the foreseeable future, provided the materials in question cannot be reused beneficially elsewhere in the DOE complex. The particular technical alternative recommended by Peretz (1996c) is a melting and fluorination process to strip uranium from the salt as UF_6 gas. The uranium fluoride would be converted to an oxide and stored with other ^{233}U inventories, while the stripped salt would be stored in a "gettered" mode in shielded cells.

This alternative, and others, would involve remediation work using the MSRE facility and equipment. Project personnel have begun testing and maintenance, such as replacement of deficient pressure sensors. However, the operability and status of some components are unknown and contributes to the panel's recommendation for a stepwise remediation approach. Present DOE practices require an assessment of the integrity of all components of the MSRE that would be vital to a remediation operation.

These considerations are at a stage where relevant scientific and technical information now under development on the identified alternatives will provide input to a future binding regulatory decision on the particular remediation option selected for the MSRE salts. This decision involves selection of the remediation alternative considered to be the best, as judged against all CERCLA criteria.[2]

ROLE OF THE NATIONAL RESEARCH COUNCIL

At the request of DOE, the National Research Council (NRC), under the auspices of the Board on Radioactive Waste Management (BRWM), has undertaken a study to provide an independent technical review of the alternatives offered in Peretz (1996c)—specifically, to examine the process by which these alternatives for MSRE salt treatment and disposition were identified and used in decision making. The complete Statement of Task describing the scope of this study is reproduced in Box 1.1. The study was undertaken by the Molten Salt Panel (hereafter referred to as the panel) of the Committee on Remediation of Buried and Tank Wastes (CRBTW). The present report, written by the panel, represents consensus positions reached as a result of

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[2] The CERCLA criteria are the following: overall protection of health and environment, compliance with applicable regulations, long-term effectiveness, reduction of hazard, short-term effectiveness, implementability, and cost.

deliberations and discussions. Two meetings (in September and October 1996),[3] parts of which were open to the public, were held to solicit input from and interaction with DOE and its contractors. The panel also heard from current and retired Oak Ridge employees, a State of Tennessee representative, and interested members of the public.

The panel used many available background materials. The problems and proposed solutions associated with the salt tanks have been discussed in some detail at various technical meetings (Peretz, 1996a,b), in the reports of a Senior Review Board review (February 20, 1995), and in briefings on MSRE fuel salt disposition to the CRBTW during 1996. Chemical and technical aspects of the problem, including the current state of the molten salt reactor fuel and flush salts, tanks, and related equipment (e.g., associated tubing, valves, and sensors), have been discussed and summarized in Peretz (1996c) and references therein. Presentations to the panel (Rushton et al., 1996a,b) have reviewed the history of facility operations and have outlined a targeted timeline for safe removal and disposition of the MSRE fuel and flush salts that is consistent with CERCLA requirements. The future schedule is intended to encompass actions subject to the approval of the two agencies with regulatory authority over these actions, the State of Tennessee and the U.S. Environmental Protection Agency.

SCOPE AND ORGANIZATION OF THIS REPORT

To address the three key questions posed in the Statement of Task (Box 1.1), this report is organized as follows.

Some of the scientific challenges common to most of the alternatives are discussed in this report first. Radiolysis and nuclear reactions are treated in Chapter 2. Fluoride salt chemistry, partitioning, and system corrosion are treated in Chapter 3. The assessment of the present condition of the salts and the drain tanks that is contained in these two chapters is relevant to any remediation approach.

Other challenges are discussed as they would pertain to the execution of a remediation plan. In Chapter 4, the logical process steps are presented, from which the panel develops a preferred, stepwise

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[3] The September meeting included a tour of the MSRE facility.

BOX 1.1 ROLE OF NATIONAL RESEARCH COUNCIL

This report responds to the statement of task reproduced below:

The study panel will review the DOE alternatives for remediation of fuel and flush salts in drain tanks as part of the decommissioning of the Molten Salt Reactor Experiment (MSRE) facility at the Oak Ridge National Laboratory. DOE has presented specific options for the fuel and flush salt removal from drain tanks and potential options for disposition during remediation of the MSRE facility. These options are identified and evaluated in "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).[1]

The panel is asked to review the current state of the Department's evaluations for removal, separation, and stabilization of the MSRE salts to determine the extent to which (1) appropriate technologies and options have been identified and evaluated; (2) evaluations are sufficiently complete to form a basis for decision-making; and (3) potential hazards associated with fuel and flush salt removal have been identified and addressed. Topics relevant to this determination include criticality, radiolysis, and nuclear reactions associated with the radioactive species in the facility, and the chemistry and partitioning of the salts and fluorinated compounds that exist in various phases and compositions in the facility.

The chair of the National Research Council appointed a panel of 12 scientists and engineers to perform this technical review. This panel, which operated under the auspices of the NRC's Board on Radioactive Waste Management, included experts in relevant disciplines such as risk assessment, inorganic fluoride chemistry, nuclear chemistry, nuclear and chemical engineering, nuclear criticality safety, materials science, and health physics. Biographical sketches of the committee members are given in Appendix H.

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[1] Cited in this report as Peretz (1996c).

approach based on the understanding that some decisions are best postponed until after further information on the system is acquired. Chapter 5 presents selected technical processing approaches to strip uranium, with commentary on the relative advantages and disadvantages of each. Issues pertaining to nuclear criticality safety provide one of the most significant constraints in some of the future processing options; therefore, these considerations are explicitly treated in Chapter 6.

The scientific and technical background information in Chapters 2 through 6 is important to the assessment of strategic alternatives, which are discussed in Chapter 7. Several of the various alternatives in Peretz (1996c) are compared and contrasted to provide the basis for a recommended alternative.

Chapter 8 addresses the management of potential hazards associated with MSRE salt cleanup operations. This chapter also lists several specific information-gathering activities recommended to reduce hazards and provide experimental evidence to better inform the decision-making process.

The final chapter (Chapter 9) contains a summary discussion with commentary on the waste management strategy appropriate for the molten salt cleanup efforts. To the extent that future experimental evidence confirms the anticipated condition of the salt and drain tanks, a preferred approach is recommended for consideration. The three questions posed in the Statement of Task are also answered explicitly.

2—

Radiolysis and Nuclear Reactions

This chapter provides technical details about current information available on the salts in the tanks. This assessment is important for any remediation strategy. The discussion that follows focuses on the radioactive species and nuclear reactions relevant to cleanup operations.

The now solid 4650 kg[1] of fuel salt in two of the drain tanks contains nearly all of the uranium, plutonium, and fission products, with a minor amount in the flush salt in the third tank. Ongoing radiolysis effects have had important chemical consequences on the contents of the drain tanks. Substantial amounts of both fluorine gas and uranium hexafluoride (UF_6) have been produced, allowing vapor transport of more than 10 percent of the original 37.1 kg of uranium (see Table 2.1) from the fuel salt storage tanks. An unknown fraction of the uranium is in connecting piping and traps, with approximately 2.6 kg in the auxiliary charcoal bed (ACB) located at the end of the off-gas vent line (see Figure 1.5).

Salient features of the Peretz (1996c) report that are pertinent to this discussion are summarized here and cover radioactive source terms, radiation effects, and general comments, including discussion of radiation-induced liberation of fluorine (F_2) and uranium hexafluoride gases, radiation decomposition of solid uranium hexafluoride, the effects of an excess of reducing species in the salt, and the difficulties associated with a simple remelting operation.

RADIOACTIVE SOURCE TERMS

When reactor operation was terminated in late 1969, the molten fuel salt was transferred from the reactor to two drain tanks and

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[1] 1000 kg (one metric ton) is approximately equal to 2205 pounds, slightly smaller than the English long ton (2240 pounds) and larger than the short ton (2000 pounds).

allowed to cool and solidify. During the intervening years, the short-lived radioactive fission products have decayed to insignificant levels. This has left strontium-90 (^{90}Sr; with a 28.5-year half-life) and cesium-137 (^{137}Cs; with a 30-year half-life) and their short-lived daughters as the primary sources of fission product radioactivity (mostly beta and gamma radiation). According to Table 2.2, a total of 23,985 curies (Ci) exists in the fuel salt (in the inventory projected for December 1999),[2]

TABLE 2.1 Mass (kg) of Uranium and Plutonium in Fuel and Flush Salt

	Mass (kg) if No Losses			Mass (kg) if 4.4 kg U Lost from Fuel Salt[a]		
Isotope	In Fuel Salt	In Flush Salt	Total	In Fuel Salt	In Drain Tank 1	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

[a] Based on transport of 2.6 kg to the auxiliary charcoal bed and presence of 1.8 kg as UF_6 vapor in the off-gas piping and vessels.

[b] The ^{232}U/^{233}U ratio is assumed to be the same in both the fuel and the flush salts. This implied, as of 1995, a ^{232}U content of 160 ppm (pans per million) of the total uranium content in the fuel salt and 75 ppm of the total uranium content in the flush salt (the ^{233}U isotopic fraction in the flush salt is approximately half that in the fuel salt clue to the higher concentrations of ^{235}U and ^{238}U in the flush salt).

SOURCE: Modified from Peretz (1996c, Table 1.4).

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[2] A curie is a measure of radioactivity that is now defined as 3.7 × 1010 disintegrations per second; it originated historically as a representation of the radioactivity of one gram of radium (226Ra).

approximately 99 percent of which is contributed by the isobaric pairs ^{90}Sr/Y and ^{137}Cs/Ba.[3] Uranium, plutonium, americium, and their decay products contribute substantially less radioactivity (1496 Ci, primarily alpha activity from the ^{232}U and ^{233}U decay daughters) in the fuel salt (see Table 2.3) but contribute a major radiation hazard (the 2.6-million electron volt [MeV] gamma from thallium-208) that affects worker safety.

TABLE 2.2 Inventory of Fission and Activation Product Isotopes[a]

Isotope	Half-Life	Radioactivity (Ci)	Inventory in Fuel Salt (98.3%)	Inventory in Fuel 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_{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

NOTE: d = day; m = minute; y = year.

[a] Based on decay to December 1999.

SOURCE: Peretz (1996c, Table 1.6).

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[3] Y = yttrium; Ba = barium.

TABLE 2.3 Inventory of Actinide Isotopes Based on Decay to December 1999.

Isotope	Half-Life	Radioactivity (Ci)[a]	Activity Fuel Salt (Ci)[b]	Activity in Flush Salt (Ci)[b]
^{232}U and its daughter chain			*27.4 kg ^{233}U*	0.2 kg ^{233}*U*
^{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
^{233}U and its primary daughter chain				
^{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 ms	0.8	0.70	0.01
^{209}Pb	3.25 h	0.8	0.70	0.01
Other significant uranium and transuranic isotopes			2.5 kg ^{234}*U*	0.02 kg ^{234}U
^{234}U	2.45×10^5 y	17.4	15.2	0.11
			98.2% Pu	1.8% Pu
^{238}Pu	87.7 y	0.89	0.87	0.02
^{239}Pu	24,110 y	41.7	40.9	0.75
^{240}Pu	6540 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
Summary of actinide inventories				
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	1672	1496	14.0	

NOTE: d = day; h = hour; m = minute; ms = millisecond; s = second; y = year.

[a] Based on the total inventory of 31.3 kg ^{233}U and 2.8 kg ^{234}U. ^{232}U/^{233}U ratio assumed to be constant.

[b] This assumes a migration of approximately 4 kg ^{233}U from the salt.

SOURCE: Modified from Peretz (1996c, Table 1.7).

RADIATION EFFECTS AND GENERAL COMMENTS

Radiation-induced changes to salt chemistry from fission energy and fission events ceased at reactor shutdown, leaving radioactive decays (from alpha, beta, and gamma particle radiation sources) to continue to drive chemical effects. Such chemical effects result from ionization processes that occur within the salts as the radiation energy is absorbed in the solids. In a gross view, one can speak of the distances (ranges[4]) within which the energies of the alpha and beta particles are expended and in which the particles are stopped. In the fuel salt, which has a density of nearly 2.5 g/cm^3 (Table 2.4), the range of an alpha particle is very short, nominally a few milligrams per square centimeter, whereas that of beta particles is longer and can be several grams per square centimeter. By contrast, gamma radiation is much more "penetrating," with intensity diminished primarily by the vessel wall thickness rather than by the salt mass. Consequently, the energy from gamma rays are not all be expended within the volume of the fuel salt. The gamma levels at the surface of the fuel salt tanks due to fission products are approximately 640 roentgens (R) per hour[5] (Williams, 1995), largely due to the 0.66-MeV gamma rays from ^{137}Cs.

The existence of a high radiation field from the gamma radiation external to the fuel salt storage vessels makes it difficult for personnel to work on nearby equipment within the shielding except by remote-handling techniques or by brief operations designed to limit the episodic exposure to acceptable levels. Equipment can deteriorate over an extended period of time in the presence of radiation-induced chemically reactive gases such as fluorine and uranium hexafluoride. It would not be unusual for this to result in mechanical problems such as stuck valves, malfunctioning gauges (giving faulty readings), plugged lines (often at right-angle joints), and welds with pinholes. It is prudent to design for extensive equipment repair or replacement prior to any actual treatment of the radioactive salt.

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[4] This range is often given as a weight per square centimeter.

[5] Human exposure to the radiation field at the external wall of the drain tanks would reach life-threatening levels in one to two hours, but such exposure is prevented because operations are performed outside the shielded drain tank cell.

TABLE 2.4 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)
Fuel salt			
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	
Flush salt			
Flush salt drain tank	4265	1.92	2.22

[a] Mass and volume estimates that best correspond to process history.

SOURCE: Peretz (1996c, Table 1.2).

Radiation-Induced Liberation of Fluorine and Uranium Hexafluoride Gases

As shown in Table 2.1, the stored fuel salt originally contained 37.6 kg of uranium isotopes (84 percent ^{233}U, 7.5 percent ^{234}U, 5.9 percent ^{238}U, 2.6 percent ^{235}U) and 0.74 kg of plutonium isotopes (90 percent ^{239}Pu, 9.6 percent ^{240}Pu, 0.4 percent ^{241}Pu, and other isotopes), which is important to radiolysis (and criticality) concerns. The radiolysis reaction is probably the most important chemical consequence (discussed further in Chapter 3) for storage of the fuel salt, causing the release of fluorine atoms and molecules and the formation of volatile UF_6. Radiolysis led to pressurization of the piping system, migration of uranium into the pipes and ultimately to the ACB, and evidence that decomposition of the volatile UF_6 had deposited some solid plugs (probably uranium tetrafluoride [UF_4]) in the reactor vent pipes.

Peretz (1996c, p. 1–11) and Williams et al. (1996) reported radiation-induced liberation of fluorine gas from simulated fuel salts. The release of F_2 apparently is due to recombination of fluorine atoms liberated by radiation effects on the fluoride salts, with each radiation source (alpha, beta, and gamma) potentially responsible for this effect.[6]

This was observed in 1964 in irradiation experiments using surrogate salt samples. At that time no uranium was found in the gas phase. With the aim of reversing this radiolysis and, in large measure, deterring the escape of fluorine from the bulk salt, the irradiated salt (Guymon, 1971) was "annealed" after reactor shutdown. Annealing was carried out by maintaining the salt for a week at 149°C, a temperature well below the melting point of the salts (Peretz, 1996c).

Annealing of the bulk fuel salt, carried out on an annual basis until December 1989, was unsuccessful in preventing the transport of F_2 and UF_6 from the salt. This procedure was done presumably so that the fluorine released by radiolysis could recombine with the reduced species in the salt. Instead, the net effect over time was that fluorine (perhaps as fluorine radicals or F_2) oxidized UF_4 to UF_6. Annealing was stopped because of concern that annual heating of the fuel salts may have aided the transport of some uranium from the fuel, which had been observed at that time, probably as volatile uranium hexafluoride. Presently, pressure sensors at different locations in the piping system indicate different overpressures, showing that the piping is plugged in several places.

In recent years, gamma radiation was detected to confirm the migration of uranium within the piping system. The high-energy gamma from the thallium-208 (^{208}Tl) daughter of ^{232}U was used to trace the movement of UF_6 through the piping. In retrospect, the difference

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[6] Radiolysis (i.e., energy deposition in the salt due to energetic alpha, beta, or gamma radiation) is the source of the energy needed to break chemical bonds, resulting in the release of fluorine and UF_6. However, the particular radioactive species (e.g., alpha particles from actinides, beta particles from fission products, or gamma rays from gamma emitters such as those in the ^{232}U decay chain) that caused the most radiolytic decomposition is uncertain. It can be argued that alpha particle decays are partially responsible for fluorine radiolysis. Compared to gamma radiation, alpha particles have a shorter range and a denser ionization track, considerations that are important because individual fluorine atoms must be produced in close proximity to combine to form F_2. Another argument in favor of alpha (over gamma) radiolysis of UF_6 to lesser fluorides is that the uranium nucleus provides the alpha particle source, which is therefore always in close proximity to uranium fluoride compounds.

These considerations are reflected in quantitative data. Trowbridge et al. (1995, Table 2, p. 19) summarize fluoride radiolysis, focusing solely on uranium fluorides and Molten Salt Reactor Experiment (MSRE) salts. They show *G* values (molecules of fluorine produced per 100 eV of absorbed radiation) as being highest for alpha radiation energy expended in solid UF_6 ($G = 1.5$). For x-ray and gamma energies expended in solid fluorides to yield fluorine, the *G* values are much lower, of the order of 0.02 with large uncertainties. One experiment, cited without details, provided a *G* of zero for the effects of ^{238}Pu alpha radiation on MSRE salts. However, since the observed yields of F_2 and UF_6 were both extraordinarily greater than anticipated, other mechanisms are clearly at play; nevertheless, the effects of alpha radiation will have major consequences particularly on a condensed UF_6 phase.

between the simulated test (showing a benefit from annealing) and the real salt system (in which annealing may have aided migration of uranium away from the drain tanks) was probably the existence of a cold chemical trap in the Molten Salt Reactor Experiment (MSRE) system that the simulated test did not contain. An alternative explanation is that tests on the simulated salt using reactor radiation did not adequately model the enhanced fluorine generation from alpha (over gamma) radiolysis.

In March 1994, a gas sample was taken from an off-gas system that was connected to the vapor space existing over the solid fuel salts in the drain tanks. The analysis (Peretz, 1996c, Table 1.1) showed that fluorine gas was present[7] at a pressure of 350 mm of mercury. Furthermore, the gas sample had the relatively high UF_6 gas pressure of 69 mm at 21°C, which is significant because it is only a few millimeters lower than the vapor pressure of UF_6 gas in equilibrium with its solid phase at that temperature. This may represent a major concern because, where UF_6 gas is in true equilibrium with its solid phase, the pressure would *not* provide a measure of the amount of uranium present. Thus, other methods of measurement would be required to establish the amount and location of UF_6 as a solid and of any of the three lower fluorides of uranium (i.e., UF_5, UF_4, and UF_3) that do not contribute importantly to the vapor pressure.

Pressure-volume relationships (Peretz, 1996c, p. 1–12) established that a *minimum* of 1.8 kg of uranium exists as vapor in the vessels and piping. Further radiation and thermal measurements established that 2.6 kg of uranium had been transported from the fuel salts and was deposited in the upper 1-foot section of the ACB located outside the main reactor building. Both fluorine and uranium hexafluoride react with charcoal, forming CF_x and nonvolatile uranium fluorides. The charcoal provided a "sink" (by greatly lowering both the F_2 and the UF_6 pressures) to collect the uranium as UF_4 or UF_3 (uranium trifluoride). The ACB currently is isolated from any source of additional UF_6. Planning and process design are in progress at Oak Ridge National Laboratory (ORNL) to remove the charcoal fraction containing the uranium deposit. Relief of the different overpressures observed in the vent piping (currently greater than the one

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[7] As reported to the panel by Rushton et al. (1996b), the pressure over the drain tank fuel salts had increased to about two atmospheres, as measured on October 3, 1996.

atmosphere pressure found in 1994) is being addressed by work in progress at ORNL.

Once solid UF_6 is deposited on surfaces throughout the apparatus, there is no driving force for its migration, provided all surfaces are at the same temperature. Temperature differences (currently several Celsius degrees) between the interior of the salts and the upper tank shell that caps the vapor space could provide a mechanism for buildup of solid UF_6. Even though only small temperature differences result from energy deposited in the salt by radiation, time favors transport.[8]

Radiation Decomposition of Solid Uranium Hexafluoride

The reverse of radiation-induced formation of UF_6 from the fuel salts also can be a problem. In deposits of solid UF_6, decomposition by its alpha radiation from the uranium must be considered. Whereas this effect is negligible in the case of depleted uranium and minimal in the case of ^{235}U, it is enhanced greatly in the current situation where ^{233}U and ^{232}U (with its decay chain of six alpha-emitting daughters) are involved (see Figure 2.1). Although ^{232}U is present to only 160 parts per million (ppm) in the uranium, radiation from ^{232}U (and its daughters) exceeds that from ^{233}U (see Table 2.3), which is the major uranium isotope (84 weight percent).

The data in Peretz (1996c) indicate about 8 Ci of alpha activity per mole of uranium. The neutrons produced by (,n) reactions on fluorine and beryllium can be measured to show uranium deposition. Perhaps of more importance from a process aspect, a deposit of solid UF_6 that has migrated from the salt and has aged sufficiently for the ^{232}U daughter chain to be reestablished, would have released in its lattice the energy from 3×10^{11} alpha particles per second per mole. If 6 MeV is used as the average alpha energy, in 100 days about 25 eV per molecule of UF_6 will have been deposited.

This energy far exceeds the chemical bond strengths of UF_6. Trowbridge et al. (1995) cite a value of 1.5 molecules of F_2 produced for

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[8] Here again, the alternative explanation of alpha radiolysis from ^{232}U daughters can be invoked to explain transport. Reduction of a solid UF_6 deposit to lower fluoride salts (UF_5, UF_4, and UF_3), if it were to lower the vapor pressure, would provide a driving force for transport and a mechanism to build deposits that cause eventual plugging.

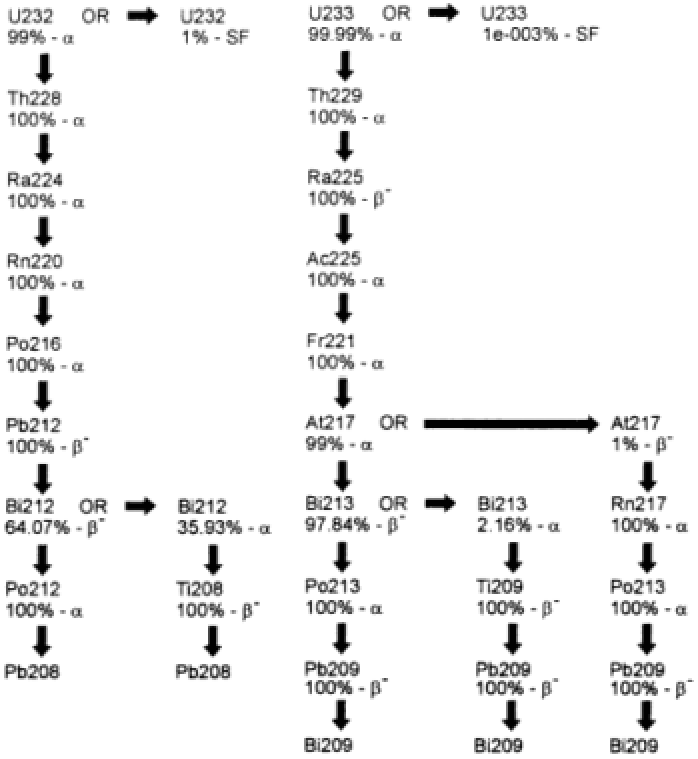

Figure 2.1
Decay chains for ^{232}U and ^{233}U. Note: SF = spontaneous fission. During reactor operations, ^{233}U(n,2n) reactions produced small quantities of ^{232}U, which decays by successive alpha and beta particle emissions to ^{208}Tl, an emitter of a penetrating 2.6-MeV gamma ray. Source: Peretz (1996c, Figure 1.12).

100 eV deposited in solid UF_6. Thus, in spite of inefficiencies of bond breaking and the occurrence of back-reactions, substantial radiolytic decomposition of the deposited UF_6 will be observed in aged deposits. This decomposition results in deposits of nonvolatile uranium fluorides (e.g., UF_4 and UF_3) that cannot be removed readily from unheated pipes and vessel surfaces by use of room-temperature fluorine in an inert purge gas. In piping or equipment where heating is difficult or impossible, the use of fluorinating agents such as krypton difluoride (KrF_2), bromine pentafluoride (BrF_5), or chlorine trifluoride (ClF_3) (see Appendix B) to refluorinate the lower fluoride salts may prove useful, if the reaction with fluorine at room temperature does not produce UF_6.

If oxygen has been introduced through minor leaks back-streaming from the vent line, or through oxide coatings or adsorbed moisture, uranyl difluoride (UO_2F_2) may be formed, which—along with uranium in reduced oxidation states—an be converted to UF_6 upon refluorination, as with KrF_2 or BrF_5 at room temperature (see Chapter 3 and Appendix B).

Long-Term Effects of Leaving Plutonium in the Salt After Uranium Removal

Plutonium migration in the MSRE system has not received significant attention because the formation and migration of quantities of UF_6 dominate nuclear criticality safety implications. Prior to migration from the salt, the initial uranium concentration was about 7100 ppm, far exceeding the plutonium concentration of 155 ppm. Indeed, competition leading to the formation of UF_6 would have suppressed formation of transient PuF_6, which is known to be reduced by the lower fluorides of uranium.

In anticipation of uranium removal, it is prudent to anticipate effects of radiation on the plutonium remaining in the fluoride salts. Radiation effects are known to disturb the normal PuF_6 ` $PuF_4 + F_2$ equilibrium with two opposing results. One is that radiation is known to decompose PuF_6. Conversely, radiation effects on F_2 gas in contact with PuF_4 at ambient temperature will lead to PuF_6 in concentrations *exceeding* those calculated from the equilibrium constant (Katz and Seaborg, 1986, and extensive references cited therein).

It is likely that radiation effects on the plutonium remaining in the fluoride fuel salts will lead eventually to formation of *some* PuF_6 and its migration from the stored salt. Criticality will not occur because of the limited amount of plutonium in any one container. The getters provided for fluorine also will react with any PuF_6, which would be an alpha particle hazard (and not a criticality hazard) at low plutonium concentrations. Cautious handling of the fluorine getter material on subsequent opening of the interim storage vessels is warranted.

EXCESS OF REDUCING SPECIES IN THE SALT AND HAZARDS OF SIMPLE REMELTING

The loss of F_2 and UF_6 has left a reservoir of reducing agents distributed throughout the mass of fuel salt that can have some chemical effects on salt remelt. Whether these reducing agents are isolated metal atoms as described in Peretz (1996c, p. 1–30) or electrons located in fluoride lattice vacancies is less important than their potential effects. The current estimate (Rushton et al., 1996a) is that 290 equivalents of excess reductant have been produced in the fuel salt. In reacting with 135 moles of total uranium in the two fuel drain tanks, all of the uranium initially present as UF_4 would be reduced to the less soluble UF_3, precipitation of which is unlikely at a uranium concentration of approximately 0.12 mole percent.[9]

Further reaction of the 155 remaining unsatisfied equivalents of chemical reducing agents could yield 12 kg of uranium metal. Melting of the salts without eliminating this excess of reducing equivalents could result in formation of some uranium metal, although it is not clear that uranium metal would be formed in preference to zirconium metal or possibly the zirconium fluoride ZrF_3.

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[9] This number can be calculated two ways. One way uses 4650 kg of salt and 39.5 as the quasi molecular weight of the mixture, derived from the mole percent of the constituents, to calculate 118,000 moles of salt and 142 moles of uranium. The ratio of these mole numbers is 0.0012, or 0.12 mole percent. The second calculation uses data from Hollenbach and Hopper (1994, Table 1) to deduce 118,400 moles of salt, of which ^{233}UF4, at 309 g/mole, would constitute 150 moles. The ratio of these mole numbers is 0.0013, or approximately 0.13 mole percent. This uranium concentration is a factor often higher than the value quoted in Liebenthal et al. (1994).

The conclusion that there may be significant amounts of metallic uranium present in the salt (Peretz, 1996c, p. 1–30) is based on the assumption that all reducing potential available as a by-product from fluorine generation results in preferential uranium reduction. The panel does not concur with the use of such an extreme assumption. The fact that zirconium fluoride reduces before uranium fluoride is well established and is one of the reasons that zirconium fluoride is present in the melt. The melt composition is almost certainly different than at reactor discharge and may contain metallic zirconium, but even if single atoms of uranium metal were formed locally in the solid phase, there does not appear to be any mechanism that could cause this material to agglomerate into a dense metal phase.

Surrogate samples of fuel salt were irradiated (in 1963) in the Materials Test Reactor (MTR) in Idaho to a fluoride removal of 2.1 percent (Peretz, 1996c, p. 3–4). This value is to be compared with the current (minimum) estimate of 0.13 percent fluoride removal from the fuel salts. Only about half of the salt was recovered on remelt of the irradiated sample, leaving a high-melting residue that could not be removed by draining. Recent tests (Peretz, 1996c, p. 3–6; Williams et al., 1996) of irradiated surrogate fuel salts indicate similar behavior because insoluble, metallic-appearing precipitates are observed on remelt. These tests involve the melting behavior of surrogate salts when irradiated to a fluorine deficiency of 0.1 percent, more closely resembling the 0.13 percent fluorine loss estimated for MSRE fuel salt. In these experiments (Williams et al., 1996, p. 12), the gray-black irradiated salt melted to form an opaque pool. With these results, there is currently no experimental knowledge of the rate at which chemical treatment (e.g., fluorination) will restore the melted irradiated salt to the homogeneous condition of the melted unirradiated salt. As of this writing, further information is desirable on the composition of the nonmelting precipitate.

In summary, nuclear decays of radioactive constituents of the salt have resulted in radiolytic formation of F_2 and UF_6 gases, which have migrated out of the solid salt. This migration implies a loss of fluorine and formation of associated reducing agents in the salt. These conditions could lead to both chemical and physical problems accompanying a simple remelt, since the phases that result from melting of a reduced salt mass could cause line plugging and prevent the transfer of molten salt. Based on considerable past experience in this area, it would be desirable to obtain a homogeneous melt that is likely to be handled successfully by routine, well-established procedures. The goal would be to restore the salt to its previous process condition, in which melting was straightforward and the desired oxidation states in the melted salts were maintained readily. Cautious approaches to attaining this condition were suggested (Peretz, 1996c) and are discussed in greater detail in Chapters 4 through 6, after further elaboration of salt chemistry in Chapter 3.

3—

Fluoride Salt Chemistry, Partitioning, and System Corrosion

To provide a technical evaluation of the options identified for the disposition of stored fluoride and flush salts, the chemistry of these salts needs to be understood. The effects of radiolysis and the processing steps required for remediation of these salts, as well as the corrosive interactions of the salts with the piping, storage tanks, and other components, also lead to important chemical changes in the salts.

CHEMISTRY RELEVANT TO THE PRESENT STATUS

As shown in Table 3.1, the composition of the flush salt in mole percent is 65.9 lithium fluoride (LiF), 33.9 beryllium fluoride (BeF_2), and 0.18 zirconium fluoride (ZrF_4). The fuel salt has the mole percent composition 64.5 LiF, 30.4 BeF_2, 4.9 ZrF_4, and 0.12 uranium tetrafluoride (UF_4). The LiF and BeF_2 components were chosen to be thermodynamically more stable than UF_4, with a liquidus temperature for the flush salt of about 460°C. The 4.9 mole percent ZrF_4 in the fuel salt reduces the liquidus temperature slightly but otherwise serves two functions:

1. For the composition of the fuel salt, depending on the temperature, zirconium may be reduced slightly more readily than uranium (tending to minimize the formation of metallic uranium).
2. The ZrF_4 component reacts more readily with oxygen than UF_4 and can serve as a getter to scavenge any oxygen impurity.

An unusual and favorable property of these salts is that their solidification shrinkage for the given compositions is only about 2 percent.

TABLE 3.1 Composition of the Fuel and Flush Salts

	Fuel Salt	**Flush Salt**
Current salt composition (mol %)		
LiF	64.5	65.9
BeF_2	30.4	33.9
ZrF_4	4.9	0.18
Mass of fissile elements in salt (kg)		
Uranium	33.2[a]	0.5
Plutonium	0.724	0.013
Current distribution of uranium and plutonium isotopes (wt %)		
^{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

[a] Assumes 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.

SOURCE: Peretz (1996c, Table 1.3).

The fuel salt solids can be viewed as a matrix of closely packed fluoride ions with the much smaller Be^{2+} and Li^{+} ions occupying interstices. At their low concentrations, Zr^{4+} and the larger U^{4+} cation contribute little to spatial requirements (Zachariasen, 1948). Indeed, on the basis of fluoride volume alone, the fuel salt density is estimated (Robert Penneman, unpublished), using the data of Zachariasen (1948), as 2.52 g/cm^3, close to the 2.48-g/cm^3 density reported (Peretz, 1996c).

Chemical Consequences of Radiolysis

As a consequence of the radiolysis reaction, some cations of the stored crystalline salt may be reduced to metal atoms. Peretz (1996c) suggests that any of the metal atoms lithium, beryllium, uranium, or zirconium could be formed; this is uncertain because the reduction potentials for the metals in fused salt at 500°C are not relevant in the crystalline solid phases. Perhaps the identity of the metal atoms is not important, since they can be considered simply as electronic point defects in the crystalline salt phases, not metal particles.

Another important consequence of the radiolysis reaction, besides the loss of gaseous fluorine and uranium hexafluoride (UF_6) by migration to the piping system, is that the highly reduced multiphase salt has physical and chemical properties, such as an apparent reduction in the solubility of various fluorides in the melt, that differ from the properties of the original, single-phase fused salt. To better inform remediation strategy, it is important to gain additional information on the (as yet) poorly defined chemical properties of the remelted salts.

PARTITIONING OF URANIUM FROM THE SALT

As noted in Chapter 2, sampling of the gas phase near the end of the off-gas vent line indicated high concentrations of F_2 essentially saturated with UF_6 vapor at the current temperature of the vent system (~21°C). This gaseous product results from radiolysis reactions in the solidified salt phase, and it would be prudent to assume that UF_6 has been distributed to, and condensed in, all regions of the system, including the freeboard volume in the upper regions of the drain tanks as well as areas of restricted flow in the off-gas vent system preceding the auxiliary charcoal bed (ACB). Due to the significant amount of alpha decay arising from the $_{232}$U daughters that grow into the chain with a 1.9-year half-life, radiolysis effects make it probable that a significant fraction of the initial UF_6 may now be present as non-volatile lower uranium fluorides.

It is possible that back-migration of oxygen or water vapor from the ACB into the vent line has occurred. This could result in the precipitation of uranyl difluoride (UO_2F_2) as one of the species currently restricting flow in the vent line and in the production of hydrogen fluoride (HF) gas. Today the ACB is isolated from the vent line.

The staff at Oak Ridge National Laboratory (ORNL) proposes to clear the off-gas line by initially purging with an inert gas (helium or argon), followed by evacuation to volatilize any UF_6 residing in the off-gas system; this approach should remove all UF_6, but it would not remove lower fluorides that may be present in the system.

Several chemical options can be considered for the removal of nonvolatile uranium residues remaining after the initial pumping. Considerable fluorination technology that has been developed over the last 20 years at other Department of Energy (DOE) sites may be applicable to the Molten Salt Reactor Experiment (MSRE) remediation effort. These options may be of use both for clearing the piping and traps in the off-gas lines and for recovering ^{233}U from the remelted MSRE salt fractions by volatility processing methods.

Concern exists about whether the solidified salt can be remelted to form a homogeneous liquid since significant fluorine has been lost from the original melt (Chapter 2). To address this issue, Chapter 4 describes a recommendation to attempt to refluorinate the salt components during a heating phase short of actual melting by addition of HF gas in helium (He) at a slightly positive pressure. It is expected that HF-He would oxidize all uranium or plutonium compounds to the IV oxidation state at 400°C (just below the melting temperature) if adequate permeability exists in the solidified salt. Additionally, refluorination can be continued during progressive melting with a rock-melting, laser, or calrod apparatus to ensure that significant quantities of fissile material do not accumulate as a critical deposit.[1] Hydrogen fluoride will not oxidize uranium or plutonium to the hexafluorides UF_6 or PuF_6, and molecular fluorine at temperatures less than 300°C may not be effective in producing UF_6 or PuF_6.[2]

In order to generate UF_6 from UF_4, especially at the temperature existing in the off-gas piping, alternative fluorination agents should be considered to boost the reaction rate. These would include atomic

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[1] As is well known to MSRE project personnel (Rushton et al., 1996a, b), any such central heat source to induce localized melting need not be powerful enough to supply all the requisite heat energy to the salts. The resistance heaters on the external tank wall could be used to elevate the salt temperature.

[2] Fluorine reacts with UF_4 to produce UF_6 in argon-neon mixtures at temperatures as low as 12 K. Large-scale, efficient production of UF_6 may require higher temperatures or ultraviolet irradiation (Margrave et al., 1976, 1977).

fluorine, bromine pentafluoride (BrF_5), chlorine trifluoride (ClF_3), fluorine dioxide (O_2F_2), dioxygen monofluoride (O_2F), and krypton difluoride (KrF_2). All of these have significant advantages and disadvantages, as discussed in Appendix B.

PLUTONIUM PARTITIONING BY FLUORINATION

Peretz (1996c, p. 3–24) referred to laboratory and pilot plant studies involving fluorination of surrogate salt containing both uranium and plutonium. The results showed that very little plutonium was removed, even after most of the uranium was volatilized as UF_6.[3] Furthermore, the high-temperature fluorination yield of PuF_6 was low, and long fluorination times caused increased corrosion.

These results are consistent with the understanding that, because PuF_6 is a powerful fluorinating agent, little PuF_6 would be expected to be volatilized from the molten salt phase until all other volatile fluoride gases (including all the UF_6) are volatilized and driven out of the molten salt solvent. Experience at Los Alamos (Mills, 1996) suggests that volatilization of such small amounts of PuF_6 (at the level of 155 parts per million [ppm] in the existing salt) is difficult, especially if plutonium exists in the salt phase as a double salt with one of the major components (e.g., LiF). Ambient-temperature fluorination using the reagent O_2F_2 is also unlikely to be successful in removing plutonium from the bulk salt (see Appendix B).

Based on these considerations, fluorination does not appear to be usable for removing plutonium from the salt. The depleted salt will retain the plutonium (and fission products).

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[3] A 45-hour fluorination of 2000 liters of MSRE molten salt removed 216 kg of uranium and left a uranium residue of 26 parts per million (ppm; Peretz, 1996c). No uranium was volatilized during the first 7 1/2 hours while conversion of lower oxidation state uranium to uranium pentafluoride (UF_5) occurred. Subsequently, UF_6 was volatilized at about 6–7 kg per hour. During the last 6 hours, fluorine utilization dropped to nearly zero, and essentially no plutonium was removed (the final plutonium concentration was 110 ppm, compared to an initial value of 112 ppm).

NONFLUORINATION OPTION FOR PLUTONIUM SEPARATION

If plutonium separation becomes essential, the following work at Los Alamos might be the basis for development: Los Alamos investigators (Joel Williams, Los Alamos National Laboratory, personal communication with Melvin Coops) have found that it is feasible to strip small amounts of plutonium from molten salt electrorefining residues (a eutectic salt of sodium chloride and potassium chloride [NaCl-KCl]) by bubbling oxygen through the molten salt to precipitate plutonium (and americium) as the insoluble dioxide. The salt is then evaporated for recycle, leaving the oxide residues as a waste product. Since oxygen gas has a low solubility in the molten salt, addition of sodium carbonate to the molten salt has been found at Los Alamos to be a suitable way to precipitate the plutonium-americium oxides.

If the MSRE molten salt is sufficiently fluid to be either filtered or centrifuged to separate a precipitate of zirconium-plutonium oxide, the method utilized at Los Alamos may be an applicable technique for isolation of the small amount of plutonium present in the MSRE drain salt. Addition of lithium carbonate (Li_2CO_3) to the salt after uranium removal is complete may be a simple and effective method of adding oxygen to precipitate plutonium oxide (PuO_2), with zirconium oxide (ZrO_2) also likely.

SYSTEM CORROSION ISSUES

In considering the recommendation for in situ melting of the stored salts (first the flush salt and then, if successful, the fuel salt) and pressurization of the tanks to push the molten salt through the existing (cleaned and heated) valves and pipes, it must be ascertained that these Hastelloy N components have not suffered severe corrosion damage during their use and storage periods. Hastelloy N was a good choice of material initially, because the high-nickel alloy is least susceptible to fluorination attack at high temperature (Lai, 1990). Although fluorine corrosion at high temperature is accelerated significantly by the presence of water vapor (HF is formed), in this case water vapor would also have been removed from the gas phase by the formation of ZrO_2 and UO_2F_2. Any significant corrosion of the alloy at ambient (or warm, 200°C) temperature would require the presence of an aqueous (or water vapor) phase.

There is no evidence that system internals have been exposed to moisture via any leak in the system. ORNL corrosion researcher James Keiser inspected one valve that had been plugged and cut out of the system and found no evidence of observable corrosion attack. As one possible means of observing on a gross scale the condition of the Hastelloy and the salt inside the storage tanks, an optical fiber inspection system could be considered. A cored salt sample taken from the center of a storage tank could not be expected to contain the chromium, iron, and other solutes that would indicate tank corrosion because any corrosion products (particularly nonvolatile compounds or those that complex with fluoride salts) would be localized to the immediate surface of the alloy.

Radiation-Induced Corrosion Questions

The 30-year-old drain tanks have been experiencing a radiation field and radiation-produced compounds, and one can ask what effect these compounds have on the integrity of the Hastelloy N walls. As noted previously, there is about one atmosphere of excess pressure over the fuel drain tanks. This is likely to be largely F_2 combined with the saturation pressure of UF_6 (and HF-O_2 [molecular oxygen] if there has been any leakage of moist air). Chapter 2 addresses the effects of alpha self-radiation on decomposing, solid UF_6. However, radiation effects on the F_2 gas could cause some reversal of UF_6 decomposition. Indeed, F_2 plus radiation, especially in the presence of O_2, is an aggressive reaction mixture. Even at ambient temperature, at which F_2 itself will not react, enhanced chemical attack of the fuel tank wall might take place in a radiation field, liberating molybdenum or chromium hexafluorides (MoF_6 or CrF_6) as volatile gases and possibly corroding the nickel by forming Li_2NiF_6.

The F_2 and UF_6 gases are more reactive and corrosive than the solid salt, and it is unknown at the present time whether these gaseous species are in contact with the interior drain tank wall. Because the fuel salt shrinks approximately 2 percent on solidifying, a gas space may exist between the solid salt surface and the interior tank walls. Alternatively, a coating or film of solid salt may be deposited, protecting the tank wall from reactive gas attack.

Some laboratory-scale corrosion tests could be performed, but these would take time and would be of only limited value, since it would be difficult for such tests to duplicate stresses or other local conditions such as pitting. The ideas[4] presented below are offered for consideration by ORNL staff to weigh the merits of obtaining this information against the time and efforts required for meaningful results. Corrosion tests would be conducted over irradiation times short compared with the 27-year radiation exposure of the fuel tank walls, even though the integrated dose could be similar. For example, samples of metal of composition equivalent to the tank and thimble tubes could be prepared and sealed in contact with a variety of gas environments, such as F_2, F_2+ O_2, and 50–50 mixtures of UF_4 and UF_6. Then these samples could be irradiated with gamma rays (for example, from the High Flux Isotope Reactor [HFIR] spent fuel elements) or with a source of alpha particles to simulate the history of the drain tank walls in the presence of radiation fields. Over time, the samples could be tested for metal corrosion and for formation of volatile UF_6.

To provide perspective on the severity of these corrosion issues, the fact that the tanks and associated piping continue to hold gases at a pressure of more than one atmosphere after more than 25 years suggests that there are no leaks in the metal confinement at this time.

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[4] Many techniques, such as standard procedures in nondestructive testing, are not practical due to the intensity of the radiation field at the tank wall (see Chapter 2), necessitating the use of remote operations to access the drain tanks.

4—

Preferred Technical Approach

Based on present understanding of the condition of the system and its salts, a number of observations are offered that are relevant to any decision on remediation options and strategy.[1] As further information is obtained, these observations may have to be modified. These comments form the basis for a preferred technical approach developed by the panel.

COMMENTS ON PROCESS STEPS

As discussed earlier, it is possible to conclude the following:

1. Since the charcoal trap is "at the end of the line" (Peretz, 1996c, Figure 1.9, p. 1–13) and all the migrated uranium salts originated in the drain tank, it is prudent to assume that all the piping contains uranium in volatile and nonvolatile forms such as uranium hexafluoride (UF_6; solid and gas), uranyl difluoride (UO_2F_2), uranium pentafluoride (UF_5), uranium tetrafluoride (UF_4), and uranium trifluoride (UF_3).
2. Since the freeboard gas space above the salt is at a lower temperature than the salt, there are probably significant uranium compounds deposited on the walls of the tanks and the thimbles and on the underside of the tank cover.
3. Current plans to resolve issues 1 and 2 above (with collection of uranium compounds in the piping and the auxiliary charcoal bed [ACB], for use in a mass balance estimate) are important to determine the

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[1] The panel is aware that Oak Ridge National Laboratory (ORNL) documents (e.g., ORNL, 1996b) have used various assumptions about technology and process steps for remediation. It is the panel's understanding that these assumptions were made for administrative reasons such as budgeting and staffing and do not represent actual decisions for implementation.

appropriate strategy for dealing with the uranium in the salts. Indeed, it is conceivable that there may not be as much uranium left in the salt as initially anticipated; the uranium may be concentrated in certain regions exterior to the bulk salt. A directional, high-resolution gamma survey (e.g., using a well-shielded, small-bore collimated germanium [Ge] detector) could help clarify this question.

4. Separation of uranium from the salt and from the system should be one of the major milestones, because it would eliminate subsequent criticality concerns and reduce the rate of radiolysis. Doing this without first moving the salt mixture to another location is attractive because it avoids the hazards (and costs) of any transfer operation and avoids leaving a residue of residual uranium and salt that is inherent in such liquid salt transfers.
5. Except for fluorination in place, all other separation technologies appear to require extensive new facilities with resulting long times and high costs. With the present state of knowledge, the panel considers that some type of fluorination procedure to extract UF_6 from the salt is the most promising technical approach to address comment 4 above.

DEVELOPMENT OF A PREFERRED APPROACH

With consideration given to the present state of knowledge of the condition of the Molten Salt Reactor Experiment (MSRE) system and salts and to the above-mentioned list of technical approaches that seem credible, several information-gathering exercises are recommended to assist the decision-making process, as discussed further in Chapter 8. Subject to confirming evidence yet to be gathered, the panel recommends that the following considerations, outlining a cautious, stepwise strategy, be taken into account in the development of a preferred approach:

1. Additional chemical, physical, and process data on the distribution of uranium and the remelting and refluorinating behavior of the salts, as discussed in Chapters 2 and 3, are essential to validate assumptions and reduce uncertainties; therefore, the plan must be developed in stages either as the information becomes available or as it becomes clear that such information cannot be made available.

2. Venting of the off-gas system piping and the gas space above the salt in the drain tanks, together with volatile UF_6 removal from these areas, is an essential first step for any alternative, and the resulting reduction in system pressure will be a significant safety step. The collection of uranium will also provide the first data point in an ongoing material balance program.
3. The next step depends on the success of step 2 and an assessment of system integrity. If possible, it should involve removing the presently nonvolatile uranium salts from the piping and tank freeboards and obtaining a material balance.
4. During steps 2 and 3 above, noninvasive methods of locating significant uranium salt inventory (e.g., high-resolution gamma spectroscopy scans) should be undertaken as feasible.
5. After "cleaning" of the piping and tank gas space, obtaining a sample of the fuel salt could be considered. This sample seems useful for evaluating the methods and possible hazards of salt melting, but such merits should be weighed against the hazards of taking a sample and of contamination problems.

   Specifically, the gaseous radon hazard (see Appendix C), and contamination with alpha- and beta-gamma-emitting residues, should be considered. With an inventory of 5 g of uranium-232 (^{232}U; 130 curies) in the salt, a 1-pound sample (0.01 percent by weight) would contain approximately 13 millicuries (mCi), not only of ^{232}U, but also of the decay products thorium-228 (^{228}Th), radon-224 (^{224}Rn), and ^{220}Rn, the latter of which is a highly radioactive, alpha-emitting gas. The ^{220}Rn gas permeates neoprene gloves and distributes rapidly to the air even in countercurrent air flows. It then decays rapidly to polonium-216 (^{216}Po) and on to a 3.3-hour half-life daughter, lead-212 ($^{212'}$ Pb), that finally decays (with a 36 percent yield) to thallium-208 (208 TI), which emits a 2.6-MeV (million electron volt) gamma ray (see Figure 2.1).
6. The alternatives for salt melting include the following, but choices cannot be made until more information is available:

a. Melt as is.
b. Hydrofluorinate below the liquidus temperature and then melt.

   c. Use pool melting by either heater or laser, and hydrofluorinate as melting occurs.
   d. Perform step 6b without melting, and then step 6c.

7. At this point, if melting seems feasible, the decision can be made whether to fluorinate in place or to transfer the molten salt to another vessel for fluorination.

   a. If the decision is to fluorinate in place, choices must be made concerning fluorinating agents (see Chapter 3 and Appendix B), melting methods (all at once or stepwise), and whether to use existing tank heaters or a new heat source.
   b. If the decision is to fluorinate elsewhere, the choice must be made as to where and how.

   Hydrofluorination in place, followed by melting (to test the salt solubility), followed by transfer of the melt to a new vessel of ensured integrity for fluorination is a strategy with merit if corrosion concerns persist, because the hydrofluorination step, which may enhance the melt, is a less corrosion-aggressive process than fluorination. The options of thoroughly inspecting the vessel walls for localized thinning, and possibly plugging the thimbles or filling them with HF-resistant material, could be used to reduce any likelihood of leakage.

8. If melting either does not appear to be possible or does not appear to be safe, the solid removal alternative would have to be developed.

In the development of steps 6 through 8, some laboratory and mockup tests and use of these test results in deciding what large-scale process to apply to the drain tank salts would seem to be in order. For example, the flush salts might be a preliminary surrogate, but because of the (assumed) large difference in constituent concentration and oxidation state, either melting or fluorination of the flush salts is only a demonstration of the equipment and technique and does not confirm the chemistry of the fuel salts. If all else fails and solid salt removal becomes the proposed operation, it may be necessary to conduct a mockup test to determine the mechanical problems (such as those introduced by the cooling thimbles; the mechanical challenge is greater to remove solids from regions interior to the tank that are behind cooling tube arrays, as compared with regions directly under a flange on the tank head). Because of the uncertainties inherent in a solid removal operation, it would be prudent to do the work in stages and not to commit to doing the drain tanks until after the mockup and the flush tanks have been done successfully.

A particularly significant issue in carbon dioxide (CO_2) blasting or other solid removal techniques is gaseous radon contamination. Whereas fine particles of salt can be filtered from a gas stream, radon cannot. This consideration alone could well preclude the use of such means of breaking up the salt if fluorination (with all the caveats regarding melting) fails.

Also there should be efforts to determine the status of the system (leak-tightness, pressure worthiness, corrosion damage to date) and projected damage, as well as complete assurance of the absence of water from the cells or the systems (since essentially all the credible postulates of criticality excursions require the presence of water).

Tests on surrogate samples can be useful to address some of the uncertainties associated with the fuel salts. For example, such tests could be used to bound the range of redox conditions under which hydrofluorination and fluorination would be successful and to probe the extent of segregation that could be tolerated. Peretz (1996c, p. 1–30) noted that segregation was observed on freezing surrogate salt samples (uranium concentration varied by a factor of two, from top to bottom). This effect would likely have been enhanced by the slow (melt refining) process of cooling the several tons of irradiated salt. Radiation effects and transport of UF_6 from the mass may have further increased the inhomogeneity of the uranium and fission product distribution.

A sample of the actual fuel salt, preferably a core sample down through the mass, would make it possible to test several remedies on the actual salt itself before committing to major action that could be irreversible. However, as noted earlier, the decision to obtain a core sample should consider the disadvantageous consequences of possible ^{228}Th, ^{224}Ra, and ^{220}Rn contamination.

Chapter 5 discusses specific technical processes mentioned above that are under consideration (Peretz, 1996c) for stripping uranium from the salt.

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Comments on Specific Separation Technologies

Because separation of uranium from the fluoride salts is a key step in the remediation plans, the panel has considered in detail the candidate technologies for this activity, and comments on them here.

FLUORINATION

The best candidate option based on current data and Molten Salt Reactor Experiment (MSRE) status information seems to be recovery of the uranium fraction by fluoride volatility techniques. This technology is thoroughly demonstrated and can be performed safely.

Although removal of uranium from the molten irradiated salt has been done in the past, another question exists—can aged, solidified salt be remelted and brought to a homogeneous melt condition? If the answer is yes, then the chemistry and process of fluorination can proceed—given adequate vessel integrity. This also assumes that the piping is unblocked and free of leaks. Lower-temperature fluorinating agents may be backups if vessel integrity indicates that high-temperature direct fluorination with fluorine may be dangerous (see Chapter 3 and Appendix B). Salt hydrofluorination, discussed below, may be advantageous prior to melting.

Small-scale laboratory tests in gas-tight enclosures with samples of actual salt, even if not truly representative, are important to evaluate whether the salt can be remelted and, if so, under what conditions. As noted elsewhere (Appendix C), collecting samples poses a possible radon daughter contamination hazard. Prior to obtaining an actual salt sample, tests with irradiated surrogate salts should be continued.

The possibilities of direct fluorination, hydrofluorination, and use of alternative fluorinating agents are discussed in further detail below.

Direct Fluorination

One technical approach (Peretz, 1996c, 3–7,8), as elaborated by Rushton et al. (1996a), involves initially forming a small puddle of liquid salt by partially melting a small area on the surface of the fuel salt and treating the slurry (melt and precipitate) with fluorine gas (F_2), a mixture of hydrogen fluoride and hydrogen[1] ($HF\text{-}H_2$), or a mixture of hydrogen fluoride and helium (HF-He). If this produces a clear melt, then melting would be increased slowly. Rather than first solubilizing all the uranium, use of fluorine results in removal of uranium hexafluoride (UF_6) as the melting proceeds.

Even though hydrogen would be produced in the restoration of a metal atom site into a cation, there is concern that introducing an $HF\text{-}H_2$ mixture would be hazardous because of the fluorine sites existing within the salt. Diluting the HF in helium could lessen the hazard associated with hydrogen gas, which is introduced to control corrosion. It is possible that HF treatment would remove the reducing sites by reacting with the metal atoms. Possible uranium trifluoride (UF_3) precipitation is unlikely because of its solubility in the salt, although local solubility excess could occur.

Use of an internal heat source for remelting the solidified MSRE salts directly within the two drain tanks has been suggested by Oak Ridge National Laboratory (ORNL) staff. This heat source would be used in parallel with the externally mounted tank heaters to ensure that melting initiates in the center of the tank and progresses outward. It is believed that this approach would permit a single puddle to be formed in the center of the tank. This would have two benefits: the melt could be monitored for insoluble species that might be encountered on remelt, and a solid salt coating would be maintained against the walls, with the salt serving as its own container as long as possible.

This puddle would be fed a fluorinating gas stream continuously to reoxidize any uranium in the salt to uranium tetrafluoride (UF_4) and UF_6, as well as to stir the melt. Because of the hot fluorine and HF that

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[1] The hydrogen is introduced (Peretz, 1996c) to adjust the redox potential.

are expected to be used for this purpose, elements that could form volatile fluoride gases (i.e., the hexafluorides of chromium, molybdenum, tungsten, tantalum, and niobium [CrF_6, MoF_6, WF_6, TaF_6, NbF_6] and carbon fluorides) should not be used in the central heater assembly. For this purpose, probably the best material is pure nickel or Hastelloy N. Electrical heating is assumed, and a good thermal conductor will be needed to fill the gap (between the resistance element and the tubular nickel jacket) that does not short out the resistance unit. Several suitable choices of material are available.

Hydrofluorination

Another approach, which might precede the one just described, could involve the following steps: after testing the tank with vacuum and helium purge to remove any volatile uranium fluoride and fluorine, some modest pressure of HF or F_2 could be applied to the warmed (but not melted) salt to permit diffusion to decrease the residual reducing equivalents in the fuel salt. Considerable time is available even for slow reactions. Because HF does not oxidize uranium beyond the IV oxidation state, this hydrofluorination procedure would be primarily a measure to ensure that any uranium in diffusive contact with gas in the system is not reduced below that state.

Alternative Fluorinating Agents

As discussed in Chapter 2, radiolysis of transported UF_6 would produce a variety of lower uranium fluorides, some of which can be refluorinated easily to UF_6 and some that might not react at temperatures below 500°C unless fluorinating agents stronger than F_2 are used (e.g., bromine pentafluoride [BrF_5] and chlorine trifluoride [ClF_3], as discussed in Appendix B). This is a critical point, since much of the condensed UF_6 and associated degradation products probably are present in the piping and upper regions of the drain tanks (see comments 1 and 2 in Chapter 4). Lower-temperature fluorination might also be important in evaluating vessel integrity for the fluorination step. Removal of fissile material from the MSRE system will require a stronger fluorination treatment than melting with simultaneous hydrofluorination by use of $HF\text{-}H_2$ mixtures. Several refluorination steps may be needed, such as (1) partial melting with simultaneous HF-argon or HF-He treatment to convert the lower fluorides or metal to UF_4; followed by (2) treatment with F_2 or BrF_5 in argon or helium at melt temperature to convert UF_4 to volatile UF_6 (which would then be trapped in sodium fluoride traps); followed by (3) treatment with BrF_5 or KrF_2 (krypton difluoride) to remove deposits from the cooler surfaces, valves, and unheated plumbing constituting the balance of the system.

Monitoring the effectiveness of the proposed refluorination treatments may be possible without actually penetrating the containment vessels, by inspecting the vessel walls with collimated precision gamma spectroscopy. Core samples of the solid melt may provide valuable information on both the amount of segregation that has occurred and the state of reduced material present in the tanks, if the radon daughter contamination (Appendix C) hazard can be managed.

ELECTROREFINING

Preliminary information was provided to the panel concerning the possible use of the Argonne National Laboratory (ANL) electro-metallurgical process for treatment of MSRE salts. The panel believes that its application to MSRE salts should not be considered unless fluorination treatment fails and only after use of an electrorefining system has been demonstrated on MSRE salts. Pilot plant demonstration of this technique on chloride-based pyrochemical processing of spent fuels from the Experimental Breeder Reactor (EBR-II) is under way. The National Research Council (NRC, 1995) Committee on Electrometallurgical Treatment of DOE Spent Fuels has recommended that additional possible applications of this technique be deferred until the demonstration on EBR-II spent fuel has been shown to be successful. Consistent with this recommendation, electrometallurgical treatment of MSRE salts should be viewed as a future alternative pending farther testing and development.

The current ANL demonstration is being performed by use of chloride salt electrorefining (ER). The proposed treatment of MSRE salt would use fluoride salt ER, with a liquid bismuth cathode to isolate the uranium and plutonium from the lithium fluoride-beryllium fluoride-zirconium fluoride (LiF-BeF_2-ZrF_4) salt solvent. Although the equipment is similar, the chemistry is not. Since the kinetics, thermodynamics, and solubilities of the fluorides are not the same as those of the chlorides, the proposed fluoride process has to be demonstrated satisfactorily in the laboratory before any commitment to the technology can be considered. Insufficient process data are available to make an evaluation of this concept at present.

The ER process necessarily would be carried out in an inert atmosphere by remote operation behind heavy shielding. No suitable facility of this nature now exists at ORNL. It is too early to estimate what the costs of such an operation might be, but facility costs on the order of tens of millions of dollars are not unreasonable. Use of the ANL facility in Idaho faces major problems of shipping and of coordinating operations at two separate sites in addition to problems of the technology.

For these reasons, the panel considers ERa possible backup technology, but it is too early to give any further consideration to its application for MSRE cleanup.

DISTILLATION OF MOLTEN SALT

Very little information was provided on distillation of the molten salt. The few data concerning this alternative that are discernible from basic chemistry imply that this operation would not provide clean separations because of the wide range of vapor pressures for the salt constituents. It would also require very high temperatures, up to approximately 1500°C; thus, serious containment problems would arise. It would appear that both process (or flow sheet) conditions and process equipment would have to be developed, and the potential benefits are not apparent. The panel recommends that consideration be given to dropping this process from the list of alternatives unless significant and favorable additional information becomes available.

AQUEOUS DISSOLUTION AND SEPARATION

Another alternative is to dissolve the 4650 kg of fluoride salt in an aqueous solvent and isolate the uranium and plutonium by known aqueous processing techniques. Because the separation of uranium and plutonium from fission products and other ions is well demonstrated for precipitation, solvent extraction, and ion exchange, there is little danger that such separations cannot be accomplished. Aqueous separation is also the only ensured way to isolate the plutonium if that is an objective. However, getting the salt into a soluble form suitable for processing without segregation may be a major challenge. It may also be a significant challenge to dissolve the plutonium if any of it has aged to the reduced state. Some plutonium compounds become refractory upon aging, and although soluble when first formed, they become insoluble with aging.

If the aqueous work is done off-site, the salt removal (without segregation) and shipping concerns must be addressed as well as the technology for the dissolution and feed preparation steps. It would also be necessary to resolve the question of disposal of the fluoride-bearing liquid waste.

If aqueous processing is done on-site, questions of what to do with the waste still remain, except that the volume of waste generated would be much greater than from nonaqueous means. This larger volume is derived from the low solubility of MSRE fluoride salts in dilute mineral acids, which implies that significant dilution with water is required. The neutron-moderating capability of water poses a criticality concern, discussed in more detail below. Facilities at ORNL that were used for aqueous processing of ^{233}U in the past may not be suitable for the current mixture of ^{233}U, ^{232}U, and plutonium. New facilities would be very expensive.

Criticality Concerns in Aqueous Processing

The issue of criticality prevention would have to be addressed in dissolving the salts. If it is possible mechanically to retrieve the salt from the existing MSRE system for external chemical treatment, dissolution in a favorable geometry[2] for aqueous treatment would be required to ensure criticality safety. This problem arises from the fact that BeF_2 present in the salt is readily soluble in many aqueous solvents, whereas LiF and ZrF_4 (zirconium fluoride) are not. In any mineral acid (for example, 3 molar nitric acid) the fluoride ion produced by BeF_2 dissolution would cause immediate precipitation of all uranium, plutonium, and lanthanide elements as insoluble fluoride salts. These precipitates have high density, are insoluble in nearly all mineral acids, and could aggregate rapidly to form a critical mass. As little as approximately 600 g of ^{233}U in aqueous solution could go critical if the dissolver vessel is not configured as a favorable geometry (ANS-8.1 Working Group, 1993).

Fluoride Removal

The amount of fluoride present in MSRE fluoride salts would cause major complications in current aqueous processing methods, such as a solvent extraction process (e.g., the plutonium and uranium recovery by extraction, or PUREX, process) or ion-exchange systems. Uranium fluoride can be dissolved by metathesis of the fluoride to the hydroxide followed by acid dissolution, or by reacting UF_3 or UF_4 with warm borate salts to volatilize fluorides as boron trifluoride (BF_3) gas. Another possible approach is addition of aluminum nitrate to sequester the fluoride and provide the concentrated aqueous salt concentrations necessary to put uranium and plutonium into the solvent phase. In either case, the fluoride ions present in the solution must be removed prior to continued aqueous chemical processing, whether by ion exchange, solvent extraction, or precipitation.

Conclusions on Aqueous Processing

Because aqueous processing is the basic technology for separations work in this field, it was reviewed as a candidate for application to MSRE salts. Because of the extensive experience (worldwide) with reprocessing nuclear fuels of many materials and compositions, the panel believes that a workable flow sheet could be developed, but due to complications introduced by the large amount of

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[2] A *favorable geometry* is said to exist when a container or piece of equipment cannot hold enough fissile material to be critical regardless of enrichment, concentration, or amount of water-equivalent external reflection. For example, a long thin cylinder 11.7 cm in diameter and of unlimited length (an "infinite cylinder") will be subcritical if filled with ^{233}U in nitrate solution of *any* concentration (i.e., with any amount of uranium that can actually be dissolved in an aqueous or organic fluid) with a water reflector. The term *safe geometry,* although often used synonymously, is discouraged because such a container would not necessarily be "safe" (i.e., subcritical) if other nearby containers (of fissile species) were also present.

fluorides in the system, the result would be very complex, would produce great amounts of waste, and would necessitate new facilities because of the corrosive nature of the solutions required. Such chemical processing would have to be performed not only in critically safe vessels, but also by remote means behind heavy shielding, because of the fission products present. For these reasons, the panel considers aqueous dissolution to be one of the costliest and least desirable process options currently under consideration.

STABILIZATION TECHNOLOGIES

Most of the stabilization technologies listed in Peretz (1996c) involve shipping material off-site, making both transportation and acceptance issues of concern. Because it might not be permissible to ship the salts in their present unstable form, stabilization should be planned as a near-term necessity. Stabilization (as with a chemical getter) may also be required for on-site interim storage and may be possible in association with another operation.

Some nuclear criticality safety issues are specific to a particular processing route, such as aqueous processing. As another example, solubilizing the entire salt mass prior to any uranium removal in a fluorination process would pose a greater hazard than remelting and fluorinating a smaller mass. Further remarks on nuclear criticality safety are offered in the next chapter.

6—

Nuclear Criticality Considerations

As discussed in this chapter, the panel finds that the probability of a critical excursion during the processing of the Molten Salt Reactor Experiment (MSRE) salt is extremely low. Even if such an event were to occur, the safety and technical consequences would be insignificant. Additionally, certain process options (e.g., see Appendix D) can reduce the likelihood of criticality even further. However, the public concerns and political consequences could be very large; thus, the panel has addressed the question in some detail.

CRITICALITY ISSUES IN PROCESSING

Nuclear criticality safety considerations provide significant restrictions to the process designs to be implemented for each of the processing options. Nuclear criticality safety issues are determined by the chemical and physical behavior of the constituents, for example, the potential for uranium hexafluoride (UF_6) evolution and condensation, the lower uranium fluorides produced, uranium reduction to metal, and zone refining as a result of melting. Table 6.1 outlines some specific concerns for each remediation operation.

A more general nuclear criticality issue that is not specific to any one processing option is the potential consequence of a nuclear criticality excursion. Two elements of relevance are the shutdown mechanism that would limit the consequences of such an excursion in the salt medium and the range of energy releases from such an event.

Pruvost and Paxton (1996) describe initiating mechanisms and consequences for historical and other postulated nuclear criticality accidents. Augmented neutron flux, heat generation, and production of new fission products would be signs of an excursion were it to happen.

If the MSRE salt is inhomogeneous, it is not evident that a mechanism exists that would vary the composition to concentrate

TABLE 6.1 Nuclear Criticality Safety Implications: A Sample of Concerns Considered by the Panel

Remedial Operation	Criticality Hazard/ Concern	Compensatory Measures
General: Verify current subcritical configuration	*Baseline*: Establish (best-estimate) critical mass values for potential compositions of ^{233}U in dry salt in (unrestricted) aqueous solution with effects of water and other moderators Apply adequately conservative safety factors (e.g., based on assumptions that bound uncertainties in supporting data, which are known to be inadequate, and calculations)	Maintain configurations and compositions Monitor for changes Prevent additions of moderators
1. Remove reactive gases	Ingress of water or other moderator to drain tanks	Strict control of moderator sources Favorable geometry in NaF traps, alumina, and zeolite bed
2. Remove solid UF_6 deposits	Redistribute existing material to critical configuration Accumulate external critical mass Ingress of water or other moderator	Apply batch/mass limits Remove to favorable geometry containers Strict control of moderator sources

3. Sample solid salt	Ingress of water or other moderator Collapse of salt Mechanical reconfiguration of salt	Strict control of moderator sources
4. Remove residual uranium in piping	Ingress of water or other moderator Accumulate external critical mass	Strict control of moderator sources Remove to favorable geometry containers
5. Fluorinate in place to UF_6	Ingress of water or other moderator Redistribution or precipitation of uranium or plutonium	Strict control of moderator sources Fluorinate carefully with HF, followed by F_2 Apply batch/mass limits Remove to favorable geometry containers
6. Remove salt as liquid for fluorination elsewhere	Uranium redistribution, segregation, or precipitation to form critical mass Ingress of water or other moderator	Analyze and establish controls for new external system(s) Strict control of moderator sources Control geometry and/or mass of removed liquid material
7. Remove salt as solid	Ingress of water or other moderator Collapse of solid	Strict control of moderator sources Salt removal procedures to stabilize geometry and prevent collapse

8. Convert UF_6 to U_3O_8	Accumulate critical mass Ingress of water or other moderator Note: This conversion step is well established, having been conducted frequently at ORNL (for ^{235}U-bearing materials as well as for ^{233}U-bearing materials) over the last several decades	Strict control of sources of water and other moderators (or apply limits and/or geometries that accommodate optimum moderation) Apply batch/mass limits and/or use favorable geometry containers

NOTE: F_2 = molecular fluorine; HF = hydrogen fluoride; NaF = sodium fluoride; ORNL = Oak Ridge National Laboratory; U = uranium; UF_6 = uranium hexafiuoride; U_3O_8 = uranium oxide.

fissile material at the rapid rate required to sustain a nuclear chain reaction (i.e., to go critical). Without a rapid assembly or concentration mechanism, even if a chain reaction is achieved the resulting energy release would be very small and a breech of the drain tank containment would not occur. Further, the configuration of the MSRE system includes both distance and heavy shielding, which were enough to provide protection during operations at a steady power level of 8 MW. The radiation effects of a potential critical excursion would be unlikely to spread beyond the enclosed vessels; evacuation of surrounding rooms and buildings would be unnecessary. Thus, the consequences of a criticality excursion within the drain tanks are manageable. The panel concludes that, even if such an event were to occur, the safety and technical consequences would be insignificant.

CRITICALITY HAZARD OF REMELTING THE FLUORIDE SALTS IN THE DRAIN TANKS

Aside from these criticality issues for various process alternatives, an assessment can be provided on the low nuclear criticality hazard when remelting the salt. The salt mixture is less effective as a moderator than water. However, three of its four constituents are "good" moderators. Specifically, the effectiveness of lithium and beryllium is explained because they are lower in atomic number than the carbon (graphite) used to provide extra moderation for the MSRE core during operation. Fluorine comes after carbon in the periodic table, but it is still of low enough mass to be considered a moderator. Zirconium has a relatively high mass, with reduced moderating effectiveness. The overall combination of the elemental salt constituents provides a somewhat less effective moderator than graphite, which is one reason graphite was added as a moderator to the MSRE core design (at some substantial cost and inconvenience).

The composition and concentrations of the salt mixture are such that even in the optimum configuration, criticality could not be achieved in the MSRE reactor vessel without the addition of a graphite moderator. Without as good moderation as in the graphite core, and with reduced uranium content (each drain tank originally contained only approximately half the uranium inventory, and more than 10 percent of that has migrated out of the salt), the probability of a criticality excursion in each drain tank is further reduced. Additionally, the panel notes that the shielding was designed to be adequate for sustained criticality during reactor operations.

One approach to assessing criticality potential is to use model calculations that generate a k_{eff} value for a particular geometry of fissile material (here, ^{233}U, ^{235}U, and ^{239}Pu [plutonium-239]); neutron-moderating material (here, water, lithium, beryllium, and fluorine), and reflecting material (here, salt and concrete). Presentations to the panel (Rushton et al., 1996a,b) have included such calculations. Criticality is possible for the case of water intrusion into the salt (interior to the tanks), and for this reason, moderator controls are important. However, these calculations have shown (i.e., have generated a k_{eff} value much less than one) that external moderation alone cannot cause criticality.

The nominal uranium-in-salt concentration (i.e., approximately 15 g of uranium per liter, if half of the original uranium content is assumed to be distributed equally among the two tanks) is insufficient to be critical in a drain tank. A local increase in concentration could lead to a critical configuration in a tank. Should the concentration increase by a factor of two in a large enough, sphere-like configuration, criticality might be possible. Conversely, if the current uranium concentration in the drain tank remains relatively uniform (or, as is possible, is well below the nominal value), a well-controlled melt is unlikely to lead to a critical configuration.

RATIONALE FOR TECHNICAL INSIGNIFICANCE OF A CRITICALITY EXCURSION

The panel believes that a criticality excursion, even were it to occur, would have no important technical consequence.

Any operation would be done by remote means; that is, no human would be inside the drain tank cell. The drain tank cell provides massive concrete shielding (several feet thick; see Figure 1.3) and a gas-tight steel liner. Any criticality excursion event would be totally contained and well shielded. The building ventilation system provides the necessary secondary containment. This containment system was designed for an operating reactor and thus should contain any plausible criticality excursion in the drain tanks.

A comparison of the MSRE drain tank system to that of previous criticality accidents provides perspective. The latter involved mechanisms to concentrate fissile material, for example, by a continuous feed to a reaction. From a historical and practical point of view (Stratton and Smith, 1989; Frolov et al., 1995; Knief, 1985; Pruvost and Paxton, 1996) a configuration similar to the MSRE reactor vessel is required for this. Such a configuration is absent in the case of the MSRE drain tanks. For example, were the tank wall to leak or to rupture (as a worst-case scenario), the material would disperse inside the drain tank cell and be subcritical in a slab geometry configuration. The cleanup problem would be transferred from the tanks to the cell.

Even the rupture of the half-inch-thick Hastelloy N drain tank wall (which, if it did occur, would still pose no significant risk to the public) is a conservative scenario for a criticality excursion, with the following rationale: any criticality burst could take place only if the salt were liquid (i.e., at a temperature greater than 460°C), but beryllium fluoride [BeF_2] sublimes at 800°C (at one atmosphere). Therefore, a temperature rise of 340C, obtained from any fission burst, would automatically disassemble the salt system, just as it would in an aqueous system (the BeF_2 gas void would be similar to the steam void in a water system). In both systems the nuclear reaction automatically shuts down after an initial burst.

Without a breach of vessel walls, a criticality event may be detectable only by the presence of fresh fission products.

CONCLUDING COMMENTS

The panel had neither the resources nor the charter to perform a quantitative risk assessment (of criticality or of any other hazard) and notes that a rigorous effort is premature until the specific event scenarios and process conditions are defined. Nevertheless, the basis for the panel's position is found in the approach suggested in Appendix E to evaluate the criticality probability and to limit it to less than 10^{-6} per year. The likelihood of a significant dose to someone at the site boundary is several orders of magnitude lower, due to the small fission product inventory, the relatively low energy release (on the order of megawatt-seconds) that is hypothetically possible from criticality (as a worst case), and the presence of significant containment barriers.

Detailed analyses of credible uranium and salt configurations are continuing at Oak Ridge National Laboratory (ORNL). Based on a review of previous nuclear criticality safety evaluations, the panel has confidence in the ORNL analysis and evaluation capabilities. Further, it is assumed that with whatever processing option is employed, the associated nuclear criticality safety measures will include (1) requirements that all activities proceed with caution; (2) measures to prevent intrusion of water moderator into the drain tank, which Crume (1994) reported could make the current configuration critical; and (3) appropriate consideration of the potential value of monitoring neutron multiplication or of adding neutron poison either for normal operation or in response to an upset condition. One potential poison, gadolinium (described further in Appendix D), is a uniquely powerful neutron absorber. The stable compound gadolinium trifluoride (GdF_3) would be soluble in, and heavier than, the molten salt and would behave chemically very much like uranium trifluoride (UF_3). The management of nuclear criticality safety hazards during processing is addressed further in Chapter 8 and Appendix E.

7—

Strategic Alternatives

Seven principal alternatives for Molten Salt Reactor Experiment (MSRE) salt remediation have been identified (Peretz, 1996c) and are quoted below. Some of the defined alternatives address in general a range of treatment options. These alternatives are grouped according to the disposition of MSRE fuel salts.

The chapter then offers commentary on these alternatives, with a basis for rejecting all but the last and with a discussion of why permanent geologic disposal end points are too far in the future to derive meaningful strategy.

PERMANENT DISPOSAL IN THE DRAIN TANKS

> *Alternative 1: No Action.*
> Continue to store the MSRE fuel and flush salts 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.

DISPOSAL OF ALL KEY CONTAMINANTS IN THE FEDERAL REPOSITORY

> *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 [Idaho National Engineering Laboratory] as spent fuel,[1] in accordance with the Programmatic EIS [Environmental Impact Statement] for DOE [Department of Energy] 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.

DISPOSAL OF KEY CONTAMINANTS IN THE SALT RESIDUE IN THE WASTE ISOLATION PILOT PLANT (WIPP)

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 [uranium hexafluoride] to U_3O_8 [uranium oxide] and place the oxide in storage at ORNL [Oak Ridge National Laboratory] Radiochemical Development Facility (RDF) for future disposition in the Materials Disposition Program (MDP). Stabilize the salts and store (in RH-TRU [remote-handled transuranic] canisters) at ORNL until WIPP is available. Ship to WIPP for permanent disposal.

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[1] Chemical reactions in the salt can lead to separation (via volatile compounds) of the fissile material from the matrix. In most commercial spent fuels (oxides), this hazard does not exist. The instability of the fluoride salts may limit or preclude transportation options.

DISPOSAL OF KEY CONTAMINANTS IN SALT RESIDUE IN THE FEDERAL REPOSITORY

Alternative 5a: Transfer the Uranium to the MDP, Vitrify the Salt in the DWPF [Defense Waste Processing Facility], 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 at ORNL Radiochemical Development Facility (RDF) for future disposition in the Materials Disposition Program (MDP). Stabilize the salts and ship to Savannah River. Dissolve the salts and bleed into the waste stream being fed into the DWPF. 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: Transfer the Uranium to the MDP, Process the Salt by Electrorefining, and Dispose of the Salt Residue in the Federal Repository.

Remove the MSRE fuel and flush salts from their drain tanks. Construct an electrorefiner [facility] at ORNL. Separate the zirconium and rare earths from the salt by. electrorefining and convert them to a metal waste form to be managed with similar wastes at ANL-W [Argonne National Laboratory-West]. Separate the uranium and other radioactive materials from the salt. Electrorefine this material in a chloride salt electrorefiner to separate the uranium. Convert the uranium to U_3O_8, place the oxide in storage at the ORNL RDF, and interface with the national ^{233}U repository for disposal. Dispose of the chloride salt along with similar wastes generated at ANL. 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 program 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.

REUSE OF THE SALT

Alternative 6: Transfer the Uranium to the MDP and Transfer the Salt to Another Program for Reuse.

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 RDF. Interact as necessary with the uranium MDP, as in alternatives 4 and 5a. Stabilize the salts and transport the salt to Los Alamos for use.

INTERIM STORAGE

Alternative 7: Transfer the Uranium to the MDP and Place the Salt Residue in Interim Storage.

Remove the MSRE fuel and flush salts from the 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 national ^{233}U repository at the ORNL RDF. 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.

There are five general options for interim storage that appear representative, as given below. Alternatives 7b, 7c, and 7d all require shipping of waste products for interim storage off-site and revised acceptance criteria for storage. Alternative 7e is based on additional proposals for new forms of processing at ORNL.

Alternative 7a: Transfer the Uranium to the MDP, Stabilize the Salt Residue with a Fluorine Getter, and Store at ORNL.
Alternative 7b: Transfer the Uranium to the MDP, 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 the Uranium to the MDP, Incorporate the Salt Residue in Borosilicate Glass, and Store at Savannah River.
Alternative 7e: Transfer the Uranium to the MDP, Construct a Salt Conversion Facility at ORNL, Convert the Salt Residues to Glass or Phosphate Waste Forms, and Store at ORNL.

RATIONALE FOR REJECTING THE FIRST SIX ALTERNATIVES

Alternatives 1 and 2 are not attractive as permanent solutions because the drain tanks lie below the water table (creating a criticality hazard) and constitute shallow subsurface storage of transuranic waste (which is contrary to present DOE practice).

For alternatives 3, 4, and 5, ultimate disposition requires the availability of repositories not yet in operation or constructed. Other problems with these options include off-site transportation of the chemically unstable salt medium and the incompatibility of fluoride salts with a glass waste form. Alternatives 3 and 4 are mutually exclusive ideally, because the fuel salts should be classified legally either as defense-related TRU waste or as high-level waste or spent fuel, not both. A definitive classification decision would appear to aid the decision-making process here by eliminating one of these alternatives.

If there were other uses for the radioactive salt mixture (this is doubtful because it contains plutonium and fission products) and if transportation requirements would allow the transport of a salt medium that is unstable in the presence of radiation (this too seems doubtful), alternative 6 would be attractive, as noted in Peretz (1996c).

Thus, it is advisable to evaluate interim storage as a realistic objective (Peretz, 1996c) in selecting technical process options.

INTERIM VERSUS PERMANENT STORAGE AND DISPOSAL

In reviewing the alternatives for longer-term remediation activities, proposed or planned, the panel excluded consideration of the multiple issues involved in very long term or "permanent" waste disposal. That topic comes under the jurisdiction of many groups and agencies and involves time scales well beyond the year 2000. Waiting for a better definition of the regulatory and technical issues involved in the acceptability of a waste form for ultimate disposal is *not*, in the panel's judgment, a satisfactory decision at this time, given the known and anticipated hazards of the MSRE. The panel notes that determination of the ultimate geologic waste disposal system is not essential to the selection of a process to be used in the cleanup of the fuel and flush salt tanks, although the process chosen will affect waste disposal costs.

The panel assumes that the eventual long-term disposal procedures will be adaptable to handling a variety of materials, in some cases requiring well-established methods for further processing. Accordingly, the panel believes that attempts to anticipate possible eventual long-term storage criteria and disposal processes are fruitless at this time and are secondary to efforts to evaluate options for near-term remediation work and interim, on-site storage.

In summary, a final disposal form cannot be selected at this time because final repository criteria are not yet established. Definitive criteria, though desirable, remain conjectural, with final resolution probably beyond the time horizon of the MSRE cleanup project. However, cleanup work on the salts need not be driven by these considerations. The panel notes that chemical reactions that are going on can lead to further separation of the fissile material from the salt matrix. In most commercial spent fuels (oxides), this hazard does not exist. It appears feasible to isolate the uranium from the solvent salt and to convert both of these fractions to stabilized materials suitable for safe and secure interim storage on-site.

Of the on-site interim storage possibilities, combining the MSRE mixture of ^{232}U and ^{233}U with existing inventories of ^{233}U in the MDP program may be undesirable due to the containment and measurement challenges created by the gaseous daughters of ^{232}U (see Appendix C).

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Management of MSRE Hazards

Several hazards associated with the fissile and toxic content of the inactive Molten Salt Reactor Experiment (MSRE) facility have been recognized (Liebenthal et al., 1994; Peretz, 1996c). Some of the hazards listed here are hypothetical, not confirmed by direct observations or measurements and not necessarily significant *risks* at this time.[1] In part, steps have already been taken that reduce the possibility or likelihood of occurrence of some hazards by substantial safety factors. Other hazards (such as melting effects) become possible risks only when that step is taken. Still others are likely to be proven hypothetical and can be removed from further consideration when better information is developed. Essentially all of these hazards, both real and hypothetical, appear to be readily open to better definition of their significance or nonsignificance as risks by means of types of measurements available for assessment of condition and tests for process behavior.

CURRENT HAZARDS

The hazards[2] identified, some of which come from Peretz (1996c), include the following:

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[1] An important distinction is drawn between "hazards" and "risks." For this section, "hazards" are defined and identified as events that could or might go wrong, so as to produce damaging consequences to people, environment, facilities, or the ability to complete the desired remedial actions as planned, initially without regard to the likelihood or importance (or size) of the consequences. "Risks" are defined as the product of the likelihood of a hazard scenario occurring and a measure of the importance (or size) of the possible consequences (i.e., risk equals probability times consequence). In this report, the main evident hazard scenarios are identified, and preliminary judgments of their manageability are discussed. These judgments are provided with the caveat that normal good safety practices and certain noted risk-limiting precautions be implemented rigorously.

[2] Some hazards have been identified for the auxiliary charcoal bed, which is outside the scope of this report and for which a remediation plan is already in effect. These hazards are a possible criticality configuration for uranium accumulated on the carbon absorption bed if water were to enter the vessel; the potential for a vigorous exothermic reaction of fluorine with the carbon bed due to the stored chemical or Wigner effect energy, which could result in the dispersal of uranium and fluorine (ammonia treatment may eliminate these concerns of chemical reactivity); and the potential for reactions of UF_6 with the carbon bed to form UF_4, solid CF_x, $C(F_2)$ (i.e., F_2 absorbed on an activated carbon surface), and ultimately gaseous CF_4, with the release of a large amount of energy.

1. the alpha and gamma radiolysis-induced reduction of fluorides, probably including the tetrafluorides of uranium and plutonium (UF_4 and PuF_4), with the emission of fluorine and the formation of uranium hexafluoride (UF_6);
2. the low solubility of the radiolyrically produced reduced components in the salt, causing possible precipitation of segregants on melting and resulting in a possible criticality hazard (thought to be of low probability, as derailed in Chapter 6);
3. a possible critical configuration in the salt tanks due to intrusion of water into the salt drain tanks;
4. the potential for radiotoxicity and chemical toxicity hazards in the event of system leakage (e.g., radon-220 [^{220}Rn]);
5. the potential for radiation and chemical exposures of personnel in connection with monitoring, characterization, or remediation activities;
6. the potential for chemical or physical reactions of the salt with the containment, piping, and proposed processing systems, which could excessively delay or preclude orderly completion of a selected plan for remediation (e.g., system plugging by nonvolatiles involving significant inventories of uranium);
7. the potential behavior and criticality hazard of uranium deposited on tank freeboards or headspace (the void above the solidified salts) in the form of radiolytically generated fluorides of uranium that are reduced to oxidation states of less than VI; and
8. the migration of uranium as UF_6 from the salt, driven by the temperature differential maintained between the interior of the drain tanks and the ambient temperature of connected piping and hardware.

HAZARD MANAGEMENT ACTIVITIES

A number of important remedial hazard control operations[3] have been completed or are well under way, including

1. measures to reduce the potential for flooding of the drain tank cells;
2. installation of new pressure sensors at several points in the off-gas system; and
3. plans for steps to reduce pressure and to clear known plugs in the system piping.

This list is not exhaustive; other measures have been taken or are in progress (ORNL, 1995; ORNL, 1996b).

The panel assumes that standard safety precautions for handling fluorine compounds and fissile material will be followed. Considerable experience with these materials is available not only at the Oak Ridge Reservation, but also (for fluorine, hydrogen fluoride[HF], fluorinating agents, and other fluoride compounds) in industrial and chemical manufacturing applications. The quantitative evaluation of such well-known hazards lies outside the scope (see Box 1.1) of the panel's Statement of Task. However, the panel perceives no obstacles to attaining safety standards equivalent to those required by law for all licensed facilities.

CRUCIAL ROLE OF FURTHER ACTIVITIES FOR CONDITION AND PROCESS ASSESSMENT

An important part of the evaluation of remediation alternatives involves the extent to which significant known hazards of the alternative process steps may differ and some estimation of the relative degree of

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[3] The list excludes operations associated with the auxiliary charcoal bed (ACB) since this hazard is outside the scope of this report and remediation measures are under way. Regarding the ACB, its isolation from the rest of the system, measures to reduce the potential for waterflooding, the installation of a restraining ring and reinforcements on the cell plug, and an intensive analysis of the hazards associated with it have been done.

predictability and manageability of these hazards that can result in different levels of risks.

The state of knowledge of the salt system and the hardware systems is incomplete in several important characteristics, which limits the evaluation of some of the hazards. The panel believes that qualitative judgments of the manageability of many of the hazards (and thereby, the likely relative risks) are possible at this time. These judgments are contingent on further definition of specific process parameters as well as on expected improvements in equipment (or hardware) assessment. However, improved knowledge of the system condition and of process behaviors may uncover additional hazards that are unrecognized at present.

MAJOR RECOMMENDATION CONCERNING HAZARDS

Accordingly, the panel's principal recommendation for the management of hazards[4] is to focus on available means for measurements and tests to reduce the present uncertainties in basic physical and chemical conditions and to better define the physical and chemical behavior for the major remediation alternatives. The panel supports a process of information-gathering activities that would define hazards better, reduce unknowns or uncertainties, and confirm (or refute) assumptions (e.g., that the salt can be remelted successfully) that guide present thinking and are testable prior to large-scale remediation operations.

An illustration of this concept is provided in Appendix E, where a course of actions consistent with the preferred approach of Chapter 4 is revisited to show how such a course manages hazards. The level of technical detail is greater than in Chapter 4, with explicit emphasis on how such actions provide for hazard mitigation and control.

The panel notes the developing nature of the remediation program at the MSRE and believes that the present narrow focus on efforts to define hazards by condition assessment, testing, and the use of available resources could be broadened by planned feasibility studies,

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[4] The third issue in the Statement of Task addresses the hazards associated with the technical alternatives for salt removal.

safety plans, risk analyses, and process activities in the near future. Given adequate condition assessment and planning for the remediation campaign, the panel's opinion is that the hazards of any of the process alternatives reported so far do not appear to exhibit sufficient attributes that preclude bringing them to the status of well-controlled risks by using available techniques. However, control measures for the different alternatives may be found to differ substantially in their required costs and times.

DETAILED RECOMMENDATIONS REGARDING HAZARDS

The likelihood of unexpected off-normal conditions that can transform hazards to actual damaging event scenarios and consequences is still subject to a range of uncertainties. These uncertainties can be reduced by available and practical diagnostic measurements to overcome inadequate information on some system conditions and on the behavior of some materials under desired process conditions.

Accordingly, the principal and urgent mitigation activities recommended for consideration at this time are near-term actions[5] focused on improving the state of knowledge of the controlling uncertainties. These include (in a partial listing) the following:

1. better data on the physical and chemical conditions of the drain tanks, cells, and piping, to limit the present unknowns; and
2. a structured campaign of bench- and pilot-scale laboratory testing with salt mixtures (using irradiated surrogates or actual drain tank samples) to limit unknowns in compositions, reaction rates, and physical behaviors. This campaign could seek to extend existing data on the following:

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[5] Regulatory procedures of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) allow these information-gathering activities to be accomplished as removal actions, whether time critical or non-time critical, if it is even necessary to invoke CERCLA requirements (due to any potential for releases) (Ed Carreras, Environmental Protection Agency Region IV, private communication with Thomas Kiess). The panel offers no further discussion of the regulatory framework, noting that flexibility is available to implement an appropriate strategy.

- the composition of actual salt samples (or irradiated surrogates) along with their critical physical and chemical properties, and the likely degree and types of inhomogeneities (with particular attention to the degree to which the radiation-caused particulates or phases are amenable to redissolution);
- the corrosion rates for alternative practical fluorination conditions;
- any enhancements to corrosion due to the history of radiation breakdown of the salts (this could be mocked up by using irradiated samples from the High Flux Isotope Reactor [HFIR] facility);
- the established diffusion and reaction rates for fluorination at melting and annealing temperatures, by using various fluorinating agents;
- initial testing with simulated nonradioactive salt to maximize the rates of learning and explore optimum ranges for process parameters;
- confirmatory bench-scale process testing using actual salt samples; and
- possible confirmation of overall process behavior using the flush tanks for pilot runs with added natural or depleted uranium and pretreatment to simulate the reduced condition in the drain tanks.

Longer-term recommendations include the preparation of well-modeled hazard scenarios for the processes selected in the form of sequence-of-event tree diagrams, supplemented by success path sequences for the development of procedures. This type of effort would provide the orderly assurance that all foreseeable and suspected hazards have been identified and that means for their control or mitigation have been defined.

The panel recommends that ongoing reevaluation be part of the planning process and be applied periodically as additional measurements and test results become available. This is also desirable during the implementation and monitoring of selected procedures.

The panel also recommends that hold point and contingency plans and emergency response plan revisions be defined at appropriate times. This recommendation results from the judgment that a final inflexible plan for a remediation campaign cannot be defined fully in advance, even after a preferred approach is selected and ratified. This uncertainty results from the unavoidable presence of several first-of-a-kind situations in the alternatives considered so far.

Finally, the panel recommends, as a long-term measure, that cleanup strategies for the MSRE project provide one or more sets of logical approaches for the removal, processing, and interim storage of fuel and flush salts in a safe manner, by taking into account the need for alternative and backup strategies. During this strategy development, all pertinent factors should be considered, including criticality potential, remediation effectiveness and implementability, risk management, uncertainties, trade-offs, and duration of actions. Of equal importance is the need to include full consideration of possible process perturbations, failures, contingencies, resource requirements, and other factors warranting backup support or alternative approaches to offset possible factors that might deter success. Because the final resolution of disposal may take considerable time, the panel suggests that the Department of Energy use a phased decision approach strategy focused on interim storage, with the flexibility it provides, rather than try to select a final disposition alternative in the near future. It appears that final resolution of ultimate site criteria and characteristics lies beyond the time horizon of the MSRE cleanup project.

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Summary and Responses to Questions in Statement of Task

The Statement of Task for this study (Box 1.1) asks the panel "to review the current state of the Department's (DOE's) evaluations of alternatives" (presented in Peretz, 1996c) "for removal, separation, and stabilization of MSRE salts to determine the extent to which (1) appropriate technologies and options have been identified and evaluated; (2) evaluations are sufficiently complete to form a basis for decision-making; and (3) potential hazards associated with fuel and flush salt removal have been identified and addressed." Following a technical summary and some general perspectives that summarize panel views, specific answers to these questions are presented.

TECHNICAL SUMMARY

In brief, the Molten Salt Reactor Experiment (MSRE) salts contain uranium, transuranium elements, and fission product radioactivity, as well as fluorides of lithium, beryllium, and zirconium, and should not remain indefinitely in the drain tank cell where they have been kept for more than 25 years. Major reasons for this conclusion include the continuing migration of fluorine and uranium from the bulk salt, its location *below* the natural water table, and the potential critical configuration upon the intrusion of water. The permanent disposition of transuranics well in excess of 100 nanocuries per gram at shallow depths, just below grade, is also likely to be disallowed.

Removal alternatives for the salt are

1. melting, fluorination to form uranium hexafluoride (UF_6), and removal of the molten salt with its plutonium and fission products; or

2. breaking up the bulk fuel salt and removing it as solid particles.

The first alternative is preferred, with or without preliminary uranium removal in situ, with option 2 as a backup procedure.

Radiation effects continue to move fluorine and uranium from the bulk salt. In October of 1996, there was nearly one atmosphere of excess gas pressure over the fuel drain tanks, almost twice that observed in 1994. The pressure is contributed largely by molecular fluorine (F_2) and the saturation pressure of UF_6, which suggests solid deposits in the piping of UF_6 and its radiation-induced lower fluorides. Any removal alternative must start with the gases, including whatever uranium can be removed by pumping. The uranium material balance is poorly known, especially the amounts in and the locations of nonvolatile forms. Partial decomposition of solid UF_6 by the effects of alpha radiation (from ^{233}U and daughters) is expected to form nonvolatile uranium fluoride deposits essentially throughout the equipment. Because fluorine is more effective in reforming UF_6 when such locations can be heated, alternate reagents for UF_6 formation (e.g., BrF_5 [bromine pentafluoride] and KrF_2 [krypton difluoride]; see Appendix B) should be considered to treat nonvolatile plugs in unheated regions.

Removal of uranium from the molten fuel salt by F_2 sparging to produce UF_6 was accomplished routinely in the past. Hence, this approach would normally be favored. However, melting of an *irradiated* surrogate salt sample did not yield a clear melt but yielded at least two phases, one a metallic-appearing precipitate. To date, it has yet to be established that refluorination treatment of the salt containing such precipitate(s) will be successful in reestablishing a homogeneous melt.

Experiments should be performed on additional irradiated surrogate salt samples in attempts to redissolve the precipitate and restore the salt melt to a homogeneous condition so that transfer to another container or uranium removal by fluorination could ensue. It should be emphasized that the MSRE fuel salt, probably in a highly reducing chemical condition, remains a major problem, which will only worsen with time.

Even if uranium removal is accomplished, the residual salt will still contain activity from 0.7 kg of plutonium and from fission products. Formation of fluorine and volatile fluorides will continue. Plans to "getter" the fluorine formed from the interim stored fuel salt should also provide for the possible formation of some plutonium hexafluoride (PuF_6), although a significant quantity of volatile PuF_6 is not expected (Mills, 1996).

STRATEGY FOR REMEDIATION

There is insufficient knowledge in hand to outline, in detail, a series of processes that, if followed, would lead clearly to a satisfactory outcome of nonhazardous removal, separation, and stabilization of MSRE salts. Information gathering in the near future should allow better decisions concerning these alternative actions. Indeed, relevant alternatives have been identified in Peretz (1996c), but final evaluation awaits further information. No important options or technologies seem to have been omitted from Peretz (1996c).

There is a preferred approach within which some options exist. Of the several alternative processes, fluorination to extract UF_6 from the molten salt is the leading option. However, choices are available for specifics of the processes for salt pretreatment, salt melting, and fluorination.

Although Peretz (1996c) contains a baseline hazard section that identifies present hazards, evaluations are not yet sufficiently complete to allow for thorough knowledge of the extent of hazards associated with various alternative processes. However, the information required is well defined and can be obtained by available methods. Three information needs are (1) locating the uranium within the system, (2) further work in assessing the condition of the fuel salts and their containment, (storage tanks, piping, and associated hardware), and (3) bench-scale testing of possible remediation processes.

Where Is the Uranium?

As the charcoal trap and the piping system are cleaned up, some related information will be obtained. As the volatile components are taken from the system, identified, and quantified, more information will follow. The amount of uranium removed from the piping as the hexafluoride plus that in the charcoal trap will help determine the remaining total inventory. This inventory could be present in lower oxidation states, either in the salt or deposited in the headspace and piping. If there is much uranium remaining in the system external to the tanks, it might be feasible to map its distribution by radiation surveys. The distribution of uranium-containing species in the salt could be determined with gamma monitoring supplemented by neutron monitoring. Of possible relevance to a remediation strategy is whether inhomogeneities in uranium concentration exceed the variations in distribution that were observed in surrogate salt samples. Core and/or radial samples could also provide this information, but gaseous radioactive contamination is a significant hazard associated with sampling the salt.

How Can a Condition Assessment Affect Remediation Plans?

Information related to the condition of the system, obtained as work has progressed (ORNL, 1996a), has established that plugs from deposits in the piping remain and interfere with the removal of volatile substances by pumping.

Fluorination may remove lower oxidation state uranium that could remain in the plugs and headspace. Although fluorine, hydrogen fluoride (HF), and BrF_5 are the preferred fluorination agents, corrosion and temperature concerns[1] and the extent to which uranium-containing deposits resist reaction may lead to consideration of other fluorinating agents, such as atomic fluorine or KrF_2 (see Appendix B). Plutonium is present in such low concentrations (approximately 155 ppm [parts per million]) that it is not likely to form PuF_6 readily with any of these possible fluorinating agents.

Although it seems unlikely since gases above atmospheric pressures remain in the system, there may be cracks or pinholes in the apparatus and piping above the salt. These would not be revealed if they were plugged by the uranium-containing species. If it were determined that corrosion damage is not a problem, consideration could be given to plugging the thimble tubes physically and fluorinating the gradually melting salt in the storage tanks. The panel recommends, prior to

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[1] Fluorine is a better oxidizer at elevated temperature. If the pipes and valves cannot be heated, fluorinating agents more active than F_2 at ambient temperature may be required.

fluorination, consideration of an annealing procedure of heating the solid salt in an atmosphere with a gradually increasing concentration of fluorine or HF. The panel recommends an initial atmosphere with an HF-inert gas mixture, rather than the proposed HF-H_2 (hydrogen) mixture. This would be succeeded by a HF-F_2-inert gas mixture to ensure that all uranium was oxidized at least to uranium(IV). Omitting hydrogen from the hydrofluorination step would reduce the hazards associated with the explosive reactivity of hydrogen gas.[2]

The Panel's Preferred Alternative

Because one does not know at this time what options will be available for final disposition of the actinides, fission and decay products, and the salt, the panel considers that interim storage of separated uranium and of the residual salts is the only realistic option available at this time. Interim storage of the separated uranium as an oxide in existing sites at Oak Ridge seems acceptable, as does interim storage of the fluoride salts (containing radioactive species other than uranium) with a getter for radiation-produced fluorine gas that would be expected to form and migrate out of the solid salt residue.

In short, the panel finds that the general approach given in Peretz (1996c) is acceptable but backup alternatives must be available. The scheme should have hold points to confirm that the expected process behavior is being realized. Given adequate preparations, the intended processes are likely to perform as planned. However, it would be prudent to add fallback and contingency plans to the intended operational scenario.

Hazards

The panel considered various hazards. Criticality, in particular, was given considerable attention. The panel finds that, in the absence of water, there is no appreciable likelihood of the occurrence of a critical excursion. As stated in Chapter 6, the panel believes that the probability

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[2] The HF-F_2-inert gas mixture would produce hydrogen via the reaction $2UF_3 + 2HF$ ` $2UF_4 + H_2$. This evolved hydrogen would then be consumed by F_2 to form HF. The addition of F_2 thus serves to reduce the hazard of excessive hydrogen concentration.

of such an excursion during remediation of the MSRE salt is extremely low and, even if such an event were to occur, the safety and technical consequences would be insignificant.

The panel finds that the available documentation (Peretz, 1996c) shows an awareness of the hazards and how to deal with them. The panel has some concern over the use of hydrogen as a diluent and anticorrosion agent in the proposed treatment with mixtures of hydrogen and hydrogen fluoride. An evaluation of the specific hazards associated with each step of the planned work, and of the branches in the scheme to be developed, should be laid out in further detail.

RESPONSES TO QUESTIONS IN STATEMENT OF TASK

The Statement of Task for this study (Box 1.1) asked the panel to address three questions concerning the scoping activities of the Department of Energy (DOE) and DOE contractors to date on the remediation techniques and strategy that could be applied to MSRE fuel and flush salts. These questions (and answers) are intended to assist the decision-making process involving DOE and regulatory agencies. Of course, selection of a proper cleanup approach is of interest to others, such as workers and the general public.

The material in preceding chapters provides the necessary background for answers to these questions. The panel provides brief answers to each question below. More detailed discussions can be found elsewhere in the report.

Question 1

To what extent have the appropriate technologies and options been identified and evaluated?

The overall technical alternatives seem to have been identified, but the actual details and steps are not clear enough for final evaluation.

In some cases, alternatives exist within a technology: for instance, if fluorination in the drain tanks is not feasible by using fluorine, fluorination with another agent such as BrF_5 or fluorination in a separate vessel may be possible.

Because the source of volatile uranium fluoride was the drain tank and uranium migrated through the system to the carbon trap, there is a high probability that substantial amounts of uranium compounds are located on the cover and walls in the freeboard area of the drain tank. This issue may be important in assessing technical options.

The alternative of solid salt removal by mechanical fragmentation and particle evacuation was conceptual and not specific. If there are data or experience to support the concept, they were not presented to the panel.

Question 2

To what extent are the evaluations sufficiently complete to form a basis for decision making?

The development of additional information, now in progress, is needed to support decisions about alternatives. The final selection of one method—for example, direct fluorination with F_2—is subject to the acquisition of additional information about the condition of the system and the hazards, which appears to be feasible given adequate resources. The literature documents the procedure, and personnel at Oak Ridge National Laboratory (ORNL) have had extensive experience in the direct fluorination of uranium tetrafluoride (UF_4) to produce UF_6. Nevertheless it is important to be aware of alternative possibilities.

The Consequences of Failure to Complete According to Plan

Additional assessment is needed to address an important hazard, the hazard of *failure,* to explore whether the selected remediation method precludes a desirable backup option in the event that unexpected or undesirable behavior is encountered. For instance, could the failure of one technological alternative preclude using another? Could failure to reoxidize the reduced metals sufficiently result in a sludge in the melted salt such that liquid removal becomes impractical?

Cost Estimates

Because of the lack of details it is not possible for the panel to assess the credibility of cost estimates. For example, it is not obvious how to compare the cost of an as-yet-undefined mechanical process with the cost of liquid removal.

A Possible Strategy

In Peretz (1996c), the strategy being used by the project is not defined. Each strategy should have a primary alternative and one or more backup alternatives to cover the hazard of failure of the primary alternative. A preliminary cost estimate should be done for each case. The decision maker can then optimize the choice of strategies based on probable success, initial costs, and possible ultimate costs. The decision maker can then choose between strategies of lowest base cost but higher potential total cost versus strategies with higher base costs but lower potential overall costs. An alternative technology that is primary in one case might be the backup in another case.

Question 3

To what extent have the potential hazards associated with fuel and flush salt removal been adequately identified and addressed?

The Peretz (1996c) report contains a baseline hazard section that identifies the present hazards, but there is almost no discussion of the hazards associated with various alternatives. A preliminary hazards screening has also been made (ORNL, 1995). The term hazard is used instead of risk because the probability of a hazard becoming a risk is best determined only after operation steps are detailed for execution. Identification of the hazards associated with various process alternatives awaits further development of those alternatives.

The hazards associated with radioactivity and criticality are not unique to this project. However, the complex mechanical and chemical questions elevate the importance of the hazard of failure, a concept not developed in detail in Peretz (1996c).

The Peretz (1996c) report contains a cursory risk analysis of potential future human exposure in which there are indications that unduly conservative (i.e., beyond credible) assumptions may have been used. One stated assumption is a scenario in which a component of the now pressurized off-gas system suddenly fails and releases the entire radioactive inventory within the building. It is further assumed that 50 percent of this inventory is retained, and 50 percent is lost as a ground-level release under typical conservative atmospheric conditions (Peretz, 1996c, p. 1–36).

These assumptions are unduly pessimistic; at ambient temperature, only a small fraction of the uranium is in the gas phase, and exposure to moist air rapidly converts most of the uranium to nonvolatile oxides. In addition, all system components are in sealed cells inside a building. Any highly exothermic process with carbon (e.g., decomposition of CF_x to form carbon compounds and CF_4 [carbon tetrafluoride]) that could volatilize a large amount of radioactive fluoride salts is a potential hazard that has already been mitigated by isolation of the activated charcoal bed from the majority of the radioactive material.

A major overestimate of a hazard is not a conservative strategy when using the results to choose a line of action. It easily can result in selecting a course of action more dangerous than the discarded action. In the absence of more complete data (e.g., realistic probability distribution functions for every uncertain parameter), and for present decisions, the panel believes that estimates of risk that provide the best basis for decision making should be on an expected value basis, bracketed by an uncertainty range.

PANEL PERSPECTIVE

These findings and recommendations are offered to enable the parties involved (DOE, contractors, and regulatory agencies) to clean up the MSRE fluoride salts safely and expeditiously, with due regard for the hazardous materials (such as reactive F_2 and UF_6 gases and fissile ^{233}U).

Fluorination procedures, subject to important caveats and further information-gathering activities advocated in this report, appear at this time to be a preferred technical approach worthy of further consideration. However, without the additional information that comes from testing and experimentation, it is too early to make a final, sound decision. Thus, it is still too soon to eliminate backup remediation methods.

A hazard management strategy is recommended by the panel as an appropriate way to develop a decision-making process that is phased, or "gated." A period of further testing and information-gathering activity would provide for a more informed decision that could be deferred until the relevant information is received. Candidate technologies can be in view during this time and, subject to the receipt of confirming evidence, could be used in the MSRE salt cleanup. The aim of acquiring more information with additional scoping studies is to affect the choice of technical alternatives and enable project personnel to gain increased confidence in the success of the chosen technical approach. As new information becomes available on the fuel and flush salts and on the status of the rest of the MSRE system, additional reviews of the major issues may be warranted.

OVERALL CONCLUSION

After reviewing Peretz (1996c) and discussing the problems with responsible personnel, the panel concludes that the evaluations done to date are adequate for proceeding with the remediation program and that work needs to go forward on a timely schedule. As discussed in the report, the panel recommends a phased program with each phase designed to do those things and acquire the information that will make going on with the next phase an action with acceptable risks. The technical capabilities of Oak Ridge National Laboratory are quite adequate to ensure that the measures needed to prevent or control all likely hazards can be implemented practically and safely.

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- Correspondence to W. H. Hamilton from J. E. Rushton, January 24, 1996: Molten Salt Reactor Experiment Senior Review Board.

Appendixes

Appendix A—

List of Materials Reviewed

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Appendix B—

Alternative Fluorinating Agents

Fluorinating agents other than molecular fluorine and hydrogen fluoride (HF) are identified and discussed briefly below. The challenge of volatilizing the uranium by fluorination in the Molten Salt Reactor Experiment (MSRE) system, particularly in places where heating is ineffective, may provide an opportunity to use one of these fluorinating agents. As a general rule, the short-lived fluorinating agents listed below would be more effective in a flow system rather than a closed system. The list below is not exhaustive; for example, xenon fluorides, because they are reasonably well known in fluoride chemistry work, are not included.

- Chlorine trifluoride (CIF_3) is a liquid that boils at 11.7°C and is a good oxidizer that converts uranium tetrafluoride (UF_4) to uranium hexafluoride (UF_6) even at room temperature. Its main drawback is that if oxygen-containing compounds are present, it may produce chlorine dioxide (ClO_2) or chlorine monoxide (Cl_2O) as a reaction by-product. Gaseous ClO_2 is condensed easily to liquid at about 9°C, which can be achieved by fluids boiling under vacuum. Liquid ClO_2 is a potent explosive, whereas gaseous ClO_2 appears to be reasonably safe. Therefore, CIF_3 should not be used in systems containing oxygen in any form, and cold trapping (which would condense moisture) should not be used for collection of volatile compounds (UF_6).
- Bromine pentafluoride (BrF_5) is a liquid at room temperature (melting point, -61.3°C; boiling point, 40.5°C) and is a good oxidizing agent capable of converting all uranium fluorides, including uranyl difluoride (UO_2F_2,) to uranium hexafluoride at room temperature; its oxidizing capability improves with temperature (Jarry and Steindler, 1967, 1968; Holmes et al., 1969). If excess BrF_5 is used, the reduction

by-product is bromine trifluoride (BrF_3), which is also a strong oxidizing agent; if oxidizable materials are present in excess, the product is bromine, which can be seriously corrosive to stainless steels, less so to high-nickel alloys. The BrF_3 can be refluorinated with fluorine and recycled for reuse if desired. It does not have any known explosive reaction products.

- Atomic fluorine can be produced from diatomic fluorine (F_2) at low pressure, up to 1 or 2 mm (of mercury) in 20 mm of argon, by the use of microwave heating in a sapphire tube, ultraviolet (UV) light, laser activation, or a furnace at 300–600°C. Because of its low dissociation energy, diatomic fluorine (F_2) can be dissociated extensively into atomic fluorine, with a reasonably long lifetime (several minutes) that is dependent on its partial pressure in an inert gas stream. Atomic fluorine is a strong oxidizing agent, capable of oxidizing both UF_4 and PuF_4 (plutonium tetrafluoride) to the hexafluoride at room temperature, and the equipment to produce it is very simple to use and easy to place close to the point of use. Atomic fluorine is practically noncorrosive to most alloys and can be used with copper or stainless piping. Unused fluorine can be redissociated easily by any of the generation mechanisms noted above; for example, if UF_6 is trapped from the gas stream in carbon dioxide (CO_2) or sodium fluoride (NaF) traps, the unused fluorine can be reactivated.
- Dioxygen difluoride (O_2F_2; FOOF) is a fast-acting oxidizing agent capable of converting either UF_4 or PuF_4 to its hexafluoride (UF_6 or PuF_6) at room temperature (Eller et al., 1988). This compound is stable at liquid nitrogen temperatures but has a life of only a few seconds at room temperature. It can be generated at a few hundred grams per hour in a simple coaxial reactor consisting of a liquid nitrogen-cooled, 1 1/2-inch outer-diameter stainless steel jacket with an inner cal-rod-heated, 3/4-inch nickel tube. The O_2F_2 condenses on the inner surface of the outer jacket at liquid nitrogen temperatures and can be eluted for later use, or the reactor can be operated in a continuous production mode. It can be transported easily in stainless equipment held at liquid nitrogen temperature.
- Dioxygen monofluoride (O_2F; FOO) can be made in the same type of reactor that is also equipped with a sapphire window for

injecting UV light from a mercury discharge lamp. It is considerably longer lived than, but has similar oxidizing capabilities to, O_2F_2.

- Krypton difluoride (KrF_2) is a powerful oxidizing agent capable of producing UF_6 or PuF_6 at room temperature from any lower fluoride or oxide. It has a room-temperature lifetime of many hours or even days and can be piped considerable distances in standard copper or stainless tubing. It can be made in the same UV-pumped system described for O_2F production. The production efficiency is much lower than for O_2F, but better stability makes KrF_2 usable at a considerable distance from the generation area. It was used at Los Alamos National Laboratory (LANL) to decontaminate the prototype M-LIS (Molecular Laser Isotope Separation) plutonium isotopic enrichment equipment and remove internal plutonium contamination from the processing equipment at room temperature.

KrF_2 may be a practical (but costly) candidate for stripping uranium residues from MSRE off-gas pipes, traps, and valves after a more readily available agent is used to oxidize the bulk deposits (e.g., BrF_5). The production rates of KrF_2 should be able to be scaled up from the current LANL coaxial laboratory-type reactor systems to enable sufficient feed for stripping lower uranium fluoride residues from the freeboard regions in MSRE drain tanks and off-gas traps. Krypton difluoride cannot be used to fluorinate the molten salt at 460°C because it is not stable at elevated temperature.

Appendix C—

Contamination Concerns Relating to Radon Gas Spread

From Tables 2.4 and 3.1, an upper-bound estimate of the amount of uranium-233 (^{233}U) present in Molten Salt Reactor Experiment (MSRE) drain tanks is 33 kg, 160 parts per million (or 5.28 g) of which is ^{232}U. This ^{232}U emits 114 curies (Ci) of alpha particle decays that, when added to the decays of the six alpha-emitting equilibrium daughters, gives a total alpha emission of 684 Ci at full equilibrium (about 20 years). Radon (^{220}Rn) gas is a member of this decay chain and has a half-life of about 1 minute but grows a daughter product, lead-212 (^{212}pb), with a half-life of 10.5 hours that feeds thallium-208 (^{208}Tl), which emits a 2.6-MeV (million electron volt) gamma ray. As long as the decay chain is intact from thorium-228 (^{228}Th) onward, ^{220}Rn gas and ^{208}Tl gamma rays are emitted with a 1.9-year half-life (about a 20-year total life).

Radon is a monoatomic gas that permeates organic polymers such as neoprene gloves and Plexiglas windows and causes many safety problems because of its highly radioactive particulate daughters. A 4.5 kg sample of salt will contain about 0.5 Ci of alpha emitters of which 0.11 Ci (2.5×10^{11} alpha disintegrations per minute) will be gaseous radon. If analytical evaluations on kilogram-sized samples are performed in a standard hot cell," a large fraction of this gas, at least 10^{10} alphas per minute, will be released to the cell atmosphere and spread throughout the facility by rapid diffusion through the atmosphere. Radon is known to spread upwind through ventilation ducts and other equipment, leaving alpha particulate contamination wherever it was present.

Although the short-lived daughters may not be considered a real hazard, they are impossible to distinguish from an actual particulate spill, since the alpha contamination will appear everywhere and the ^{228}Th parent has a 1.9-year half-life. For this reason, great caution should be exercised with any MSRE salt samples taken for analysis or evaluation

Contamination spread from the radon gas will contaminate all equipment with alpha-emitting daughters, some of which emit 2.6-MeV gamma rays as well. The implications of sampling MSRE drain salts should be considered carefully before a commitment to sample the salts is made, and adequate containment enclosures should be available to handle and analyze samples of this type.

Appendix D—

Use of a Nuclear Poison to Inhibit Nuclear Criticality

Careful evaluation of the behavior of Molten Salt Reactor Experiment (MSRE) salts during remelting operations suggests that the risk of a critical excursion is very low. However, it is desirable to perform neutron criticality calculations to confirm this conclusion by modeling the salt system in *real* terms. Without introduction of a moderator such as water, there is no criticality hazard associated with the solidified salt system at present. A small possibility exists for aggregation of uranium compounds such as uranium trifluoride (UF_3) during melting or fluorination. The addition of an excellent nuclear poison on top of the salt should provide additional insurance that criticality cannot be achieved during melting. If this is deemed necessary, the panel advocates consideration of gadolinium trifluoride (GdF_3) for this purpose. The advantages of GdF_3 addition to the drain tanks would be the following:

- It has a 49,000-barn thermal neutron capture cross section, with an additional 400-barn resonance integral.
- The chemical solubility of GdF_3 in the LiF-BeF_2-ZrF_4 (lithium fluoride-beryllium fluoride-zirconium fluoride) salt is expected to be high; additionally, the density is about 5.0, which implies that the gadolinium will descend rapidly through the molten fluid, dissolving as it falls through the liquid salt.
- The chemical properties of GdF_3 are very similar to the properties of UF_3, which would prevent segregation of poison and fissile materials.
- Only 1 kg of GdF_3 would be needed to provide adequate protection; this material can be obtained as a fine powder that can be dispersed easily over the entire solidified cake of existing salt.

- The compound GdF_3 is not a listed chemical in any of the Environmental Protection Agency or supplementary state regulations (it is a natural fission product already present in the MSRE salt).

Because of these desirable features, GdF_3 appears to be a very useful poison for MSRE remediation purposes and does not have any known negative characteristics for this application. For the above reasons, the panel believes that the addition of GdF_3 should be considered if detailed reactivity calculations suggest the possibility of a criticality excursion due to precipitation and aggregation of a fissile species.

Appendix E—

Hazard Scoping of Major Actions for Remediation

This appendix provides a more in-depth view of the detailed technical considerations for each of the process steps outlined in Chapter 4 in the development of a preferred approach. The execution of any remediation program involves many detailed selections in chemistry, engineering, and safety and monitoring provisions. A typical sequence (not necessarily optimal or comprehensive) of such selections is outlined here but is not intended to provide a definitive recommendation for any step in the process. Such decisions are best made by project personnel as new information is obtained.

The suggested actions, some of which are already being planned or are under way at Oak Ridge National Laboratory (ORNL), include the following:

Action 1: Removal (principally from the piping and the freeboard of the tanks) and analysis of the reactive gases fluorine (F_2) and uranium hexafluoride (UF_6) from the vent lines of the salt drain tanks, now under pressure.

The amount and composition of the gases can provide important but partial information about conditions of the stored fuel salts and some clues as to the condition of equipment (including possible leakage or exposure to water via a pressure of hydrogen fluoride [HF] and oxygen [O_2]).

Action 2: Removal of UF_6 gas specifically from the piping and tank freeboard.

The gas should be collected and its amount and composition determined. These determinations will improve the estimates of the degree of reduction of the salt relative to the oxidation state while the reactor was in operation. These data would aid a uranium mass balance calculation, and significant uranium recovery would reduce the criticality potential associated with the drain tank remediation alternatives.

Action 3: Removal of nonvolatile uranium (if it exists) from the piping by fluorination.

If any aggregate amount remaining is small relative to criticality (e.g., less than 250 g), it may be left for the last step after the tank contents are processed unless the residue results in plugged lines. Final removal may be either by fluorination or by dissolution.

If simpler measures (such as addition of any of the fluorinating agents of Appendix B as gases) fail, another possible approach for removing nonvolatile plugs in the lines is to introduce an aggressive oxidizer such as krypton difluoride (KrF_2) in anhydrous HF, to carry KrF_2 to the plugs in a liquid solution. This approach is not without difficulty—it would require cooling of the lines below the 19°C boiling point of HF (or working at greater than atmospheric pressure), and in the presence of a base such as lithium fluoride (LiF), it would enhance the attack of KrF_2 on nickel surfaces.

Action 4: Obtain information about the distribution and segregation of uranium in the salt, by one or both of the following methods:

- *Option 4A*. Gamma spectroscopy
- *Option 4B*. Collection of a salt sample

Obtaining a solid sample of the fuel salt in the drain tank appears to be an operation with hazards that result from gaseous radon contamination, as discussed in Chapter 4 and Appendix C. The sampling method considered here by the panel is a simple core drilling operation, with the drill and contained sample removed from the drain tank to a hot cell for sample handling and analysis, conducted after the reactive gases F_2 and UF_6 have been removed from the piping and the drain tank freeboard.

Obtaining fully representative samples of the drain tank salt in its present solid condition is highly desirable but may not be possible without significant spreading of radioactive contamination. Any bulk sample provides some information on the extent of segregation present, some of which might be expected due to zone refining effects during initial solidification. The ideal goal of such characterization is to map the spatial distribution of uranium-233 (^{233}U) and plutonium within the tanks, and their chemical states. If practical, several full-length core samples, at different radial distances from the center of the tanks, can provide a more precise measure of possible inhomogeneity in elemental composition and chemical state and, therefore, of the potential for segregation (and possible degree of precipitation) on melting. Because of solubility uncertainties, melting the salt may not by itself ensure homogeneity. Even though it may not be truly representative of the entire salt mass, one full-length core sample can provide significant data on the extent of segregation.

Gamma spectroscopy and mapping are mentioned as actions that are less hazardous than core sampling. They can provide information on uranium distribution that will help inform a decision on remediation strategy.

Action 5: Determination of the structural integrity of the fuel and flush salt tanks and their potential for leakage during subsequent operations (see options 6A, 6B, and 6C).

Several hazards to tank integrity must be evaluated. One hazard is that the tank may have experienced some degree of corrosion during operation or during exposure to fluorine (and possibly to nascent fluorine species and fluorine radicals formed by radiolysis) and to ionizing radiation over the extended storage period. Another hazard of tank failure is associated with the melting of the salt. This hazard includes possible differential thermal expansion effects, depending on the directionality and overall pattern of the melting process. These effects can be monitored during melting and the heat inputs arranged so as to minimize differential effects by relieving most volumetric effects on the free surface of the salt bed. A third hazard is that tanks may leak due to progressive corrosion during fluorination operations. A water leak could seriously complicate these problems.

It is recommended that all available techniques for condition assessment be considered. Analyses of cell gas, tank gas, and any salt samples can provide bounding information on tank condition and possible general corrosion and on possible existing leaks. Ultrasonic testing, where feasible, could provide more direct evidence of general wall thinning. None of these methods is able to provide reliable evidence that there is not some localized pitting or cracking that may progress to leaks. However, if the measured rate of general corrosion is low and in accord with prior laboratory results, the likelihood of unexpected severe localized corrosion is reduced.

The most likely failure mode is projected to be corrosion of the thinnest members, the cooling thimbles, and the more highly stressed region in and near the welds. This hazard can be eliminated by removing the bayonet coolers or by plugging thimble penetrations at the vessel wall. Corrosion rates might be reduced by using a lower-temperature fluorinating agent (such as bromine pentafluoride [BrF_5]; see Appendix B) than fluorine. The relative corrosion rates for different time-temperature-reagent compositions for alternative fluorination processes should be tested and confirmed, and the process conditions optimized, by using small-scale laboratory tests.

In risk terms, this hazard appears likely to remain seriously uncertain unless creative inspection methods are found or developed. This fact suggests that procedures having minimum reliance on tank integrity be given priority; these include the following:

- *Fluorination at annealing temperatures without melting*. Because some fluorine species have been able to diffuse out of the solid salt near room temperature, it is reasonable to test whether fluorine (or HF) will diffuse into the solid salt and react at useful rates at annealing temperatures lower than the melting point.
- *Controlled zone melting and simultaneous fiuorination, using the unmelted portion of the salt bed as a "skull" or frozen crust for most of the melting and fiuorination operation*. With proper monitoring, this can be used to bound the possible extent of segregation and precipitation of reduced species.
- *Contingency plans for coping with leaks of reagent gas and UF_6.*
- *Contingency plans for stopping melting and fluorination and reverting to removal of salt as a solid, if unavoidable*. As mentioned in Chapter 4, solid removal by carbon dioxide (CO_2) blasting is a contingency that it is preferable to avoid, because of the potential spreading of contamination of gaseous radioactive radon.

Action 6: In-tank fluorination for extraction and collection of ^{233}U. At least three methods can be identified:

- *Option 6A*. Preliminarily conduct hydrofluorination without melting to recover normal "oxidation" states of UF_4 and PuF_4 (uranium and plutonium tetrafluorides) (e.g., using HF or fluorine-helium mixtures at annealing temperatures), followed by options 6B or 6C to extract uranium.
- *Option 6B*. Zone melt the salt in place progressively and fluorinate the uranium content to UF_6 using an appropriate fluorination gas mixture at elevated temperature (e.g., fluorine at 500°C).
- *Option 6C*. Zone melt the salt in place progressively and fluorinate the uranium content to UF_6 in place using alternative fluorinating agents (e.g., BrF_5 or KrF_2; see Appendix B).

There are two noteworthy hazards to this operation. The first is failure of the vessel due to preexisting corrosion damage and the effect of accelerated corrosion during fluorination. Analysis of the hazard of vessel failure requires information about the present condition of the vessel and the projected corrosion rates for fluorinating conditions.

The second hazard is the possibility of criticality due to possible segregation of fissionable material. The criticality hazard can be limited by using a low salt melting rate and by progressively fluorinating out the uranium content of the melt zone before further melting occurs. By operating in a quasi-batch size mode, it should be possible to monitor the uranium removed from the melted volume and avoid having a critical mass of uranium accumulating in the melt and subject to precipitation.

This does not necessarily address the question of the behavior of possible insoluble plutonium species. The amount of plutonium appears small enough (650 g divided among the two drain tanks, as reported in Peretz, 1996c) that by itself it would be safely subcritical in any configuration in the absence of moderator. However, the case of incomplete dissolution and fluorination of uranium leaves open the possible scenario of a mixture of plutonium and uranium segregating in the drain tank vessel. Only if an effective fissile concentration of tens of grams per liter were achieved in a large enough, sphere-like configuration could criticality be possible. The detailed analyses under way at ORNL address the presence of plutonium along with the credible uranium and salt configurations.

Regarding option 6A, even if recovery of the normal oxidation state is only partial, when combined with zone melting and monitoring it appears likely to eliminate the possibility of criticality caused by precipitation. Remaining uncertainties in the conditions required for this process can be determined by a series of laboratory melting tests with simulated "reduced" uranium in salt so as to permit measurement of diffusion and reaction rates.

A continuous monitor of the degree of subcriticality of the system, such as sensitive neutron monitoring, would provide a measurement to support calculations and provide additional assurance of safety. The (,n) reactions with fluorine and beryllium provide an internal neutron source that is augmented slightly by the subcritical neutron flux (k_{eff} approximately 0.85) from fission events. Significant increases in neutron flux might be readily observable far from the critical configuration. The sensitivity of such a measurement could be enhanced further, if necessary, by introducing a stronger external neutron source (e.g., a pulsed neutron source).

If the processes of melting and fluorination to separate and recover the uranium and transfer it to another vessel are acceptable for selection on the basis of other criteria, means to ensure large margins of criticality safety appear feasible, subject mainly to further detailing of the process steps.

To support this position, a series of conditions that the panel considers unlikely would all have to occur simultaneously without the exercise of detection or control measures. These conditions are

1. substantial segregation of the fissile species, on the order of a large fraction of the total inventory in the drain tanks;
2. attainment of high density of the fissile material;
3. absence of continuous tracking of the location of the inventory;
4. absence of monitoring of possible increased neutron multiplication; and
5. failure to take available corrective actions if trends toward any of these conditions were to occur.

Given the normal disciplines of carrying out the intended types of operations with intensive planning and training and with the usual multiple levels of internal and external review and monitoring, the panel believes that the risk of criticality can be kept acceptably small. Specifically, it should be readily feasible to maintain less than 1 percent chance each for conditions 3, 4, and 5 above. Condition 2 may be physically impossible and is subject to experimental verification. The combined chance of the occurrence of criticality can be estimated reasonably to be substantially below the target levels generally considered satisfactory by nuclear safety authorities worldwide. This preliminary estimate is assumed to be subject to documentation and verification by a Safety Analysis Report, or its equivalent, normally required for all operations involving the processing or transport of fissile materials. Accordingly, the panel believes that criticality poses negligible risk to the planned operations.

The hazards of uranium-depleted salt removal appear to be substantially smaller than the hazards of "loaded" (i.e., fissile material bearing) salt removal discussed in the next action.

Action 7: Processing of fuel and flush salt external to the present drain tanks. Here two options have been identified:

- *Option 7A*. Melt and transfer the salt to a separate vessel for fluorination of uranium to UF_6, preferably using option 6C or well-monitored zone melting to prevent undetected segregation, and subsequent recovery of uranium. The following procedural comments are offered:

1. Conduct a series of trial runs with melting of simulated reduced-state salt to establish possible segregation behavior.
2. Consider a possible option for further evaluation: run a fullscale pilot melting test with the flush tank salt, preceded by an annealing treatment with a gas atmosphere to simulate the partially reduced conditions of the fuel salt.

Option 7B. Excavate the salt as a solid from the drain tanks (e.g., by CO_2 blasting) and transfer to a new vessel for

1. conventional fluorination of the uranium to UF_6 with options similar to options 6A, 6B, and 6C above;
2. electrorefining according to methods proposed by Argonne National Laboratory; or
3. no further treatment operations beyond stabilization for storage.

The following principal hazards in option 7B are noted:

1. It may be impractical to effect complete removal of the salt by CO_2 blasting due to internal tank structures or to impractically low rates of salt removal.
2. Carbon dioxide could react with F_2 to form carbonyl fluoride (COF_2) or even carbon tetrafluoride (CF_4) in an exothermic reaction.
3. Containment of radioactive species (in particular, dispersal of radon, as discussed in Chapter 4 and Appendix C) would seem to be aggravated by a technique such as CO_2 blasting.
4. The large volumes of gas to be handled could be subject to leaks or mechanical blowouts and subsequent material releases. Secondary containment may be required to limit this hazard.
5. This procedure may not entirely eliminate the hazards of segregation. In fact, segregation may be caused by density differences of solid particulates.
6. Dry runs with simulated salts can establish optimum removal conditions and likely rates of removal.
7. A full-scale test can be done by using the flush tank and salt, avoiding criticality hazards, and minimizing corrosion and leakage hazards. However, the flush tank may not be a good surrogate for the physical removal test because of the absence of thimbles.

The mitigation measures already taken are recognized as useful, but the panel believes that preventive measures are also needed because an unexplained event, even if well mitigated, can raise concerns of institutional credibility that could render it difficult for the Department of Energy to proceed with fuel and flush salt remediation on an orderly schedule and budget.

Action 8: Interim storage of the separated ^{233}U.

Transport of UF_6 to the existing on-site ^{233}U storage facility without further chemical conversion is a convenient option with well-defined and experienced protocols and generally well-controlled hazards. Radiation decomposition would be expected if the uranium were left as a fluoride. This could be avoided by conversion to the uranium oxide (U_3O_8), a standard operation.

The option of converting UF_6 to U_3O_8 for storage is also a practical one with experienced conversion and transport techniques, generally well-defined procedures and equipment, and well-controlled hazards. Stabilization of the salt residues after fluorination by chemical gettering is a less practiced operation but with less significant hazards.

Appendix F—

List of Acronyms and Abbreviations

ACB	auxiliary charcoal bed
ANL	Argonne National Laboratory
arm	atmosphere
BRWM	Board on Radioactive Waste Management
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
Ci	curies
CRBTW	Committee on Remediation of Buried and Tank Wastes
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility, at the Savannah River Site
EBR	Experimental Breeder Reactor
EIS	Environmental Impact Statement
EPA	U.S. Environmental Protection Agency
ER	electrorefining
eV	electron volts
HFIR	High Flux Isotope Reactor at Oak Ridge National Laboratory
INEL	Idaho National Engineering Laboratory
LANL	Los Alamos National Laboratory
MDP	Materials Disposition Program
MeV	million electron volts
M-LIS	Molecular Laser Isotope Separation
MSRE	Molten Salt Reactor Experiment
MTR	Materials Test Reactor, at Idaho National Engineering Laboratory

MW	megawatt
NRC	National Research Council
ORNL	Oak Ridge National Laboratory
ppm	parts per million
psia	pounds per square inch absolute
psig	pounds per square inch gauge
PUREX	plutonium and uranium recovery by extraction
R	roentgen
RDF	Radiochemical Development Facility (at ORNL)
RH-TRU	remote-handled transuranic
UV	ultraviolet
WIPP	Waste Isolation Pilot Plant

Appendix G—

Glossary

annealing	a procedure to encourage the diffusion of a substance into a solid matrix by heating below the melting point
barn	a unit of area, equal to 10^{-24} cm^2, used to measure nuclear cross sections
criticality	the presence of a self-sustaining fission chain reaction
criticality accident	an unplanned criticality
curie	a measure of the quantity of radioactive material in a sample, equal to 3.7×10^{10} disintegrations per second
eutectic	a mixture of two substances in the proportion that establishes a compound with the lowest possible melting point. The liquid is a single phase; the constituent solids separate upon equilibrium cooling.
favorable geometry	a shape of a container holding fissile material in which the geometric dimensions prevent a criticality excursion regardless of enrichment, concentration, or water-equivalent external reflection
fissile material	any mixture of fissile nuclides (uranium-233, uranium-235, and plutonium-239) capable of criticality
fission cross section	a measure (in units of area) of the probability that a fission event occurs upon collision of a neutron and a fissile nucleus

fluorination	a process using any of a number of chemical agents to introduce fluorine into a substrate (producing fluoride compounds, as by halogen exchange or oxidation)
getter	a chemically active material that reacts to trap an evolved gas
hydrofluorination	a process using hydrogen fluoride (HF). In this application, HF reoxidizes reduced centers that have been formed in the former melt. It does not take uranium to an oxidation state higher than IV.
isobars nuclei	of two different elements (i.e., differing atomic number Z) with the same mass number (A)
kilogram	a metric unit of mass
liquidus	line the boundary in a phase diagram of a binary system that separates a two-phase region from a single-phase liquid region
mole	a unit of measure equal to Avogadro's number of particles
oxidation	state a measure of the number of electrons needed to share in bonds to establish the electronic neutrality of the pure species
psia	literally, pounds per square inch absolute, a measure of pressure (a vacuum = 0 psia; 1 atmosphere [atm] = 14.7 psia)
psig	literally, pounds per square inch gauge, a measure of pressure from a gauge that compares to an ambient atmospheric reading (psig = psia — 1 atm; 1 atm = 0 psig)
radiolysis	any chemical reaction induced by the effects of ionizing radiation
reductant	a substance participating in a chemical reaction by reducing, or adding an electron to, a species of interest, thereby lowering its oxidation state

roentgen	a unit of radiation exposure; currently defined as 2.58×10^{-4} coulombs per kilogram and derived historically as the amount of gamma radiation that produces 1 electrostatic unit of charge (via production of ions) in 1 cm^3 of air at 1 atm and 0° C
torr	millimeters of mercury, a measure of pressure (1 atm = 760 torr)

Appendix H—

Biographical Sketches of Molten Salt Panel Members and Consultants

John L. Margrave, *Chair*, is the E.D. Butcher Professor of Chemistry at Rice University. His professional interests lie in areas of physical-inorganic chemistry including matrix-isolation spectroscopy and metal atom chemistry; fluorine chemistry; high-temperature chemistry, including mass spectrometry; levitation calorimetry and fluorine bomb calorimetry; laser applications; chemical vapor deposition of thin films; and environmental chemistry. Dr. Margrave was a member of the founding board of directors of Houston Advanced Research Center, where he has also served as vice president for research, director of the Materials Science Research Center, and currently serves as chief scientific officer. He has edited the journal *High Temperature and Materials Science* since its founding and has received numerous professional awards. A member of the National Academy of Sciences, Dr. Margrave has served on many National Research Council committees. He received his B.S. in engineering physics and Ph.D. in chemistry from the University of Kansas.

Sol Burstein is a registered professional engineer and currently does consulting work mainly in the areas of nuclear and mechanical engineering management. He retired as vice chairman of the board of directors of Wisconsin Energy Corporation and spent 21 years of his career with Wisconsin Electric Power Company. Dr. Burstein is the recipient of numerous awards and honors, including distinguished service awards from the University of Wisconsin, Marquette University, and the Engineering and Scientific Societies of Milwaukee. He has served on numerous industry and government advisory committees, including the Nuclear Safety Research Review Committee of the U.S. Nuclear Regulatory Commission, several committees of the National Research Council, and its Board on

Radioactive Waste Management. Dr. Burstein is a member of the National Academy of Engineering. He received his B.S.M.E. from Northeastern University and an honorary D.Sc. from the University of Wisconsin, Milwaukee.

Robert Catlin is a licensed medical physicist and certified health physicist. He retired in 1995 as executive director, clinical and laboratory safety, at the University of Texas Health Sciences Center, Houston, where he also served as executive director of the Positron Diagnostic and Research Center and taught radiological science at the School of Public Health. Previously, he served as scientific adviser for the Electric Power Research Institute and had careers in federal service and industry. Mr. Catlin is a member of Sigma Xi, the American Academy of Health Physics, and other professional societies. He has participated as a consultant to the former Soviet Union and to the U.S. Department of Energy (DOE) on radiological matters for incidents at Chernobyl and at Chelyabinsk. He has served on numerous industry and government advisory committees, including those of the National Council on Radiation Protection and Measurements and the National Research Council's Board on Radioactive Waste Management. Mr. Catlin received his A.B. degree in biology from Princeton University and an M.S. equivalent in health physics at Oak Ridge National Laboratory.

Gregory R. Choppin is the R. O. Lawton Distinguished Professor of Chemistry at Florida State University. Dr. Choppin's research includes nuclear chemistry, physical chemistry of the actinides and lanthanides, environmental behavior of actinides, chemistry of the f-Elements, separation science of the f-Elements, and concentrated electrolyte solutions. During a postdoctoral period at the Lawrence Radiation Laboratory, University of California, Berkeley, he participated in the discovery of mendelevium, element 101. His research activities have been recognized by the American Chemical Society's Award in Nuclear Chemistry and Southern Chemist Award, the Manufacturing Chemists award in Chemical Education, and a Presidential Citation Award of the American Nuclear Society. He has served on numerous National Research Council committees and currently is a member of the Board on Chemical Sciences and Technology and the Board on Radioactive Waste Management's Committee on Remediation of Buried and Tank Wastes. He received his B.S. in chemistry from Loyola University, New Orleans; his Ph.D. in chemistry from the University of Texas, Austin; an honorary degree from Chalmers University, Goteborg, Sweden; and an honorary D.Sc. from Loyola University.

Melvin S. Coops is currently a part-time staff member with Lawrence Livermore National Laboratory and a consultant with Los Alamos National Laboratory and, through the University of Chicago, is a technical reviewer of the Nuclear Technology Program at Argonne National Laboratory. Mr. Coops's experience in chemical separations of radioactive materials, actinide metallurgy, and remotely operated processing systems spans more than 40 years. He is an expert in nuclear fuel cycle chemistry using both aqueous methods and pyrochemical techniques. His experience includes separations chemistry of the fission product and lanthanide and actinide elements, with a special interest in the chemistry, metallurgy, and nuclear properties of the isotopes of uranium, neptunium, plutonium, americium, and curium. Mr. Coops is retired from Lawrence Livermore National Laboratory but continues to work there part-time. He has been a member of the American Nuclear Society since its inception. He holds a B.S. degree in chemistry from the University of California at Berkeley and an Sc.D. equivalent from Lawrence Livermore National Laboratory.

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