DEFENSE NUCLEAR FACILITIES SAFETY BOARD

February 14, 1995

MEMORANDUM FOR: G. W. Cunningham, Technical Director

COPIES: Board Members

FROM: Mark T. Sautman

SUBJECT: Molten Salt Reactor Experiment: Potential Safety Issues

1. **Purpose:** This reports documents a review of the Molten Salt Reactor Experiment by Wayne Andrews, Andrew De La Paz, James McConnell, Cindy Miller, Mark Sautman, and William Yeniscavich. The review included two informal visits by the Defense Nuclear Facilities Safety Board staff to Oak Ridge National Laboratory, a video conference on January 4, 1995, and review of relevant documents.

2. **Summary:** Since the Molten Salt Reactor Experiment shut down 25 years ago, several kilograms of fissile uranium (mostly ^{233}U) have migrated from the Fuel Drain Tanks through the piping of the off-gas system and deposited in a short section of a charcoal bed. The possibility of an accidental criticality will not be eliminated until all sources of water which could enter the charcoal bed or Fuel Drain Tanks are identified and removed. In addition, the Fuel Drain Tanks are believed to be corroding and the potential exists for stress corrosion cracking in the off-gas system piping and charcoal bed vessel. High radiation levels and reactive F_2 and HF gas in the piping will also pose serious worker hazards during remediation activities.

3. **Background[1,2]:** The Molten Salt Reactor Experiment (MSRE) at the Oak Ridge National Laboratory (ORNL) is a graphite moderated, homogeneous-fueled reactor built to investigate the practicality of the molten salt reactor concept for commercial power applications. It was operated from June 1965 to December 1969. The circulating fuel solution was a mixture of lithium-, beryllium-, and zirconium-fluoride salts, containing uranium and plutonium fluoride as the fuel (Table 1). The primary reactor components, the reactor vessel, auxiliary equipment, fuel drain tanks, and liquid waste storage tank are located below grade in reinforced concrete cells lined with stain-less steel (Figure 1). After operations were terminated in 1969, the facility was placed in a shutdown status with the fuel left in the fuel drain tanks. The 4600 kg of fuel salt was divided between two tanks and contains 37 kg of uranium (mostly ^{233}U) and 0.7 kg of plutonium.

Table 1: Salt Composition

	Fuel Salt	Flush Salt
Total mass, kg	4650	4290
Composition, mole %		
LiF	64.5	66
BeF_2	30.3	34
ZrF_4	5.0	0
UF_4	0.13	0
Uranium contents, kg		
U-232	160 ppm	160 ppm
U-233	30.82	0.19
U-234	2.74	0.02
U-235	0.85	0.09
U-236	0.04	0.00
U-238	2.01	0.19
Total Uranium, kg	36.46	0.49
Plutonium content, g		
Pu-239	657	13
Pu-240	69	2
Other Pu	2	0
Total Plutonium	728	15

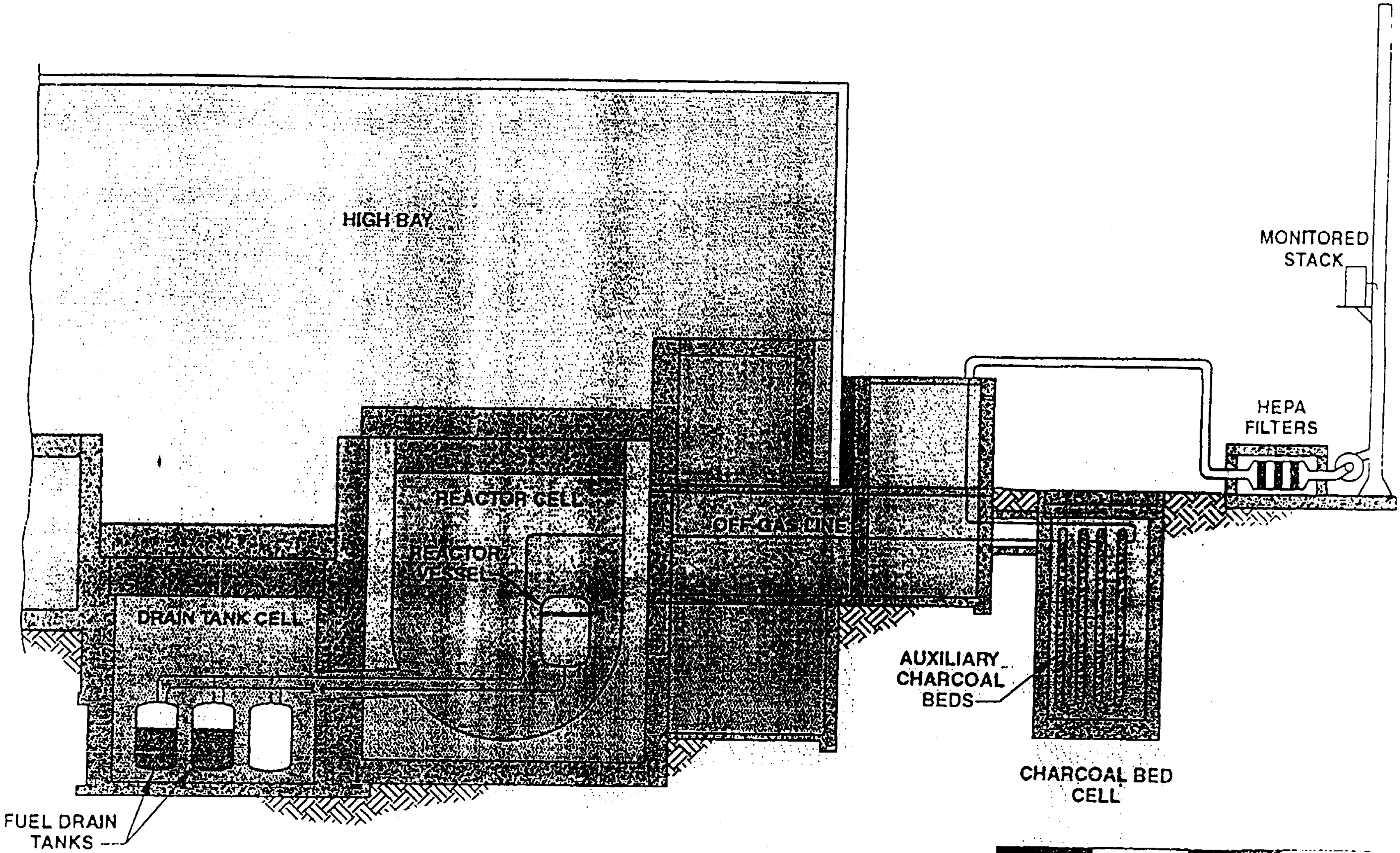


Figure 1: Molten Salt Reactor Experiment Layout

In 1987, abnormal radiation levels (5R/hr) were detected in a room adjacent to the Fuel Drain Tanks. A part of the annual surveillance and maintenance program was an annual annealing, or reheat, of the salt mixture with the intent of recombining the fluorine generated by radiolysis of the fuel salt. The annual annealing was suspended after 1989 when it was suspected that it was responsible for the abnormal radiation levels. Subsequent investigations finally concluded in 1994 that significant concentrations of reactive gases (UF_6 and F_2) are present in the piping and approximately 2.6 kg of uranium are located in the Auxiliary Charcoal Bed (ACB) (Figures 1 and 2). Under certain credible conditions, the uranium in the ACB could conceivably have gone critical. Additional uranium deposits may be located in piping and other areas that are interconnected with the Fuel Drain Tanks, such as the off-gas piping. These deposits are expected to be smaller than the ACB deposit, although this has not been verified.

The ACB, part of the off-gas treatment system, consists of two U-tube charcoal traps which are fabricated from six-inch diameter stainless steel pipe. They are approximately 20 ft long per leg. The ACB is located in a 10 ft diameter, 24 ft deep underground concrete pit. The ACB pit was filled with water to cool the charcoal traps and provide shielding during reactor operation. The ACB pit remained full of water until recently. Therefore, the charcoal traps were fully submerged when the uranium was discovered to be located in the ACB.

Department of Energy (DOE) and Martin Marietta Energy Systems (MMES) personnel investigating the MSRE hypothesize that uranium tetrafluoride (UF_4) combined with fluorine (F_2), creating uranium hexafluoride (UF_6) and was driven out of the drain tanks during the annual annealing process. The UF_6 then migrated throughout the piping between the drain tanks and the Vent House. When the UF_6 reached the ACB, it was reduced by the charcoal to UF_4. There do not appear to be any visible defects in the charcoal bed (observed remotely). DOE estimates that, in addition to the 2.6 kg of ^{233}U in the ACB, approximately 2 kg may exist throughout the piping and the head space areas of the Fuel Drain Tanks.

4. Discussion:

a. Criticality Safety Issues: There are three potential areas in the MSRE of concern from the standpoint of criticality: the ACB, the off-gas system piping, and the Fuel Drain Tanks. It is estimated that about 2.6 kg of ^{233}U has been deposited in the ACB while, at a minimum, another 2 kg exists in other sections of the off-gas system, as well as the head space of the two Fuel Drain Tanks. The single parameter mass limit for a uniform aqueous solution of ^{233}U is about 550 grams[3]. However, the deposits of ^{233}U are very undermoderated. For a solid piece of water-reflected ^{233}U metal, the single parameter mass limit increases to 6.0 kg. The single

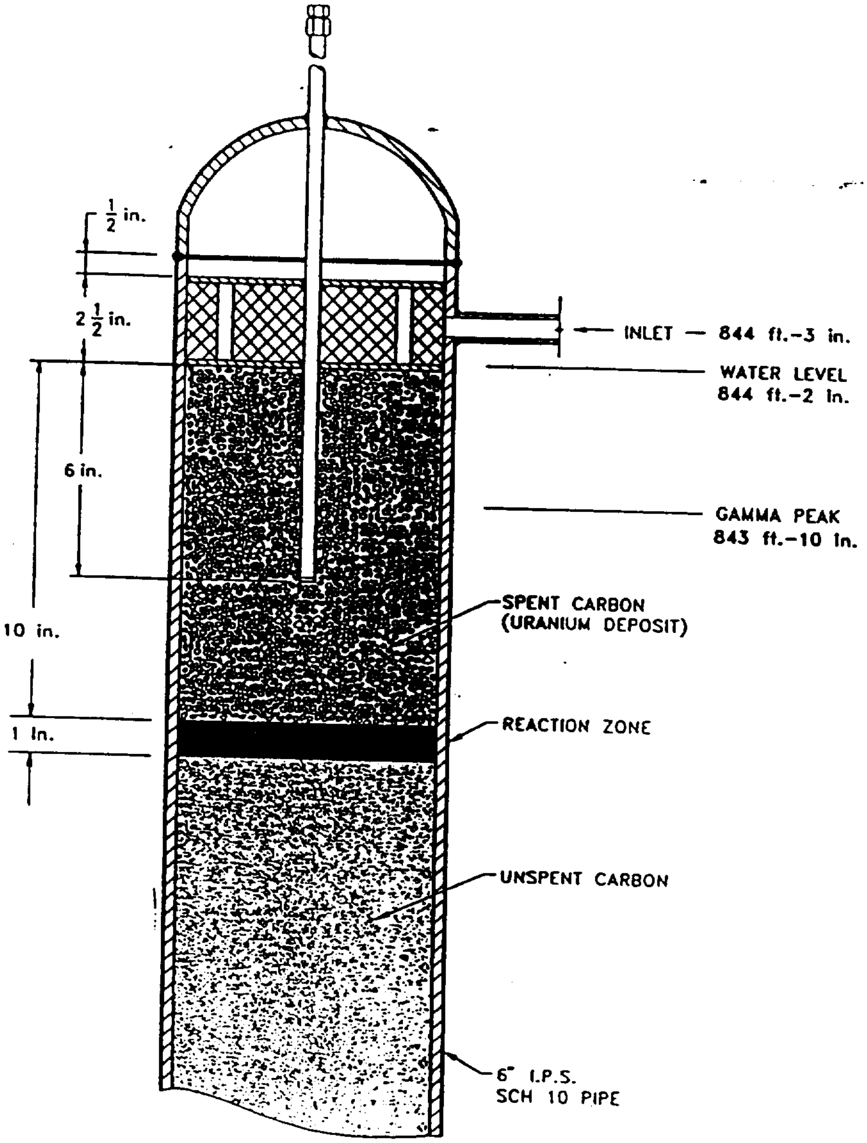


Figure 2: The Molten Salt Reactor Experiment Auxiliary Charcoal Bed

parameter mass limit for a fully reflected mass of dry UF_4 would be expected to be larger than for pure uranium metal because of the decreased uranium atom density in the compound.

In the North Electric Service Area (NESA -- the area of the reactor where the initial high radiation levels were detected), the specific location and amounts of ^{233}U present in the off-gas system lines have not been quantified. As stated previously, a deposit outside of the Fuel Drain Tanks and the ACB is not expected to be larger than 2 kg of ^{233}U. However, if water gets into the off-gas system piping, the critical mass of ^{233}U decreases from that required for dry UF_4 and may become a concern.

For the ACB, UF_4 and UF_6 are mixed with the charcoal. The charcoal acts to reduce the uranium atom density. ORNL examined the potential for a criticality for both water inside the ACB and water outside the ACB. ORNL criticality calculations indicate that the only credible criticality scenario for the 2.6 kg of ^{233}U is when water enters the ACB and fills the void spaces in the charcoal bed. ORNL calculations also indicate that water reflection alone, i.e., water completely surrounding the outside of the ACB, is insufficient to cause a criticality event. Thus, the current mass of uranium is theoretically sufficient for a criticality, but sufficient moderation is not present. The recent draining of the ACB pit has significantly reduced the amount of reflection.

ORNL criticality calculations for the Fuel Drain Tanks assume that 30.5 kg of ^{233}U, 0.9 kg of ^{235}U, and 0.6 kg of ^{239}Pu are present. ORNL personnel determined that optimal reflection conditions in the drain tank cell would occur if the two drain tanks and the flush tank broke loose from their supports and formed a planar array in the corner of the drain tank cell. Such a configuration would yield a k_{eff} value of 0.86 using the most conservative set of available cross sections. (k_{eff} is the effective multiplication factor; a system is supercritical when k_{eff} is larger than one.) ORNL criticality calculations have also been performed assuming that a layer of UF_6 formed on top of the fuel salt in a single fuel drain tank in this optimally reflected condition. For a layer with 2 kg of ^{233}U, k_{eff} does not increase appreciably. However, if water is mixed with this 2 kg layer, a critical configuration may be obtained. Also, if the uranium and about 10 gallons of water are assumed to be uniformly distributed in the fuel drain tanks, a critical configuration may be attained. It is important to note that optimal reflection (drain and flush tanks moving to the corner of the drain tank cell) may not be required for these configurations to go critical.

ORNL personnel stated that the MSRE nuclear criticality safety approvals (NCSAs) are being revised to incorporate additional accident scenarios. These NCSAs will be completed within the next couple of months. However, it is important that ORNL identify all potential water sources that could enter the off-gas piping, the ACB, or the Fuel Drain Tanks. This includes the consideration of natural water sources, such as groundwater in close proximity to the drain tank cell and the ACB pit. The controls in place to isolate each of these water sources from the three suspected locations of uranium need to be assessed, documented, and positively controlled. From review of existing documentation and discussions with ORNL personnel, it is not apparent that such an action will be completed promptly. A MSRE Remediation Project Summary Schedule presented to the Board staff on January 4, 1995, noted that the partition of the off-gas system and the elimination of water sources would not be completed until the end of the calendar year.

b. Metallurgical Issues: The Fuel Drain Tanks and the Fuel Flush Tank are made of the nickel base alloy HASTELLOY Alloy N (Table 2). The off-gas system and the charcoal bed filter vessel are made of type 304 stainless steel. The components were assembled by welding without using post-weld stress relief anneals.

Grimes reported that HASTELLOY Alloy N has shown excellent corrosion resistance to molten-fluoride salts at MSRE operating temperatures (1200°F) in numerous long-term tests (20,000 hours)[4]. Attack was uniform and about 0.1 mil/year. Haubenreich and Engel reported results where the chromium concentration in the actual fuel salt was used as an indicator of corrosion of (HASTELLOY Alloy N[5]. The chromium content increased from 38 to 85 ppm over a three year period between May 1965 and March 1968. Assuming general corrosion, this corresponds to a 0.2 mil layer of HASTELLOY Alloy N. However, the data suggested that much of the chromium appeared in the salt while it was in the Fuel Drain Tanks between runs.

A recent analysis of vapor in the off-gas system line from the Fuel Drain Tanks showed 10 mm Hg pressure of MoF_6. This is an indication that the HASTELLOY Alloy N is corroding at room temperature. The analysis also showed the presence of nitrogen and HF in the off-gas system vapor. These results indicate that moist air is leaking into the system.

The corrosion test data on HASTELLOY Alloy N indicate that it is fairly corrosion resistant to molten salt at 1200°F. However, the MoF_6 in the off-gas system line indicates corrosion is occurring at room temperature even though the salt is solidified. It should not be assumed that the room temperature corrosion mechanism is the same as the high temperature molten-salt corrosion mechanism. The room temperature corrosion does not necessarily have to be uniform, and the moist air inleakage could have a significant effect on room temperature corrosion.

Table 2: Composition of HASTELLOY Alloy N

Element	Percent
Ni	66-71
Mo	15-18
Cr	6-8
Fe, max	5
C	0.04-0.08
Ti + Al, max	0.5
S, max	0.02
Mn, max	1.0
Si, max	1.0
Cu, max	0.35
B, max	0.01
W, max	0.5
P, max	0.015
Co, max	0.2

The off-gas system lines and ACB vessel are made of type 304 stainless steel and would be expected to be immune to corrosion by fluorine gas and UF_6 at room temperature. However, the presence of moisture and HF in the off-gas system creates the potential for stress corrosion cracking.

The Board staff believes that: 1) HASTELLOY Alloy N is corroding, 2) there is an inleakage of moist air into the system, and 3) the potential exists for stress corrosion cracking in the stainless steel off-gas system. However, no quantification of the room temperature corrosion rate of HASTELLOY Alloy N has been made except to say it is small. No effort has been made to determine if the stainless steel components are cracked, and no effort has been made to identify the source of the moist air.

c. Chemical and Radiological Issues: The circulating fuel solution was a mixture of lithium and beryllium fluorides containing uranium fluoride as the fuel and zirconium fluoride as a chemical stabilizer. The initial fuel charge was highly enriched ^{235}U, which was later replaced with ^{233}U. Small amounts of plutonium fluoride were added to the ^{233}U to gain experience with plutonium in a molten salt reactor. Following reactor shutdown, the fuel salt was drained into two storage tanks. The flush salt, which contained 1 to 2 percent of the uranium and fission products, was drained into a third tank. The salts were allowed to cool to room temperature and solidify.

Including the uranium that has migrated, the fuel salt and flush salt contain about 37 kg of uranium and 0.74 kg of plutonium. Approximately 87 percent of the uranium and 90 percent of the plutonium are fissile. The salts also contain over 27,000 Ci of fission products, predominately ^{90}Sr and ^{137}Cs.[6]

The uranium contains about 160 ppm of ^{232}U. The presence of ^{232}U and ^{233}U creates very high radiation fields. ^{232}U and ^{233}U have specific alpha activities that are 10 million and 4400 times higher, respectively, than ^{235}U and they each have several daughter products with relatively short half lives. The neutron activity of the salts from (alpha,n) reactions is much greater than normal because of the presence of ^{9}Be, ^{19}F, and ^{7}Li. One of the daughter products of ^{232}U of particular interest is ^{208}Tl because it has a three minute half-life and emits a 2.6 MeV gamma.

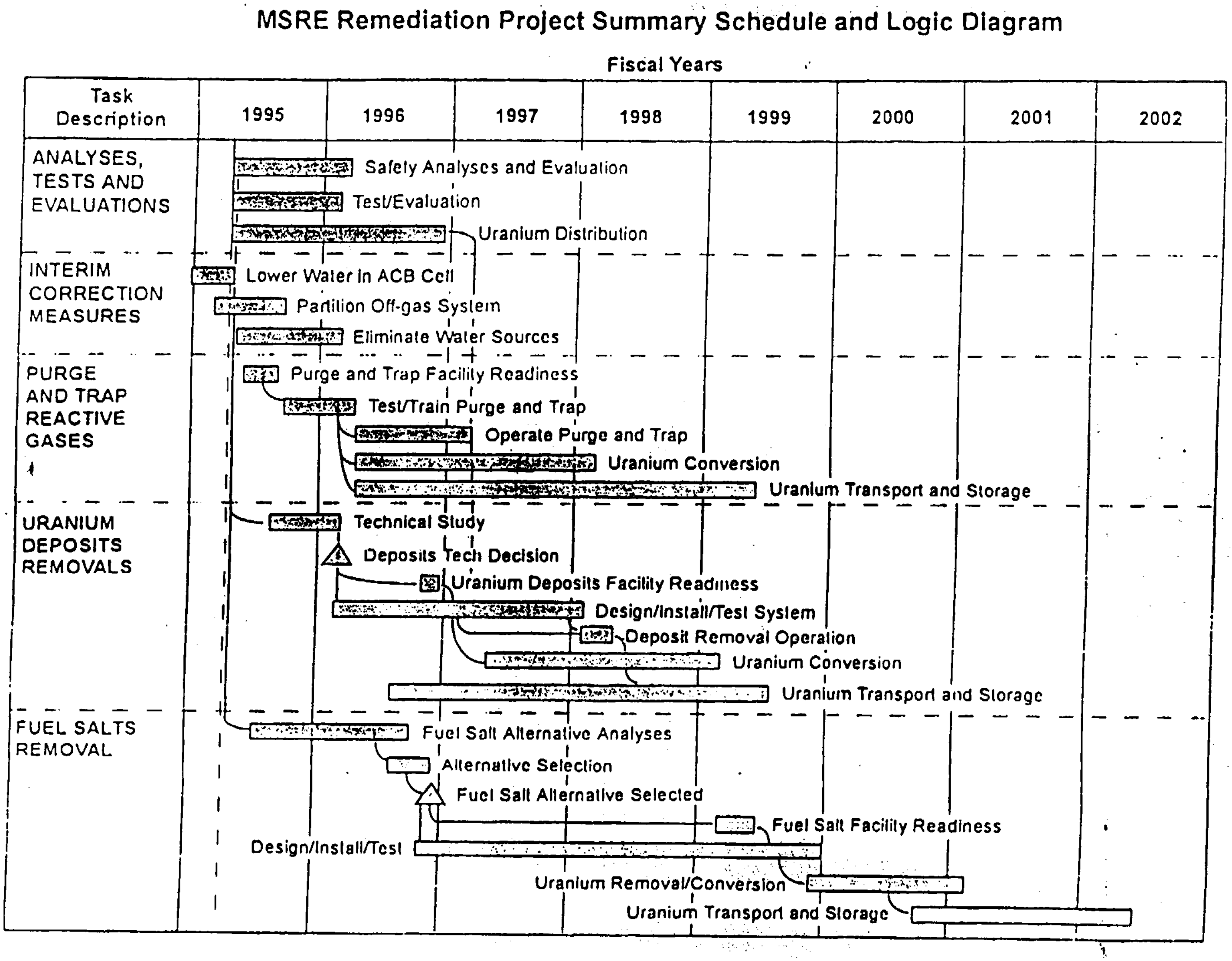
Radiolysis of the fluorine salts by gamma rays produces fluorine radicals, which can recombine with the salt or form fluorine gas. For a number of years, the salt was annealed annually to 350° - 500° F, but not melted, to promote the recombination of the fluorine radicals. As discussed previously, this practice was suspended after 1989 when DOE began to suspect that the annealings were increasing radiation levels in nearby off-gas system lines. DOE suspects that fluorine radicals in the salt lattice reacted with the UF_4 to form UF_6. The high temperatures of the annealings may have allowed the UF_6 to sublime and enter the head space above the salt in the tank. The UF_6 could then be carried by the outgas flow through a 0.5-inch off-gas system line until it reached the ACB. There the UF_6 was reduced by the charcoal to UF_4.

Although the off-gas system valves between the Fuel Drain Tanks and the ACB are still open, ORNL personnel believe that uranium migration only occurred during the annealings. This is because normal temperatures are not expected to drive the UF_6 from the salt and through the narrow pipe. This belief is supported by high accuracy radiological monitoring data taken on the piping in the North Electric Service Area which have not shown any increase in radiation levels during the past 12 months.

DOE currently estimates that 2.6 kg of uranium have been deposited in a 6-inch diameter by one foot long section of the ACB. DOE estimates an additional 2 kg of uranium (as UF_6 gas) are in the piping and the head space above the Fuel Drain Tanks. The amount of uranium in the ACB has been determined by: 1) calculating the amount of ^{232}U present from ^{208}Tl, a daughter product which emits a high energy gamma ray; and 2) measuring the ratio of $^{232}U/^{233}U$ in a gas sample from the off-gas system piping. Although it takes about 15 years for the ^{232}U-^{208}Tl pair to reach secular equilibrium, ORNL believes that this has occurred[7]. The basis for this belief is that radiation levels and temperature differentials in the ACB have not noticeably increased during the last couple of months. However, any uranium deposited more recently than 1979 would not have reached equilibrium. For example, any ^{232}U deposited during the last annealing would have only reached about 80 percent of secular equilibrium with ^{208}Tl. Board staff estimates indicate that the overall amount of underestimation is minor (i.e., less than 10 percent) if the uranium was deposited evenly during annealings. If some other mechanism has allowed uranium to migrate recently during non-annealing periods, however, the amount of underestimation would increase.

There are other important chemical reactions occurring in the system. Very reactive fluorine gas is present at nearly 0.5 atm. HF gas, which is very corrosive if it condenses, has been detected in the piping. This indicates that water has entered the system unintentionally. Furthermore, fluorine gas reacts readily with the charcoal. This reaction can become very energetic, leading to a possible deflagration, if a criticality or other incident raised the temperature above 300° C. No plutonium has been found in the gas samples so far.

d. Programmatic Plan: DOE and ORNL have established a plan to address the various issues associated with the MSRE. They have near and long term integrated plans for remediation (Figure 3), along with an associated work breakdown schedule (Figure 4). The key issues are funding for this initiative beyond FY1995 and the lack of urgency with respect to the elimination of water sources.



MSRE Remediation Project Summary Schedule and Logic Diagram

Figure 3

MSRE URANIUM MIGRATION REMEDIATION
WORK BREAKDOWN STRUCTURE

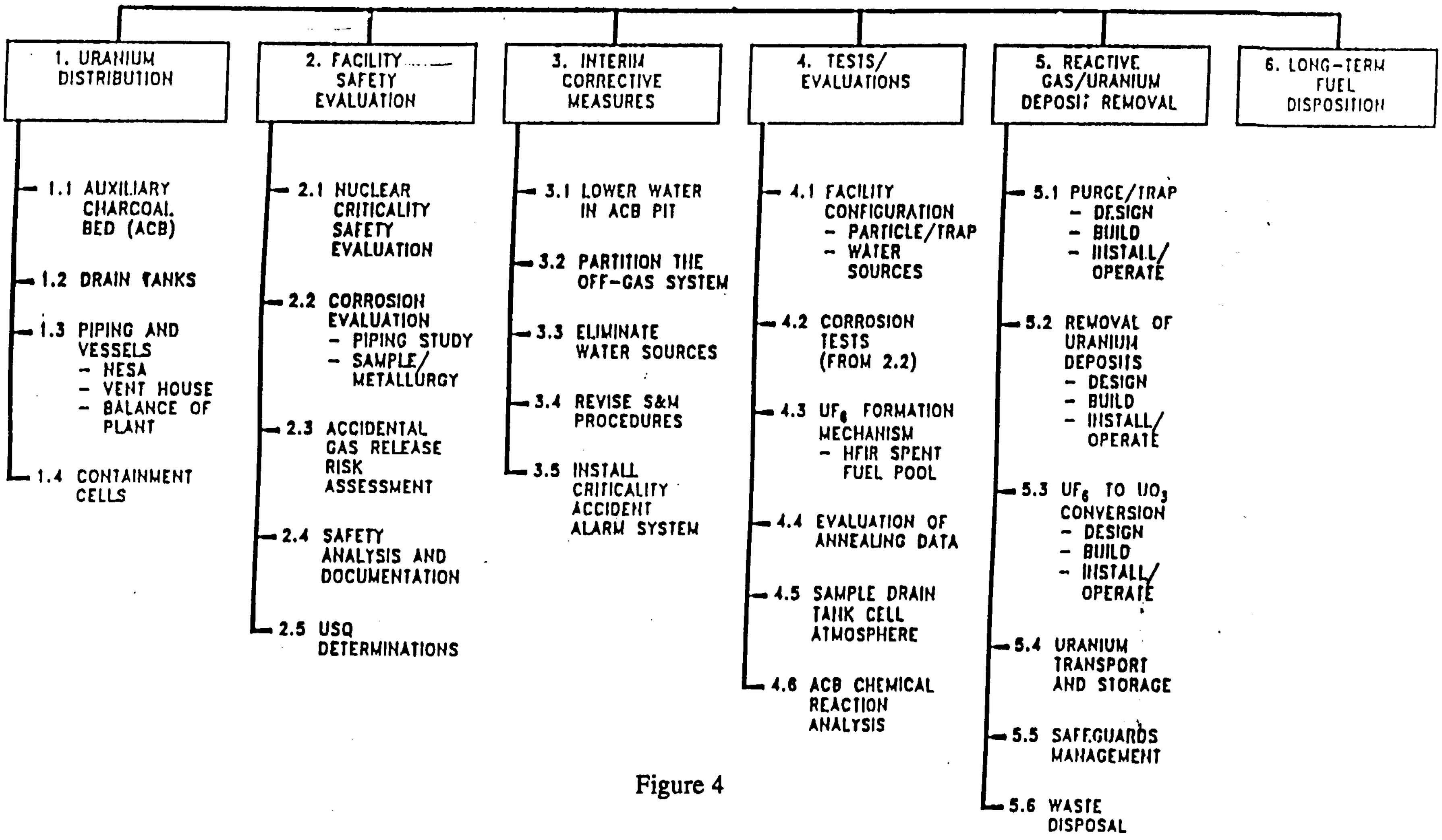


Figure 4

6. References:

1. K. J. Notz, "Extended Storage-in-Place of MSRE Fuel Salt and Flush Salt", ORNL/TM-9756, September 1985.

2. T. Burwinkle, "Molten Salt Reactor Experiment UF_6 Migration Remediation Preliminary Work Plan (Draft)", September 30, 1994.

3. ANSI/ANS-8.1-1983, *Nuclear Criticality Safety in Operations with Fissionable Materials Outside Reactors*

4. W. R. Grimes,"Molten-Salt Reactor Chemistry", Nuclear Applications and Technology, Vol 8, February 1970, P 137-155.

5. P. N. Haubenreich and J. R. Engel, "Experience with the Molten-Salt Reactor Experiment", Nuclear Applications and Technology, Vol 8, February 1970, P 118-136.

6. K. J. Notz, "Decommissioning of the Molten Salt Reactor Experiment - A Technical Evaluation", ORNL/RAP-17, January 1988.

7. ORNL Nuclear Criticality Safety Approval, No. 11, September 16, 1994, p. 20.