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DECONTAMINATION OF THE ORNL
MOLTEN-SALT FLUORIDE-VOLATILITY PILOT
PLANT AFTER PROCESSING IRRADIATED
ZIRCONIUM-URANIUM ALLOY FUEL

S. Mann
E. L. Youngblood

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

OAK RIDGE NATIONAL LABORATORY

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for the

U.S. ATOMIC ENERGY COMMISSION

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CHEMICAL TECHNOLOGY DIVISION

PILOT PLANT SECTION

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FLUORIDE-VOLATILITY PILOT PLANT AFTER PROCESSING
IRRADIATED ZIRCONIUM-URANIUM ALLOY FUEL

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FEBRUARY 1966

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PILOT PLANT AFTER PROCESSING IRRADIATED ZIRCONIUM-URANIUM ALLOY FUEL

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1. ABSTRACT

The molten-salt fluoride-volatility process for recovering uranium from irradiated zirconium- or Zircaloy-2-clad fuel elements was demonstrated successfully in the ORNL Molten-Salt Fluoride-Volatility Pilot Plant. This report describes decontamination methods that have been used twice, following two periods of "hot" operation, to reduce radiation levels in excess of 2000 r/hr to values sufficiently low to permit extensive direct maintenance and equipment modification. Radiation dosage to individuals who did the mechanical work in no case exceeded the quarterly 1.3-r allowance. Final backgrounds were less than 100 mr/hr in the majority of cell locations, with maximum readings of 500 mr/hr adjacent to some parts of the process equipment.

The decontamination sequence was based on laboratory development work. It includes flushing with a molten salt, followed by treatment with three types of aqueous solutions for removing salt film, metal scale, and deposited radiation emitters. The respective compositions were:

Ammonium oxalate, 0.3 to 0.35 M;

Aluminum nitrate, 0.1 M; or $\text{Al}(\text{NO}_3)_3\text{-HNO}_3$, 0.1-0.01 M;

Sodium hydroxide-hydrogen peroxide-sodium tartrate, about 5-1-1 wt %.

This procedure is suitable for radiation levels at least as high as those encountered in the two radioactive operating periods cited.

2. INTRODUCTION

The ORNL Molten-Salt Fluoride-Volatility Pilot Plant has been used in developing the molten salt process for recovering uranium from irradiated reactor fuel. From early 1960 through 1963, operations included dissolution of zirconium- or Zircaloy-2-clad fuel elements in molten

NaF-LiF-ZrF_4 at 500 to 650°C, and volatilization of uranium as UF_6 .

Anhydrous HF vapor was employed for dissolution and fluorine for volatilization. Two series of hot runs successfully demonstrated the process.

This, of course, resulted in highly contaminated equipment.

The plant was designed originally for direct maintenance, which requires intermittent decontamination to a radiation level sufficiently low to provide working time for (1) maintenance and repairs, (2) corrosion measurements and inspection of process vessels, and (3) equipment modification. The necessary connections were built into the system initially so that lines for circulating the decontamination solutions could be attached in areas with low radiation background. Decontamination was successfully carried out after each of the two series of hot runs, the first on fuel that had been cooled for 6 to 7 yr, and the second on fuel cooled for 6 to 13 months. Each decontamination took about 4 months.

After the first hot series and decontamination, extensive work of all three of the above types was carried out in cell 1 of building 3019. This cell contained most of the equipment involved with high radiation levels and that required no manual operation. During hot operation the cell was inaccessible; the general radiation background for the Zr-U program varied from 15 to 500 r/hr, with some specific spots up to 2200 r/hr. All work in this cell had to be done during a planned shutdown. Equipment that required manual operation or periodic maintenance such as valves, pumps, filters, etc., was located in cell 2, where the radiation background normally was low enough for unlimited access; unit shielding was required for some cell-2 equipment.

For all work performed in cell 1 after decontamination, personnel radiation dosage was kept well within Health Physics allowances. No one

exceeded 300 mr/week, and only once did a daily dose (225 mr) exceed 200 mr. Quarterly exposure for all craftsmen was held at or below half the 1300 mrem allowance, with one supervisor reaching about 1150 mrem. The use of additional craftsmen on overtime was required to complete the work in a shorter period of time; this had the added benefit of distributing individual radiation exposure where, otherwise, exposure would have been limiting.

The method of decontamination was developed in Chemical Development Section A,¹ Chemical Technology Division, with only minor modifications made in the field. Corrosion due to the process itself² was within expectations except for fluorinator seam welds, but even there did not restrict continued operation. Subsequent laboratory work at ORNL and at Battelle Memorial Institute³ (BMI) showed that most of the seam-weld corrosion could have resulted from decontamination, particularly from the nitrate solutions; elimination or careful use of nitrate solution should control such corrosion in the future. Somewhat related work at Argonne National Laboratory⁴ (ANL) indicated weld corrosion of comparable severity might result from fluorine exposure alone.

Corrosion resulting from decontamination² was negligible (less than 1 mil) in the hydrofluorinator. But, as to the fluorinator, data are insufficient to separate the contributions to corrosion by process operation and by decontamination; however, the above-mentioned work at BMI clearly indicated that the $\text{Al}(\text{NO}_3)_3\text{-HNO}_3$ decontaminant must have contributed substantially to general fluorinator corrosion, though not to the extent encountered in the seam welds.

The second decontamination was less extensive since no craft work had to be done in cell 1. Corrosion measurements of the hydrofluorinator were

obtained remotely from the cell roof with pulse-echo equipment.

Both decontaminations demonstrated that radiation backgrounds can be reduced enough to make direct maintenance of a volatility plant feasible.

3. PLANT EQUIPMENT AND OPERATION

3.1 Description of Equipment and Flowsheet

Volatility Pilot Plant equipment can be divided into two major groups according to function. In the first group, or hydrofluorination system, metallic fuel elements are dissolved by submerging the elements in molten NaF-LiF-ZrF_4 at 500 to 650°C and passing gaseous HF through the melt. The reaction takes place in the hydrofluorinator, or dissolver, which is shown in the flowsheet (Fig. 1).

The second major group is the fluorination system, in which the salt is contacted with fluorine to remove the uranium as UF_6 . The UF_6 is further purified by a sorption-desorption cycle in a bed of NaF pellets, FV-105, located atop the fluorinator, FV-100 (Fig. 1). Waste salt from the fluorinator is transferred into a shielded can in cell 1A for disposal.

The fuel elements are dissolved in the lower, narrower section of the hydrofluorinator. The final salt batch has a volume of about 60 liters and weighs about 160 kg. During the reaction, hydrogen is produced from conversion of the fuel metal to fluorides by the HF.

During hot operation, the bottom and conical sections of the hydrofluorinator become highly contaminated by contact with molten salt, and the top section from splashing salt and from dust particles. The HF recycle equipment (scrubber and reboiler) becomes quite contaminated from

NOTES Shaded vessels are those which were decontaminated

NORMAL FLOW LEGEND

U

HF

F₂

Molten Salt

Service

Fig. 1. Flowsheet of Volatility Pilot Plant.

the radioactive dust in the off-gas, but the rest of the recycle system becomes only slightly contaminated (less than 20 mr/hr). The HF neutralizer tank (FV-1009) is highly contaminated by the solids periodically dumped from the scrubbing system catch tank (FV-1003). This tank contains a solution of KOH.

Similarly, the bottom of the fluorinator (FV-100) is highly contaminated from salt contact, and the upper section from salt splash, entrainment and condensed vapor. The first, or lower, portion of the sorber (FV-105) becomes hot from sorbing volatile fission products and filtering out the dust. From this point on, the equipment, consisting of various chemical and cold traps and associated piping, is at a much lower level of radioactivity, but high in uranium holdup; all this equipment is located in cell 2 and is decontaminated separately from that in cell 1.

Materials of construction are listed in Table 1.

3.2 Sequence and History of Operating Runs

The operational history of the volatility pilot plant for the zirconium program consisted of a series of shakedown and equipment-demonstration runs on dummy elements (no uranium), a series of complete flowsheet demonstration runs on nonirradiated fuel elements, and then two series of hot runs, each followed by decontamination. Various interruptions for trouble-shooting and equipment modification occurred during the shakedown and flowsheet-demonstration periods, and major repairs were made after the first hot series. Table 2 presents a brief outline of this history.

Table 1. Materials of Construction, ORNL Molten-Salt Volatility Pilot Plant

Equipment Item	Material of Construction											
Hydrofluorinator	INOR-8 ^a											
Fluorinator ⁵	L-Nickel ^b											
Fluorinator welds ⁵	Nickel filler metal 61 ^c											
HF Storage (outside)	Mild steel											
HF system tanks, condensers	Inconel/Monel											
Caustic tanks, pumps	Inconel/Monel											
Process piping	Inconel, monel, INOR-8, mild steel											
Instrument lines	Copper tubing, inconel and INOR-8 pipe											
Gaskets, low temperature	Teflon, copper, aluminum, monel											
High temperature	Copper (ring joint)											
Valves	Monel, bronze bellows, mild steel											
<u>Nominal Compositions (wt %)</u>												
	Ni	Cr	Fe	Mo	Co	Cu	Mn	Si	C	S	Al	Ti
^a INOR-8 (Hastelloy-N)	70	7	5	16	0.2	0.35	0.8	0.3	0.06	0.01		
^b L-Nickel (Nickel-201)	99.47		0.11				0.17	<0.01	0.023	0.007		
^c Nickel filler metal 61	93 min		1.0			0.25		0.75	0.15	0.01	1.5	2-3.5

Table 2. Sequence of Zirconium Runs
for the Molten-Salt Volatility Pilot Plant

Run Designation ^a	Initial Salt Composition		Remarks
	NaF-LiF-ZrF ₄ (Mole %)	Uranium Content, (wt%)	
Salt Transfer Studies	27-27-46	0	No HF, F ₂ operation
T-1	43-22-35	0	No contamination, HF operation only to dissolve dummy Zr or Zircaloy-2 elements, F ₂ used only for equipment check-out.
T-2	38-30-32	0	
T-3	39-39-22	0	
T-4	38-37-25	0	
T-5	38-37-25	0	
T-6	38-37-25	0	
T-7	37-37-26	0	
TU-1	40-35-25	0.3	Installed FV-105; complete flow- sheet demonstration and equipment check-out; no radioactivity.
TU-2	37-38-26	0.2	
TU-3	33-41-26	0.3	
TU-4	42-34-24	0.5	
TU-5	42-35-23	0.2	
TU-6	38-37-25	0.3	
TU-7	39-38-23	0.2	
			Installed dissolver off-gas scrubbing system FV-1001, 2001, 1003, 1005.
T-8 ^b	28-30-42	0	Equipment check-out, dummy disso- lution only.
T-9	32-33-35	0	
T-10	38-37-25	0	
TU-8	35-41-24	0.2	Same as previous TU runs.
TU-9	35-42-23	0.2	
TU-10	36-40-24	0.2	
TU-11	35-42-23	0.3	
TU-12	39-38-23	0.3	Final demonstration run with cell 1 locked.
R-1	38-35-27	0.1	6 to 7 year cooled fuel, finishing 7-1-62. No entry to cell 1.
R-2	37-35-28	0.2	
R-3	37-35-28	0.2	
R-4	37-35-28	0.1	
R-5	36-35-29	0.1	
R-6	32-38-30	0.1	
T-11	40-32-28	0.03	Clean-out dummy element run.
--	--	Heel Only	Barren salt flush, no run number by oversight.
First major decontamination, after 29 runs.			Installed FV-9002 rod-out equipment.
TU-13	39-33-28	0.4	Complete demonstration runs, beginning 2-25-63.
TU-14	29-32-29	0.2	
TU-15	40-31-29	0.2	
R-7	41-31-28	0.4	6 to 13 months cooled fuel, finishing 9-30-63. No entry to cell 1.
R-8	39-33-28	0.4	
R-9	38-32-30	0.5	
R-10	41-31-28	0.4	
R-11	39-33-28	0.3	
T-12	40-33-27	0.04	Clean-out dummy element run.
T-13	--	Heel Only	Barren salt flush.
T-14	--	Heel Only	Barren salt flush.
Second major decontamination, after 40 runs.			

^aT-series runs used simulated (dummy) fuel elements of Zircaloy-2 with no uranium.

TU-series runs used non-irradiated uranium alloy elements with Zircaloy-2 cladding.

R-series runs used irradiated elements similar to TU-series elements.

^bAbnormal salt composition due to operational error.

4. REACTOR OFF-GAS SOLIDS

4.1 Origin of Off-Gas Solids^{*}

Off-gas solids from the hydrofluorination and fluorination reactors are of interest because they are the source of nearly all downstream-equipment contamination. Of the two, contamination due to dissolver off-gas solids was much more severe than that from the fluorinator. In both cases, the solids are formed by entrainment of salt particles containing fission products, and condensation of vaporized salt and fission product fluorides, or both; the dissolver solids, in addition, show the presence of some metallic-particle entrainment.

These metallic solids are thought to be formed by the reduction of metallic fluoride impurities less chemically active than the zirconium and deposition of these impurities on the zirconium at the site of dissolution reaction. Once deposited, the metallic impurities may flake off the surface of the fuel element, migrate to the surface of the molten salt, and be entrained in the off-gas.^{6, 7}

4.2 Characteristics of Hydrofluorinator Off-Gas Solids

The off-gas solids are deposited to a large extent as a dust, and thus require special consideration when any part of the system is opened to the atmosphere. Such opening is a regular part of certain operations: charging fuel elements, recharging pellets to the movable-bed sorber, connecting and disconnecting barren salt or product vessels, etc.

^{*}This term is used to denote both entrained particles and condensed vapors.

During the cold shakedown runs, considerable information was obtained about the hydrofluorinator off-gas solids. Usually about 200 to 400 g per run were discharged into the off-gas system. Electron micrographs showed that the solids ranged in size from $0.01\ \mu$ to agglomerates in excess of $10\ \mu$. Analyses of two samples collected in the off-gas system during cold runs are as follows:

Sample After Run No.	Sn	Mo	Ni	Fe	Zr	Na	Li	Cr	F ⁻
TU-4, 5 ⁸ (wt %)	12.8	2.7	7.5	10.4	7.2	2.5	< 1	< 1	36.3
TU-8, 9, 10 ⁹ (wt %)	10.4	4.4	25.3	0.3	17.5	0.6	0.03	0.09	22.5

Generally, it appears that with Zr-U fuels the bulk of the solids lost to off-gas varies widely in percentage composition but is composed mainly of Sn, Mo, Ni, Fe, Zr, and Na. Stoichiometric balances based on analyses like those above indicate that these metals exist in varying proportions both as fluorides and as metal.

4.3 Distribution of Radioactivity from Solids in the Hydrofluorinator Off-Gas

During processing of the 6-to-7-year-cooled fuel, a gamma scan of the FV-7001-C filter after the first hot run, R-1, showed that the source of radioactivity was as follows: 42% ¹²⁵Sb, 42% ¹⁰⁶Ru, 16% ¹³⁷Cs.¹⁰ After run R-3 airborne activity* from the element-charging-chute valve was due largely to ¹²⁵Sb (more than 80%), with some ruthenium. Airborne activity*

*The airborne activity resulted from operational mishaps that were eliminated thereafter by improved controls and procedures.

from the barren-salt transfer line after R-4 was $\geq 60\%$ ^{125}Sb , 30% ^{106}Ru , $\leq 10\%$ ^{60}Co , about 3% ^{90}Sr .¹¹

The percentage of activity in the fuel that was transferred to the dissolver off-gas system during the work with fuel cooled 6 to 7 yr is given in Table 3 below:

Table 3.^{12, 13} Transfer of Radioisotopes to Dissolver
Off-Gas System

Based on calculated feed activity and samples from off-gas scrubber

Activity	Approximate % of Total Feed Activity Transferred ^a						
	R-1	R-2	R-3	R-4	R-5	R-6	T-11
Gr β	0.1	0.08	0.01	0.01	0.1	0.01	0.2
G γ	0.1	0.2	0.1	0.1	0.1	0.3	0.9
^{106}Ru	4.6	0.6	0.2	0.8	0.8	0.8	55.0
^{125}Sb	3.8	18.9	11.6	17.8	12.6	28.8	220.0
^{95}Nb	0.1	0.5	0.1	0.01	1.2	0.2	514.0
^{137}Cs	--	0.1	0.001	0.02	0.02	0.06	0.2
U	<0.03	<0.02	<0.03	<0.03	<0.03	<0.03	<0.01

^aCalculated activities assume no specific fission product decay prior to fuel discharge from reactor.

Approximately 0.1 to 0.3% of the gross gamma activity was transferred to off-gas. Antimony-125 was the only element showing an appreciable percentage loss. In processing the 6-yr-cooled fuel, ^{106}Ru and ^{125}Sb contributed most to the activity. Apparently some deposited ruthenium, antimony, and niobium are liberated from the dissolver during dummy runs that follow hot

runs as indicated by T-11 results and by the increase in radiation level of the crossover-line for T-11 and other dummy runs.

Detailed information on the composition of off-gas solids and distribution of activity was not obtained on the shorter-cooled runs, R-7 through R-11. Since the relative picture of equipment radiation did not change much except for the expected overall higher level, and since the bulk of solids and accompanying activity continued to wash down during-- and flush out after--each run with comparative ease, the HF and off-gas system is not considered a major problem in decontamination. However, the bottom of some tanks, particularly the neutralizer FV-1009, obviously provided a place for radioactive solids to settle out and be retained. Some design improvement should be possible for these vessels.

4.4 Fluorinator Off-Gas Solids and Fluorination-System Contamination

The fluorinator off-gas solids, compared with those from the dissolver, present a much less serious problem if only equipment contamination is considered. The major problem in this part of the system is to prevent contamination of the product with even small amounts of fission or corrosion products. On a percentage basis, nearly all the radioactivity was confined within the fluorinator or trapped in the lower part of the movable-bed absorber. Certain more volatile corrosion or fission product fluorides, notably molybdenum, ^{237}Np and ^{99}Tc , either pass through the NaF pellets during fluorination or are desorbed later with the UF_6 . In turn, some part of that which escapes the movable-bed sorber deposits in the downstream equipment, but not sufficiently to prevent direct handling or maintenance. This activity is relatively "soft" and, even with the fuel that had been

cooled 6 to 13 months, "Cutie Pie" readings at contact with the outside walls of the equipment seldom rose above 1 r/hr; all readings at 1 ft from the equipment were considerably below 1 r/hr, with the exception of the vacuum pump for the cold-trap, which was not even shielded by thermal insulation.

Therefore, all fluorination equipment downstream from the absorber, namely, the product-collection equipment in cell 2, was handled separately and not included in the decontamination of cell-1 equipment.

5. DECONTAMINATION: GENERAL PREPARATIONS

The primary concern here was with decontamination for beta and gamma radioactivity, as differentiated from the alpha-emitting contamination of the UF_6 recovery equipment. Therefore the recovery system was only flushed with demineralized water to reduce retention of ^{235}U to practically zero. However, ammonium fluoborate is added to the water if the calculated or estimated retention is more than 3.5 kg (ref 14) despite the fact that measures are taken beforehand to render the recovery system noncritical. No attempt was made to reduce the already low level of radioactivity, although washing with water effects some reduction.

The UF_6 recovery system in cell 2 is separated from cell-1 equipment by installing blanks in interconnecting lines. All instruments for cell 1, except a few required level transmitters are valved off, and blanks are installed in the fluorine supply lines.

Utilizing the neutralizer tank (FV-1009), which normally contains caustic, for surge capacity, tubing lines are run from the caustic pump (FV-4201) discharge manifold to various points of the system. This is

shown in Fig. 2. The necessary connections were provided in the original design where it meant cutting into the piping. Other connections use flanges and similar convenient points that also were in the original design, though primarily for operational purposes. The arrangement makes it possible to circulate solution through all process lines and vessels in cell 1, as well as accessory lines that belong to the cell-1 system but are located in adjacent areas.

The caustic pump (FV-4201) normally used in processing is a Chem-pump, model SF-3/4-3/4M, with a 30-to-40-ft head and normal capacity of 10 to 15 gpm. For decontamination, a larger pump is desirable and a model SF-3/4K-751-1S with a 94-ft head and 30-gpm capacity was used.

The waste nozzle must be enclosed to make solution containment complete. The nozzle terminates within an inverted "cup." The open bottom is sealed by a rubber gasketed plate, pressed against the rim by an air-operated jack.

Separate provision must be made to wash and clean, at least to some extent, the space behind the piston in the movable-bed absorber. Since it would be impractical to circulate solution through this section in the same way as for other equipment, the method employed was to pump fresh solution (usually ammonium oxalate or plain water) at a low rate into the space. The rate must be restricted to an amount that can conveniently pass the piston rings and join the main stream. The foregoing was accomplished from the operating gallery with a Lapp Microflo pump, taking suction from the solution makeup tank and discharging into the nitrogen purge line to the rear of the piston.

Fig. 2. Diagram of the Volatility Pilot Plant Decontamination System.

6. DECONTAMINATION: SPECIFIC PROCEDURES

The same general procedure was used for both aqueous decontaminations in cell 1 during the zirconium processing program. At the completion of a series of radioactive runs, several dummy-element runs and salt flushes were made to recover any remaining uranium and to reduce radioactivity by diluting the salt heels. These cleanout runs also permitted disposal of all NaF pellets from the movable-bed sorber in the waste salt. Any liquid HF remaining in the surge tank (FV-1006), and possibly in the storage tank (FV-1600), was used after each dummy run or salt flush to wash FV-7001-C, FV-1003 and FV-1005; some reduction in radioactivity resulted. In transferring salt for the last run, the two freeze valves between hydrofluorinator and fluorinator and waste nozzle were blown empty to permit circulation of decontamination solutions. The waste-nozzle seal assembly was installed at this time.

Next, the HF system was flushed with water to eliminate the chemical hazard and possible corrosion risk due to HF. Also, the salt-sampling cubicle (FV-951) was sprayed with water, and the cubicle floor was soaked with ammonium oxalate (amm ox) solution. Since it was unnecessary to further decontaminate the HF recirculation system, the exchangers FV-2004 and FV-2005, tank FV-1006, and reboiler FV-1207 were valved off.

With the connections made for circulating aqueous solutions, as described in the preceding section, criticality precautions were taken if required.¹⁴ If less than 820 g of ^{235}U remained, no poison would be necessary. Above that figure, a suitable poison (ammonium fluoborate) would be charged to both the hydrofluorinator and fluorinator in an amount dependent on the calculated maximum holdup of uranium. For the first

decontamination, 8 liters of poison solution (200 g/liter) was added to both hydrofluorinator and fluorinator before charging the first and second batches of amm ox solution; then, additional ammonium fluoborate was added in making up the circulating solutions to bring the final concentration to 5 g/liter.

For the second decontamination, no poison was required.

The three types of decontaminating solutions and the conditions under which they were used were in general conformity with methods developed by Chemical Development Section A of the Chemical Technology Division.¹ The solutions, described in detail in Table 4, are:

- a. ammonium oxalate (amm ox),
- b. aluminum nitrate, with or without nitric acid, and
- c. sodium hydroxide--hydrogen peroxide-sodium tartrate (caustic peroxide-tartrate, or c-p-t).

The purpose of each type is as follows:

Ammonium oxalate satisfactorily dissolves many if not all of the fluoride salts remaining as solid film or dust on equipment surfaces.

The aluminum nitrate-nitric acid solution dissolves metallic scale and small masses of redeposited metallic particles, particularly in the hydrofluorinator. The metallic deposits are believed formed by oxidation-reduction in the presence of HF and zirconium. Further, this solution removes by corrosive action a thin film of metal from vessels and piping, thus partially exposing radioactivity that had penetrated the surface.

Caustic-peroxide-tartrate solution complexes radioactive material exposed on metal surfaces or redeposited from the $\text{Al}(\text{NO}_3)_3\text{-HNO}_3$ solution.

These solutions were used in the order given until all three kinds had been used once, although any number of fresh batches of any type might

Table 4. Decontamination Solutions:
Composition and Recommended Temperature

Ammonium Oxalate

Concentration: 0.3 to 0.35 M

Recommended temperature: Closest approach to boiling

Standard make-up: $(\text{NH}_4)_2 \text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ 8 kg/50 gal batch

Aluminum Nitrate-Nitric Acid ($\text{Al}(\text{NO}_3)_3\text{-HNO}_3$)

Concentration: $\text{Al}(\text{NO}_3)_3$ 0.1 M

HNO_3 0.01 M (if used)

Recommended temperature: 50-60°C

Standard make-up: $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ 7.1 kg/50 gal batch

HNO_3 (conc.) 12 cc/50 gal batch

Note: When $\text{Al}(\text{NO}_3)_3$ is used alone it should be adjusted to

3-3.5 pH; try 0.75 liter conc. KOH per 50 gal batch and
determine pH.

Sodium Hydroxide-Hydrogen Peroxide-Sodium Tartrate

Concentration: 5-1-1 wt% c-p-t

Recommended temperature: Ambient

Standard make-up: NaOH (50%) 13.8 liters/50 gal batch

Tartrate 2.5 kg/50 gal batch

H_2O_2 (30%) 5.1 liters/50 gal batch

Note: The total H_2O_2 requirement should be added in equal
increments spaced over the total circulating time
because of the high decomposition rate. This improves
effectiveness of the solution and decreases possible
difficulty from too-rapid release of oxygen.

be used. After completing the first cycle of the three types, the order of further use was determined by apparent effectiveness for continued removal of radioactivity.

Note that $\text{Al}(\text{NO}_3)_3\text{-HNO}_3$ solution is particularly corrosive toward nickel, the fluorinator material of construction. Therefore, this solution should not be used in the fluorinator except for unusually difficult decontamination, and even then should be restricted to low nitric acid content, short exposure time, and ambient temperature. Aluminum nitrate alone is preferred if it will perform satisfactorily, but the same restrictions are advisable here, too. Even with metals or alloys not so severely attacked, exposure time and acid concentration should be held to a minimum.

As mentioned earlier, work at ORNL and BMI,³ and at ANL,⁴ showed that the severe corrosion of the fluorinator seam welds (nickel filler metal 61), discovered after the first decontamination, could have resulted from the use of $\text{Al}(\text{NO}_3)_3\text{-HNO}_3$ decontaminating solution or the fluorine exposure during regular operation. The BMI work used actual samples of the pilot plant fluorinator, nickel 201 plate with nickel filler metal 61, under exposure to decontamination solutions of ORNL pilot plant composition. ANL used test specimens of nickel 200 plate with nickel filler metal 61 or nickel 200 weld metal, under exposure to a fluorine atmosphere at about 475°C. The BMI seam weld corrosion was about 900 mils/yr; ANL corrosion for the nickel filler metal 61 ranged from about 1300 to 700 mils/yr, and for nickel 200 weld metal was less than 5 mils/yr. This indicates that weld metals of superior corrosion resistance should be substituted in future nickel vessels.

During the second decontamination nitric acid was not used in the fluorinator.

Some variation in concentration of the different solutions was tried but with no real difference noted in effectiveness. Eventually, solution makeup and recommended temperature were standardized as shown in Table 4.

All solutions were charged to the system at room temperature. When required, heat was supplied by steam in vessel jackets for FV-1009, -1005, -7001-C, and by the furnace and Calrod heaters on FV-100, -1000, and -105. Circulation rates up to 4 gal/min were achieved, varying with system head and vapor-lock. Time of circulation for each solution charge, and static or holding time, varied considerably, depending on radiation level of the solution and availability of operators. Solution sometimes was allowed to remain stagnant overnight or weekends. Generally, each batch was circulated one day before being discharged and replaced. Not all parts of the equipment were contacted by every batch because of the numerous paths of circulation, but the paths were varied as much as practical.

When the type of solution was to be changed, the system was rinsed by circulating water. Also, when successive batches of amm ox solution during the second decontamination continued cloudy with suspended matter, two batches of water containing dishwasher detergent were circulated and dumped. The first came out quite dark, the second much clearer.

Table 5 presents the data for circulation of the solutions during the first decontamination, following processing of the 6-year-cooled fuel. Table 6 presents similar data for the next decontamination, following the 6-month-cooled fuel. The first program was the more extensive because of the craft work required in cell 1; no craft work was necessary after the second decontamination.

Table 5. Decontamination Procedure for Volatility Pilot Plant Equipment After Processing
of 6-Yr Cooled Zirconium-Clad Fuel

Moisten Salt Runs						
Run Number	Purpose					
R-1 through R-6	Six processing runs for recovery of uranium from 6-year cooled fuel					
T-11	Run with dummy element to clean system					
Salt Flush	Salt flush to clean system, using waste salt from cold U-run TU-12					
Aqueous Decontamination						
Type of Wash	Solution Concentration	Solution Volume (liters)	Time Solution Was in System (hr)			Equipment Contacted by Solution (Vessel Numbers as Shown in Fig. 2)
			Circulating at 25-50°C	Static at 25°C	Total	
KOH	2.0 N	~200	5			FV-1003, 1005, 1009, 7001-C
Water Flush			Once through			FV-1003, 1005, 1009, 7001-C
Ammonium Oxalate	0.35 M	~200	3			FV-1003, 1005, 1009, 7001-C
Water Flush			Once through			FV-1003, 1005, 1009, 7001-C
1st Ammonium Oxalate poisoned ^b	0.35 M	1350		45		FV-100, FV-1000, FV-1009, FV-105 ^a
2nd Ammonium Oxalate poisoned ^b	0.35 M	1000 (est.)		60	60	FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1350		15		FV-100, FV-1000, FV-1009, FV-105 ^a
3rd Ammonium Oxalate	0.35 M	1270		65		FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1300	5		50	FV-100, FV-1000, FV-1009, FV-105 ^a
4th Ammonium Oxalate	0.35 M	1345		43		FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1475	5		5	FV-100, FV-1000, FV-1009, FV-105 ^a
5th Ammonium Oxalate	0.35 M	1365		52	30	FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1300 (est.)		40		FV-100, FV-1000, FV-1009, FV-105 ^a
6th Ammonium Oxalate	0.35 M	1370		33	52	FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1350	6		6	FV-100, FV-1000, FV-1009, FV-105 ^a
1st Al(NO ₃) ₃ Solution	0.03 M	1350		70		FV-100, FV-1000, FV-1009, FV-105 ^a
	0.10 M			20	52	72
2nd Nitrate Solution						
Al(NO ₃) ₃	0.10 M	1350		35	11	FV-100, FV-1000, FV-1009, FV-105 ^a
HNO ₃	0.01 M					
Water Flush		1475	2			FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1475	2			FV-100, FV-1000, FV-1009, FV-105 ^a
1st c-p-t Solution ^c	NaOH 5 wt % H ₂ O ₂ 1 wt % Sodium Tartrate 1 wt. %	1350	10			FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1300 (est.)	2			FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1300 (est.)	2			FV-100, FV-1000, FV-1009, FV-105 ^a
3rd Nitrate Solution	Al(NO ₃) ₃ 0.10 M HNO ₃ 0.01 M	1350		58		FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1350 (est.)	2			FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1350 (est.)	2			FV-100, FV-1000, FV-1009, FV-105 ^a
2nd c-p-t Solution ^{c, d}	NaOH 5 wt % H ₂ O ₂ 2 wt % Sodium Tartrate 2 wt. %	1335	20			FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1350 (est.)	2			FV-100, FV-1000, FV-1009, FV-105 ^a
Water Flush		1350 (est.)	2			FV-100, FV-1000, FV-1009, FV-105 ^a

^a Circulation of any solution always included the bottom section of FV-100, FV-1000 up to the middle or top of slug chute, and FV-1009 tank. Since the flow paths in-and-out of FV-100 and FV-1000 were varied, the upper half of FV-100 and FV-105 were contacted only an estimated fifty percent of the time. Part of the circulating time (est. 25%) solution would be static in FV-100 while circulating in FV-1000, part-time (est. 15%) it would be static in FV-1000 while circulating in FV-100 and FV-105. In some flowpaths, FV-1001, 1003, 1005, and 7001-C were also contacted, but these are of minor consideration.

^b Both FV-100 and FV-1000 were neutron-poisoned by adding to each vessel 1600 g of ammonium fluoborate (8 liters at 200 g/liter) before charging the ammonium oxalate solution.

^c c-p-t caustic-peroxide-tartrate, or sodium hydroxide-hydrogen peroxide-sodium tartrate, solution.

^d H₂O₂ added in evenly spaced increments of 0.5 wt. % to a total of 2%.

Table 6. Decontamination Procedure for Volatility Pilot Plant Equipment
After Processing of 6- to 13-Month Cooled Zirconium-Clad Fuel

Molten Salt Runs						
Run Number ^a	Purpose					
R-7 through R-11	Five processing runs for the recovery of uranium from 6- to 13-month cooled fuel					
T-12	Run with dummy element to clean systems					
T-13	Salt flush and HF sparge to clean system					
T-14	Salt flush and HF sparge to clean system					
Aqueous Decontamination						
Type of Wash ^a	Solution Concentration	Solution Volume (liters)	Time Solution Was in System (hr)			Equipment Contacted by Solution (Vessel Number as Shown in Fig. 2)
			At 25 to 80°C	80 to 95°C	Total	
Water wash of FV-1003 and FV-1005						
1st Ammonium Oxalate	0.3 M	200	92.5	--	92.5	FV-1000 ^{b, c} , FV-100 ^{b, c} , FV-1009
2nd Ammonium Oxalate	0.3 M	1098	30	13	43	FV-100 ^b , FV-1000, FV-1003, FV-1009
3rd Ammonium Oxalate	0.3 M	936	244	20	264	FV-100 ^b , FV-1000, FV-1009
4th Ammonium Oxalate	0.3 M	900	7	20	27	FV-1000, FV-1009
5th Ammonium Oxalate	0.3 M	732	72	20	92	FV-1003, FV-1005, FV-1009
6th Ammonium Oxalate	0.3 M	990	9	10	19	FV-100, FV-105, FV-1000 ^c , FV-1009
Water wash of FV-1009		378				
7th Ammonium Oxalate	0.3 M	1020	6	13	19	FV-100, FV-105, FV-1000 ^c , FV-1009
Water wash of FV-1009		378				
8th Ammonium Oxalate	0.3 M	1152	5	12	17	FV-100, FV-105, FV-1000 ^c , FV-1009
Washed hydrofluorinator slug chute valves with water--washed FV-1009 with ammonium oxalate solution						
9th Ammonium Oxalate	0.3 M	1101	6	35	41	FV-100, FV-1000, FV-105, FV-1003, FV-1009
Ammonium Oxalate wash of FV-1009		378				
1st Detergent wash	d	1334	--	1.5	1.5	FV-100, FV-1000, FV-105, FV-1003, FV-1009
2nd Detergent wash	d	1232	3	16.5	19.5	FV-100, FV-1000, FV-105, FV-1003, FV-1009
Water wash	--	1007	~3	16	~19	FV-100, FV-1000, FV-105, FV-1003, FV-1009
			(below 50°C)	(near 50°C)		
1st Al(NO ₃) ₃	0.1 M pH >3.5	567	~3	~5	~8	FV-1009
2nd Al(NO ₃) ₃	0.1 M pH >3.5	220	3.2	15.2	18.4	FV-1009, FV-1000
			(room temp.)			
NaOH-H ₂ O ₂ -Na ₂ C ₄ H ₄ O ₆	5-1-1 wt %	1235	20	--	20	The entire system that was decontaminated
				(80-95°C)		
Water wash	--	~1000	~3	~20	23	The entire system that was decontaminated

^aListed in chronological order. See Fig.2 for flow diagram during washing.

^bBottom section only.

^cSolution static in vessel.

^dApproximately 1.25 lbs of dishwasher detergent was used.

7. RESULTS

Effectiveness of decontamination was followed in three ways:

1. equipment and cell background radiation readings,
2. radiation (Cutie Pie) readings of samples of spent decontamination solution, and
3. radiochemical and chemical analysis of spent solution.

The first of these three was by far the most informative for it determined allowable working time in the cell and was the "control" measure. Solution radiation readings were of interest but of little practical use. Solution analyses were quite erratic; otherwise, these analyses might have provided useful information on corrosivity of solutions, the physical and chemical form in which the radioactivity was retained, and removed from the system, and the relative ease of removal of different fission products.

The equipment and cell radiation readings were obtained in several ways, partly dictated by the degree of decontamination reached in the program. At first, readings could be taken only by inserting a detector on a long pole or chain through a penetration in the cell roof, or into the 6 in. sched-40 steel pipe (with the last 18 in. of sched-10 aluminum pipe) used for the threshold-detector unit (TDU) extending about 20 ft down into the cell. As soon as the hydrofluorinator had been cleaned sufficiently to reduce the hazard, the detector head on a chain was lowered through the slug chute inside an aluminum pipe or plastic sleeve; in this way, readings inside the hydrofluorinator were taken at 1-ft intervals from top to bottom at several significant stages. Finally, when cell background dropped to a tolerable level, readings were taken at more than 30

specified locations by direct entry to the cell, at arbitrary time intervals. An electrometer, permanently installed in the cell on the south wall about 2 ft from the hydrofluorinator bottom section, provided one reading continuously throughout the program.

Table 7 shows the radiation readings for the first decontamination, after run R-6, taken within the cell. Table 8 shows the readings taken inside the hydrofluorinator. Except for a few specific readings, the first dummy cleanout run reduced the average reading inside the hydrofluorinator by a factor of about 3 to 4, as shown in Table 8. The following data summarizes briefly the benefits derived just from the dummy dissolution run, T-11, and from the barren-salt flush following T-11:

	Radiation Level (r/hr)				
	Inside			Cell 1	
	Hydrofluorinator			(by Electrometer)	
	Maximum	Average	Decontamination Factor	Reading	Decontamination Factor
During R-6	--	--	--	19	--
After R-6	360	59.3	--	3	6.3
After dummy run T-11	117	16.8	3.5	2.2	1.4
After salt flush	27	8.0	2.1	1.1	2.0

In both tables, 7 and 8, some readings that appear to be out of order are actually correct; the apparent discrepancies result mostly from the removal of insulation, self-shielding in tank FV-1009, and movement of radioactive material from one area to another as a direct result of using some particular circulating path for the solutions.

Table 7. Cell-1 Radiation Data During Decontamination After Processing 6-Year-Cooled Zirconium-Clad Fuel

All values in mr/hr

Location	After Hot Run R-6 From Cell Roof and Doorway (7-3-62)	After Clean-out Run T-11 From Cell Roof and Brief Cell Entry (7-16-62)	After Salt Flush From Cell Entry (7-24-62)	After Caustic and Amm Ox Washing of HF Recycle System and FV-1009 (8-3-62)	Before First Amm Ox Wash (9-11-62)	After First Amm Ox Wash (9-19-62)	After Third Amm Ox Wash (10-1-62)	After Sixth Amm Ox Wash (10-16-62)	After Two Al(NO ₃) ₃ -HNO ₃ and One c-p-t Washes (10-26-62)	After Three Al(NO ₃) ₃ -HNO ₃ and Two c-p-t Washes* (10-31-62)	During Run TU-15, Before Run R-7*** (3-28-63)
Waste Nozzle			100,000				700	900	460-560	300-700	
Cell 1 Door (open)							900	300	150	300*	70
MS-1000-1 (horizontal section)	20,000	4,000			1,000	1,000	900	700	4,000	1,800	100
FV-1003 (top)				800	800		700	600	420	600	100
FV-1003 (center)					1,800		500	400	350	350	150
FV-1003 (bottom)			100,000	9,000	8,500		1,000	300	200	250	500
Center of Cell (1st level)			800		300		300	250	100	150	30
HFV-2207-1 (horizontal)				750			500	400	1,800	500	120
FV-1005 (top)							800	700	700	650	160
FV-1005 (center)							600	450	350	450	100
FV-1005 (bottom)			25,000	700	1,100		900	1,000	950	900	200
FV-1006 (center)							350	200	160	175	30
FV-1006 (bottom)			1,500	350	350	500	450	300	300	300	95
FV-1009 (center)					100	200	200	150	60	60	15
FV-1009 (bottom)			6,000**	60,000	50,000	2,000	1,500	700	900	400	85
FV-500 (bottom)	2,000	<1,000			250		60	50	30	30	10
FV-500 (center)			850		600		150	100	90	60	10
FV-500 (top)			2,000		175		400	250	100	300*	40
Center of Cell (Mezzanine)							40	30	20	20	10
FV-2004 (center)							90	65	45	45	20
FV-2005 (center)							70	45	30	40	20
Center of Cell (2nd level)	19,500	2,000					40	30	20	25	10
FV-100 (middle neck)							600	400	170	140	40
FV-100 (upper enlarged part)							350	250	150	110	60
FV-100 (top neck)	4,000		2,500				900	500	160	110	70
FV-105 (above FV-100)	2,500						500	300	200	240	50
FV-105 (horizontal)					1,600		450	300	330	300	50
FV-105 (vertical)	1,500	2,000					300	200	220	150	40
FV-105 (top)		<1,000	<1,000				100	80	35	35	25
FV-5000 (bottom)	9,000	2,000	1,500		2,000		1,800	1,500	1,000	1,000*	80
FV-5000 (3' above bottom)	5,000	1,000	500			300	350	250	160	300*	65
FV-5000 (top of cone)	2,000						200	100	65	40*	20
FV-5000 (top of furnace)	68,000	<1,000	<1,000				500	300	75	80*	20
FV-1000 (middle of 24" section)	55,000	3,000	3,000				400	300	120	190*	25
FV-1000 (top of 24" section)							400	300	100	115*	40
FV-1000 (neck)	51,000	15,000	9,000				400	300	80	80*	80
FV-1002 (slug chute middle)							100	150	60	70	
HFV-1002-1 (near FV-1002)							300	200	200	250	60
HFV-1002-1 (near FV-1001)							600	150	800	3,000	75

* Insulation removed from fluorinator and hydrofluorinator before these readings. This also affects readings at other near-by locations.

**FV-1009 tank full for this reading; empty for all later readings.

***Not part of decontamination program, but an example of cleaning and shielding effect of the first cold run.

Table 8. Radiation Level Inside the Hydrofluorinator During the Decontamination After Run R-6

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Radiation Level, R/hr				With Probe in Plastic Sleeve		
Run R-6	Run T-II	Barren Salt Flush	1/2 in. Aluminum Pipe, after Ammonium Oxalate Wash No 2	after Ammonium Oxalate Wash		
				No. 2	No. 4	No. 6
<1	<1	<1	<1	3	2.5	<1
2	2	1	1	3	1	<1
3	3	3	<1	2	<1	<1
3	3	3	<1	1.5	<1	<1
3.5	4	2	<1	1.5	<1	<1
6	5	3	<1	1.5	<1	<1
13	10	5	<1	1.5	<1	<1
37	25	8	<1	2	<1	1
105	41	11	<1	2	<1	1
147	49	16				
130	60	19	<1	3	1	2
38	17	14	1.5	4	2	2
43	10	10	1.5	4.5	2	3
85	7	8	1.5	4.5	2	3
153	5	6	1.5	5	2	2
162	4	6				
129	3	5	1.5	4.5	2	3
48	3	4	1.5	5	3	2
26	5	4	1	6	3	3
39	10	4	1	3	<1	a
17	6	5	1	3	<1	a
9	4	7	1	3	<1	a
12	8	6	1	3	<1	a
12	8	7	1	4	<1	a
6	8	7	1.5	6	<1	a
8	8	8	1.5	4.5	<1	a
3	12	8	2	7	2	a
17	50	12	4	10	2	a
50	117	12		28		
171		17	11	18	7.5	a
360		27			6.0	a

Average — 59.3 16.8 8.0 1.7 5.1 1.9 1.7

a. Readings were not taken because of instrument trouble.

The readings in the next-to-last column of Table 7 are those that prevailed during the extensive craft work in cell 1. Of great significance here are the background readings for the center of the cell at the first level, the mezzanine, and the second level: 150, 20 and 25 mr/hr, respectively. These are the locations where the craftsmen would try to stand and organize the job to be done, before actually approaching the hotter equipment. The higher readings shown for specific equipment were taken at "contact," but were very much lower at distances of even 1 ft. Proof that these radiation figures represent a satisfactory level for direct, extensive craft work is shown in Table 9, which lists the highest individual exposures for the job categories requiring significant in-cell time.

The ability to hold maximum quarterly exposure of any craftsman to about one-half of allowable was partly due to the distribution of the work load; extra craftsmen were used in overtime to shorten total shut-down time. Pipefitting was the craft most in demand; a tabulation of exposure rate over a large number of in-cell jobs for which accurate data were kept showed the following:

Total time of exposure, 192.2 hr

Total exposure, 6346 mr

Average dose rate, 33 mr/hr

For the second decontamination, Table 10 shows radiation readings from inside cell 1, and Table 11 from inside the hydrofluorinator, similar to Tables 7 and 8 for the first decontamination. It is obvious, and expected, that the final radiation levels in the second case are

Table 9. Personnel Radiation Exposure for
Direct Maintenance Work After First Decontamination

These figures represent the highest individual
exposures for the major job categories, during the
quarters of greatest work load

Job Category	Quarterly Exposures (1962), mr		
	2nd	3rd	4th
HP surveyor	170	110	590
Technical supervisor	210	250	1110
Pipe fitter	150	340	680
Pipe fitter	110	190	650
Electrician	100	10	520
Instrument technician	60	10	180

severalfold higher than the first. This is because of the much higher levels at the start, and the purposely less extensive decontamination effort the second time because no work was planned in the cell.

Additional data during the second decontamination are given in Tables 12 and 13. Table 12 shows radiation readings taken inside the TDU tube in cell 1, measured at one-foot intervals beginning at the top of the cell. Readings after the last amm ox wash are not reported because the detector in use did not have a scale of lower range. Table 13 presents some information on radiation levels and zirconium and nickel concentrations in various wash solutions; the data are too erratic to be of value and are reported simply for the record.

Table 10. Cell 1 Radiation Data During Decontamination After Processing 6- to 13-Month Cooled Zirconium-Clad Fuel

Location	All Values from Cell Roof Are Given in r/hr						All Values from Cell Entry Are Given in mr/hr		
	After Cleanout	After Salt Flush	After Salt Flush	After First	After Third	After Eighth	After Deter-	After Final	Prior to Hot
	Run T-12 (10-17-63)	Run T-13 (11-1-63)	Run T-14 (11-11-63)	Arm Ox Wash (12-19-63)	Arm Ox Wash (1-3-64)	Arm Ox Wash (1-17-64)	gent Washes (1-23-64)	Wash (4-9-64)	Run RA-1 (8-31-64)
Waste Nozzle							12,000	10,000	10,000
Cell 1 Door (open)							200	140	200
FV-1003 (top)							600	840	500
FV-1003 (center)							600	500	180
FV-1003 (bottom)							500	350	180
FV-1005 (top)							1,100	1,600	630
FV-1005 (center)							800	940	470
FV-1005 (bottom)							1,000	800	260
FV-1006 (center)							800	340	200
FV-1006 (bottom)							1,800	650	400
FV-1009 (center)							600	1,200	280
FV-1009 (bottom)							20,000	10,000	10,000
FV-500 (bottom)							110	80	55
FV-500 (center)							350	120	70
FV-100 (middle neck)							1,200	850	290
FV-100 (upper enlarged part)							1,200	750	270
FV-100 (top neck)							3,000	600	920
FV-2004 (center)							650	240	160
FV-2005 (center)							300	190	100
FV-105 (above FV-100)	53	34	19	6	4	2			
FV-105 (horizontal)	44	22	18	6	4	4	3,500	1,800	440
FV-105 (vertical)	53	37	27	4	2	1	900	600	460
FV-105 (top)	50	30	23	3	2	1			360
*FV-5000 (bottom)							250	250	200
*FV-5000 (3 ft above bottom)							300	200	150
*FV-5000 (top of cone)							500	220	110
*FV-5000 (top of furnace)		15	16	7	6		850	330	140
FV-1000 (middle of 24-in. section)	33	37	50	16	7	4	850	900	240
FV-1000 (top of 24-in. section)	37	58	110	29	9	4			660
FV-1000 (neck)	700	400	500	9	4	4			
FV-1002 (slug chute middle)	150	63	55	6	3	3			680
HFV-1002-1 (near FV-1002)	1,250	1,900	2,200	11	4	5			1,300
HFV-1002-1 (near FV-1001)									
Center of Cell (first level)							6,000	530	160
Center of Cell (mezzanine)							90	50	35
Center of Cell (second level)							250	160**	65
Electrometer	6					0.5	270	160**	

*FV-5000 furnace was closed for these readings.

**This reading on 1-28-64, before washing program was terminated.

Table 11. Radiation Level Inside the Hydrofluorinator During the Decontamination After Run R-11

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	Radiation Level, R/hr. after		
	Ammonium Oxalate Washes	Detergent Washes	Aluminum Nitrate and Caustic-Peroxide-Tartrate Washes
	0.3	0.3	0.3
	0.3	0.3	0.3
	3.3	3.5	3.3
	1.2	1.2	1.3
	1.4	1.3	1.2
	2.5	2.5	2.4
	3.0	3.2	2.8
	3.0	3.3	2.8
	4.0	4.5	3.4
	13.0	12.5	7.6
	9.5	9.3	5.0
	11.0	11.0	5.4
	14.0	14.0	7.6
	17.0	16.0	11.0
	14.0	14.0	10.0
	13.0	14.0	9.8
	15.0	16.0	10.0
	18.0	25.0	12.0
	30.0	35.0	15.0
	16.0	15.0	11.5
	20.0	17.0	12.0
	11.0	8.8	4.7
	10.0	12.0	3.2
	8.0	9.6	2.3
	16.0	15.0	2.2
	13.0	10.0	2.2
	9.0	6.8	2.5
	8.0	13.0	15.0
Average —	10.2	10.5	6.0

Table 12. Radiation Readings Inside TDU Tube in Cell 1 for Decontamination
After Processing 6- to 13-Month-Cooled Zirconium-Clad Fuel
Readings in r/hr

Distance Down From Cell 1 Roof (ft)	After Dummy Run T-12 (10-16-63)	After Salt Flush T-13 (11-1-63)	After Salt Flush T-14 (11-11-63)	After Second Amm Ox Wash (12-19-63)	After Fourth Amm Ox Wash (1-3-64)	After Eighth Amm Ox Wash (1-10-64)	After Ninth Amm Ox Wash (1-17-64)
1	0.3	0.3	0.3	0.3	--	--	--
2	0.3	0.3	0.3	0.3	0.3	--	--
3	0.3	0.3	0.3	0.3	0.3	--	--
4	0.3	0.3	0.3	0.3	0.3	--	--
5	2.3	1.5	1.2	0.3	0.3	0.3	0.3
6	5.5	3.0	2.3	0.5	0.3	0.3	0.3
7	8.0	5.0	4.1	0.5	0.3	0.3	0.3
8	15.0	8.5	6.1	0.6	0.3	0.4	0.3
9	15.0	7.5	6.3	0.8	0.3	0.4	0.3
10	13.5	7.5	6.1	0.9	0.6	0.4	0.4
11	16.0	9.0	7.5	1.0	0.6	0.5	0.5
12	16.0	9.0	7.1	1.0	0.7	0.6	0.5
13	15.0	7.5	5.9	1.0	0.7	0.5	0.5
14	14.0	7.0	5.0	1.0	0.7	0.5	0.5
15	12.3	6.0	4.2	1.0	0.7	0.6	0.5
16	11.0	5.0	3.6	1.0	0.7	0.5	0.4
17	7.5	4.5	3.1	0.8	0.6	0.5	0.4
18	5.5	3.5	2.6	0.7	0.6	0.4	0.3
19	4.5	3.0	2.3	0.6	0.5	0.4	0.3
20	3.5	3.0	2.2	0.6	0.5	0.4	0.3
21	4.5	4.5	3.1	0.7	0.7	0.5	0.3
22	6.8	5.0	3.8	0.8	0.8	0.7	0.5
22.3	7.3	5.0	4.2	1.1	0.8	0.7	0.5
Maximum Reading	16.0	9.0	7.5	1.0	0.7	0.6	0.5
Average Reading	8.0	4.6	3.6	0.7	0.5	0.4	0.3

Table 13. Wash Solution Data for Decontamination After Processing
6- to 13-Month-Cooled Zirconium-Claad Fuel

Wash Solution Identification	Gross Beta Counts/min/ml ($\times 10^4$)	Scintillation Alpha Counts/min/ml ($\times 10^4$)	Cutie Pie Reading of 25 ml Sample (mr/hr)	Zirconium Concentration (mg/ml)	Nickel Concentration (mg/ml)	Wash Solution Volume (liters)
2nd Amm Ox	224	511	2,000	0.48	0.095	1,098
3rd Amm Ox	94	228	700	0.042	0.034	936
4th Amm Ox	74	125	460	0.007	0.023	900
5th Amm Ox	59	86	175	0.004	0.013	732
6th Amm Ox	82	127	200	0.042	0.035	990
7th Amm Ox	42	70	800	0.001	0.013	1,020
8th Amm Ox	50	67	420	<0.001	0.006	1,152
9th Amm Ox	22	31	200	<0.002	0.015	1,101
1st Detergent	162	167	7,000	<0.002	<0.01	1,334
2nd Detergent	14	9	450	<0.002	<0.01	1,232
Water Wash	7	6	170	--	--	1,007
A1 Nitrate Wash of Caustic Neutralizer	29	35	200	<0.002	0.050	610
A1 Nitrate Wash of Hydrofluorinator	5	17	120	<0.004	0.022	790
Caustic-Peroxide- Tartrate Wash	45	79	170	<0.004	<0.006	1,235
Final Water Wash	17	20	92	<0.004	<0.006	1,080

The tabulated data immediately below summarize briefly for the second decontamination the benefits in cell 1 from the dummy run and the two barren-salt flushes made directly after hot run R-11. This can be compared with similar data for the first decontamination following run R-6. Decontamination factors are about the same in both cases:

	Radiation Level, r/hr				
	Inside TDU Pipe			Cell-1	
	Maximum	Average	Decontamination Factor	Electrometer	
				Reading	Decontamination Factor
During R-11				480	
After R-11				20	
After dummy run T-12	16.0	8.0		5	4.0
After first salt flush T-13	9.0	4.6	1.7	3.2	1.6
After second salt flush T-14	7.5	3.6	1.3	2.5	1.3

Information of value on equipment corrosion directly attributable to decontamination is almost nonexistent except for that on the fluorinator seam weld³ mentioned in the Introduction. It is indeed unfortunate that the results of the analyses of decontamination wash solutions (Table 13) are so undependable; accurate nickel concentrations alone would give good indication of corrosivity of each batch of solution. The main reason for the poor reliability was in the sampling, wherein wide variation existed in the amount of suspended solids, depending on the degree of turbulence of the circulating solution. Wide variation could be observed visually in samples taken in rapid succession.

No leakage of equipment was observed during the first decontamination, but one manual-valve bellows and two ring-joint flanges developed leaks during the second decontamination. The valve (V-4201-4) was in the caustic pump manifold, and the corrosion that caused bellows failure could have taken place to a large extent during preceding operation. A number of such failures had occurred during regular operation. The leaking ring joints could possibly be explained similarly.

During fluorine conditioning of the system after the second decontamination at least seven failures of bellows or bellows gaskets occurred in manually and remotely operated valves. Inspection showed all failures to be the result of corrosion, but it would be pure speculation to try to apportion this among regular operation, decontamination, and fluorine conditioning.

8. CONCLUSIONS AND RECOMMENDATIONS

The overall results of the decontamination methods described in this report are effective enough to justify the concept of direct maintenance for a molten-salt volatility plant, at least for fuel cooled as long as six months. However, improvement in methods is desirable in some instances; specifically, a less corrosive solution for descaling of the nickel fluorinator is needed, and better temperature control of the circulating aqueous solutions would improve decontamination efficiency noticeably. Nitric acid should not be used in the nickel fluorinator except for extreme cases.

The total elapsed time required to decontaminate the pilot plant (about four months in each case) is too great for practicality. At the

same time, the pilot plant demonstration was not planned for time-efficiency in this area, and little doubt exists that the elapsed time could be reduced by half or less.

If commercial plants for molten-salt volatility processing become a reality, and if direct maintenance is planned, a laboratory development program will be necessary to find either a suitable solution for descaling a nickel fluorinator or another material of construction for the vessel. However, this work should not be done until there is reasonable certainty that a commercial plant is to be built.

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