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Work Plan for Denaturing Waste  
in the Old Hydrofracture Tanks  
at Oak Ridge National Laboratory,  
Oak Ridge, Tennessee

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**Work Plan for Denaturing the Waste  
in the Old Hydrofracture Tanks  
at Oak Ridge National Laboratory,  
Oak Ridge, Tennessee**

Date Issued—June 1998

Prepared for the  
U.S. Department of Energy  
Office of Environmental Management

Environmental Management Activities at  
OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37831  
managed by  
BECHTEL JACOBS COMPANY LLC  
for the  
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## ABBREVIATIONS

ETTP	East Tennessee Technology Park
HASP	health and safety plan
MVSTs	Melton Valley Storage Tanks
OHF	Old Hydrofracture Facility
ORNL	Oak Ridge National Laboratory
RCRA	Resource Conservation and Recovery Act
RWP	radiation work permit

## EXECUTIVE SUMMARY

The Environmental Management Program at Oak Ridge National Laboratory (ORNL) is managing a project to remove the contents of the Old Hydrofracture (OHF) Tanks, located in Melton Valley. CDM Federal is responsible for sluicing the sludge and supernate from the OHF Tanks and transferring the slurry into the Melton Valley Storage Tanks (MVSTs), ORNL's active liquid low-level waste system. Before the material can be sluiced to the MVSTs, it must meet the requirements of WM-LWS-WAC, *Waste Acceptance Criteria for Liquid Low-Level Waste System, Process Waste Treatment Complex-Building 3544, and Process Waste Treatment Complex-Building 3608*, which contains requirements for ratios of fissile to nonfissionable isotopes. This work plan describes the denaturing activities to be performed to ensure that the material meets these requirements. Personnel from the ORNL Chemical Technology Division are responsible for the denaturing activity described in this work plan.

## 1. OBJECTIVE

The Environmental Management Program at Oak Ridge National Laboratory (ORNL) is managing a project to remove the contents of the Old Hydrofracture (OHF) Tanks, located in Melton Valley. CDM Federal is responsible for sluicing the sludge and supernate from the OHF Tanks and transferring the slurry into the Melton Valley Storage Tanks (MVSTs), ORNL's active liquid low-level waste system. Before the material can be sluiced to the MVSTs, it must meet the requirements of WM-LWS-WAC, *Waste Acceptance Criteria for Liquid Low-Level Waste System, Process Waste Treatment Complex-Building 3544, and Process Waste Treatment Complex-Building 3608*. WM-LWS-WAC contains requirements for ratios of fissile to nonfissionable isotopes. More specifically, the amount of  $^{238}\text{U}$  must be sufficient to have 110 parts by weight  $^{238}\text{U}$  per part  $^{235}\text{U}$ , plus an additional 200 parts  $^{238}\text{U}$  per part  $^{233}\text{U}$ . The sludge and supernate in the OHF Tanks contain uranium with increased ratios of  $^{233}\text{U}$  and  $^{235}\text{U}$  to  $^{238}\text{U}$ , so depleted uranium (99.8%  $^{238}\text{U}$ ) must be added to the tanks to dilute the isotopic ratio of the contents (i.e., denature) before they can be sluiced. Personnel from the ORNL Chemical Technology Division are responsible for the denaturing activity.

## 2. BACKGROUND

The OHF Facility is located in Melton Valley and includes five underground tanks in sizes ranging from 13,000- to 25,000-gal capacity. Two recent sampling campaigns have provided information on the chemical and physical characteristics, and volumes of the sludge and supernate in the tanks (Keller et. al. 1997). Appendix A shows a summary of the volume measurements and uranium analytical results for the five tanks. The sludge volumes were calculated using the maximum sludge height measured in each of the tanks. To ensure conservatism, the highest uranium concentration and highest isotopic results for  $^{233}\text{U}$  and  $^{235}\text{U}$  and the maximum sludge volume and density for each tank were used to calculate the amount of  $^{233}\text{U}$  and  $^{235}\text{U}$  present. The amount of depleted uranium that will be required to denature the contents of each tank (prior to planned supernate transfers), based on the requirements of WM-LWS-WAC, is also shown in Appendix A. The depleted uranium will be added as a uranyl nitrate solution, but most of the uranium will precipitate after mixing with the tank contents because of the high pH of the solution in the OHF Tanks. Following mixing of the tank contents by CDM Federal, the depleted uranium will be distributed between the supernate and sludge in the same ratio as the original uranium, so both the supernate and the sludge will be denatured. The tank sludges also contain  $^{239}\text{Pu}$ , but the plutonium is adequately denatured by the large amount of thorium present in the waste. Nuclear Criticality Safety Approval 56 for the OHF Tanks specifies that the depleted uranium used for denaturing shall not contain  $>0.4$  wt%  $^{235}\text{U}$ .

A large volume of depleted uranyl nitrate waste solution was generated by the ORNL Robotics and Process Systems Division in the past. A total of 51 drums (labeled 150759.01 through 150759.51) of this waste solution, which came from one tank, are stored at East Tennessee Technology Park (ETTP). All of the drums contain the same solution, except for the last drum (150759.51), which contains mostly rinse water. The uranyl nitrate solution is a mixed waste, classified as hazardous under the Resource Conservation and Recovery Act (RCA) due to chromium and corrosivity, and classified as radioactive due to the uranium content. As such, the drums must

be stored in a RCRA-permitted facility until they are used. Four of these drums have been sampled and analyzed at the ORNL Radioactive Materials Analysis Laboratory to determine the concentration and isotopic ratio of the uranium, the acid concentration, and the presence of trace metals in the waste solutions. A composite sample from the drums was also analyzed by the Lockheed Martin Energy Systems Analytical Services Organization. The solution in the drums is primarily uranyl nitrate, with small amounts of other heavy metals, as shown in Appendix B, and contains a maximum concentration of 0.20 wt%  $^{235}\text{U}$ . To ensure conservatism, a uranium concentration of 350 g/L will be used to calculate the amount of uranyl nitrate solution required for each OHF tank. Selected drums of this solution will be shipped from ETTP to the OHF site at ORNL as needed. The Tennessee Department of Environment and Conservation has given permission to store the drums for up to 3 days. If the solution in the drums cannot be used within 3 days, the drums must be returned to ETTP for storage in a RCRA-permitted area until they are needed.

### 3. ENVIRONMENTAL AND SAFETY REQUIREMENTS

The uranyl nitrate solution will be handled as a RCRA hazardous waste until it is pumped into the OHF tanks. The drums from ETTP will be manifested for shipment to ORNL and must be used within 3 days or returned to ETTP. After the drums are emptied, adsorbent will be added to solidify any residual liquid, and the drums will then be disposed of as solid low-level waste through the ORNL Radioactive Waste Operations Group.

The denaturing activity will be covered under the health and safety plan (HASP) prepared by CDM Federal and the project radiation work permit (RWP) prepared by the Lockheed Martin Energy Research Office of Radiation Protection. This will eliminate duplication of effort and provide clear lines of authority by having only one site safety and health officer and health physics technician responsible for all of the work at the site. Level 2 Nuclear Criticality Safety training is required for personnel supervising the denaturing activity. Personal protective equipment for the denaturing work will be specified by the HASP and RWP.

### 4. PROCEDURES

A detailed work instruction for the denaturing activity will be prepared by Chemical Technology Division personnel. Chemical Technology Division personnel will arrange for the drums of uranyl nitrate to be delivered to the OHF site by the Hazardous Waste Operations Group. The volume of solution needed for denaturing each tank, following planned supernate transfers by CDM Federal, is shown in the work instruction. The required volumes range from 26 to 113 gal per tank. Chemical Technology Division personnel will transfer the solution into the selected OHF tank using a drum pump, and the volume will be monitored using a battery-powered, digital flowmeter/totalizer. The uranyl nitrate will be added to each tank just prior to mixing and sluicing operations by CDM Federal personnel. The hose used to transfer the uranyl nitrate solution will be multi-layer to provide chemical compatibility and resistance to abrasion and puncture. The current site plan indicates that less than 100 ft of hose will be required. Movement of the drums on site will be coordinated with CDM Federal personnel. Between uses, the pump, totalizer, and hose will be rinsed with water, drained, sealed, bagged, and stored on site as radioactively contaminated equipment.

Chemical Technology Division personnel will be responsible for decontaminating or disposing of the pump, flowmeter and hose, and for disposing of the empty drums and used personal protective equipment generated during the denaturing activities.

All activities, results, and calculations will be documented in a registered logbook, and a copy of the relevant pages will be provided to the OHF Tanks Contents Removal Project Manager for placement in the project file.

## 5. REFERENCES

Keller, J. M., J. M. Giaquinto and A. M. Meeks, *Characterization of the Old Hydrofracture Facility (OHF) Waste Tanks Located at ORNL*, ORNL/TM-13394, Oak Ridge National Laboratory, April 1997.

**APPENDIX A. OLD HYDROFRACTURE TANKS -  
RESULTS OF ANALYSES AND CALCULATIONS**

Old Hydrofracture Tanks - Results of Analyses and Calculations							
	Tank #	T-1	T-2	T-3	T-4	T-9	Total
Liquid Volume (gal)		10780	10630	1960	14790	4930	43090
(L)		40806	40238	7419	55985	18662	163109
pH		9.3	9.5	11.6	10.4	9.1	
U (mg/L)		281	221	7.7	216	303	
U-233 (%)		0.35	0.35	0.22	0.37	0.45	
U-235 (%)		0.58	0.5	0.62	0.58	0.55	
U-238 (%)		99.17	99.15	99.16	99.15	99	
U (Kg)		11.47	8.89	0.06	12.09	5.65	38.16
U-233 (Kg)		0.040	0.031	0.000	0.045	0.025	0.142
U-235 (Kg)		0.067	0.044	0.000	0.070	0.031	0.213
U-238 (Kg)		11.37	8.82	0.06	11.99	5.60	37.83
Amount of Additional Depleted Uranium (0.20% U-235) Required for Denaturing Liquid							
Uranium (Kg)		4.8	2.7	0.0	5.7	3.5	16.7
Amount of Depleted Uranium Solution (350 g/L U) Required for Liquid							
(L)		13.7	7.7	0.0	16.2	10.1	47.7
(gal)		3.6	2.0	0.0	4.3	2.7	12.6
Sludge Volume (gal)		1410	1560	3120	2310	1140	9540
(L)		5337	5905	11810	8744	4315	36112
Density		1.33	1.33	1.31	1.25	1.58	
Sludge Weight (Kg)		7099	7854	15471	10930	6818	
U (mg/Kg)		2420	2090	5920	7870	2700	
U-233 (%)		1.23	1.07	0.74	0.89	1.2	
U-235 (%)		0.51	0.4	0.44	0.52	0.5	
U-238 (%)		98.26	98.53	98.82	98.59	98.3	
U (Kg)		17.18	16.41	91.59	86.02	18.41	229.61
U-233 (Kg)		0.211	0.176	0.678	0.766	0.221	2.051
U-235 (Kg)		0.088	0.066	0.403	0.447	0.092	1.096
U-238 (Kg)		16.88	16.17	90.51	84.81	18.10	226.46
Total Volume (gal)		12190	12190	5080	17100	6070	52630
Tank Capacity (gal)		15000	15000	25000	25000	13000	93000
Amount of Additional Depleted Uranium (0.20% U-235) Required for Denaturing Sludge.							
Uranium (Kg)		43.7	32.6	110.5	146.1	45.2	378.0
Amount of Depleted Uranium Solution (350 g/L) Required for Sludge							
(L)		125	93	316	417	129	1080
(gal)		33	25	84	110	34	286
Amount of Depleted Uranium Solution (350 g/L) Required For Sludge and Liquid							
(L)		139	101	316	434	139	1128
(gal)		37	27	84	115	37	298

<b>Old Hydrofracture Tanks - Results of Analyses and Calculations (Cont.)</b>								
	Tank #	T-1	T-2	T-3	T-4	T-9	Total	Reserve In T-3
Liquid Volume (gal)		5290	5850	1960	8660	14020	35780	7310
(L)		20024	22144	7419	32781	53070	135438	27632
pH		9.3	9.5	11.6	10.4	9.1		
U (mg/L)		281	221	7.7	216	303		217
U-233 (%)		0.35	0.35	0.22	0.37	0.385		0.367
U-235 (%)		0.58	0.5	0.62	0.58	0.55		0.567
U-238 (%)		99.17	99.15	99.16	99.15	99		
U (Kg)		5.63	4.89	0.06	7.08	14.48	32.14	6.00
U-233 (Kg)		0.020	0.017	0.000	0.026	0.056	0.119	
U-235 (Kg)		0.033	0.024	0.000	0.041	0.080	0.178	
U-238 (Kg)		5.58	4.85	0.06	7.02	14.34	31.85	
<b>Amount of Additional Depleted Uranium (0.20% U-235) Required for Denaturing Liquid.</b>								
Uranium (Kg)		2.4	1.5	0.0	3.4	6.7	16.7	2.7
<b>Amount of Depleted Uranium Solution (350 g/L U) Required for Liquid</b>								
(L)		6.9	4.3	0.0	9.7	19.2	47.7	
(gal)		1.8	1.1	0.0	2.6	5.1	12.6	
<b>Sludge Volume (gal)</b>								
(L)		5337	5905	11810	8744	4315	36112	
Density		1.33	1.33	1.31	1.25	1.58		
<b>Sludge Weight (Kg)</b>								
U (mg/Kg)		2420	2090	5920	7870	2700		
U-233 (%)		1.23	1.07	0.74	0.89	1.2		
U-235 (%)		0.51	0.4	0.44	0.52	0.5		
U-238 (%)		98.26	98.53	98.82	98.59	98.3		
U (Kg)		17.18	16.41	91.59	86.02	18.41	229.61	
U-233 (Kg)		0.211	0.176	0.678	0.766	0.221	2.051	
U-235 (Kg)		0.088	0.066	0.403	0.447	0.092	1.096	
U-238 (Kg)		16.88	16.17	90.51	84.81	18.10	226.46	
<b>Total Volume (gal)</b>								
		6700	7410	5080	10970	15160	45320	
<b>Tank Capacity (gal)</b>								
		15000	15000	25000	25000	13000	93000	
<b>Amount of Additional Depleted Uranium (0.20% U-235) Required for Denaturing Sludge.</b>								
Uranium (Kg)		43.7	32.6	110.5	146.1	45.2	378.0	
<b>Amount of Depleted Uranium Solution (350 g/L) Required for Sludge</b>								
(L)		125	93	316	417	129	1080	
(gal)		33	25	84	110	34	286	
<b>Amount of Depleted Uranium Solution (350 g/L) Required For Sludge and Liquid</b>								
(L)		132	97	316	427	148	1128	
(gal)		35	26	84	113	39	298	

**APPENDIX B. ANALYTICAL RESULTS FOR  
URANYL NITRATE SOLUTIONS**

Analytical Results for Uranyl Nitrate Solutions											
Drum ID Number	Laboratory	U (g/L)	U-238 (%)	U-235 (%)	Acid (M)	Al (mg/L)	Ca (mg/L)	Cr (mg/L)	Fe (mg/L)	Mg (mg/L)	Na (mg/L)
150759.47	RMAL	414	99.82	0.18	5.71	1450	274	367	1830	582	4040
150759.48	RMAL	394	99.80	0.20	5.80	1390	259	349	1740	551	3880
150759.49	RMAL	372	99.81	0.19	5.81	1110	247	331	1650	525	3760
150759.50	RMAL	352	99.81	0.19	4.96	1190	193	241	1230	407	2420
Composite	ASO	362	99.81	0.19	NA	1450	210	568	3850	2340	2830

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