MARTIN MARIETTA

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**ENVIRONMENTAL
RESTORATION
PROGRAM**

**Characterization Summary Report
for Pond Waste Commercial
Disposal Project**

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MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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**Characterization Summary Report for Pond Waste
Commercial Disposal Project**

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**MARTIN MARIETTA ENERGY SYSTEMS, INC.
managing the**

**Oak Ridge K-25 Site
Oak Ridge Y-12 Plant
Oak Ridge National Laboratory
under contract DE-AC05-84OR21400**

**Paducah Gaseous Diffusion Plant
Portsmouth Gaseous Diffusion Plant
under contract DE-AC05-76OR00001**

**for the
U.S. DEPARTMENT OF ENERGY**

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EXECUTIVE SUMMARY

This report is prepared to summarize information on the existing sampling and analysis results for the K-1407B and K-1407C ponds, which were used as settling and holding basins before their closure. The purpose of the document is to compare the existing data to commercial disposal facility criteria so that off-site disposal options for pond waste drums can be examined. This action is taken in response to a letter (with an action plan) sent from F. S. Patton to L. L. Radcliffe and R. C. Sleeman on July 24, 1992.

There are ~45,795 drums of stabilized sludge and ~31,954 drums of raw sludge at the Oak Ridge K-25 Site. There have been corrosion and storage problems associated with these drums. The U. S. Department of Energy would like to transport all waste drums that meet regulatory requirements to a commercial disposal facility.

The pond wastes are classified as mixed waste because of their radioactive constituents and their classification under the Resource Conservation and Recovery Act regulations as "listed hazardous waste" (F006 listed waste).

Analytical analysis of raw sludge for hazardous constituents indicated that both wet and dried sludge failed Land-Disposal Restriction (LDR) criteria for nickel and silver. Because of the failure to meet LDR requirements, it is concluded that wet and dried sludge cannot be sent to a land-disposal facility without further exemption or stabilization. Analytical analysis of stabilized sludge cubes, which were prepared during the actual field stabilization work, indicated that these cubes met LDR requirements for hazardous constituents. Because stabilized sludge cubes met the LDR requirements, stabilized sludge drums could potentially be land disposed (additional sampling/analysis will determine if the cubes are representative of the stabilized drum population).

The concentrations of specific radionuclides contained in the stabilized sludge cubes are within the maximum concentration limits listed in the Radioactive Material License of Envirocare. However, there are several radionuclides contained in the stabilized sludge that are not specifically listed in the license. Additional analytical data are required from Energy Systems to quantify the total concentrations of these radionuclides. These sampling and analysis requirements have been incorporated into the action plan for off-site disposal of pond waste. Clarification and modification of the Radioactive Material License by the disposal site is necessary to meet all Energy Systems radiological disposal requirements for radionuclides.

1. INTRODUCTION

Martin Marietta Energy Systems Inc., is pursuing implementation of an action plan that was attached to the letter from F. S. Patton to L. L. Radcliffe and R. C. Sleeman, entitled "Specific Initiative to Support Off-site Commercial Mixed Waste Disposal," dated July 24, 1992. Task IA of the action plan, to be completed by August 14, 1992, involved (1) a comparison of existing pond waste characterization data vs Envirocare criteria and (2) submittal of a report to the U. S. Department of Energy Oak Ridge Field Office (DOE-OR). In addition, any modifications to the pond waste disposal action plan resulting from necessary characterization are to be identified in a revised action plan and submitted along with the August 14, 1992 report. This report is prepared to fulfill task IA of the referenced action plan.

The key findings of this report were discussed in a briefing on July 30, 1992, which included Energy Systems personnel and representatives from DOE-OR Environmental Restoration and Waste Management divisions. This report includes a brief background on past pond waste sampling and analysis activities, summarizes analytical results on both the hazardous and the radiological constituents, provides a comparison of pond waste constituents to the Envirocare disposal facility criteria, and provides conclusions for the disposal action.

2. BACKGROUND

The K-1407B and K-1407C ponds were used as settling and holding basins at the Oak Ridge K-25 Site to receive wastes from the neutralized waste streams from the K-1501 Steam Plant, K-1401 metals cleaning facility, K-1420 plating shop, and the sludge generated from the cascade scrubber blowdown treatment system. To meet 1984 Hazardous and Solid Waste Amendments closure requirements for the Resource Conservation and Recovery Act (RCRA) by November 1988, pond wastes were removed from the basins. From 1987 to 1989, the sludge was excavated from the ponds and subsequently treated at the K-1419 Sludge Treatment Facility by mixing it with cement and fly ash to form a grout and placing the composite into 89- and 96-gal steel drums for curing and storage. The facility ran from February 1987 through March 1989. To meet closure schedules negotiated by DOE and the Tennessee Department of Environment and Conservation, fixation was halted after ~45,795 drums had been solidified; the remainder of the raw sludge was placed directly in drums.

Presently there are ~45,795 drums of stabilized sludge and ~31,954 drums of raw sludge. There have been corrosion and storage problems associated with these drums. DOE would like to transport all waste drums that meet regulatory requirements to a commercial disposal facility.

3. HAZARDOUS WASTE CONSTITUENTS SAMPLING/ANALYSIS

3.1 DESCRIPTION OF SAMPLING

Pond wastes are classified as mixed waste because of their radioactive constituents and their classification under RCRA regulations as "listed hazardous waste" (F006 listed waste).

To land dispose pond waste samples and satisfy hazardous waste concerns, the waste must meet Land-Disposal Restriction (LDR) criteria. Waste would also need to be tested for the Toxic Characterization Leaching Procedure (TCLP) to ascertain that it is not characteristically hazardous. (Earlier it was determined that pond waste meets characteristics criteria; ignitability, corrosivity, reactivity, and Extraction Procedure-Toxicity (EP-TOX) limits. However, since then the TCLP has become the standard method of testing.) Finally, the waste must be tested to determine if it can be treated as California-listed waste.

Necessary analytical information for radionuclides and hazardous constituents is found in the July 1991 sampling results¹. To characterize the waste drums, analytical analyses were conducted on (a) statistically based random samples collected from drums containing raw sludge and (b) stabilized sludge cubes that were prepared and archived during Sludge Treatment Facility operation. Figure 1 provides an overview of pond waste sampling. Stabilized sludge cubes were tested by TCLP to represent stabilized sludge drums. Raw sludge samples were analyzed after the separation of the liquid and wet sludge by decantation. An aliquot of the liquid was tested for constituents to meet California-listed waste criteria and the wet sludge was tested by TCLP and for the total constituent analysis (TCA). Following drying, the sludge was tested by TCLP.

3.2 RESULTS/CONCLUSIONS

Analytical analysis of raw sludge (wet and dried) (see Tables 1, 2, 3, and 4) indicated the following results:

- wet and dried sludge failed LDR criteria for nickel and silver (dried sludge sample results for silver were not conclusive because of high detection levels of the instrument; however, because nickel did not meet LDR requirements, analyses were not repeated);
- met TCLP limits;
- determined not to be characteristically hazardous waste; and
- determined not to be California-listed waste.

Because of the failure to meet LDR requirements, it is concluded that sludge, wet or dry, cannot be sent to a land-disposal facility without an exemption or further stabilization.

Analytical analysis of stabilized sludge cubes (see Table 5) indicated the following results:

- met LDR requirements;
- met TCLP limits; and
- determined not to be characteristically hazardous waste.

Stabilized sludge cubes met the LDR requirements and TCLP limits; therefore, stabilized sludge drums could possibly be land disposed. This disposal would be contingent on sampling stabilized sludge drums to support data obtained from stabilized sludge cubes and to meet disposal site requirements.

Fig. 1. Overview of pond waste sampling

Table 1. TCLP K-1407B Pond wet sludge result summary

Parameters	Mean (mg/L)	Maximum (mg/L)	Minimum (mg/L)	Standard	TCLP limits (mg/L)	LDR limits (m/L)
Arsenic	<0.50	<0.50	<0.50	0	5.0	NA
Barium	1.02	1.10	<1.0	0.038	100.0	NA
Cadmium	0.032	0.038	<0.030	0.003	1.0	0.066
Chromium	<0.10	<0.10	<0.10	0	5.0	5.2
Lead	<0.50	<0.50	<0.50	0	5.0	0.51
Nickel	4.4	11.0	2.1	3.1	NA	0.32*
Selenium	<0.50	<0.50	<0.50	0	1.0	NA
Silver	0.14	0.56	<0.10	0.13	5.0	0.072*
Mercury	<0.020	<0.020	<0.020	0	0.2	NA

* Does not meet Land Disposal Restriction limits.

Source: *Characterization of the K-1407 B and C Ponds Raw Sludges and Laboratory cured Concrete Cubes*, KTCD-1019, March 1992, Oak Ridge K-25 Site, Oak Ridge, Tennessee.

Table 2. TCLP K-1407/B Pond dry sludge result summary

Parameters	Mean (mg/L)	Maximum (mg/L)	Minimum (mg/L)	Standard	TCLP limits (mg/L)	LDR limits (mg/L)
Arsenic	<0.50	<0.50	<0.50	0	5.0	NA
Barium	<1.0	<1.0	<1.0	0	100.0	NA
Cadmium	0.035	0.051	<0.030	0.007	1.0	0.066
Chromium	<0.10	<0.10	<0.10	0	5.0	5.2
Lead	<0.50	<0.50	<0.50	0	5.0	0.51
Nickel	9.6	14.0	3.6	2.7	NA	0.32*
Selenium	<0.50	<0.50	<0.50	0	1.0	NA
Silver	<0.10	<0.10	<0.10	0	5.0	0.072*
Mercury	<0.020	<0.020	<0.020	0	0.2	NA

* Does not meet Land Disposal Restriction limits.

Source: Characterization of the K-1407 B and C Ponds Raw Sludges and Laboratory cured Concrete Cubes, KTCD-1019, March 1992, Oak Ridge K-25 Site, Oak Ridge, Tennessee.

Table 3. TCLP K-1407C Pond wet sludge result summary

Parameters	Mean (mg/L)	Maximum (mg/L)	Minimum (mg/L)	Standard	TCLP limits (mg/L)	LDR limits (m/L)
Arsenic	<0.50	<0.50	<0.50	0	5.0	NA
Barium	1.03	1.20	<1.0	0.072	100.0	NA
Cadmium	<0.030	<0.030	<0.030	0	1.0	0.066
Chromium	<0.10	<0.10	<0.10	0	5.0	5.2
Lead	<0.50	<0.50	<0.50	0	5.0	0.51
Nickel	3.9	9.0	0.66	1.99	NA	0.32*
Selenium	<0.50	<0.50	<0.50	0	1.0	NA
Silver	0.105	0.18	<0.10	0	5.0	0.072*
Mercury	<0.020	<0.020	<0.020	0	0.2	NA

* Does not meet Land Disposal Restriction limits.

Source: Characterization of the K-1407 B and C Ponds Raw Sludges and Laboratory cured Concrete Cubes, KTCD-1019, March 1992, Oak Ridge K-25 Site, Oak Ridge, Tennessee.

Table 4. TCLP K-1407B Pond dry sludge result summary

Parameters	Mean (mg/L)	Maximum (mg/L)	Minimum (mg/L)	Standard	TCLP limits (mg/L)	LDR limits (m/L)
Arsenic	<0.50	<0.50	0.50	0	5.0	NA
Barium	<1.0	<1.0	<1.0	0	100.0	NA
Cadmium	<0.030	<0.030	<0.030	0	1.0	0.066
Chromium	0.11	0.25	<0.10	0.040	5.0	5.2
Lead	<0.50	<0.50	<0.50	0	5.0	0.51
Nickel	4.9	16.0	0.59	4.3	NA	0.32*
Selenium	<0.50	<0.50	<0.50	0	1.0	NA
Silver	<0.10	<0.10	<0.10	0	5.0	0.072*
Mercury	<0.020	<0.020	<0.020	0	0.2	NA

* Does not meet Land Disposal Restriction limits.

Source: Characterization of the K-1407 B and C Ponds Raw Sludges and Laboratory cured Concrete Cubes, KTCD-1019, March 1992,
Oak Ridge K-25 Site, Oak Ridge, Tennessee.

Table 5. TCLP K-1407B and C Ponds stabilized sludge cubes result summary

Parameters	Mean (mg/L)	Maximum (mg/L)	Minimum (mg/L)	Standard	TCLP limits (mg/L)	LDR limits (m/L)
Arsenic	<0.50	<0.50	<0.50	0	5.0	NA
Barium	<1.0	<1.0	<1.0	0	100.0	NA
Cadmium	<0.030	<0.030	<0.030	0	1.0	0.066
Chromium	<0.10	<0.10	<0.10	0	5.0	5.2
Lead	<0.50	<0.50	<0.50	0	5.0	0.51
Nickel	<0.10	<0.10	<0.10	0	NA	0.32*
Selenium	<0.50	<0.50	<0.50	0	1.0	NA
Silver	<0.10	<0.10	<0.10	0	5.0	0.072*
Mercury	<0.020	<0.020	<0.020	0	0.2	NA
Uranium	<10.000	<10.000	<10.000	0	NA	NA

* Silver concentration is 0.060 mg/L (analysis redone April 1992).

Source: Characterization of the K-1407 B and C Ponds Raw Sludges and Laboratory cured Concrete Cubes, KTCD-1019, March 1992,
Oak Ridge K-25 Site, Oak Ridge, Tennessee.

4. RADIOLOGICAL CONSTITUENTS SAMPLING/ANALYSIS

4.1 DESCRIPTION OF ANALYSIS

As described in Sect. 3.1, the pond wastes are classified as mixed wastes because of their radionuclide content and classification as a listed hazardous waste. This section provides a comparison between existing analytical data for stabilized sludge radionuclide content and the maximum concentrations set forth in the Radioactive Material License of Envirocare.

The stabilized sludge cubes produced during Sludge Treatment Facility operation were used for testing to determine the radionuclide content of the stabilized sludge and the hazardous constituent content¹. The stabilized sludge cubes were leached in hot nitric acid for a specified length of time. The leachate was then analyzed for specific activity of certain radionuclides.^{1,2}

4.2 RESULTS/CONCLUSIONS

A copy of the Radioactive Material License issued to Envirocare by the state of Utah was used for comparison with the analytical results from the stabilized sludge cubes. A detailed breakdown of the stabilized sludge cubes data and Envirocare's concentration limits are contained in Table 6. This comparison yielded the following results.

- Technetium-99, Neptunium-237, and Plutonium-238, -239, -240, -241, and -242 are not currently included in the Envirocare license; these radionuclides are present in the stabilized sludge cubes.
- Several radionuclides contained in the stabilized sludge cubes are listed in Envirocare's license; the concentrations of these specific radionuclides were less than the concentration limits in the license.
- Envirocare can currently accept Uranium-235 at concentrations <770 pCi/g; however, no more than 350 g of Uranium-235, as related to special nuclear material, can be present in any one shipment; Uranium-233 is not listed in their license.
- The sum of fractions of radionuclide concentration must be used to determine the total concentration of radionuclides per shipment.
- Envirocare is currently talking to the state of Utah with regards to including Technetium-99 and Neptunium-237 into their groundwater model for inclusion in the Radioactive Material License; Plutonium-238, -239, -240, -241, and -242 were originally included in the groundwater model but are not currently included in Envirocare's license.
- Envirocare is currently talking to the Nuclear Regulatory Commission with regards to increasing the quantity of special nuclear material they can have on site.
- Envirocare requires gamma spectral analysis for all natural and manmade radionuclides; this is not a requirement of the license but is necessary for total radionuclide

concentration calculations. Any available testing information and characterization data for pond waste should be included with each shipment.

This comparison identified several areas that need to be addressed. It is necessary for Energy Systems to analyze for Uranium-233, -234, -235, and -238 separately so that the concentration of each can be calculated. It is also necessary to calculate the total quantity of special nuclear material per shipment. This number is somewhat dependent on the mode of shipment, whether by rail or truck. The total quantity of special nuclear material contained in each stabilized sludge drum will need to be calculated once the stabilized sludge sampling and analysis is complete. The leachant extraction procedure currently used to determine radionuclide content may need to be supplemented with gamma spectral analysis. However, this additional analytical technique may not be necessary if Envirocare concurs with the current technique.

Table 6. Radionuclide Data Comparison

Radioactive material	K-1407-B sludge mean concentration (pCi/g)	K-1407-C sludge mean concentration (pCi/g)	Stabilized sludge mean concentration (pCi/g)	ENVIROCARE Radioactive Material License	
				maximum concentration (pCi/g)	
Uranium (total)	---	---	100.7	(Not required)	
Uranium-234	---	---	---	3.70E+04	
Uranium-235	20.8	14.8	---	7.70E+02	
Uranium-238	---	---	---	2.80E+04	
Uranium-natural	---	---	---	1.80E+04	
Uranium-depleted	---	---	---	1.10E+05	
Cesium-137	7.28	19.1	3.73	5.60E+02	
Technetium-99	2860	1110	160.2	NA	
Neptunium-237	10.87	24.3	2.38	NA	
Plutonium-238	2.78	54.9	0.13	NA	
Plutonium-239/240	10.3	24.4	2.68	NA	
Thorium-228	1.07	12.3	---	(1)	
Thorium-230	66.8	67.1	---	1.50E+04	
Thorium-232	3.23	4.1	---	6.80E+02	
Thorium-234	200.7	132	---	(1)	
Protactinium-234m	379	438	---	(1)	

NA = Not in license

(1) = Parent radionuclide included in license.

5. SUMMARY AND REVISED ACTION PLAN

On the basis of analytical results obtained from the stabilized sludge cubes and raw sludge samples (wet and dried), it is concluded that raw sludge did not meet LDR requirements and, therefore, cannot be land disposed. Stabilized sludge cubes did meet LDR requirements. Commercial disposal of the stabilized sludge at a permitted/licensed mixed waste disposal site is viable.

Additional sampling and analysis is necessary to characterize the stabilized sludge drums so that analytical results obtained from the stabilized sludge cubes can be confirmed. A quality assurance plan² and a statistical analysis report³ to support the sampling and analysis plan are prepared for characterizing stabilized drums. Sampling of stabilized drums was initiated on July 20, 1992, and is expected to be finalized by March 19, 1993.

The comparison of existing analytical results from the stabilized sludge cubes with the Radioactive Material License of Envirocare signifies the need for additional radiological sampling by Energy Systems and modification of Envirocare's license. Energy Systems will determine if Envirocare will substitute leachate extraction radionuclide analysis for the gamma spectral analysis; however, if this substitution is not acceptable, gamma spectral analysis will be performed.

The revised action plan for off-site disposal of stabilized pond waste at a commercial disposal facility is presented on the next page. This action plan has been revised to include sampling and analysis milestones (see 1C, 1D, and 1E for sampling, analysis, and report preparation). Revised items are designated on the left side. The Energy Systems Environmental Restoration Program will continue implementation of off-site disposal actions following the indicated milestones in the subject plan. Any future revisions to this plan will be incorporated by Energy Systems and resubmitted to DOE-OR.

Action Plan for Off-Site Disposal of K-25 Waste

	Task name	Start date	Finish date
	IA. Energy Systems to compare existing pond waste characterization data vs Envirocare criteria and submit report to DOE-OR.	07/24/92	08/14/92
	IB. DOE-OR to review Energy Systems report and approve modifications of tasks on action plan.	08/14/92	08-18/92
R1	IC. Stabilized sludge sampling.	07/20/92	12/18/92
R1	ID. Stabilized sludge analysis.	07/20/92	02/05/93
R1	IE. Laboratory analysis report.	02/05/93	03/19/93
	IIA. DOE-OR to obtain contract for commercial mixed waste disposal with Energy Systems support.	07/24/92	03/93
	IIB. Energy Systems/DOE Envirocare facility inspection to verify acceptability.	12/01/92	12/18/92
	IIIA. Energy Systems to prepare 5820.2A exemption for pond waste and submit to DOE-OR.	07/31/92	08/28/92
	IIIB. DOE review 5820.2A exemption and submit to DOE-HQ for approval.	08/28/92	09/30/92
	IIIC. DOE-HQ review and approve 5820.2A exemption for pond waste disposal at Envirocare.	09/30/92	02/93
	IVA. Energy Systems to submit NEPA categorical exclusion to DOE-OR covering transport of pond waste from ORR to Envirocare.	09/01/92	09/30/92
	IVB. DOE-OR to review and approve NEPA categorical exclusion.	09/30/92	11/30/92
	V. Energy Systems to prepare and approve shipping documentation (procedures, certification plan, safety assessment, quality assurance plan) to ship pond waste to Envirocare.	11/01/92	04/93
	VI. Energy Systems to obtain contract for transportation of pond waste to Envirocare.	12/31/92	06/93
	VII. Energy Systems training for off-site waste disposal.	05/93	06/93
	VIII. Energy Systems to conduct operational readiness review for off-site disposal of pond waste.	06/93	07/93
	IX. DOE-OR to approve initiation of shipments to Envirocare.	07/93	08/93
	X. Energy Systems to complete 13 pond waste shipments to Envirocare (10,400 ft ³) pending funding in FY 1993.	08/93	09/93

6. REFERENCES

1. C. R. Kirkpatrick, et. al. *Characterization of the K-1407 B and C Ponds Raw Sludges and Laboratory Cured Concrete Cubes*, KTCD-1019, Martin Marietta Energy Systems, Inc., Oak Ridge K-25 Site, Oak Ridge, Tenn., March 1992.
2. Analytical Chemistry Department of the Technical Division, *Quality Assurance Project Plan for Sampling and Analysis of K-1407-B and -C Ponds Raw and Stabilized Sludges at the K-25 Site*, AP:Q4-91-003, Martin Marietta Energy Systems, Inc., Oak Ridge K-25 Site, Oak Ridge, Tenn., Oct. 1991.
3. J. W. Zolyniak. *Sampling Plans, Statistical Models, and Data Analysis Outlines for Statistical Characterization of the Drums of Solidified Concreted Sludge from the K-1407-B Holding Pond and the K-1407-C Retention Basin K/QT-393*, Martin Marietta Energy Systems, Inc., Oak Ridge K-25 Site, Oak Ridge, Tenn., February 1992.

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