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Department of Energy
Albuquerque Operations Office
Los Alamos Area Office
Los Alamos, New Mexico 87544

SEP 27 1996

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CERTIFIED MAIL - RETURN RECEIPT REQUESTED

Mr. Benito Garcia, Bureau Chief
Hazardous and Radioactive Materials Bureau
New Mexico Environment Department
2044 Galisteo St., Bldg. A
P. O. Box 26110
Santa Fe, NM 87505

Dear Mr. Garcia:

Subject: Treatability Study Notification

The purpose of this letter is to provide notification of intent to conduct seven mixed waste treatability studies at Los Alamos National Laboratory (LANL), pursuant to Title 20 of the New Mexico Administrative Code, Chapter 4, Part 1, which incorporates Title 40 of the Code of Federal Regulations, 261.4(f). The studies will be conducted jointly by the Materials Research and Processing Science Group (MST-5) and the Environmental Systems and Waste Characterization Group (CST-7). The waste samples to be studied contain highly enriched uranium as well as regulated hazardous waste constituents. These waste streams were generated at the Department of Energy's Portsmouth Gaseous Diffusion Plant (PORTS) in Piketon, Ohio, and are covered wastes in PORTS' Site Treatment Plan (STP).

These treatability studies are intended to determine the effectiveness of various treatment technologies associated with the new Uranium Line for Special Separation Science (ULISSES) located in the CMR Building at Los Alamos National Laboratory (LANL) on a variety of mixed wastes. These technologies will treat the waste to reduce the health and safety concerns associated with mixed waste by separating the radionuclides for recovery and reuse, thereby making the secondary residue from these treatment processes more amenable for subsequent treatment, storage, and disposal. Treatment processes specified in the enclosed treatability studies include:

1. Degreasing with dodecane, filter to collect the solid material, calcine the filtered solids at 900°C in air, leaching of the solids with nitric acid, precipitation with either ammonium hydroxide or hydrogen peroxide, filtration of the solids, calcination of the precipitate to U_3O_8. Ammonium hydroxide precipitation of the filtrate, drying of precipitate (hazardous constituents), or ion exchange and/or extraction chromatography of filtrate and elution of non-actinide and non-lanthanide constituents, followed by hydroxide precipitation, and calcination (hazardous constituents);

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2. Fluorination at 300°C with F_2, collection at -40°C of UF_6, calcination of the residue solids at 900°C in air, followed by leaching of the solids with nitric acid, if necessary, precipitation with either ammonium hydroxide or hydrogen peroxide, filtration of the solids, ammonium hydroxide precipitation of the filtrate, drying of the precipitate (hazardous constituents), or ion exchange and/or extraction chromatography of filtrate and elution of non-actinide and non-lanthanide constituents, followed by hydroxide precipitation, and calcination (hazardous constituents);

3. Calcination, followed by leaching of the solids with nitric acid, precipitation with ammonium hydroxide or hydrogen peroxide, filtration of the solids, ammonium hydroxide precipitation of the filtrate, drying of the precipitate (hazardous constituents), or ion exchange and/or extraction chromatography of filtrate and elution of non-actinide and non-lanthanide constituents, followed by hydroxide precipitation, and calcination (hazardous constituents);

4. Leaching of the solids with nitric acid, precipitation with ammonium hydroxide or hydrogen peroxide, filtration of the solids, ammonium hydroxide precipitation of the filtrate, drying of the precipitate (hazardous constituents), or ion exchange and/or extraction chromatography of filtrate and elution of non-actinide and non-lanthanide constituents, followed by hydroxide precipitation, and calcination (hazardous constituents);

5. Pyrohydrolysis to convert fluorides to their metal oxides, accompanied by scrubbing of hydrogen halides with aqueous potassium hydroxide, leaching of the solids with nitric acid, precipitation with ammonium hydroxide or hydrogen peroxide, filtration of the solids, ammonium hydroxide precipitation of the filtrate, drying of the precipitate (hazardous constituents), or ion exchange and/or extraction chromatography of filtrate and elution of non-actinide and non-lanthanide constituents, followed by hydroxide precipitation, and calcination (hazardous constituents);

6. Fluorination at 300-500°C with F_2 or ClF_3, collection at -40°C of UF_6, followed by calcination, leaching of the solids with nitric acid, precipitation with either ammonium hydroxide or hydrogen peroxide, filtration of the solids, ammonium hydroxide precipitation of the filtrate, drying of the precipitate (hazardous constituents), or ion exchange and/or extraction chromatography of filtrate and elution of non-actinide and non-lanthanide constituents, followed by hydroxide precipitation, and calcination (hazardous constituents).

The waste streams generated at PORTS to be treated are described below:

1. "Oil Leak Gunk" consists of lubrication oil that leaked into uranium hexafluoride process lines where their subsequent reaction generated a solid mixed waste.

2. "X-710 Gunk" is a solid mixed waste routinely generated during filtration and evaporation operations occurring in the PORTS analytical chemistry laboratory.

3. "Filter Ash" consists of nonvolatile metal fluorides and U_3O_8 generated by filtration of particulates from UF_6 materials using a metallic filter.

4. "Freon Degrader Residue" consists of metal fluorides and nonvolatile uranium fluorides generated during the degradation process applied to various Freon compounds used at PORTS. Fluorine gas reacted with Freon-114 to form carbon tetrafluoride (CF_4). Gaseous metal fluorides reacted with the degrader surface to form nonvolatile transition metal fluorides.

Because "Oil Leak Gunk" will be included in two different treatment processes and "Freon Degrader Residue" will be included in three different treatment processes, LANL will be conducting seven separate treatability studies. Descriptions of these studies are enclosed.

A total of 95.4 kilograms (kg) of waste samples will be treated in the seven studies. The enclosed descriptions of individual treatability studies list the total amount of waste to be accepted on-site at LANL per waste stream. Although "Oil Leak Gunk" and "Freon Degrader Residue" are included in more than one study, the total amount being accepted at LANL is specified in each study. Thus, please note that the total amount for both studies using "Oil Leak Gunk" is 75.7 kg and the total amount for all three studies using "Freon Degrader Residue" is 5.2 kg. each

Although unlikely, should any untreated waste samples not be used during the treatability study, they will be returned to PORTS. All treated secondary wastes, effluents, and scrubber solutions will be analyzed for proper characterization. If the secondary wastes, effluents, and scrubber solutions do not exhibit the characteristics of a hazardous waste, they will be managed as radioactive waste. If the secondary wastes do exhibit the characteristics of a hazardous waste, they will either be sent directly off site to a permitted treatment, storage, and disposal facility, or sent back to the generator (PORTS). After determining the uranium content, effluent from the treatment process will be profiled and submitted with analysis to the Chemistry and Mixed Waste Science Group for approval prior to discharge to the TA-50 Radioactive Waste Treatment Plant. Treatment technologies will be used to minimize the amount of waste that will be returned to Portsmouth. Wastes, returned to PORTS, will be in a form that will allow for facile disposal.

If you have any questions, please contact me at (505) 665-5042.

Sincerely,

H. L. "Jody" Plum
Office of Environment and Projects

LAAMEP:6JP-017

Enclosures

cc :
See page 4

SEP 27 [illegible]

cc w/enclosures:
S. Dinwiddie
Hazardous and Radioactive
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2044 Galisteo St., Bldg. A
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J. Archuleta
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ENCLOSURE

TREATABILITY STUDIES PROCESS DESCRIPTION

RECOVERY AND RECYCLING OF HIGHLY ENRICHED URANIUM FROM MIXED WASTE: OIL LEAK GUNK

Los Alamos
NATIONAL LABORATORY

Hazardous & Solid Waste Group
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Facility Name:	**Los Alamos National Laboratory (LANL)** **Materials Science & Technology Division, Group: MST-5** **Chemical Science & Technology Division, Group: CST-7**
Facility EPA ID Number:	**NM0890010515**
Project Title:	**Recovery and Recycling of Highly Enriched Uranium from Mixed Waste: Oil Leak Gunk**
Location of Project:	**Technical Area (TA)-3, Building SM-29 (the Chemistry, Metallurgy, Research Building [CMR Building]), Wings 4 and 9 in the Basement**
Project Contacts:	**Mike H. West, Ph.D.** **MST-5, Mail Stop G730** **(505) 665-5734** **John R. FitzPatrick, Ph.D.** **CST-7, Mail Stop G739** **(505) 665-1761**

Project Description:

This project consists of one (1) treatability study involving a mixed waste that was generated at the Portsmouth Gaseous Diffusion Plant in Portsmouth, Ohio (PORTS). The PORTS facility is operated by Lockheed Martin for the Department of Energy. This project is intended to determine the effectiveness of various treatment technologies, associated with the new Uranium Line for Special Separation Science (ULISSES), located in the CMR Building at LANL, on a variety of mixed wastes (i.e., wastes that contain both hazardous constituents and radioactive constituents). This technology may concentrate the hazardous constituents in the waste and will treat the mixed waste to reduce the health and safety concerns, associated with mixed waste, by separating the radionuclides for recovery and re-use at LANL or other Department of Energy facilities.

Project Goals and Objectives:

The goals of this project are to demonstrate:

1. The feasibility of this treatment technology for the safe, economical, and efficient treatment of some special types of lubricating oil-based mixed waste, and

2. To evaluate the ease of recovering and recycling radionuclides from this process waste using standard aqueous recovery processes. The objective of this treatability study is to evaluate this uranium recovery technology on mixed waste created by

exposure of uranium hexafluoride (UF_6) to pump oils (Oil Leak Gunk). Furthermore, the proposed treatment technology will reduce the radionuclide concentration in the mixed waste and will recover the radionuclides making the secondary residue from this treatment process more amenable for subsequent waste management and/or treatment capabilities. To facilitate any subsequent treatment and storage, the hazardous constituents will be isolated from the original matrix in as small a volume and mass as possible.

At the completion of this study, this technology will be compared with other residue treatment technologies that have been proposed for use in ULISSES. The goal is to identify the most effective recovery processes for highly enriched uranium with respect to these mixed waste types. The information, obtained from the study, will be shared with other uranium processing facilities in the public and private sectors. LANL is generating waste similar to the Oil Leak Gunk. Thus, the technology developed in this treatability study will have applicability to mixed waste currently generated or stored at LANL.

Project Tasks:

Obtain mixed-waste samples from the generator. Treat the mixed waste using the technology listed below. Determine the uranium and hazardous constituent removal efficiency of the treatment process and identify the treatment products.

Project Milestones:

1. Start date will be a minimum of 45 days after submittal of the treatability study notification to NMED.
2. Complete testing of Oil Leak Gunk by June 1, 1997.

Qualifications:

Key Staff Experience: Mike H. West: Ph.D. in Inorganic Chemistry, Washington State University, 1976. Current position, LANL technical staff member in MST-5. Over 13 years experience in process development and fundamental actinide research. For the past two years focused on developing treatment processes for radioactive and mixed waste and on recovering and recycling strategic metals.

John R. FitzPatrick: Ph.D. in Inorganic Chemistry, University of Utah, 1976. Current position, LANL technical staff member in CST-7. Eighteen years experience in actinide processing, flowsheet development, equipment design, set-up and operation for the recovery of plutonium and uranium from various process residues.

Equipment and Facilities:

Bench scale equipment is located in Wing-4 of the Uranium Laboratory at the CMR Building for performing various experiments on mixed waste samples. In addition, gloveboxes are available in the same area for demonstrating the most appropriate treatability approach on a larger scale for each type of waste. Analytical chemistry analyses are available in Wings-3, -5, -7, or -9 to measure the amount of hazardous constituents remaining in both the secondary process waste and in the recovered enriched uranium fraction. For example, inductively coupled plasma-atomic emission spectrometry,

inductively coupled plasma-mass spectrometry, and quantitative uranium assays by Davies-Gray titration are available. The uranium in solution can be easily measured using Liquid Scintillation Counting (LSC) techniques, available in Wing-5. By early calendar year 1997, glove boxes will also be available in Wing-9 of the CMR Building.

Project Discussion:

Description of Waste to Be Treated: Oil Leak Gunk - Oil Leak Gunk consists of lubrication oil that leaked into uranium hexafluoride (UF_6) process lines where their subsequent reaction generated a solid mixed waste.

Sample Waste Amounts to be Treated: 75.7 kg

RCRA Waste Code(s): Mixed - D007 (Cr) and D008 (Pb)

Site Treatment Plan Information: Because this waste stream was generated at PORTS, it is not covered by the Compliance Plan Volume of LANL's Federal Facility Compliance Order Site Treatment Plan.

Description of The Waste Treatment Technology: Preliminary work at PORTS (Letter from Keith Banks to Ralph Wilcoxon, April 10, 1996) has shown that reaction of this matrix with H_2SO_4 until the disappearance of fumes and subsequent leaching of the residue with dilute and concentrated nitric acid (HNO_3) removed 84.6 to 103.7% of the uranium. According to Lockheed Martin, extraction with trioctylphosphine oxide (TOPO) also appeared to be feasible. Degreasing of the oil leak gunk with dodecane or some other non-regulated solvent (i.e., not regulated as a hazardous waste in accordance with Title 20 of the New Mexico Administrative Code, Chapter 4, Part 1 [20 NMAC 4.1]) should also be successful, assuming there are no organometallic uranium compounds present. This is the approach that will be taken for this treatability study. After degreasing, filtration, and washing, one or two subsequent leaching steps with dilute HNO_3 will then remove uranium from the residue. The uranium can be recovered from the nitric acid solution by precipitation with ammonium hydroxide (NH_4OH) or hydrogen peroxide (H_2O_2), followed by filtration through appropriate filtration media, and calcination to U_3O_8 at temperatures up to 900°C. The U_3O_8 is a stable product for storage and/or recycle.

Hydrogen peroxide precipitation of uranium allows for separation from metallic impurities relative to NH_4OH precipitation, and the filtrate can be subjected to a basic precipitation step where the hazardous constituents are collected in a hydroxide precipitate. This precipitate is then dried for storage. Alternatively, the filtrate from the H_2O_2 precipitation can be acidified to 4M HNO_3 and loaded onto a column of TRU-Spec or Actinide-Spec resins, supplied by Eichrom Industries (Reference: Procedure 620.1, "Extraction Chromatography Cleanup of Homogeneous Solids and Soil/Gravel Samples Undergoing Total Metals Analysis," from: Transuranic Waste Characterization Sampling and Analysis Methods Manual, Report No. DOE/WIPP-91-043, May 1995). The hazardous constituents are eluted from the column with 4M HNO_3, and the actinide elements are retained by the resin. The acidic eluate is subjected to a basic precipitation step as discussed above. The actinides are either left on the resin or subsequently removed by a low acidity eluent. The degreasing solution can be appropriately treated (destroyed) by techniques such as molten salt oxidation.

Because the CMR-Building Wings contain filter towers with HEPA filters, there is virtually no chance that hazardous or radioactive air emissions could occur from this treatment process. In addition, the glove boxes have a separate HEPA filtration system.

Waste Management: Although unlikely, should any untreated Oil Leak Gunk waste samples not be used during the treatability study, they will be returned to PORTS. All treated secondary wastes, effluents, and scrubber solutions will be analyzed for proper characterization. If the secondary wastes, effluents, and scrubber solutions do not exhibit the characteristics of a hazardous waste, they will be managed as radioactive waste. If the secondary wastes do exhibit the characteristic of a hazardous waste, they will either be sent directly off-site to a permitted treatment, storage, and disposal facility, or sent back to the generator (PORTS). After determining the uranium content, effluent from the treatment process will be profiled and submitted with analysis to the Chemistry and Mixed Waste Science Group for approval prior to discharge to the TA-50 Radioactive Waste Treatment Plant. Treatment technologies will be used to minimize the amount of waste that will be returned to Portsmouth. Wastes, returned to PORTS, will be in a form that will allow for facile disposal.

ENCLOSURE

TREATABILITY STUDIES PROCESS DESCRIPTION

RECOVERY AND RECYCLING OF HIGHLY ENRICHED URANIUM FROM MIXED WASTE: FLOURINATION OF OIL LEAK GUNK

Los Alamos
NATIONAL LABORATORY

Hazardous & Solid Waste Group
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Facility Name:	**Los Alamos National Laboratory (LANL)** **Materials Science & Technology Division, Group: MST-5** **Chemical Science & Technology Division, Group: CST-7**
Facility EPA ID Number:	**NM0890010515**
Project Title:	**Recovery and Recycling of Highly Enriched Uranium from Mixed Waste: Fluorination of Oil Leak Gunk**
Location of Project:	**Technical Area (TA)-3, Building SM-29 (the Chemistry, Metallurgy, Research Building [CMR Building]), Wings 4 and 9 in the Basement**
Project Contacts:	**Mike H. West, Ph.D.** **MST-5, Mail Stop G730** **(505) 665-5734** **John R. FitzPatrick, Ph.D.** **CST-7, Mail Stop G739** **(505) 665-1761**

Project Description:

This project consists of one (1) treatability study involving a mixed waste that was generated at the Portsmouth Gaseous Diffusion Plant in Portsmouth, Ohio (PORTS). The PORTS facility is operated by Lockheed Martin for the Department of Energy. This project is intended to determine the effectiveness of various treatment technologies, associated with the new Uranium Line for Special Separation Science (ULISSES), located in the CMR Building at LANL, on a variety of mixed wastes (i.e., wastes that contain both hazardous constituents and radioactive constituents). This technology may concentrate the hazardous constituents in the mixed waste and will treat the mixed waste to reduce the health and safety concerns associated with mixed waste by separating the radionuclides for recovery and reuse at LANL or other Department of Energy facilities.

Project Goals and Objectives:

The goals of this project are to demonstrate:

1. The feasibility of this treatment technology for the safe, economical, and efficient treatment of special types of lubricating oil-based mixed waste, and

2. To evaluate the ease of recovering and recycling radionuclides from this process waste using standard aqueous recovery processes. The objective of this treatability study is to evaluate this uranium recovery technology on wastes created by

exposure of uranium hexafluoride (UF_6) to pump oils (Oil Leak Gunk). Furthermore, the proposed treatment technology will reduce the radionuclide concentration in the mixed waste and will recover the radionuclides making the secondary residue from this treatment process more amenable for subsequent waste management and/or treatment capabilities. To facilitate any subsequent treatment and storage, the hazardous constituents will be isolated from the original matrix in as small a volume and mass as possible.

At the completion of this study, the technology used will be compared with other residue treatment technologies that have been proposed for use in ULISSES. The goal is to identify the most effective recovery processes for highly enriched uranium with respect to these mixed-waste types. The information obtained from the study will be shared with other uranium processing facilities in the public and private sectors. LANL is generating waste similar to the Oil Leak Gunk; thus, the technology developed in this treatability study will have applicability to mixed waste currently generated or stored at LANL.

Project Tasks:

Obtain mixed-waste samples from the generator. Treat the mixed waste using the technologies listed below. Determine the uranium and hazardous constituent removal efficiency of the treatment process and identify the treatment products.

Project Milestones:

1. Start date will be a minimum of 45 days after submittal of the treatability study notification to NMED.
2. Complete testing of Oil Leak Gunk by June 1, 1997.

Qualifications:

Key Staff Experience: Mike H. West: Ph.D. in Inorganic Chemistry, Washington State University, 1976. Current position, LANL technical staff member in MST-5. Over 13 years experience in process development and fundamental actinide research. For the past two years focused on developing treatment processes for radioactive and mixed waste and on recovering and recycling strategic metals.

John R. FitzPatrick: Ph.D. in Inorganic Chemistry, University of Utah, 1976. Current position, LANL technical staff member in CST-7. Eighteen years experience in actinide processing, flowsheet development, equipment design, set-up and operation for the recovery of plutonium and uranium from various process residues.

Equipment and Facilities:

Bench scale equipment is located in Wing-4 of the Uranium Laboratory at the CMR Building for performing various experiments on mixed waste samples. In addition, gloveboxes are available in the same area for demonstrating the most appropriate treatability approach on a larger scale for each type of waste. Analytical chemistry analyses are available in Wings-3, -5, -7, or -9 to measure the amount of hazardous constituents remaining in both the secondary process waste and in the recovered enriched uranium fraction. For example, inductively coupled plasma-atomic emission spectrometry,

inductively coupled plasma-mass spectrometry, and quantitative uranium assays by Davies-Gray are available. The uranium in solution can be easily measured using Liquid Scintillation Counting (LSC) techniques, available in Wing-5. By early calendar year 1997, glove boxes will also be available in Wing-9 of the CMR Building.

Project Discussion:

Description of Waste to Be Treated: Oil Leak Gunk - Oil Leak Gunk consists of lubrication oil that leaked into uranium hexafluoride (UF_6) process lines where their subsequent reaction generated a solid mixed waste.

Sample Waste Amounts to be Treated: 75.7 kg

RCRA Waste Code(s): Mixed - D007 (Cr) and D008 (Pb)

Site Treatment Plan Information: Because this waste stream was generated at PORTS, it is not covered by the Compliance Plan Volume of LANL's Federal Facility Compliance Order Site Treatment Plan.

Description of The Waste Treatment Technology: The organic matrix (i.e., paraffin hydrocarbons) of Oil Leak Gunk may be converted to volatile carbon tetrafluoride (CF_4) by direct use of fluorine at elevated temperatures (300°C). However, the uranium would likely be converted to UF_6 which then must be removed cryogenically at -40°C. Every effort will be made to trap the CF_4 generated by the reaction with F_2. Since PORTS is the national storage center for UF_6, the UF_6 will be returned to PORTS. MST-5 is presently consolidating UF_6 holdings at LANL and returning the UF_6 to PORTS for storage.

The residue, remaining from the reaction with F_2, will be calcined at 800°C to remove any remaining organic material or carbon. The calcination product will be analyzed for uranium content and processed further if recoverable quantities are found. Any recoverable uranium will be removed by one or two leaching steps with dilute HNO_3. The uranium can be recovered from the nitric acid solution by precipitation with ammonium hydroxide (NH_4OH) or hydrogen peroxide (H_2O_2), followed by filtration through appropriate filtration media, and calcination to U_3O_8 at temperatures up to 900°C. The U_3O_8 is a stable product for storage and/or recycle.

Hydrogen peroxide precipitation of uranium allows for separation from metallic impurities relative to NH_4OH precipitation, and the filtrate can be subjected to a basic precipitation step where the hazardous constituents are collected in a hydroxide precipitate. This precipitate is then dried for storage. Alternatively, the filtrate from the H_2O_2 precipitation can be acidified to 4M HNO_3 and loaded onto a column of TRU-Spec or Actinide-Spec resins, supplied by Eichrom Industries (Reference: Procedure 620.1, "Extraction Chromatography Cleanup of Homogeneous Solids and Soil/Gravel Samples Undergoing Total Metals Analysis," from: Transuranic Waste Characterization Sampling and Analysis Methods Manual, Report No. DOE/WIPP-91-043, May 1995). The hazardous constituents are eluted from the column with 4M HNO_3, and the actinide elements are retained by the resin. The acidic eluate is subjected to a basic precipitation step as discussed above. The actinides are either left on the resin or subsequently removed by a low acidity eluent.

Because the CMR-Building Wings contain filter towers with HEPA filters, there is virtually no chance that hazardous or radioactive air emissions could occur from this treatment process. In addition, the glove boxes have a separate HEPA filtration system.

Waste Management: Although unlikely, should any untreated Oil Leak Gunk waste samples not be used during the treatability study, they will be returned to PORTS. All treated secondary wastes, effluents, and scrubber solutions will be analyzed for proper characterization. If the secondary wastes, effluents, and scrubber solutions do not exhibit the characteristics of a hazardous waste, they will be managed as radioactive waste. If the secondary wastes do exhibit the characteristic of a hazardous waste, they will either be sent directly off-site to a permitted treatment, storage, and disposal facility, or sent back to the generator (PORTS). After determining the uranium content, effluent from the treatment process will be profiled and submitted with analysis to the Chemistry and Mixed Waste Science Group for approval prior to discharge to the TA-50 Radioactive Waste Treatment Plant. Treatment technologies will be used to minimize the amount of waste that will be returned to Portsmouth. Wastes, returned to PORTS, will be in a form that will allow for facile disposal. The UF_6 will be returned to PORTS for consolidation and storage.

ENCLOSURE

TREATABILITY STUDIES PROCESS DESCRIPTION

RECOVERY AND RECYCLING OF HIGHLY ENRICHED URANIUM FROM MIXED WASTE: X-710 GUNK

Los Alamos
NATIONAL LABORATORY

Hazardous & Solid Waste Group
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Facility Name:	**Los Alamos National Laboratory (LANL)** **Materials Science & Technology Division, Group: MST-5** **Chemical Science & Technology Division, Group: CST-7**
Facility EPA ID Number:	**NM0890010515**
Project Title:	**Recovery and Recycling of Highly Enriched Uranium from Mixed Waste: X-710 Gunk**
Location of Project:	**Technical Area (TA)-3, Building SM-29 (the Chemistry, Metallurgy, and Research Building [CMR Building]), Wings 4 and 9 in the Basement**
Project Contacts:	**Mike H. West, Ph.D.** **MST-5, Mail Stop G730** **(505) 665-5734** **John R. FitzPatrick, Ph.D.** **CST-7, Mail Stop G739** **(505) 665-1761**

Project Description:

This project consists of one (1) treatability study involving a mixed waste that was generated at the Portsmouth Gaseous Diffusion Plant in Portsmouth, Ohio (PORTS). The PORTS facility is operated by Lockheed Martin for the Department of Energy. This project is intended to determine the effectiveness of various treatment technologies, associated with the new Uranium Line for Special Separation Science (ULISSES), located in the CMR Building at LANL, on a variety of mixed wastes (i.e., wastes that contain both hazardous constituents and radioactive constituents). This technology may concentrate the hazardous constituents in the mixed waste and treat the mixed waste to reduce the health and safety concerns associated with mixed waste by separating the radionuclides for recovery and re-use at LANL or other Department of Energy facilities.

Project Goals and Objectives:

The goals of this project are to demonstrate:

1. The feasibility of this treatment technology for the safe, economical, and efficient treatment of special types of mixed waste from analytical residues, and

2. To evaluate the ease of recovering and recycling radionuclides from this process waste using standard aqueous recovery processes. The objective of this treatability study is to evaluate this uranium recovery technology on mixed wastes generated

by analytical chemistry procedures (X-710 Gunk). Furthermore, the proposed treatment technology will reduce the radionuclide concentration in the mixed waste and will recover the radionuclides making the secondary residue from this treatment process more amenable for subsequent waste management and/or treatment capabilities. To facilitate any subsequent treatment and storage, the hazardous constituents will be isolated from the original matrix in as small a volume and mass as possible.

At the completion of this study, the technology used will be compared with other residue treatment technologies that have been proposed for use in ULISSES. The goal is to identify the most effective recovery processes for highly enriched uranium with respect to these mixed-waste types. The information obtained from the study will be shared with other uranium processing facilities in the public and private sectors. LANL is generating waste similar to the X-710 Gunk; thus, the technologies developed in this set of treatability studies will have applicability to mixed waste currently generated or stored at LANL.

Project Tasks:

Obtain mixed-waste samples from the generator. Treat the mixed waste using the technology listed below. Determine the uranium and hazardous constituent removal efficiency of the treatment process and identify the treatment products.

Project Milestones:

1. Start date will be a minimum of 45 days after submittal of the treatability study notification to NMED.
2. Complete testing of X-710 Gunk by June 1, 1997.

Qualifications:

Key Staff Experience: Mike H. West: Ph.D. in Inorganic Chemistry, Washington State University, 1976. Current position, LANL technical staff member in MST-5. Over 13 years experience in process development and fundamental actinide research. For the past two years focused on developing treatment processes for radioactive and mixed waste and on recovering and recycling strategic metals.

John R. FitzPatrick: Ph.D. in Inorganic Chemistry, University of Utah, 1976. Current position, LANL technical staff member in CST-7. Eighteen years experience in actinide processing, flowsheet development, equipment design, set-up and operation for the recovery of plutonium and uranium from various process residues.

Equipment and Facilities:

Bench scale equipment is located in Wing-4 of the Uranium Laboratory at the CMR Building for performing various experiments on mixed waste samples. In addition, gloveboxes are available in the same area for demonstrating the most appropriate treatability approach on a larger scale for each type of waste. Analytical chemistry analyses are available in Wings-3, -5, -7, or -9 to measure the amount of hazardous constituents remaining in both the secondary process waste and in the recovered enriched

uranium fraction. For example, inductively coupled plasma-atomic emission spectrometry, inductively coupled plasma-mass spectrometry, and quantitative uranium assays by Davies-Gray are available. The uranium in solution can be easily measured using Liquid Scintillation Counting (LSC) techniques, available in Wing-5. By early calendar year 1997, glove boxes will also be available in Wing-9 of the CMR Building.

Project Discussion:

Description of Waste to Be Treated: X-710 Gunk - X-710 Gunk is a solid mixed waste generated during routine operations in the PORTS analytical chemistry laboratory. Routine operations included filtration and evaporation.

Sample Waste Amounts to be Treated: 2.8 kg

RCRA Waste Code(s): Mixed - D007 (Cr) and D008 (Pb)

Site Treatment Plan Information: Because this waste stream was generated at PORTS, it is not covered by the Compliance Plan Volume of LANL's Federal Facility Compliance Order Site Treatment Plan.

Description of The Waste Treatment Technology: According to recent work at Portsmouth (Letter from D. L. Riepenhoff to Jim Applegate, December 18, 1995), the major constituents in the two X-710 Gunk wastes in addition to uranium are nickel, iron, titanium, calcium, silicon, aluminum, and chromium. One major concern with wastes from analytical chemistry laboratories is the potential presence of organic materials. Calcination at elevated temperatures (up to 900°C) will oxidize any residual organic compounds. Leaching of the remaining solids with 3M HNO_3 will solubilize the majority of the uranium present. The uranium can be recovered from the nitric acid solution by precipitation with ammonium hydroxide (NH_4OH) or hydrogen peroxide (H_2O_2), followed by filtration through appropriate filtration media, and calcination to U_3O_8 at temperatures up to 900°C. The U_3O_8 is a stable product for storage and/or recycle.

Hydrogen peroxide precipitation of uranium allows for separation from metallic impurities relative to NH_4OH precipitation, and the filtrate can be subjected to a basic precipitation step where the hazardous constituents are collected in a hydroxide precipitate. This precipitate is then dried for storage. Alternatively, the filtrate from the H_2O_2 precipitation can be acidified to 4M HNO_3 and loaded onto a column of TRU-Spec or Actinide-Spec resins, supplied by Eichrom Industries (Reference: Procedure 620.1, "Extraction Chromatography Cleanup of Homogeneous Solids and Soil/Gravel Samples Undergoing Total Metals Analysis," from: Transuranic Waste Characterization Sampling and Analysis Methods Manual, Report No. DOE/WIPP-91-043, May 1995). The hazardous constituents are eluted from the column with 4M HNO_3, and the actinide elements are retained by the resin. The acidic eluate is subjected to a basic precipitation step as discussed above. The actinides are either left on the resin or subsequently removed by a low acidity eluent.

Because the CMR Building contains filter towers with HEPA filters, there is virtually no chance that hazardous or radioactive air emissions could occur from this treatment process. In addition, the glove boxes contain a separate HEPA filtration system.

Waste Management: Although unlikely, should any untreated X-710 Gunk waste samples not be used during the treatability study, they will be returned to PORTS. All treated seconary wastes, effluents, and scrubber solutions will be analyzed for proper

characterization. If the secondary wastes, effluents, and scrubber solutions do not exhibit the characteristics of a hazardous waste, they will be managed as radioactive waste. If the secondary wastes do exhibit the characteristic of a hazardous waste, they will either be sent directly off-site to a permitted treatment, storage, and disposal facility, or sent back to the generator (PORTS). After determining the uranium content, effluent from the treatment process will be profiled and submitted with analysis to the Chemistry and Mixed Waste Science Group for approval prior to discharge to the TA-50 Radioactive Waste Treatment Plant. Treatment technologies will be used to minimize the amount of waste that will be returned to Portsmouth. Wastes, returned to PORTS, will be in a form that will allow for facile disposal.

ENCLOSURE

TREATABILITY STUDIES PROCESS DESCRIPTION

RECOVERY AND RECYCLING OF HIGHLY ENRICHED URANIUM FROM MIXED WASTE: FILTER ASH

Los Alamos
NATIONAL LABORATORY

Hazardous & Solid Waste Group
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Facility Name:	**Los Alamos National Laboratory (LANL)** **Materials Science & Technology Division, Group: MST-5** **Chemical Science & Technology Division, Group: CST-7**
Facility EPA ID Number:	**NM0890010515**
Project Title:	**Recovery and Recycling of Highly Enriched Uranium from Mixed Waste: Filter Ash**
Location of Project:	**Technical Area (TA)-3, Building SM-29 (the Chemistry, Metallurgy, and Research Building [CMR Building]), Wings 4 and 9 in the Basement**
Project Contacts:	**Mike H. West, Ph.D.** **MST-5, Mail Stop G730** **(505) 665-5734** **John R. FitzPatrick, Ph.D.** **CST-7, Mail Stop G739** **(505) 665-1761**

Project Description:

This project consists of one (1) treatability study involving a mixed waste that was generated at the Portsmouth Gaseous Diffusion Plant in Portsmouth, Ohio (PORTS). The PORTS facility is operated by Lockheed Martin for the Department of Energy. This project is intended to determine the effectiveness of various treatment technologies, associated with the new Uranium Line for Special Separation Science (ULISSES), located in the CMR Building at LANL, on a variety of mixed wastes (i.e., wastes that contain both hazardous constituents and radioactive constituents). This technology may concentrate the hazardous constituents in the mixed waste and will treat the mixed waste to reduce the health and safety concerns associated with mixed waste by separating the radionuclides for recovery and re-use at LANL or other Department of Energy facilities.

Project Goals and Objectives:

The goals of this project are to demonstrate:

1. The feasibility of this treatment technology for the safe, economical, and efficient treatment of special types of filter ash-based mixed wastes, and

2. To evaluate the ease of recovering and recycling radionuclides from this process waste using standard aqueous recovery processes. The objective of this treatability study is to evaluate this uranium recovery technology on a variety of mixed waste

solids arising from filtering gaseous UF_6 streams (Filter Ash). Furthermore, the proposed treatment technology will reduce the radionuclide concentration in the mixed waste and will recover the radionuclides making the secondary residue from this treatment process more amenable for subsequent waste management and/or treatment capabilities. To facilitate any subsequent treatment and storage, the hazardous constituents will be isolated from the original matrix in as small a volume and mass as possible.

At the completion of this study, the various technologies used will be compared with other residue treatment technologies that have been proposed for use in ULISSES. The goal is to identify the most effective recovery processes for highly enriched uranium with respect to these mixed waste types. The information obtained from the study will be shared with other uranium processing facilities in the public and private sectors.

Project Tasks:

Obtain mixed-waste samples from the generator. Treat the mixed waste using the technology listed below. Determine the uranium and hazardous constituent removal efficiency of the treatment process and identify the treatment products.

Project Milestones:

1. Start date will be a minimum of 45 days after submittal of the treatability study notification to NMED.
2. Complete testing of Filter Ash by October 1, 1997.

Qualifications:

Key Staff Experience: Mike H. West: Ph.D. in Inorganic Chemistry, Washington State University, 1976. Current position, LANL technical staff member in MST-5. Over 13 years experience in process development and fundamental actinide research. For the past two years focused on developing treatment processes for radioactive and mixed waste and on recovering and recycling strategic metals.

John R. FitzPatrick: Ph.D. in Inorganic Chemistry, University of Utah, 1976. Current position, LANL technical staff member in CST-7. Eighteen years experience in actinide processing, flowsheet development, equipment design, set-up and operation for the recovery of plutonium and uranium from various process residues.

Equipment and Facilities:

Bench scale equipment is located in Wing-4 of the Uranium Laboratory at the CMR Building for performing various experiments on mixed waste samples. In addition, gloveboxes are available in the same area for demonstrating the most appropriate treatability approach on a larger scale for each type of waste. Analytical chemistry analyses are available in Wings-3, -5, -7, or -9 to measure the amount of hazardous constituents remaining in both the secondary process waste and in the recovered enriched uranium fraction. For example, inductively coupled plasma-atomic emission spectrometry, inductively coupled plasma-mass spectrometry, and quantitative uranium assays by Davies-Gray are available. The uranium in solution can be easily measured using Liquid

Scintillation Counting (LSC) techniques, available in Wing-5. By early calendar year 1997, glove boxes will also be available in Wing-9 of the CMR Building.

Project Discussion:

Description of Waste to Be Treated: Filter Ash - Filter Ash is generated by the filtration of particulates from UF_6 streams using a metallic filter. The waste consists of nonvolatile metal fluorides and U_3O_8.

Sample Waste Amounts to be Treated: 11.7 kg

RCRA Waste Code(s): Mixed - D006 (Cd), D007 (Cr), D008 (Pb), D009(Hg), and D011 (Ag)

Site Treatment Plan Information: Because this waste stream was generated at PORTS, it is not covered by the Compliance Plan Volume of LANL's Federal Facility Compliance Order Site Treatment Plan.

Description of The Waste Treatment Technology: PORTS personnel have shown the feasibility of using 3M HNO_3 to remove in excess of 99% of the uranium content of filter ash (Letter from Keith Banks to Ralph Wilcoxon, April 10, 1996). The uranium can be recovered from the nitric acid solution by precipitation with ammonium hydroxide (NH_4OH) or hydrogen peroxide (H_2O_2), followed by filtration through appropriate filtration media, and calcination to U_3O_8 at temperatures up to 900°C. The U_3O_8 is a stable product for storage and/or recycle.

Hydrogen peroxide precipitation of uranium allows for separation from metallic impurities relative to NH_4OH precipitation, and the filtrate can be subjected to a basic precipitation step where the hazardous constituents are collected in a hydroxide precipitate. This precipitate is then dried for storage. Alternatively, the filtrate from the H_2O_2 precipitation can be acidified to 4M HNO_3 and loaded onto a column of TRU-Spec or Actinide-Spec resins, supplied by Eichrom Industries (Reference: Procedure 620.1, "Extraction Chromatography Cleanup of Homogeneous Solids and Soil/Gravel Samples Undergoing Total Metals Analysis," from: Transuranic Waste Characterization Sampling and Analysis Methods Manual, Report No. DOE/WIPP-91-043, May 1995). Technetium can be sorbed subsequently by strong base anion exchange resins such as Reillex-HPQ or with extraction chromatographic resins such as TEVA-Spec. The hazardous constituents are eluted from the TRU-Spec or Actinide-Spec column with 4M HNO_3, and the actinide elements are retained by the resin. The acidic eluate is subjected to a basic precipitation step as discussed above. The actinides are either left on the resin or subsequently removed by a low acidity eluent.

Because the CMR Building contains filter towers with HEPA filters, there is virtually no chance that hazardous or radioactive air emissions could occur from this treatment process. In addition, the glove boxes have a separate HEPA filtration system.

Waste Management: Although unlikely, should any untreated Filter Ash waste samples not be used during the treatability study, they will be returned to PORTS. All treated secondary wastes, effluents, and scrubber solutions will be analyzed for proper characterization. If the secondary wastes, effluents, and scrubber solutions do not exhibit the characteristics of a hazardous waste, they will be managed as radioactive waste. If the secondary wastes do exhibit the characteristic of a hazardous waste, they will either be sent directly off-site to a permitted treatment, storage, and disposal facility, or sent back to

the generator (PORTS). After determining the uranium content, effluent from the treatment process will be profiled and submitted with analysis to the Chemistry and Mixed Waste Science Group for approval prior to discharge to the TA-50 Radioactive Waste Treatment Plant. Treatment technologies will be used to minimize the amount of waste that will be returned to Portsmouth. Wastes, returned to PORTS, will be in a form that will allow for facile disposal.

ENCLOSURE

TREATABILITY STUDIES PROCESS DESCRIPTION

RECOVERY AND RECYCLING OF HIGHLY ENRICHED URANIUM FROM MIXED WASTE: FLUORINATION OF FREON DEGRADER RESIDUE

Los Alamos
NATIONAL LABORATORY

Hazardous & Solid Waste Group
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Facility Name:	**Los Alamos National Laboratory (LANL)** **Materials Science & Technology Division, Group: MST-5** **Chemical Science & Technology Division, Group: CST-7**
Facility EPA ID Number:	**NM0890010515**
Project Title:	**Recovery and Recycling of Highly Enriched Uranium from Mixed Waste: Fluorination of Freon Degrader Residue**
Location of Project:	**Technical Area (TA)-3, Building SM-29 (the Chemistry, Metallurgy, and Research Building [CMR Building]), Wings 4 and 9 in the Basement**
Project Contacts:	**Mike H. West, Ph.D.** **MST-5, Mail Stop G730** **(505) 665-5734** **John R. FitzPatrick, Ph.D.** **CST-7, Mail Stop G739** **(505) 665-1761**

Project Description:

This project consists of one (1) treatability study involving a mixed waste that was generated at the Portsmouth Gaseous Diffusion Plant in Portsmouth, Ohio (PORTS). The PORTS facility is operated by Lockheed Martin for the Department of Energy. This project is intended to determine the effectiveness of various treatment technologies, associated with the new Uranium Line for Special Separation Science (ULISSES), located in the CMR Building at LANL, on a variety of mixed wastes (i.e., wastes that contain both hazardous constituents and radioactive constituents). This technology may concentrate the hazardous constituents in the mixed waste and will treat the mixed waste to reduce the health and safety concerns associated with mixed waste by separating the radionuclides for recovery and re-use at LANL or other Department of Energy facilities.

Project Goals and Objectives:

The goals of this project are to demonstrate:

1. The feasibility of treatment technology for the safe, economical, and efficient treatment of special types of Freon Degrader-based mixed waste, and

2. To evaluate the ease of recovering and recycling radionuclides from this process waste using standard aqueous recovery processes. The objective of this treatability study is to evaluate this uranium recovery technology on mixed waste

generated from the degradation of Freons used at Portsmouth (Freon Degrader Residue). Furthermore, the proposed treatment technology will reduce the radionuclide concentration in the mixed waste and will recover the radionuclides making the secondary residue from this treatment process more amenable for subsequent waste management and/or treatment capabilities. To facilitate any subsequent treatment and storage, the hazardous constituents will be isolated from the original matrix in as small a volume and mass as possible.

At the completion of this study, the technology used will be compared with other residue treatment technologies that have been proposed for use in ULISSES. The goal is to identify the most effective recovery processes for highly enriched uranium with respect to these mixed waste types. The information obtained from the study will be shared with other uranium processing facilities in the public and private sectors.

Project Tasks:

Obtain mixed-waste samples from the generator. Treat the mixed waste using the technology listed below. Determine the uranium and hazardous constituent removal efficiency of the treatment process and identify the treatment products.

Project Milestones:

1. Start date will be a minimum of 45 days after submittal of the treatability study notification to NMED.
2. Complete testing of Freon Degrader Residue by October 1, 1997.

Qualifications:

Key Staff Experience: Mike H. West: Ph.D. in Inorganic Chemistry, Washington State University, 1976. Current position, LANL technical staff member in MST-5. Over 13 years experience in process development and fundamental actinide research. For the past two years focused on developing treatment processes for radioactive and mixed waste and on recovering and recycling strategic metals.

John R. FitzPatrick: Ph.D. in Inorganic Chemistry, University of Utah, 1976. Current position, LANL technical staff member in CST-7. Eighteen years experience in actinide processing, flowsheet development, equipment design, set-up and operation for the recovery of plutonium and uranium from various process residues.

Equipment and Facilities:

Bench scale equipment is located in Wing-4 of the Uranium Laboratory at the CMR Building for performing various experiments on mixed waste samples. In addition, gloveboxes are available in the same area for demonstrating the most appropriate treatability approach on a larger scale for each type of waste. Analytical chemistry analyses are available in Wings-3, -5, -7, or -9 to measure the amount of hazardous constituents remaining in both the secondary process waste and in the recovered enriched uranium fraction. For example, inductively coupled plasma-atomic emission spectrometry, inductively coupled plasma-mass spectrometry, and quantitative uranium assays by Davies-Gray are available. The uranium in solution can be easily measured

using Liquid Scintillation Counting (LSC) techniques, available in Wing-5. By early calendar year 1997, glove boxes will also be available in Wing-9 of the CMR Building.

Project Discussion:

Description of Waste to Be Treated: Freon Degrader Residue - The waste to be treated was generated during the degradation process applied to various Freon compounds used at Portsmouth. Fluorine gas reacted with Freon-114 to form carbon tetrafluoride (CF_4). Gaseous metal fluorides reacted with the degrader surface to form nonvolatile transition metal fluorides. The degrader wastes consist of metal fluorides and nonvolatile uranium fluorides.

Sample Waste Amounts to be Treated: 5.2 kg

RCRA Waste Code(s): Mixed - D004 (As), D007 (Cr), and D008 (Pb)

Site Treatment Plan Information: Because this waste stream was generated at PORTS, it is not covered by the Compliance Plan Volume of LANL's Federal Facility Compliance Order Site Treatment Plan.

Description of The Waste Treatment Technology: There is some difference of opinion concerning the ease with which uranium can be leached from this waste form. A letter from A.J. Saraceno to Ralph Wilcoxon (March 13, 1996, POEF-38-340-95-01) suggests the Freon degrader material is susceptible to nitric acid dissolution. However, other information indicates this is not necessarily the case.

In this study, fluorination with ClF_3 or fluorine at 300-500°C will be conducted to leach uranium from this waste matrix. Uranium hexafluoride (UF_6) thus formed will be recovered cryogenically at -40°C. Also, superior fluorinating agents such as O_2F_2, O_2F radical, or KrF_2 could be used experimentally. Since PORTS is the national storage facility for UF_6, the UF_6 will be shipped to PORTS for processing and storage. MST-5 is presently consolidating UF_6 holdings at LANL and returning the UF_6 to PORTS for storage.

The residue remaining from the reaction with the fluorinating agents will be calcined at 800°C. The calcination product will be analyzed for uranium content and processed further if recoverable quantities are found. Any recoverable uranium will be removed by one or two leaching steps with dilute HNO_3. The uranium can be recovered from the nitric acid solution by precipitation with ammonium hydroxide (NH_4OH) or hydrogen peroxide (H_2O_2), followed by filtration through appropriate filtration media, and calcination to U_3O_8 at temperatures up to 900°C. The U_3O_8 is a stable product for storage and/or recycle.

Hydrogen peroxide precipitation of uranium allows for separation from metallic impurities relative to NH_4OH precipitation, and the filtrate can be subjected to a basic precipitation step where many of the hazardous constituents are collected in a hydroxide precipitate. This precipitate is then dried for storage. Alternatively, the filtrate from the H_2O_2 precipitation can be acidified to 4M HNO_3 and loaded onto a column of TRU-Spec or Actinide-Spec resins, supplied by Eichrom Industries (Reference: Procedure 620.1, "Extraction Chromatography Cleanup of Homogeneous Solids and Soil/Gravel Samples Undergoing Total Metals Analysis," from: Transuranic Waste Characterization Sampling and Analysis Methods Manual, Report No. DOE/WIPP-91-043, May 1995). The hazardous constituents are eluted from the column with 4M HNO_3, and the actinide

elements are retained by the resin. The acidic eluate is subjected to a basic precipitation step as discussed above. The actinides are either left on the resin or removed by a low acidity eluent.

Because the CMR Building contains filter towers with HEPA filters, there is virtually no chance that hazardous or radioactive air emissions could occur from this treatment process. In addition, the glove boxes contain a separate HEPA filtration system.

Waste Management: Although unlikely, should any untreated Freon Degrader Residue waste samples not be used during the treatability study, they will be returned to PORTS. All treated wastes, effluents, and scrubber solutions will be analyzed for proper characterization. If the secondary wastes, effluents, and scrubber solutions do not exhibit the characteristics of a hazardous waste, they will be managed as radioactive waste. If the secondary wastes do exhibit the characteristic of a hazardous waste, they will either be sent directly off-site to a permitted treatment, storage, and disposal facility, or sent back to the generator (PORTS). After determining the uranium content, effluent from the treatment process will be profiled and submitted with analysis to the Chemistry and Mixed Waste Science Group for approval prior to discharge to the TA-50 Radioactive Waste Treatment Plant. Treatment technologies will be used to minimize the amount of waste that will be returned to PORTS. Wastes, returned to PORTS, will be in a form that will allow for facile disposal. The UF_6 will be returned to PORTS for consolidation and storage.

ENCLOSURE

TREATABILITY STUDIES PROCESS DESCRIPTION

RECOVERY AND RECYCLING OF HIGHLY ENRICHED URANIUM FROM MIXED WASTE: PYROHYDROLYSIS OF FREON DEGRADER RESIDUE

Los Alamos
NATIONAL LABORATORY

Hazardous & Solid Waste Group
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Facility Name:	**Los Alamos National Laboratory (LANL)** **Materials Science & Technology Division, Group: MST-5** **Chemical Science & Technology Division, Group: CST-7**
Facility EPA ID Number:	**NM0890010515**
Project Title:	**Recovery and Recycling of Highly Enriched Uranium from Mixed Waste: Pyrohydrolysis of Freon Degrader Residue**
Location of Project:	**Technical Area (TA)-3, Building SM-29 (the Chemistry, Metallurgy, and Research Building [CMR Building]), Wings 4 and 9 in the Basement**
Project Contacts:	**Mike H. West, Ph.D.** **MST-5, Mail Stop G730** **(505) 665-5734** **John R. FitzPatrick, Ph.D.** **CST-7, Mail Stop G739** **(505) 665-1761**

Project Description:

This project consists of one (1) treatability study involving a mixed waste that was generated at the Portsmouth Gaseous Diffusion Plant in Portsmouth, Ohio (PORTS). The PORTS facility is operated by Lockheed Martin for the Department of Energy. This project is intended to determine the effectiveness of various treatment technologies, associated with the new Uranium Line for Special Separation Science (ULISSES), located in the CMR Building at LANL, on a variety of mixed wastes (i.e., wastes that contain both hazardous constituents and radioactive constituents). This technology may concentrate the hazardous constituents in the mixed waste and will treat the mixed waste to reduce the health and safety concerns associated with mixed waste by separating the radionuclides for recovery and re-use at LANL or other Department of Energy facilities.

Project Goals and Objectives:

The goals of this project are to demonstrate:

1. The feasibility of this treatment technology for the safe, economical, and efficient treatment of special types of Freon Degrader-based mixed waste, and

2. To evaluate the ease of recovering and recycling radionuclides from this process waste using standard aqueous recovery processes. The objective of this treatability study is to evaluate uranium recovery technology on mixed waste

generated from the degradation of Freons used at Portsmouth (Freon Degrader Residue). Furthermore, the proposed treatment technology will reduce the radionuclide concentration in the mixed waste and will recover the radionuclides making the secondary residue from this treatment process more amenable for subsequent waste management and/or treatment capabilities. To facilitate any subsequent treatment and storage, the hazardous constituents will be isolated from the original matrix in as small a volume and mass as possible.

At the completion of this study, the technology used will be compared with other residue treatment technologies that have been proposed for use in ULISSES. The goal is to identify the most effective recovery processes for highly enriched uranium with respect to these mixed waste types. The information obtained from the study will be shared with other uranium processing facilities in the public and private sectors.

Project Tasks:

Obtain mixed waste samples from the generator. Treat the mixed waste using the technology listed below. Determine the uranium and hazardous constituent removal efficiency of the treatment process and identify the treatment products.

Project Milestones:

1. Start date will be a minimum of 45 days after submittal of the treatability study notification to NMED.
2. Complete testing of Freon Degrader Residue by October 1, 1997.

Qualifications:

Key Staff Experience: Mike H. West: Ph.D. in Inorganic Chemistry, Washington State University, 1976. Current position, LANL technical staff member in MST-5. Over 13 years experience in process development and fundamental actinide research. For the past two years focused on developing treatment processes for radioactive and mixed waste and on recovering and recycling strategic metals.

John R. FitzPatrick: Ph.D. in Inorganic Chemistry, University of Utah, 1976. Current position, LANL technical staff member in CST-7. Eighteen years experience in actinide processing, flowsheet development, equipment design, set-up and operation for the recovery of plutonium and uranium from various process residues.

Equipment and Facilities:

Bench scale equipment is located in Wing-4 of the Uranium Laboratory at the CMR Building for performing various experiments on mixed waste samples. In addition, gloveboxes are available in the same area for demonstrating the most appropriate treatability approach on a larger scale for each type of waste. Analytical chemistry analyses are available in Wings-3, -5, -7, or -9 to measure the amount of hazardous constituents remaining in both the secondary process wastes and in the recovered enriched uranium fraction. For example, inductively coupled plasma-atomic emission spectrometry, inductively coupled plasma-mass spectrometry, and quantitative uranium assays by Davies-Gray are available. The uranium in solution can be easily measured

using Liquid Scintillation Counting (LSC) techniques, available in Wing-5. By early calendar year 1997, glove boxes will also be available in Wing-9 of the CMR Building.

Project Discussion:

Description of Waste to Be Treated: Freon Degrader Residue - The waste to be treated was generated during the degradation process applied to various Freon compounds used at Portsmouth. Fluorine gas reacted with Freon-114 to form carbon tetrafluoride (CF_4). Gaseous metal fluorides reacted with the degrader surface to form nonvolatile transition metal fluorides. The degrader wastes consist of metal fluorides and nonvolatile uranium fluorides.

Sample Waste Amounts to be Treated: 5.2 kg

RCRA Waste Code(s): Mixed - D004 (As), D007 (Cr), and D008 (Pb)

Site Treatment Plan Information: Because this waste stream was generated at PORTS, it is not covered by the Compliance Plan Volume of LANL's Federal Facility Compliance Order Site Treatment Plan.

Description of The Waste Treatment Technology: There is some difference of opinion concerning the ease with which uranium can be leached from this waste form. A letter from A.J. Saraceno to Ralph Wilcoxon (March 13, 1996, POEF-38-340-95-01) suggests the Freon degrader material is susceptible to nitric acid dissolution. However, other information indicates this is not necessarily the case.

Since most of the compounds present in the degrader material are fluoride salts, use of pyrohydrolysis will remove fluoride from the material leaving an oxide residue that is susceptible to HNO_3 leaching. In pyrohydrolysis, a stream of gas, saturated with water, will be passed through the fluoride salts at elevated temperatures. This will convert the fluorides to oxides, and the fluorides form volatile hydrogen fluoride. The hydrogen halides can be scrubbed using aqueous potassium hydroxide (KOH). The uranium oxides will be soluble in dilute HNO_3. The uranium can be recovered from the nitric acid solution by precipitation with ammonium hydroxide (NH_4OH) or hydrogen peroxide (H_2O_2), followed by filtration through appropriate frit material, and calcination to U_3O_8 at temperatures up to 900°C. The U_3O_8 is a stable product for storage and/or recycle.

Hydrogen peroxide precipitation of uranium allows for separation from metallic impurities relative to NH_4OH precipitation, and the filtrate can be subjected to a basic precipitation step where the hazardous constituents are collected in a hydroxide precipitate. This precipitate is then dried for storage. Alternatively, the filtrate from the H_2O_2 precipitation can be acidified to 4M HNO_3 and loaded onto a column of TRU-Spec or Actinide-Spec resins, supplied by Eichrom Industries (Reference: Procedure 620.1, "Extraction Chromatography Cleanup of Homogeneous Solids and Soil/Gravel Samples Undergoing Total Metals Analysis," from: Transuranic Waste Characterization Sampling and Analysis Methods Manual, Report No. DOE/WIPP-91-043, May 1995). The hazardous constituents are eluted from the TRU-Spec or Actinide-Spec column with 4M HNO_3, and the actinide elements are retained by the resin. The acidic eluate is subjected to a basic precipitation step as discussed above. The actinides are either left on the resin or subsequently removed by a low acidity eluent.

Because the CMR Building contains filter towers with HEPA filters, there is virtually no chance that hazardous or radioactive air emissions could occur from this treatment process. In addition, the glove boxes contain a separate HEPA filtration system.

Waste Management: Although unlikely, should any untreated Freon Degrader Residue waste samples not be used during the treatability study, they will be returned to PORTS. All treated wastes, effluents, and scrubber solutions will be analyzed for proper characterization. If the secondary wastes, effluents, and scrubber solutions do not exhibit the characteristics of a hazardous waste, they will be managed as radioactive waste. If the secondary wastes do exhibit the characteristic of a hazardous waste, they will either be sent directly off-site to a permitted treatment, storage, and disposal facility, or sent back to the generator (PORTS). After determining the uranium content, effluent from the treatment process will be profiled and submitted with analysis to the Chemistry and Mixed Waste Science Group for approval prior to discharge to the TA-50 Radioactive Waste Treatment Plant. Treatment technologies will be used to minimize the amount of waste that will be returned to Portsmouth. Wastes, returned to PORTS, will be in a form that will allow for facile disposal.

ENCLOSURE

TREATABILITY STUDIES PROCESS DESCRIPTION

RECOVERY AND RECYCLING OF HIGHLY ENRICHED URANIUM FROM MIXED WASTE: FREON DEGRADER RESIDUE

Los Alamos
NATIONAL LABORATORY

Hazardous & Solid Waste Group
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Facility Name:	**Los Alamos National Laboratory (LANL)** **Materials Science & Technology Division, Group: MST-5** **Chemical Science & Technology Division, Group: CST-7**
Facility EPA ID Number:	**NM0890010515**
Project Title:	**Recovery and Recycling of Highly Enriched Uranium from Mixed Waste: Freon Degrader Residue**
Location of Project:	**Technical Area (TA)-3, Building SM-29 (the Chemistry, Metallurgy, and Research Building [CMR Building]), Wings 4 and 9 in the Basement**
Project Contacts:	**Mike H. West, Ph.D.** **MST-5, Mail Stop G730** **(505) 665-5734** **John R. FitzPatrick, Ph. D.** **CST-7, Mail Stop G739** **(505) 665-1761**

Project Description:

This project consists of one (1) treatability study involving a mixed waste that was generated at the Portsmouth Gaseous Diffusion Plant in Portsmouth, Ohio (PORTS). The PORTS facility is operated by Lockheed Martin for the Department of Energy. This project is intended to determine the effectiveness of various treatment technologies, associated with the new Uranium Line for Special Separation Science (ULISSES), located in the CMR Building at LANL, on a variety of mixed wastes (i.e., wastes that contain both hazardous constituents and radioactive constituents). This technology may concentrate the hazardous constituents in the mixed waste and will treat the mixed waste to reduce the health and safety concerns associated with mixed waste by separating the radionuclides for recovery and re-use at LANL or other Department of Energy facilities.

Project Goals and Objectives:

The goals of this project are to demonstrate:

1. The feasibility of this treatment technology for the safe, economical, and efficient treatment of special types of Freon Degrader-based mixed waste, and

2. To evaluate the ease of recovering and recycling radionuclides from this process waste using standard aqueous recovery processes. The objective of this treatability study is to evaluate this uranium recovery technology on waste

generated by the degradation of Freons used at Portsmouth (Freon Degrader Residue). Furthermore, the proposed treatment technology will reduce the radionuclide concentration in the mixed waste and will recover the radionuclides making the secondary residue from this treatment process more amenable for subsequent waste management and/or treatment capabilities. To facilitate any subsequent treatment and storage, the hazardous constituents will be isolated from the original matrix in as small a volume and mass as possible.

At the completion of this study, the various technologies used will be compared with other residue treatment technologies that have been proposed for use in ULISSES. The goal is to identify the most effective recovery processes for highly enriched uranium with respect to these mixed waste types. The information obtained from the study will be shared with other uranium processing facilities in the public and private sectors.

Project Tasks:

Obtain mixed-waste samples from the generator. Treat the mixed waste using the technology listed below. Determine the uranium and hazardous constituent removal efficiency of the treatment process and identify the treatment products.

Project Milestones:

1. Start date will be a minimum of 45 days after submittal of the treatability study notification to NMED.
2. Complete testing of Freon Degrader Residue by October 1, 1997.

Qualifications:

Key Staff Experience: Mike H. West: Ph.D. in Inorganic Chemistry, Washington State University, 1976. Current position, LANL technical staff member in MST-5. Over 13 years experience in process development and fundamental actinide research. For the past two years focused on developing treatment processes for radioactive and mixed waste and on recovering and recycling strategic metals.

John R. FitzPatrick: Ph.D. in Inorganic Chemistry, University of Utah, 1976. Current position, LANL technical staff member in CST-7. Eighteen years experience in actinide processing, flowsheet development, equipment design, set-up and operation for the recovery of plutonium and uranium from various process residues.

Equipment and Facilities:

Bench scale equipment is located in Wing-4 of the Uranium Laboratory at the CMR Building for performing various experiments on mixed waste samples. In addition, gloveboxes are available in the same area for demonstrating the most appropriate treatability approach on a larger scale for each type of waste. Analytical chemistry analyses are available in Wings-3, -5, -7, or -9 to measure the amount of hazardous constituents remaining in both the secondary process waste and in the recovered enriched uranium fraction. For example, inductively coupled plasma-atomic emission spectrometry, inductively coupled plasma-mass spectrometry, and quantitative uranium assays by Davies-Gray are available. The uranium in solution can be easily measured

using Liquid Scintillation Counting (LSC) techniques, available in Wing-5. By early calendar year 1997, glove boxes will also be available in Wing-9 of the CMR Building.

Project Discussion:

Description of Waste to Be Treated: Freon Degrader Residue - The waste to be treated was generated during the degradation process applied to various Freon compounds used at Portsmouth. Fluorine gas reacted with Freon-114 to form carbon tetrafluoride (CF_4). Gaseous metal fluorides reacted with the degrader surface to form nonvolatile transition metal fluorides. The degrader wastes consist of metal fluorides and nonvolatile uranium fluorides.

Sample Waste Amounts to be Treated: 5.2 kg

RCRA Waste Code(s): Mixed - D004 (As), D007 (Cr), and D008 (Pb)

Site Treatment Plan Information: Because this waste stream was generated at PORTS, it is not covered by the Compliance Plan Volume of LANL's Federal Facility Compliance Order Site Treatment Plan.

Description of The Waste Treatment Technology: There is some difference of opinion concerning the ease with which uranium can be leached from this waste form. A letter from A.J. Saraceno to Ralph Wilcoxon (March 13, 1996, POEF-38-340-95-01) suggests the Freon degrader material is susceptible to nitric acid dissolution. However, other information indicates this is not necessarily the case. Leaching of the solids with dilute HNO_3 is the first choice for treating the Freon Degrader Residue. The uranium can be recovered from the nitric acid solution by precipitation with ammonium hydroxide (NH_4OH) or hydrogen peroxide (H_2O_2), followed by filtration through appropriate frit material, and calcination to U_3O_8 at temperatures up to 900°C. The U_3O_8 is a stable product for storage and/or recycle.

Hydrogen peroxide precipitation of uranium allows for separation from metallic impurities relative to NH_4OH precipitation, and the filtrate can be subjected to a basic precipitation step where the hazardous constituents are collected in a hydroxide precipitate. This precipitate is then dried for storage. Alternatively, the filtrate from the H_2O_2 precipitation can be acidified to 4M HNO_3 and loaded onto a column of TRU-Spec or Actinide-Spec resins, supplied by Eichrom Industries (Reference: Procedure 620.1, "Extraction Chromatography Cleanup of Homogeneous Solids and Soil/Gravel Samples Undergoing Total Metals Analysis," from: Transuranic Waste Characterization Sampling and Analysis Methods Manual, Report No. DOE/WIPP-91-043, May 1995). The hazardous constituents are eluted from the TRU-Spec or Actinide-Spec column with 4M HNO_3, and the actinide elements are retained by the resin. The acidic eluate is subjected to a basic precipitation step as discussed above. The actinides are either left on the resin or subsequently removed by a low acidity eluent.

Because the CMR Building contains filter towers with HEPA filters, there is virtually no chance that hazardous or radioactive air emissions could occur from this treatment process. In addition, the glove boxes contain a separate HEPA filtration system.

Waste Management: Although unlikely, should any untreated Freon Degrader Residue waste samples not be used during the treatability study, they will be returned to PORTS. All treated wastes, effluents, and scrubber solutions will be analyzed for proper characterization. If the secondary wastes, effluents, and scrubber solutions do not exhibit

the characteristics of a hazardous waste, they will be managed as radioactive waste. If the secondary wastes do exhibit the characteristic of a hazardous waste, they will either be sent directly off-site to a permitted treatment, storage, and disposal facility, or sent back to the generator (PORTS). After determining the uranium content, effluent from the treatment process will be profiled and submitted with analysis to the Chemistry and Mixed Waste Science Group for approval prior to discharge to the TA-50 Radioactive Waste Treatment Plant. Treatment technologies will be used to minimize the amount of waste that will be returned to Portsmouth. Wastes, returned to PORTS, will be in a form that will allow for facile disposal.