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APR 1998

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

APR 21 1998

CERTIFIED MAIL - RETURN RECEIPT REQUESTED

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

Dear Mr. Garcia:

Subject: Waste Analysis Plan for Generator Treatment of Spent Chemical Oxygen Demand Waste

The purpose of this letter is to submit a Waste Analysis Plan (WAP) for generator treatment of Chemical Oxygen Demand (COD) waste at Los Alamos National Laboratory (LANL). This WAP is intended to fulfill the requirements in Title 20 of the New Mexico Administrative Code, Chapter 4, Part 1, Subpart VIII and 40 CFR 268.7(a)(4) for generator treatment in containers. Pursuant to these requirements, the WAP must be filed with the New Mexico Environment Department (NMED) a minimum of 30 days prior to the treatment activity.

The waste to be treated is a strongly acidic, aqueous solution containing dissolved silver, mercury, and chromium. LANL's Radioactive Liquid Waste Treatment Facility generates approximately 12 to 18 liters of this spent solution per year. The selected treatment process for the COD waste is electrochemical removal of silver and mercury, alkaline neutralization of acidity, and cementation of chromium. COD waste will be transported from its point of generation at LANL to a less than 90 day accumulation area at Technical Area 48 where generator treatment will occur.

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

Sincerely,

H. L. "Jody" Plum
Office of Environment

LAAME:6JP-057

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Enclosure

bcc w/enclosure:
H. Haynes, Office of Counsel, LAAO

bcc w/o enclosure:
J. Dziewinski, CST-7, LANL, MS-J514
I. Triay, CST-7, LANL, MS-J514
R. Alexander, EM-RLW, LANL, MS-E518
J. Ellvinger, ESH-19, LANL, MS-K490

WASTE ANALYSIS PLAN FOR SPENT CHEMICAL OXYGEN DEMAND WASTE

Introduction

This waste analysis plan (WAP) presents information on the chemical and physical nature of mixed waste to be treated in a less than 90 day accumulation area at Los Alamos National Laboratory's (LANL) Technical Area (TA)-48. This plan is intended to fulfill the requirements listed in Title 20 of the New Mexico Administrative Code, Chapter 4 Part 1 (20 NMAC 4.1), Subpart VIII and 40 CFR 268.7 (a)(4) that a generator treating prohibited wastes (regulated under 20 NMAC 4.1, Subpart III and 40 CFR 262.34) in tanks or containers must develop and follow a written plan.

The waste to be treated is between 12- 18 liters (L) per year of strongly acidic, aqueous solution containing dissolved silver, mercury, and chromium. It is a spent solution generated in a routine analytical procedure known as Chemical Oxygen Demand (COD). This procedure is a widely accepted and documented analysis used in the quantitation of organics in a given sample. During this procedure, known amounts of potassium dichromate and sulfuric acid are refluxed with a sample to oxidize organic components that might be present in the sample. The excess dichromate is then titrated with ferrous ammonium sulfate. For more effective oxidation of the sample, catalysts are added to the reaction. These catalysts include silver sulfate and mercuric sulfate. The resultant waste stream is a highly acidic spent solution containing dissolved chromium, silver, and mercury. The waste to be treated originates from the Radioactive Liquid Waste Treatment Facility (RLWTF). The RLWTF utilizes the COD analysis to monitor the organic concentration of the influent and effluent of the facility. This means, random water samples taken from the waste streams coming into and out of the facility are subjected to COD analysis. It is also used to monitor other LANL Environmental Protection Agency (EPA) regulated outfalls maintained by the RLWTF. The knowledge that the RLWTF prohibits the disposal of organics to the facility and the oxidizing power of the analysis itself, assures that no underlying hazardous constituents (UHC) are present in concentrations that exceed the universal treatment standards.

As part of a waste generator treatment plan introduced by the Environmental Management, Waste Management Program Office at LANL, we will remove the toxic and the corrosive characteristics from these wastes. This will be done using techniques developed in a treatability study that took place in 1996. During this treatability study, 30.5L of COD spent solutions, contained in ten various samples, were successfully treated and met the Land Disposal Restrictions (LDR) standards.

The COD waste is routinely generated each year at LANL by the RLWTF. By treating this waste, LANL will decrease it's cost of mixed waste disposal and management. Treatment will also decrease the Laboratory's impact on the surrounding environment through responsible land management by rendering the waste non-hazardous.

Description of the Waste

The waste to be treated is a solution contained in 2.5 L glass bottles. Historically, between 12-18L of COD waste are generated at LANL each year. We are anticipating treating this 12L- 18L of waste per year. It is a non ignitable, non reactive, corrosive, homogeneous, aqueous liquid containing chromium (EPA hazardous waste number D007), silver (EPA hazardous waste number D011), and mercury (EPA hazardous waste number D009). The range of metal concentrations in these COD spent solutions are provided in the table below, and are based on the following:

- documented knowledge of the COD analytical procedure
- measurements obtained from ten 2.5L samples of COD waste treated during the 1996 treatability studies, and
- recent analytical results

Test/ Analysis	Result/ Concentration (Min-Max)	Units
Chromium	0.1-1.0	g/L
Mercury	0.2 - 4	g/L
Silver	1.0 - 7	g/L

Additional chemical constituents in the waste stream include potassium and H_2SO_4.

Treatment Process

The waste will be handled according to the procedures set fourth in Standard Operating Procedure (SOP) 037, Rules for Handling Radioactive Material at TA-48. The selected treatment process for the COD waste is electrochemical removal of silver and mercury, alkaline neutralization of acidity, and cementation of chromium.

The treatment will proceed as follows: The COD waste will be transported from its point of generation at LANL to a <90 day accumulation area at TA-48 where the treatment will take place. The initial acid concentration of the COD waste is about 7 molar, which is too concentrated for electrolysis. Therefore, the solution requires pH adjustment to about pH=1 with $Ca(OH)_2$. This will result in the precipitation on $CaSO_4 \cdot 2H_2O$ (gypsum). At pH=1 the metals will not precipitate from the solution. This gypsum will be filtered from the solution and disposed of as non-hazardous waste, i.e. solid physical form low-level waste. A Toxicity Characteristic Leaching Procedure (TCLP) analysis will be performed prior to its disposal. The solution will then be moved into an electrochemical cell for metal extraction. This cell will consist of a 3 gallon rectangular vessel with titanium anodes and copper cathodes. A low voltage DC current will be applied and Ag and Hg metals will be reduced on the cathodes. The plated silver will adhere to the electrode surface and the mercury will coalesce at the bottom of the cell leaving the chromium in solution. The small amounts, a few grams, of silver and mercury recovered from this treatment will be retained in the laboratory and reused as materials during electrochemical experimentation. Any radioactive components that might be present in the original COD sample will stay in solution. The chromium which will remain in the solution will consist of hexavalent and trivalent Cr. The Cr(VI) will be reduced to Cr(III)

by addition of a small amount of sodium dithionate. Cr(III) will then be precipitated as $Cr(OH)_3$ by raising the pH of the solution to about 8 using sodium hydroxide. This $Cr(OH)_3$ will be filtered. Between 0.25 g to 1.65 g of chromium hydroxide will be formed per 2.5 L bottle of spent COD solution, depending on the initial Cr concentration. After weighing $Cr(OH)_3$, an appropriate amount of cement, sand and water will be added and mixed. The proper mixture for chromium stabilization in Portland cement is 5-10% of precipitate and 90-95% of cement/sand. This cement composition has been proven to be effective during numerous experiments with immobilization of chromium during the 1996 treatability study. The chromium-containing cement will be disposed of as a non-hazardous waste after a TCLP analysis has been performed to ensure it meets the LDR treatment standard.

Waste Sampling

Treatment of the COD waste will be considered complete when the liquid meets the Waste Acceptance Criteria (WAC) for LANL's RLWTF at TA-50, when the pH is between 4-8, and when the solid residues are below LDR treatment standards. The solid residues (gypsum and cement) will undergo TCLP analysis to ensure that leachable metals are below the concentration based LDR treatment standards and will be disposed of as a non-hazardous waste. Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) will be used to analyze both the solution before disposal to the RLWTF and to analyze the TCLP leachates.

All analytical results completed in support of LDR treatment standards will be retained by the person conducting the generator treatment as part of LANL's operating record. LANL will prepare a notice and certification with information required under 20 NMAC 4.1, Subpart VIII, and 40 CFR 268.7 (a)(2) for waste received and treated. LANL will also send a one time notification and certification, as appropriate, to the New Mexico Environmental Department by the end of the calendar year that includes information specified in 20 NMAC 4.1, Subpart VIII, and 40 CFR 268.9 (d). In case any of the treatment residues fail to meet the WAC they will be managed as mixed waste.