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A Catalytic Oxidation Study and Regulatory Analysis of Tritiated Mixed Waste

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ABSTRACT

The United States biomedical research and development community faces very limited disposal options for the mixed waste generated by their research activities. For some waste, *e.g.* tritiated mixed waste of high tritium content, there is no satisfactory disposal route. As concerns regarding land burial and potential environmental releases mount, it is essential to develop processes for ensuring that contaminated materials may be disposed in an environmentally benign manner. Scientists in the pharmaceutical industry regularly use tritium and carbon-14 in research and drug development projects, and process solvents are contaminated. These activities generate moderate volumes of mixed waste with Curies (Ci) of tritium activity, or mCi of carbon-14. In contrast, academic institutions conducting life science and biomedical research produce large volumes of mixed waste with small radioactivity levels.

When faced with unsatisfactory long-term storage or poor disposal options, the Lawrence Berkeley National Laboratory (LBNL) decided to conduct a tritiated mixed waste treatability study, using Catalytic Chemical Oxidation (CCO) technology. Along with the selection of a suitable treatment technology it was necessary to formulate a reasonable management and disposal route. We will ensure the appropriate legal status of this waste by obtaining an Equivalent Treatment Determination for the oxidation approach, and Delisting the oxidized products. Following these actions, the products will be disposed as low-level radioactive waste (LLRW), at a permitted LLRW facility.

INTRODUCTION

There are very few Resource Conservation and Recovery Act (RCRA) disposal sites which also maintain Nuclear Regulatory Commission (NRC) licenses, and the disposal limit for tritium is orders of magnitude below that required for mixed waste disposal by LBNL alone. In addition, treatment, storage and disposal options have been extremely limited by the levels of tritium. Incineration of tritiated mixed waste at a Department of Energy (DOE) contractor site in Idaho would lead to release of the tritium, and this would not meet the environmental goals of the Idaho National Engineering and Environmental Laboratory (INEEL), LBNL or DOE. Use of an industrial boiler (at DSSI) would have the same environmental outcome, while also being prohibitively expensive (1996 estimated costs exceeded $200,000,000). Similar problems in the pharmaceutical industry precipitated a small crisis, and have forced prolonged storage of tritiated mixed waste at many sites around the USA.

After review of available methods [1-3], LBNL initiated tritiated mixed waste treatability study activities in mid-1996. The study was designed to evaluate the effectiveness and efficiency of treating tritiated mixed waste with oxidation technologies, in order to generate nonhazardous LLRW, principally tritiated water, with the emission of very small quantities of carbon dioxide and other inorganic oxidation products. In combination with appropriate legal actions, the treated products could then be disposed at a permitted LLRW disposal facility.

Two sources of tritium-containing mixed waste have been tested to determine the applicability of CCO for organic solvents:

(1) Newly generated tritiated mixed waste from tritiation reactions. This waste is low in volume (< 4 liter per year) but contains relatively high levels of tritium (200-500 Ci).
(2) Tritiated mixed waste stored on silica gel (~6 liters), as legacy waste from the process described in (1) above. At the beginning of 1996 the inventory of tritiated mixed waste was estimated at 2,000 Ci.

Table I lists the hazardous solvents used at the NTLF over the past six years that have EPA RCRA waste codes [4]. A primary goal of using the CCO technology was that mixed waste streams should meet land disposal requirements (LDR) [5] after treatment.

REVIEW OF TREATMENT TECHNOLOGIES

Several technologies were evaluated for feasibility in the treatment of tritiated mixed wastes, considering their destruction efficiency for hazardous organic compounds [1-3], and their suitability for use with tritium. We havepreviously published our brief review of the following technologies: molten salt oxidation (MSO), supercritical water oxidation (SCWO), pulsed-corona plasma and inductively coupled plasma oxidation, catalyzed wet oxidation (DETOX$^{(SM)}$), and direct chemical oxidation (DCO).

Catalytic chemical oxidation (CCO) involves high-temperature decomposition of organic chemicals in the presence of a catalyst. This process has been demonstrated successfully in remediation projects for organic chemical treatment and in several facilities for mixed waste treatment [1,2,6-8]. The process can accommodate both organic and aqueous mixtures and achieves more than 99.999% DRE. The CCO system was selected for the NTLF treatability study as the best overall match to our needs, accommodating our high tritium/low volume wastes, while confining the product tritiated water. The NTLF also has a HPLC liquid mixed waste stream with high water content (40% to 80%) which is not suitable for the CCO process as it is currently implemented. Other options, including conventional off-site incineration, are being considered for treatment of this waste stream.

THE CATALYTIC CHEMICAL OXIDATION SYSTEM DESIGN

The LBNL CCO system consists of a preheater, an oxidation cell with two spark sources, a packed-bed tubular reactor filled with alumina pellets and platinum-coated alumina pellets, two condensers and a dry ice cold trap, and several emission control devices including three water bubblers and a silica gel filter. Heat was provided to the catalytic reactor through a heating jacket. The temperatures of the oxidation cell and catalytic bed were controlled near or above 500 ^{o}C. Several components were preheated to predetermined temperatures (150–300 ^{o}C).

Samples were pumped into the system with suitable flow rates (up to 2.0 mL/min). The oxidation product (tritiated water) was collected using two condensers, a dry-ice cold trap, and three bubblers in series. The liquid products were analyzed by a HP 6890 gas chromatograph (GC) equipped with both a flame ionization detector and a HP 5973 mass selective detector (MSD). The solvent oxidation efficiency was monitored continuously by testing for carbon monoxide and residual hydrocarbon in the exhaust gas.

Since it is impossible to have commercial analytical work done on highly radioactive samples, two separate CCO systems, CCO-1 and CCO-2, were built for a comparative study. The CCO-1 system was used only for non-radioactive simulated waste (surrogate) tests, and only one water bubbler was used. The CCO-2 system was used for the tritiated mixed waste samples. While the surrogate products from the CCO-1 could be subjected to both external analytical tests and in-house GC/MS analyses, the radioactive products from the CCO-2 were only analyzed using the NTLF GC/MS system. Analysis of both sets of products, obtained under the same oxidation conditions, using the NTLF GC/MS allowed comparison of the results with external analytical reports.

RESULTS OF OXIDATION STUDIES

The DRE of organic solvents treated with a catalytic oxidation system may be sensitive to the composition of the solvent mixture and some operating conditions of the CCO process [1,2,6,8]. In this study we examined several CCO parameters critical to our waste stream, such as reaction temperatures, organic flow rates, oxygen requirements, and the water content of the waste sample.

Treatment under the treatability study included the following steps:

(1) GC/MS characterization of the waste sample for organic solvent content, and liquid scintillation counting assessment for radioactivity.
(2) Oxidation of a nonradioactive simulated waste sample (surrogate) using the CCO-1 system, when necessary.
(3) Analysis of the oxidation products with the GC/MS; sending the oxidation product to an EPA-certified laboratory for result verification (Table II) when necessary.
(4) Oxidation of the tritiated mixed waste sample using the CCO-2 system.
(5) Analysis of the oxidized liquid products with GC/MS (Table III) after neutralization, if the product is acidic.
(6) Analysis of the radioactivity content of the oxidized liquid product and water used in the water bubblers of the CCO-2 system (Table III).

At the conclusion of each mixed waste treatment, the oxidation product (tritiated water) was stored in a glass bottle pending future disposal or tritium recovery activities. The glass bottle was sealed in a can that was filled with absorbents and returned to LBNL's Hazardous Waste Handling Facility. The final disposition of the oxidation product will be determined by the outcome of an EPA Delisting Petition [9].

During the treatability study to date, multiple tritiated mixed waste samples and nonradioactive simulated surrogate oxidation studies have been conducted. Tables II and III give examples of these results. From our multiple experiments (see examples shown in Tables II and III), we found that:

(1) The interaction between organic compounds, air, steam, and catalyst gave complete decomposition of the organic components (>> 99.999%);
(2) The secondary products of the experiments are carbon dioxide and water, including trace amounts of nitric or hydrochloric acid, depending on the composition of waste used in the experiments. Neither carbon monoxide nor hydrocarbons are detected down to the 1 ppm level for each experiment; and
(3) The water in the three bubblers traps 1-2% of total radioactivity of the sample. Using three bubblers in a row ensures that less than 0.01% of the sample radioactivity passes through the bubbler water for absorbtion on the silica gel.

DISCUSSION OF OXIDATION MECHANISMS

A brief discussion of the oxidation mechanisms of methanol, chloroform, and nitrogen-containing compounds has been previously presented [2]. We gathered useful information for understanding the oxidation mechanisms for some organic compounds, especially when steam was involved. This study helped us to identify the operational limits of the CCO systems, and to ensure the correct operating conditions for the tritiated mixed waste samples.

MIXED WASTE MANAGEMENT

Regulatory Constraints: Current United States regulations do not appropriately consider either the regulatory burden relative to the small scale of tritiated mixed wastes or the environmental consequences of approved technologies, such as incineration, when applied to tritiated mixed wastes (tritium or tritiated water will be released to the atmosphere). In addition, no mixed waste landfill has a license to accept large quantities of tritium. Therefore, there is no satisfactory

disposal route for tritiated mixed waste of high specific activity generated by the biomedical R&D community. Although the proposed Hazardous Waste Identification Rule (HWIR) [10,11] offers hope for resolution of some aspects of this situation, final adoption of this proposed rule in states such as California is extremely uncertain.

As a consequence of severely constrained mixed waste management options, in some instances research institutions have banned the use of tritium in research. Even in institutions where tritium is still used, the regulatory burden resulting from the generation of tritiated mixed waste has had a profoundly restrictive effect on biomedical, chemical, agricultural, and pharmaceutical research in the United States. All of these research disciplines use radioactive tracers as fundamental tools for improving knowledge of chemical properties, drug discovery, pharmaceutical transport, and a host of other essential research needs. These constraints exist in spite of the scale of the mixed waste generation, which usually only entails a small number of gallons per year at any one institution.

The Department of Energy has built various advanced incineration devices to address mixed waste. However, since the radioactive isotope in tritiated mixed waste would be released with the incineration products (*i.e.* as tritiated water) without engineering control rather than retained in the ash, we believe that from our environmental perspective these approaches are undesirable. As a result, one of the major options for most mixed waste is inappropriate for tritiated mixed waste.

Treatability Study Requirements: The path we have chosen to resolve the disposal problems is to treat the mixed waste under a treatability study [12]. Treatability studies have restrictions and requirements for annual waste shipping and treatment quantities, notification, reporting (the annual report must be submitted to the regulatory agency no later than March 15 of each year), and record-keeping requirements (for three years). In the annual report, the facility should also include the final disposition of treatment residues (they are the oxidation liquid product and bubbler water for our case) and unused samples. Our experience suggests that none of these requirements is overly burdensome, and that treatment of tritiated mixed waste is appropriately controlled under such regulations.

After the treatability study, the facility who conducted the study can determine whether any treatment residues or unused samples are hazardous waste, and therefore subject to State or Federal hazardous waste regulations. From our discussion of the results of oxidation described above, we demonstrated that the treatment residues (the oxidized liquid product and bubbler water) contain no RCRA-regulated constituents (D001 high TOC ignitable liquid, F002, F003, F005, and D022) above universal treatment standards (UTSs). Thus, we believe that the oxidized liquid product and bubbler water (both are tritiated water) can be managed as low-level radioactive waste and be disposed of at a permitted facility.

Option of Delisting Petition: Because the treatability study might not be a long term solution for our tritiated mixed waste as generated and a treatment permit might be required for the oxidation process in the future, a delisting petition [9] would be a necessary option for the management and disposal of our treatment residues. The petition will seek to obtain a decision from the Environmental Protection Agency (EPA) to delist the treatment liquid residues derived from F002, F003, and F005 listed waste that remain following oxidation of D001 high TOC nonwastewater liquid which contains F002, F003, F005, and D022 organic compounds through catalytic oxidation. As described above, these treatment liquid residues contain no RCRA-regulated constituents above UTSs. Thus, the F002 and F005 codes of the original listed solvents could be delisted based on meeting the Universal Treatment Standards listed in Table I.

Because the majority of the NTLF tritiated mixed waste was characterized as high total organic compound (TOC) ignitable liquid (D001), which has more than 10% total organic carbon, the applicable treatment standard is "RORGS, POLYM, or CMBST" [13]. Thus, in conjunction with this delisting petition, we will also seek EPA's concurrence with our conclusion that the catalytic oxidation technology used to treat the D001 high TOC nonwastewater , D022, F002, F003, and F005 samples from which the treatment liquid residues are derived is within the federal regulatory definition of "combustion". Alternatively, we can seek a determination of equivalent treatment method [14] for the catalytic

oxidation technology. Thus, the D001 or F003 code of the oxidized waste liquid residues (tritiated water) could then be deleted.

Because the F-codes of oxidized waste liquid residues (tritiated water) can be delisted and the CCO can be equivalent to CMBST, the oxidized waste liquid residues can be disposed of as low-level radioactive waste at a permitted facility. Since the CCO system efficiently decomposes organic compounds (DRE > 99.999%) and confines more than 99% of the tritium as tritiated water (see Table III), an opportunity exists for tritium recovery and recycling using existing technologies [15,16].

CONCLUSIONS

From this treatability study work and regulatory analysis, we draw the following conclusions:

(1) The CCO process can treat aqueous mixtures containing high organic contents and achieve more than 99.999% of destruction and removal efficiency. With appropriate prior investigation using surrogates, a broad range of common organic waste constituents and complex mixtures can be accommodated.

(2) The oxidized liquid product (tritium-containing water) can be confined and collected using multiple condensers, dry-ice cold traps, and bubblers in series. We have demonstrated much greater than 99% trapping efficiency for tritiated water. This will greatly increase the possibility of tritium recycling.

(3) Temperatures in the oxidation cell continued to rise even though the methanol concentration was being diluted with water (up to 30%). We believe this was due to the production of steam. Since water is always present in waste samples, this allows for the water-gas shift reaction (or steam reforming) and enhancement of organic oxidation.

(4) Since (a) our oxidation temperatures were normally high (in the range of 320 to 500 ^{o}C), and (b) the oxidation of mixtures was always in the presence of steam, we did not observe any inhibition effects (when the water content did not exceed 30%) on the destruction of organic constituents of concern.

(5) Since current regulations cannot appropriately address the problem of managing small-scale tritiated mixed wastes, we propose to combine the Treatability Study application with the Delisting Petition and Determination of Equivalent Treatment Method to accommodate long-term, low-volume tritiated waste treatment and disposal or tritium recovery.

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TABLE I: Hazardous Chemicals Common in Tritium Labelling and their RCRA Codes

Code	Solvent	Universal Treatment Standard (UTS) for Nonwastewater
F002	methylene chloride	30 mg/kg
F003	acetone ethyl acetate methanol	160 mg/kg 33 mg/kg 0.75 mg/L TCLP
F005	toluene pyridine benzene	10 mg/kg 16 mg/kg 10 mg/kg
D001	high-TOC (>10%) non-wastewater mixture which might contain one or more of the following chemicals: acetic acid, acetic anhydride, acetone, acetonitrile, benzene, bromonitromethane, chloroform, cyclohexylamine, dimethylformamide, dioxane, ethanol, ethyl acetate, hexane, isopropanol, methanol, methyl acetate, methylene chloride, pyridine, tetrahydrofuran, tetramethylethylene diamine, toluene, triethylamine, water	CMBST, POLYM, or RORGS
D022	chloroform (> 6 mg/L TCLP)	6 mg/kg

Table II: Test Results for Oxidation of Nonradioactive Simulated (Surrogate) Samples

Date & ID	Sample Composition before Oxidation	Concentrations in Oxidized Water, mg/L	Operating Conditions
07/28/97 NTLF072897	Acetonitrile (ACN) 30% Dimethylformamide (DMF) 2% Ethanol (EtOH) 4% Ethyl Acetate (EtOAc) 5% Hexane <1% Isopropanol (IPA) 20% Methanol (MeOH) 2% Tetrahydrofuran (THF) 8% Toluene <1%, Water 18%	Nondetected* (every component) DRE > 99.999% Acidic liquid, neutralized	CCO-1; 1.2–1.3 mL/min; 95% sample + 5% IPA; Oxidation Cell 496–529 ^{o}C Carbon Monoxide (CO) and Hydrocarbon (HC) nondetected
10/24/97 NTLF102497	Acetic Acid 1%, ACN 14.5%, Benzene 1%, MeOH 4.5%, THF 0.1%, Triethylamine 3% Water 75.9%	Nondetected* (every component) DRE > 99.99% Acidic liquid, neutralized	CCO-1; 1.0–1.5 mL/min; 20% sample + 80% IPA to 55% sample + 45% IPA; Oxidation Cell 462–489 ^{o}C (CO and HC nondetected)
05/21/98 NTLF052198	Benzene 4%, Chloroform 2%, EtOH 10%, EtOAc 5%, IPA 25%, MeOH 20%, THF 5%, Toluene 5%, Water 24%	Nondetected* (every component) DRE > 99.999% Acidic liquid, neutralized	CCO-1; 1.0–1.3 mL/min; 70% sample + 30% IPA to 95% sample + 5% IPA; Oxidation Cell 503–519 ^{o}C (CO and HC nondetected)
12/10-11/98 NTLF121198	ACN 14.4%, Benzene 0.6%, DMF 2.7%, Dioxane 0.7%, EtOH 0.3%, EtOAc 0.3%, IPA 14.4%, MeOH 5.5%, Pyridine 2.8%, THF 2.8%, Toluene 0.3%, Water 55.2%	Nondetected* (every component) DRE > 99.999% Acidic liquid, neutralized	CCO-1; 1.0–1.5 mL/min; 30% sample + 70% IPA to 50% sample + 50% IPA; Oxidation Cell 478–508 ^{o}C (CO and HC nondetected)

***** Verified by an independent commercial laboratory, to EPA protocols.

Table III: Catalytic Oxidation of Tritiated Mixed Waste Samples

Date & ID	Sample Composition before Oxidation	Concentrations in Oxidized Water, mg/L	Operating Conditions
(10/03/97) ***new waste*** **R016337**	ACN 16.8%, DMF 18.4%, Dioxane 0.8%, EtOH 4.5%, EtOAc 3%, IPA 0.3%, MeOH 15.1%, Water 25.5% Volume 550 mL; 20.4 Ci	<1.0 (in-house GC/MS) (all components) DRE > 99.99% Bubbler water 230 mCi	CCO-2; 1.0–1.2 mL/min; 40% sample + 60% IPA to 75% sample + 25% IPA; Oxidation Cell 472–511 ^{o}C (CO and HC nondetected)
(12/15/97) ***new waste*** **R018926**	Acetic Acid 0.7%, ACN 14.1%, Benzene 1%, MeOH 4%, IPA (added), THF 0.1%, Triethylamine 3.1%, Water 77% Volume 400 mL; 11.89 Ci	<1.0 (in-house GC/MS) (all components) DRE > 99.999% Bubbler water 113 mCi	CCO-2; 1.2–1.9 mL/min; 60% sample + 40% IPA to 90% sample + 10% IPA; Oxidation Cell 470–520 ^{o}C (CO and HC nondetected)
(03/31/98) ***new waste*** **R018382**	Acetone 2.7%, IPA 40.4%, MeOH 33.2%, THF 3.7%, Water 20% Volume 235 mL; 3.5 Ci	<1.0 (in-house GC/MS) (all components) DRE > 99.999% Bubbler water 44 mCi	CCO-2; 1.2–1.6 mL/min; 60% sample + 40% IPA to 100% sample; Oxidation Cell 506–524 ^{o}C (CO and HC nondetected)
(05/26/98) ***inventory + new waste*** **R019166**	ACN 5.4%, Benzene 6.1%, EtOH 16.2%, EtOAc 1.1%, IPA 39%, MeOH 3.9%, THF 1.2%, Toluene 2.2%, Water 25% Volume 290 mL; 14.8 Ci	<1.0 (in-house GC/MS) (all components) DRE > 99.999% Bubbler water 122 mCi	CCO-2; 1.0–1.2 mL/min; 40% sample + 60% IPA to 75% sample + 25% IPA; Oxidation Cell 472–511 ^{o}C (CO and HC nondetected)
(08/24/98) ***Inventory waste*** **R018343**	ACN 0.2%, Benzene 21.6%, EtOH 0.9%, IPA 45.9%, MeOH 10.9%, Pyridine 0.2%, THF 0.1%, Toluene 0.2%, Water 20% Volume 310 mL; 30.07 Ci	<1.0 (in-house GC/MS) (all components) DRE > 99.999% Bubbler water 827 mCi	CCO-2; 1.2–1.5 mL/min; 90% sample + 10% IPA to 95% sample + 5% IPA; Oxidation Cell 496–514 ^{o}C (CO and HC nondetected)