

## **Catalytic Oxidation of Tritiated Mixed Waste with High-specific Activity For RCRA Delisting Petition**

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### **EXTENDED ABSTRACT**

**Background.** Scientists in the United States pharmaceutical industry regularly use tritium and carbon-14 in research and 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. In the case of Lawrence Berkeley National Laboratory's (LBNL's) tritiated mixed waste, annual volumes are small (1 liter), but tritium concentrations may range up to 1,000 Ci/liter. The hazardous component of this waste includes F-listed spent solvents, is designated as high total organic compound (high TOC) ignitable D001 waste, and may occasionally contain chloroform (code D022).

As the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC) have acknowledged in regulatory guidance documents and in proposed and final rulemakings, dual regulation of mixed waste under the Atomic Energy Act and the Resource Conservation and Recovery Act (RCRA) presents a number of difficulties. Not least of these is that there are very few RCRA disposal sites which also maintain NRC licenses, and the disposal limit for tritium is orders of magnitude below that required for mixed waste disposal by LBNL alone. Hence, the US 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 with a tritium content in the 1-200 Curie range), there is no satisfactory disposal route. Commercial options for treatment and disposal of tritiated mixed waste have undesirable environmental and fiscal consequences. As an example, the only commercial option for treatment of tritiated mixed waste, incineration, would release tritium to the environment without engineering controls designed to minimize tritium air emissions. Use of such a commercial treatment facility is also prohibitively expensive (\$30 – 100 per mCi).

**Tritiated Mixed Waste Management.** 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 the most environmentally benign manner. Incineration of tritiated mixed waste at one of the Department of Energy (DOE) contractor sites would also lead to release of the tritium, and this would not meet the pollution prevention goals of LBNL and DOE. In the pharmaceutical industry these combined environmental, fiscal and legal issues have forced prolonged storage of tritiated mixed waste at many sites around the USA.

When faced with unsatisfactory storage and disposal options for tritiated mixed waste, the Lawrence Berkeley National Laboratory decided to conduct a treatability study [40 CFR261.4(f)] using a catalytic chemical oxidation (CCO) technology. We have sought to ensure the appropriate legal status of this waste by applying for an Equivalent Treatment Determination for the oxidation approach, and Delisting the treatment residues. A summary of the strategy developed for LBNL's tritiated mixed wastes in connection with the treatability study is as follows:

- (1) Evaluate the hazardous and radiological characteristics of the identified waste streams;
- (2) Evaluate the effectiveness and efficiency of the CCO and solvent extraction technologies;
- (3) Evaluate the characteristics of the oxidized and condensed liquid product;
- (4) Obtain delisting approval [40 CFR260.22(b)] for residues of waste that originally contained F-listed components, and obtain concurrence with our conclusion that the LBNL CCO technology is within the regulatory definition of "combustion" [40 CFR 268.42, Table 1] or is an acceptable alternative treatment methodology for D001 high TOC waste; and
- (5) Dispose of the delisted treatment residues at a licensed low-level waste disposal site, or send them off site for tritium recycling.

**Catalytic Oxidation Process.** LBNL's CCO system consists of (a) a preheater, (b) an oxidation cell with two spark sources, (c) a packed-bed tubular reactor filled with platinum-coated alumina catalyst, and (d) an oxidation product (tritiated water) recovery and emission reduction system which consists of two condensers, a dry-ice cold trap, three water bubblers in series, and a silica gel filter. A general operating condition for the CCO system was developed: (a) preheater set at 300 °C, (b) oxidation cell controlled near or above 500 °C, (c) catalytic bed controlled at 500 °C or above, and (d) sample flow rate set between 1 and 2 mL/min, based on the composition of the sample.

Using the suitable operating conditions for each sample, the destruction and removal efficiency (DRE) of organic solvents exceeds 99.999%. The high oxidation efficiency has also been demonstrated because we did not detect any release of CO and other hydrocarbons (HC) at or above the one mg/liter detection limit on oxidation of any waste or surrogate samples. However, achieving this DRE requires careful attention and fine tuning of the oxidation process (see Table 1). Although none of the target organic compounds was detected in the condensed liquid product (HTO) above a one mg/liter level using the in-house GC/MS, the variability in results and operating conditions indicated the effects of the unique characteristics of each sample on the oxidation and emission reduction processes.

Our results indicated that for samples (7 out of 62) containing chloroform or methylene chloride (low concentrations) prior to oxidation, no chlorinated compounds (in the µg/liter range) were detected in the oxidation liquid product using our GC/MS and using the EPA test Methods 8015,

8260, and 8270 (by a commercial laboratory). We also did not observe the formation of soot or particulate materials in our CCO process (except in three cases out of 62 tests). We believe that:

- (a) the presence of steam enhanced the conversion of CO and other hydrocarbons to CO<sub>2</sub> and water;
- (b) the preheater of our CCO process can completely vaporize the sample; thus, the oxidation efficiency is greatly enhanced; and
- (c) the Pt catalysts further enhanced the conversion of CO or other hydrocarbons to CO<sub>2</sub> and water.

We also found that the condensers, cold trap, water bubblers, and silica gel filter can confine more than 99.9% of tritium in the waste sample. Thus, this process exceeds the DRE standards for incineration (99.99%), while emission of tritium is reduced to < 0.1% of that from incineration. The emission reduction devices also minimize the emission of acidic gas (condensed as hydrochloric or nitric acid in the liquid product) along with tritium. This level of performance clearly meets the goals of LBNL's pollution prevention program. Examples of the CCO operating conditions and oxidation results are presented in Table 1.

**Delisting Petition.** Under RCRA, prior to disposal, the treatment residues must not exhibit RCRA characteristics, must meet the concentration-based land disposal restriction (LDR) treatment standards for the F-listed and D-coded components, and the universal treatment standards (UTS) for the underlying hazardous constituents. Also, the D001 high-TOC designation of the waste means that the technology-specific LDR of combustion must be met. Based on more than 80 test results (with both tritiated waste and non-radioactive surrogate samples), we have demonstrated that:

- (a) the F002 and F005 codes of the treatment residue derived from the original listed solvents could be delisted;
- (b) the D001 and F003 codes of the liquid products of oxidation could be deleted on the basis of the Determination of Equivalent Treatment Method for the CCO system; and
- (c) the treatment residue is water or tritiated water only and exhibits no RCRA characteristics (after neutralization).

Following these actions, the treatment residues from waste oxidation can be disposed as low-level radioactive waste at a permitted facility, or tritium in the liquid products might be recycled.

LBNL believes that the combination of technology application (CCO) and administrative action (Delisting Petition and Equivalent Treatment Determination) will resolve our tritiated mixed waste treatment and disposal problem in a manner that will result in a net benefit to the environment. In June 1999, LBNL submitted a "Petition to Delist Tritiated Mixed Waste Treatment Residues" to the EPA Region IX (<http://www.lbl.gov/LBL-Programs/tritium/delisting/index.html>).

Since March 1997, two sources of tritium-containing mixed waste have been tested:

- (1) Liquid tritiated mixed waste generated from tritiation reactions; and
- (2) Tritiated mixed waste absorbed on silica gel, as legacy waste generated between 1993 and February 1996 from the process described in (1) above (completed by the end of 1998).

To September 2000, 62 mixed waste samples containing more than 1,800 Ci of tritium activity have been condensed and collected from the CCO study, giving approximately 19.6 liters of liquid product (tritiated water).

**Table 1. Examples of Catalytic Oxidation Results of Tritiated Mixed Waste Samples**

Date and ID	Sample Composition before Oxidation	Concentration in Oxidized Water (mg/L)	Operating Conditions
(02/18/00) R021130	ACN 1.8%, DMF 26.5%, EtOH 1.8%, IPA 24.6%, MeOH 10.3%, water 35%  Vol. 285 ml; 81 Ci	<1.0 (in-house GC/MS) (all components) DRE > 99.999% (neither CO nor HC were detected above 1 ppm)	CCO-2; 1.5 - 1.8 mL/min; 85% sample + 15% IPA to 80% sample + 20% IPA Oxid. cell 483–538 °C
(03/16-17/00) R021144	ACN 38%, DMF 12%, EtOAc 0.6%, EtOH 0.2%, ether 0.5%, MeOH 4.2%, toluene 0.5%, THF 14%, water 30%  Vol. 375 ml; 58.2 Ci	<1.0 (in-house GC/MS) (all components) DRE > 99.999% (neither CO nor HC were detected above 1 ppm)	CCO-2; 1.5 - 1.8 mL/min; 85% sample + 15% IPA to 80% sample + 20% IPA Oxid. cell 460–521 °C (experienced water bubbler complications)
(06/30/00) R026730	ACN 24%, acetone 1%, EtOAc 6.5%, EtOH 4%, IPA 24%, MeOH 3.5%, THF 1%, water 36%  Vol: 420 ml; 43.2 Ci	<1.0 (in-house GC/MS) (all components) DRE > 99.999% (neither CO nor HC were detected above 1 ppm)	CCO-2; 1.1–1.5 mL/min; 75% sample + 25% IPA to 80% sample + 20% IPA; Oxid. cell 486 – 525 °C (experienced water bubbler complications)
(09/07/00) R026749	ACN 23%, DMF 10%, EtOAc 5%, IPA 13%, MeOH 2%, THF 7%, water 40%  Vol. 415 ml; 61.3 Ci	<1.0 (in-house GC/MS) (all components) DRE > 99.999% (neither CO nor HC were detected above 1 ppm)	CCO-2; 1.5–2.0 mL/min; 75% sample + 25% IPA to 80% sample + 20% IPA; Oxid. cell 497–527 °C (experienced oxygen flow complications)

Note: ACN = acetonitrile, CO = carbon monoxide, DMF = dimethyl formamide, EtOAc = ethyl acetate, EtOH = ethanol, HC = hydrocabons, IPA = isopropanol, MeOH = methanol, THF = tetrahydrofuran, TMEDA = tetramethylethylene diamine