

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. 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.

From this study we have identified a suitable treatment technology and a reasonable management and disposal route for tritiated mixed waste of high specific activity, which has been generated through our biomedical research and development projects. We have included a brief review of several other oxidation technologies, a discussion of oxidation mechanisms for some specific waste components, and a short guide to our interpretation of the relevant regulations.

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 (TSD) 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). In the pharmaceutical industry these issues precipitated a small crisis, and have forced prolonged storage of tritiated mixed waste at many sites around the USA.

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 (< 1 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 [1]. A primary goal of using the CCO technology was that mixed waste streams should meet land disposal requirements (LDR) [2] after treatment.

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

Code	Solvent	Universal Treatment Standard (UTS) for Nonwastewater
F002	methylene chloride	30 mg/kg
F003	acetone ethyl acetate ethyl ether methanol	160 mg/kg 33 mg/kg 160 mg/kg 0.75 mg/L TCLP
F005	toluene pyridine benzene	10 mg/kg 16 mg/kg 10 mg/kg
D001	acetic acid, acetic anhydride, acetone, acetonitrile, benzene, bromonitromethane, cyclohexylamine, dimethylformamide, dioxane, ethanol, ethyl acetate, hexane, isopropanol, methanol, methyl acetate, tetrahydrofuran, tetramethylethylene diamine, toluene, triethylamine	CMBST, POLYM, or RORGS
D018	benzene (> 0.5 mg/L TCLP)	10 mg/kg

D022	chloroform (> 6 mg/L TCLP)	6 mg/kg
D038	pyridine (> 5 mg/L TCLP)	16 mg/kg

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 [3,4], and their suitability for use with tritium. A brief review of each of these technologies is presented below.

Direct Chemical Oxidation (DCO): DCO is an aqueous organic oxidation process using acidified ammonium peroxydisulfate, which is among the strongest known chemical oxidant compounds. The process includes an electrolysis flow cell to produce ammonium peroxydisulfate from recycled ammonium sulfate, an oxidant surge, the waste oxidizer, the product surge/separator, and a hydrogen separation/recombination cell. The oxidation potential for the electrode reaction is 2.07 volts, high enough to oxidize most organic compounds.

This technology has been tested for chemical and biological warfare agents, resins, explosives, *etc.* The destruction of fully halogenated organic compounds has not been tested. DCO is complex for the following reasons: (1) Since the sulfate product is recycled to produce peroxydisulfate by electrolysis, very large quantities of hydrogen are generated in the electrolysis cell and a separation/recombination cell is needed. Separation of hydrogen and tritium may be a problem during the treatment of tritiated mixed waste; (2) A separation unit for the process solution, residues, salts, and oxidized compounds is needed to recycle the ammonium sulfate.

Catalyzed Wet Oxidation (DETOX^(SM)): An oxidation process (known as DETOX^(SM)) for the treatment of hazardous organic wastes has been examined in various DOE projects [5]. DETOX^(SM) is a wet oxidation process in strong acidic solution (HCl), with a high concentration of ferric chloride as catalyst and small amounts of platinum and ruthenium ions as co-catalysts. This process has been demonstrated at bench-scale with 99 to 99.999% destruction and removal efficiency (DRE) for liquid hydrocarbons and chlorinated organics.

DETOX^(SM) is much more aggressive with respect to most organic compounds than the normal wet oxidation processes. The oxidant is continuously generated and regenerated in solution (this process has an internal regeneration mechanism). The heat input rate from oxidation is regulated by blending wastes to a constant heating value (the new DETOX pilot plant installed at Savannah River Site utilizes direct heat exchange to remove excess heat of combustion).

While the waste characterization, sorting, storage, and blending efforts necessary for DETOX^(SM) use are worthwhile for large volumes of waste with consistent content, they would be very time intensive for small volumes of highly variable waste. In addition, the use of strong acidic solution (HCl) with a high concentration of ferric chloride as catalyst makes this process less desirable for use with tritiated mixed waste.

Molten Salt Oxidation (MSO): MSO was developed originally in the mid-1970s for coal gasification and recovery of transuranic elements from nuclear fuel residues. Shortly thereafter, Rockwell demonstrated up to 99.9999% DRE for a variety of hazardous chemicals (liquid and

solid) with MSO. More recently, Rockwell and ETEC successfully destroyed approximately 200 liters of mixed wastes (oils) with MSO equipment [6]. Lately, several national laboratories [7,8] have further demonstrated and evaluated the application of MSO to a variety of waste streams. The DREs of chlorinated compounds, alcohols, benzene, toluene, mineral oil, scintillation cocktails, combustible plastics, *etc.*, have been examined using MSO.

MSO is not a flame-combustion process. It is a liquid-phase catalytic process in which a molten electrolyte medium, such as sodium carbonate, "reacts" with the waste [9]. The chemistry of MSO involves two main types of reactions: (1) catalytic oxidation, and (2) neutralization of acidic species to form the alkali salts (NaF, NaCl, *etc.*). It can also retain metals and ash in the molten salt when solid waste streams are treated.

The complicated operation procedure and setup, possible confinement problems for tritium gas or tritiated water vapor, and the recycling and disposal of used salts were major concerns for the application of the MSO process to tritiated mixed waste.

Supercritical Water Oxidation (SCWO): SCWO works by subjecting aqueous waste streams to temperatures and pressures in the supercritical region (over 374 °C and 3250 psi or 22.1 MPa), where organic chemicals become completely miscible with water. Above its critical point, water displays properties that make it an ideal medium for the oxidation of polar and nonpolar organic molecules. The continuous-flow SCWO system is composed of three sections: a preheating section, the reactor, and a cooldown section [10].

With introduction of oxygen, air, or oxidizers, virtually any oxidizable organic hydrocarbon can be converted to carbon dioxide and water, organic nitrogen is primarily converted to N₂, and halides appear in the effluent as inorganic acids. SCWO is most promising for aqueous wastes in which the organic content is 10% or less. The oxidation of methanol, methylene chloride, phenol, and several other organic solvents with SCWO has been examined [11]. The DRE for treatment of these organic chemicals at 500 to 580 °C for 35 seconds ranged from 99.0% to 99.99% or higher. The major concerns for use of the SCWO system were operation of a high pressure process with tritium and the long cooling time of the oxidization products after the experiment.

Catalytic Chemical Oxidation (CCO): 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 [4,5,12,13]. The process can accommodate both organic and aqueous mixtures and achieves more than 99.999% DRE.

In general the CCO process consists of a preheater, an oxidation chamber, a heated packed-bed reactor filled with catalyst pellets, and an emission reduction device. Heat is provided to the preheater and catalytic reactor with separate controlled heating zones. The temperature of the catalytic reactor and oxidation unit is in the range of 450 to 750 °C. Several pharmaceutical companies are using CCO processes to perform mixed waste treatability studies.

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. Other options, including conventional off-site incineration, are being considered for treatment of this waste stream.

THE CATALYTIC CHEMICAL OXIDATION SYSTEM DESIGN

The CCO system consisted of a preheater, an oxidation cell with two spark sources, and a packed-bed tubular reactor filled with alumina pellets and platinum-coated alumina pellets. 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 °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 measuring 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. 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 in-house GC/MS system. Analysis of both sets of products using the in-house system 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 [4,5,12,13]. 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) Characterization of the waste sample with a GC/MS for organic solvent content, and a liquid scintillation counter 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 oxidation products with the GC/MS (Table II) and liquid scintillation counter.

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 [14].

Since early 1997 fifty tritiated mixed waste samples have been oxidized, and fifteen surrogate oxidation studies have been conducted. Table II gives examples of these results.

DISCUSSION OF OXIDATION MECHANISMS

A brief discussion of the oxidation mechanisms of methanol, chloroform, and nitrogen-containing compounds is presented in the following section. This review provides useful information for understanding the basis of oxidation mechanisms of some organic compounds, especially when steam is involved. The simulated nonradioactive surrogate tests (see Table III) using the CCO-1 system allowed us to identify the operation limits of both CCO systems, and to ensure the correct operating conditions for the tritiated mixed waste samples.

(A) Destroying Hazardous Waste with Steam

Currently, incineration is one of the most popular industrial technologies for destruction of hazardous organic wastes. However, in conventional incineration, liquid waste is introduced at the location of the flame and is subjected to undesirable effects, such as solid particulate formation, products of incomplete combustion (PIC) formation, *etc.* Most of the available residence time for the waste is consumed in getting the liquid waste heated and vaporized to a high-temperature vapor state, where actual destruction chemistry can begin. PICs are also formed after combustion chemistry has occurred, so more residence time is consumed. Thus the combustion chamber is forced to operate at unreasonably high temperatures and long residence times, consuming costly fuel and creating high NO_x output.

TABLE II: Catalytic Oxidation of Simulated Waste and Tritiated Mixed Waste

#	Sample Description (component vol./total vol.; %)	Concentration in Product (mg/L)	Comments
1 Surrogate (8/97)	ACN 7.4%, Chloroform 3.2%, EtOH 3.5%, IPA 21.7%, MeOH 34.7%, THF 2.2%, Toluene 2.2%, Water 25.1% Volume: 250 mL	Nondetected (all organic components)* DRE > 99.999%	CCO-1; 1.4–1.75 mL/min; 80% sample + 20% IPA to 95% sample + 5% IPA Oxidation cell 495–508 °C Acidic liquid formed.
2 Mixed Waste F003, F005, D001, D022	ACN 7.4%, Chloroform 3.2%, EtOH 3.5%, IPA 21.7%, MeOH 34.7%, THF 2.2%, Toluene 2.2%, Water 25.1% Volume: 170 mL; Activity: 2.57 Ci	<< 1.0 (all organic components) DRE > 99.999%	CCO-2; 1.3–1.5 mL/min; 60% sample + 40% IPA Oxidation cell 514–539 °C Acidic product neutralized.
3 Surrogate (7/97)	ACN 7.8%, DMF 8.2%, EtOH 18.7%, EtOAc 1.5%, IPA 7.8%, MeOH 21%, THF 7.8%, Water 25.7% Volume: 260 mL	Nondetected (all components)* DRE > 99.999%	CCO-1; 1.2–1.4 mL/min; 70% sample + 30% IPA Oxidation cell 480–520 °C Acidic liquid formed.
4 Mixed Waste F003, D001	ACN 8 %, DMF 8%, EtOH 9%, EtOAc 1.5%, IPA 17%, MeOH 21.5%, THF 9%, Water 26% Volume: 490 mL; Activity: 51.1 Ci	<< 1.0 (all organic components) DRE > 99.999%	CCO-2; 1.3–1.8 mL/min; 70% sample + 30% IPA to 90% sample + 10% IPA Oxidation cell 466–500 °C Acidic product neutralized.
5 Surrogate (7/97)	ACN 41%, EtOAc 6%, Hexane 3%, MeOH 15%, THF 8%, Toluene 2%, Water 25% Volume: 280 mL	Nondetected (all organic components)* DRE > 99.999%	CCO-1; 1.3–1.5 mL/min; 80% sample + 20% IPA Oxidation cell 484–506 °C Acidic liquid formed.
6 Mixed Waste F003, F005, D001	ACN 42%, EtOAc 6%, Hexane 3%, MeOH 15%, THF 8%, Toluene 2%, Water 24% Volume: 300 mL; Activity: 0.63 Ci	<< 1.0 (all organic components) DRE > 99.999%	CCO-2; 1.5–2.0 mL/min; 70% sample + 30% IPA to 90% sample + 10% IPA Oxidation cell 465–508 °C Acidic product neutralized.
7 Surrogate (10/97)	Acetic Acid 1%, ACN 14.5%, Benzene 1%, MeOH 4.5%, THF 0.1%, Triethylamine 3%, Water 75.9% Volume: 240 mL	Nondetected (all components)* DRE > 99.999%	CCO-1; 1.0–1.5 mL/min; 20% sample + 80% IPA to 55% sample + 45% IPA Oxidation cell 462–489 °C Acidic liquid formed.
8 Mixed Waste F003, D001	Acetic Acid 0.7%, ACN 14.1%, MeOH 4%, THF 0.1%, Triethylamine 3%, Water 77%, (trace IPA and benzene; <1%) Volume: 400 mL; Activity: 11.89 Ci	<< 1.0 (all organic components) DRE > 99.999%	CCO-2; 1.2–1.7 mL/min; 90% sample + 10% IPA to 50% sample + 50% IPA Oxidation cell 471–520 °C Acidic product neutralized.

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

Because of these disadvantages of incineration, a steam reforming process has been developed and tested in the past few years [15]. The commercially available steam reforming process first evaporates organic waste and then provides steam at 600-1100 °F to convert the waste into CO, CO₂, H₂O, H₂, and CH₄. The main chemical reactor is heated electrically, so gases are free of fuel combustion. Thus, it avoids troublesome particulates, SO_x, and NO_x emissions. This process is also equipped with a catalytic converter that converts CO to CO₂ and releases heat that can be recovered and reused in the process.

Observations from our Study. We conducted many tests that involved both organic solvents and water in the samples (see Tables II and III). We believe the effect of steam was observed in most cases. When the water content in the mixture was high (40 to 50%) some inhibition of methanol oxidation occurred. Nevertheless, for the tests presented in Tables II and III, neither CO nor residual hydrocarbons were detected in the exhaust gas. We believe that the presence of steam enhanced the conversion of CO to CO₂ (gas-water shift reaction).

(B) Oxidation of Chloroform over Platinum Catalyst

Catalytic oxidation is used commonly for controlling industrial offgas emissions that may contain chlorinated organic molecules like chlorinated methanes and ethanes [16]. Normally in these applications it is preferable to minimize the formation of Cl₂ and favor HCl because HCl can be more easily removed from effluent streams, and thus corrosion problems in downstream operations are reduced.

Prior experiments have determined the following: (1) The presence of water had a minimal effect on catalytic activity; (2) Conversion of chloroform in the presence of water had a mild inhibitive effect on the oxidation rate; (3) Because of the presence of water, most Cl₂ was converted to HCl; (4) Performing the experiment in dry air resulted in an increase in Cl₂ concentration; therefore, the water must be supplying hydrogen to the reaction; and (5) It was also found that HCl has a strong product inhibition effect because of the adsorption of HCl on the catalyst.

Observations from our Study. We have conducted several tests on samples that contained chloroform, methanol, water, isopropanol, *etc.* (Tables II and III). We found that (i) the oxidized product (tritiated water) was acidic, which suggests the presence of hydrogen chloride, and (ii) the DREs of chloroform were greater than 99.99%. The results indicated that the presence of water could convert chloride into HCl. We did not observe any water inhibition effect on chloroform oxidation.

(C) Oxidation of Methanol over Pd Catalyst

Previous studies of methanol (CH₃OH) oxidation focused mainly on formaldehyde (HCHO) emission *via* the operation of vehicles using methanol [17]. It is relatively easy to catalytically oxidize both methanol and formaldehyde, compared to other organic chemicals. It was found that either Pt or Pd catalysts produced the highest activity and lowest HCHO yields.

Under fuel-lean conditions for different feed gas compositions, including those containing CO₂ and/or H₂O, the conversion of CH₃OH was greater than 90%. It was found that water had an inhibiting effect on methanol oxidation, probably due to mass transfer limitations.

When the feed gas contained H₂O, the CO₂ yield was increased. This effect is attributed to the water-gas shift reaction. When the experiment was conducted with multiple fuel components, the presence of CO in the feed increased the light-off temperature significantly, suggesting kinetic inhibition by CO.

Observations from our Study. From methanol oxidation experiments (on a Pt catalyst), we observed that within a broad range of oxidation temperatures (between 320 and 520 °C), methanol (with or without water) was completely (>99.999%) converted to water and CO₂. Similar observations were also true for other alcohols, such as ethanol and isopropanol (see Table III). Since water was always present in waste samples or generated in the process, this allows for the water-gas shift reaction.

It was also observed that under fuel-lean conditions (*i.e.*, with sufficient oxygen), the temperature of the oxidation cell continued to rise even though the methanol concentration was being diluted with water (up to 30%). We attribute this effect to the production of steam. From Table III, we also found that:

- (1) When the water content was raised to 40%, the temperatures of the oxidation cell were unstable. Cloudy products were also observed. The DRE of methanol was still greater than 99.99%; and
- (2) There was an inhibiting effect on methanol oxidation when water content was in the range of 40 to 50%. Soot was formed, which indicated that oxidation was incomplete. This is probably due to the water-quenching effect on the combustion reaction and the competition of oxygen.

TABLE III: Test Results for Oxidation of Nonradioactive Simulated (Surrogate) Waste

Sample Number	Original Concentration in the Simulated Waste (component vol./total vol.; %)	Concentration in Oxidation Products (mg/L)	Oxidation Cell Temperature (°C)
1	Isopropanol (100%)	<1 (DRE > 99.999%)	400–500
2	Isopropanol (60-90%), Water (10-40%)	<1 (DRE > 99.999%)	400–500
3	Ethanol (60%), Water (40%)	<1 (DRE > 99.999%)	400–500
4	Methanol (100%)	<1 (DRE > 99.999%)	400–500
5	Methanol (70%), Water (30 %)	<1 (DRE > 99.999%)	319–399
6	Methanol (50-60%), Water (40-50%)	<1 (cloudy liquid) <1 (CO & hydrocarbon) (soot formed when water content was high)	300–404 (unstable)
7	Acetonitrile 10%, Methanol 65%, Water 25%	<1 (DRE > 99.999%) (acidic product)	320–420
8	Chloroform 5%, Methanol 70%, Water 25%	<1 (DRE > 99.999%) (acidic product)	329–389

(D) Oxidation of Nitrogen-Containing Compounds

Several processes, such as incineration, pyrolysis, or steam reforming, are commonly used to treat hazardous wastes. However, none are widely used to treat nitrogen-containing waste because of the concerns of generation and emission of NO_x . In the presence of nitrogen-containing material or nitrogen and excess oxygen, oxides of nitrogen are formed during the oxidation process.

One example of the oxidation of a nitrogen-containing compound is the oxidation of ammonia. In a catalytic reactor, the oxidation of ammonia [18] will yield NO as the major product, which will be accompanied by several side products, such as N_2O and N_2 . In the nitric acid manufacturing process, any NO generated is further converted to nitric acid in the presence of water and oxygen [19].

Observations from our Study. Several surrogates, consisting of methanol, isopropanol, water, acetonitrile, *etc.*, were tested with our two CCO systems. A test result with a simple mixture is presented in Table III. We believe that the oxidation of acetonitrile follows a similar reaction route to ammonia. From our tests we found that (a) the oxidized product (water) was acidic,

which suggests the formation of nitric acid, and (b) the DREs of acetonitrile were greater than 99.99% as shown in Tables II and III.

Other studies [20] claimed that the oxidation of hydrocarbons in the mixture with nitrogen-containing compounds might be inhibited. We did not observe inhibitory effects of the nitrogen-containing compounds on the oxidation of other hydrocarbons.

REGULATORY ANALYSIS

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) [21,22] offers hope for resolution of some aspects of this situation, final adoption of this proposed rule in states such as California is extremely uncertain.

The path we have chosen is to treat the mixed waste under a Treatability Study [26]. The D001 or F003 code of the oxidized waste (tritiated water) could then be deleted on the basis of the Determination of Equivalent Treatment or Treatment Variance [23] for the CCO system. The F002 and F005 codes of the original listed solvents could be delisted based on meeting the Universal Treatment Standards listed in Table I. The residues (in this case, silica gel) and products (tritiated water) 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 much more than 99% of the tritium as tritiated water, an opportunity exists for tritium recovery and recycling using existing technologies [24,25].

Treatability Studies [26] have restrictions and requirements for annual waste shipping and treatment quantities (400 kg), waste generation and treatment processes, sampling and analysis procedures, a quality assurance plan, notification, reporting and record-keeping requirements. Our experience suggests that none of these requirements is overly burdensome, and that treatment of tritiated mixed waste is appropriately controlled under such regulations.

The further development of treatment technologies and commercial application would be greatly facilitated if Equivalent Treatment Determination and Delisting coincided with approval of the initiation of a Treatability Study using an approved technology, such as the CCO process.

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 °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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