

## **Attachment A**

### **Demonstration of Combustion Technology/ Petition for Approval of Alternative Treatment Method**

Lawrence Berkeley National Laboratory requests Environmental Protection Agency concurrence that LBNL's catalytic chemical oxidation (CCO) technology meets the definition of "combustion" set forth at 40 CFR Section 268.42, Table 1. Alternatively, LBNL requests, pursuant to 40 CFR Section 268.42(b), that EPA approve its CCO technology as an acceptable alternative to combustion.

Although California is generally authorized by EPA for regulation of hazardous wastes under RCRA, two California regulatory provisions warrant submitting this document to EPA before going to the state. First, California's hazardous waste regulations have not yet incorporated the federal change that broadened the definition of combustion at 40 CFR Section 268.42 to allow combustion in more than incinerators, boilers, and industrial furnaces. Second, one of the demonstrations an applicant to the State for approval of an alternative treatment method must make is that the US EPA Administrator has approved the use of the alternative treatment method pursuant to 40 CFR 268.42(b) (Title 22 of the California Code of Regulations, Section 66268.42(b)).

As this document will demonstrate, the LBNL CCO technology achieves a measure of performance equivalent to that of other combustion methods specified at 40 CFR 268.42, Table 1. In relation to the tritiated mixed waste generated from tritium labeling experiments and purification processes at LBNL, the CCO process achieves this measure of performance (in excess of 99.999%) without the tritium emissions associated with incineration. Treatment of tritiated mixed waste with moderate to high levels of tritium through incineration would result in emissions of tritium to the atmosphere without engineering controls. The CCO process includes strict engineering controls designed to retain nearly all of the tritium in the original waste in the residue of the CCO process.

#### **Background**

In 1996, Lawrence Berkeley National Laboratory initiated a treatability study in order to explore treating tritiated mixed wastes to meet land disposal requirements (LDRs) through use of catalytic oxidation instead of incineration.

The goal of finding an alternative to incineration is consistent with the Nuclear Regulatory Commission (NRC) and the EPA's jointly published final guidance on testing requirements for mixed waste, which emphasizes the As Low As Reasonably Achievable principle (ALARA) in connection with mixed waste management. From an environmental and ALARA perspective, incineration without engineering controls is not an environmentally desirable method for treating tritiated mixed wastes such as LBNL's to meet federal LDRs, because all or most of tritium in the waste is released into the environment during the incineration process. Incineration of mixed wastes with moderate to high tritium levels is also extremely expensive.

The primary focus of LBNL's treatability study is to evaluate the effectiveness and efficiency of oxidizing tritiated liquid mixed waste using catalytic chemical oxidation (CCO) technology. The CCO technology involves high-temperature decomposition of organic chemicals in the presence of a catalyst. CCO technology has been successfully demonstrated in many remediation projects and industrial waste treatment processes for

organic chemical treatment. Such technology should generate nonhazardous products, principally carbon dioxide and tritiated water (HTO), with the latter being trapped for disposal as low-level radioactive waste or for recycling of tritium.

### Descriptions of the Waste Characteristics

In the treatability study conducted to date, the LBNL scientists at LBNL's National Tritium Labeling Facility (NTLF) developed and used the catalytic chemical oxidation (CCO) system to oxidize multiple (52) tritiated liquid mixed waste samples (described in Section 5, Item 5a of the Delisting Petition). All of these 52 liquid mixed waste samples exhibited at least the characteristic of ignitability (D001 and F003) and were non-wastewaters with greater than or equal to 10% total organic carbon (high TOC).

Three sources of tritiated liquid mixed waste at LBNL are involved in the treatability study using the CCO system:

- 1) Inventory tritiated liquid mixed wastes absorbed on silica gel generated at the NTLF between January 1993 and February 1996 (LBNL Mixed Waste Site Treatment Plan ID Number LB-W125).
- 2) Tritiated liquid mixed wastes generated from tritium labeling experiments and purification processes at the NTLF (after February 1996 to date).
- 3) Liquid tritiated mixed waste that will be generated from future tritium labeling experiments and purification processes at the NTLF.

Before oxidation, each "as generated" mixed waste mixture studied to date contained water and one or more regulated F002, F003, or F005 constituents; was occasionally D-coded for organics; and was high-TOC D001 ignitable. Examples of hazardous constituents, as identified in 52 samples prior to oxidation, are provided in Table A-1.

Table A-1. Chemical constituents identified in multiple tritiated mixed wastes

EPA Hazardous Waste Code	Hazardous Waste Description
F002 F003 F005	methylene chloride acetone, ethyl acetate, methanol benzene, pyridine, toluene
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
D022	chloroform

It should be noted that although the mixed waste mixtures from the NTLF have, to date, always contained one or more F-listed constituents, future process changes could result in

mixed waste mixtures that are D001 high-TOC ignitable but not F-listed. Accordingly, both a delisting (to cover F-listed residues of catalytic oxidation) and approval of our CCO technology (to cover the technology-based land disposal requirement for D001 high-TOC wastes) will be necessary in order for disposal to be possible following treatment.

### **Definition of CMBST and Descriptions of the CCO System**

Title 40, Code of Federal Regulations (CFR), Section 268.40 provides that, the applicable treatment standard for D001 high-TOC ignitable waste is “RORGS, POLYM, or CMBST.” In LBNL’s case, the focus of our analysis will be on the “CMBST” treatment standard.

Under 40 CFR Section 268.42, “CMBST” is defined as “[h]igh temperature organic destruction technologies, such as combustion in incinerators, boilers, or industrial furnaces operated in accordance with the applicable requirements of 40 CFR Part 264, Subpart O, or 40 CFR Part 265, Subpart O, or 40 CFR Part 266, Subpart H, and in other units operated in accordance with applicable technical operating requirements; and certain non-combustive technologies, such as the Catalytic Extraction Process.”

The LBNL CCO system is high-temperature organic destruction technology that we believe qualifies as “CMBST.” The temperature of the CCO system for decomposition of organic chemicals in the presence of alumina pellets and platinum-coated alumina pellets as catalysts is near or above 500 °C. See Attachment B and Figures 2 and 3 in Delisting Petition for the CCO system design, operation procedure, and oxidation efficiency.

Two separate CCO systems (CCO-1 and CCO-2) were designed and constructed by the LBNL staff. The CCO-1 and CCO-2 systems are designed for treating simulated nonradioactive surrogate mixtures and tritiated mixed waste samples, respectively. Each system consists of

- sample pumps,
- a sample preheater,
- a heated oxygen source (4 liter/min flow rate),
- an oxidation cell,
- a packed-bed tubular reactor filled with platinum/alumina pellets, and
- an emission-reduction device (for exhaust gas) consisting of multiple condensers, a cold trap, water bubblers, and a silica gel filter.

Liquid samples are pumped through the preheater, at a flow rate normally regulated between 1 and 2 mL/min. The preheater temperature is maintained at near 300 °C. The temperatures of both the oxidation cell and catalytic reactor are controlled near or above 500 °C. Attachment B describes the CCO system and its oxidation efficiency.

The liquid product (water or tritiated water) is collected using multiple reflux condensers and a dry-ice cold trap in series. The trapping efficiency for tritiated water is > 98%. After these water traps, the exhaust gas goes through multiple water bubblers and silica gel before exiting to the NTLF stack.

## Regulatory Requirements

Under 40 CFR Section 268.42(b), in order to demonstrate that the CCO system qualifies as or is equivalent to “CMBST,” LBNL will show that the CCO system meets the following criteria:

- (A) The CCO system can achieve a measure of performance equivalent to that achieved by a Subtitle C incinerator, boiler, or furnace.
- (B) The CCO system is operated in accordance with applicable technical operating requirements.
- (C) The CCO system is in compliance with federal, state, and local requirements.
- (D) The CCO system is protective of human health and the environment.

**(A) Demonstration that the CCO is equivalent to the “CMBST” standard: The CCO system can achieve a measure of performance equivalent to that of an incinerator**

**(a) Performance Standards for Incinerators Under 40 CFR Part 264, Subpart O**

The 40 CFR Part 264, Subpart O incinerator performance standards are more comprehensive than the 40 CFR Part 265, Subpart O interim status standards for boilers and the 40 CFR Part 266, Subpart H performance standards for boilers or furnaces. Therefore, this discussion is focused on the more comprehensive performance standards for incinerators under 40 CFR Part 264, Subpart O.

Under 40 CFR Section 264.343, EPA requires that an incinerator burning hazardous waste be designed, constructed, and maintained so that, when operated in accordance with operating requirements specified under 40 CFR Section 264.345, it will meet the following performance standard:

Destruction and Removal Efficiency for a Subtitle C Incinerator

Under 40 CFR Section 264.343(a), an incinerator burning hazardous waste (other than F020, F021, F022, F023, F026, or F027) must achieve a destruction and removal efficiency (DRE) of 99.99% for each principal organic hazardous constituent (POHC) designated under 40 CFR Section 264.342. DRE is determined for each POHC using the following equation:

$$\text{DRE} = \frac{(W_{\text{in}} - W_{\text{out}})}{W_{\text{in}}} \times 100\%$$

where

$W_{\text{in}}$  = mass feed rate of one principal organic hazardous constituent (POHC) in the waste stream feeding the incinerator, and

$W_{\text{out}}$  = mass emission rate of the same POHC present in exhaust emissions prior to release to the atmosphere.

Also, POHCs are organic constituents in a waste stream that represent the greatest degree of difficulty of incineration; they are also present in large quantities or concentrations.

In addition, an incinerator burning hazardous waste and producing stack emissions of more than 1.8 kilograms per hour (four pounds per hour) of hydrogen chloride (HCl) must control the HCl emission rate to no greater than the larger of either 1.8 kilograms per hour or 1% of the HCl in the stack gas prior to entering any pollution control equipment.

Also, an incinerator (not operating under conditions of oxygen enrichment) burning hazardous waste must not emit particulate matter in excess of 180 milligrams per dry standard cubic meter (0.08 grains per dry standard cubic foot) when corrected for the amount of oxygen in the stack gas according to the following formula:

$$P_c = P_m \times \frac{14}{21 - Y}$$

where  $P_c$  is the corrected concentration of particulate matter,  $P_m$  is the measured concentration of particulate matter, and  $Y$  is the measured concentration of oxygen in the stack gas, using the Orsat method for oxygen analysis of dry flue gas described in 40 CFR Part 60, Appendix A (Method 3).

(b) The CCO system achieves a destruction and removal efficiency (DRE) of 99.99%.

The treatability study conducted to date has successfully demonstrated that the CCO system can oxidize organic solvent mixtures and achieve a DRE of more than 99.999%. See Tables 5-3 and 5-4 in Section 5 of the Delisting Petition, as well as Attachments I and J, for details.

The two CCO systems (CCO-1 and CCO-2) used in LBNL's treatability study are always operated in the batch mode. Each batch of simulated nonradioactive surrogate or mixed waste sample is sampled and analyzed before and after oxidation. Thus, LBNL staff sample 100% of the mixed waste and nonradioactive surrogate samples and their oxidized liquid products. In the treatability study conducted to date, 52 tritiated mixed waste samples and 17 simulated nonradioactive surrogate samples were oxidized using the CCO-2 and CCO-1 systems, respectively. See Tables 5-1 and 5-2 in Section 5 of the Delisting Petition for details. The DRE of the CCO treatability study for various organic solvent mixtures described above is >99.999%.

(c) The CCO system does not emit HCl or particulate matter.

The treatability study conducted to date also has successfully demonstrated that the CCO system does not emit HCl or particulate matter (see Item 3a-d in Section 5 of the Delisting Petition for details) because

- (1) the CCO system condenses and collects the liquid vapor (water or tritiated water) after oxidation in multiple condensers and a cold trap,
- (2) the exhaust gas (mainly CO<sub>2</sub> with some water or tritiated water vapor) flows through multiple water bubblers and a silica gel filter before being emitted through the stack, and

(3) excess oxygen (4 liters/min) is supplied to the CCO system for complete oxidation of each mixed waste or simulated nonradioactive surrogate sample.

**(B) Demonstration that the CCO is equivalent to the “CMBST” standard: The CCO system is operated in accordance with applicable technical operating requirements**

**(a) Operating Requirements**

The operating requirements specified under 40 CFR Section 264.345 include acceptable operating limits for the following conditions:

- carbon monoxide (CO) level in the stack exhaust gas
- waste feed rate
- combustion temperature
- combustion gas velocity

These conditions are designed to ensure compliance with the 40 CFR Section 264.343 performance standards. Moreover, the 40 CFR Section 264.345 operating requirements include controlling fugitive emissions from the combustion zone by

- keeping the combustion zone totally sealed against fugitive emissions,
- maintaining a combustion zone pressure lower than atmospheric pressure, or
- an alternate means of control demonstrated to provide fugitive emissions control equivalent to maintenance of combustion zone pressure lower than atmospheric pressure.

**(b) The CCO system meets the applicable technical operating requirements.**

Each CCO system has a control system with multiple (up to eleven) temperature controllers equipped with auto-tune features, dual-set-point capability, alarms, and analog outputs. The control system regulates the pumps that inject the mixed waste sample into the oxidizer. The temperature controllers, mass-flow controller, CCO, and hydrocarbon monitors are all equipped with analog output.

Liquid samples are pumped through the preheater, at a flow rate normally regulated between 1 and 2 mL/min. The preheater temperature is maintained at near 300 °C. The temperatures of both the oxidation cell and catalytic reactor are controlled near or above 500 °C. The oxygen gas flow rate is always maintained at 4 liter/min. See Attachment B and Figures 2 and 3 in the Delisting Petition for the CCO system design, operation procedure, and oxidation efficiency.

LBNL’s treatability study showed that the interaction between catalyst, organic compounds, air, water, and steam at a temperature near or above 500 °C gave complete decomposition of the hazardous components (>99.999%). The organic components of the mixed waste (or simulated nonradioactive surrogate) sample converted to low-level tritiated water (or water) were captured in the emission control device (for exhaust gas) consisting of multiple condensers, cold trap, water bubblers, and the silica gel filter. The secondary products of the experiments were

tritiated water (or water), carbon dioxide, or trace amounts of nitric acid or HCl, depending on the composition of mixed waste (or simulated nonradioactive surrogate) sample used in the experiments. The quantity of original chemical constituents in each sample prior to oxidation was in the nondetected level, and below Universal Treatment Standards (UTSs) after oxidation.

(c) Additional Monitoring and Inspection Requirements

Furthermore, the 40 CFR Part 264, Subpart O monitoring and inspection requirements include

- conducting sufficient waste analysis;
- monitoring combustion temperature, waste feed rate, and the indicator of combustion gas velocity on a continuous basis while incinerating hazardous waste;
- monitoring CO on a continuous basis at a point in the incinerator downstream of the combustion zone and prior to release to the atmosphere; and
- visually inspecting, on a daily basis, the incinerator and associated equipment for leaks, spills, fugitive emissions, and signs of tampering.

(d) The CCO system meets additional monitoring and inspection requirements.

The two CCO systems used in LBNL's treatability study are always operated in the batch mode. Each batch of simulated nonradioactive surrogate or mixed waste sample is sampled and analyzed before and after oxidation. Thus, LBNL staff sample 100% of the waste samples and their oxidized and condensed liquid products. The oxidized and condensed liquid products generated from the CCO systems to date were either water (from the CCO-1 system) or tritiated water (from the CCO-2 system). Before each sample was taken, LBNL staff thoroughly mixed the oxidized and condensed liquid product collected in the glass container; therefore, the liquid was essentially uniform and homogeneous. See Section 5 in the Delisting Petition for *Sampling Strategy*.

The efficiency of solvent oxidation is monitored continuously by measuring carbon monoxide and residual hydrocarbon in the exhaust gas. In the treatability study, LBNL staff did not detect any release of CO and hydrocarbon ( $\leq 1$  mg/liter) on oxidation of any mixed waste samples and nonradioactive surrogate samples except for a few times when the sample or oxygen transfer lines were blocked for one or two minutes. (This problem was corrected after each blockage occurred.) This is because

- (a) the oxidation temperatures were always high (in the range of 500 °C),
- (b) excess oxygen (4 liter/min) was always supplied to the oxidation cell, and
- (c) the oxidation of the mixed waste mixture was always in the presence of steam (the steam reforming effect or gas-water shift reaction).

The combustion temperature, waste feed rate, and the indicator of oxygen velocity are monitored on a continuous basis. See Tables 5-3 and 5-4 in the Delisting Petition as well as Attachments I and J for records of operating process monitoring.

LBNL staff always visually inspect, on a routine basis, the CCO system and associated equipment for leaks, spills, fugitive emissions, and signs of tampering before any oxidation. Prior to oxidation of any tritiated mixed waste samples or nonradioactive surrogate samples, LBNL staff also conduct an oxidation study of pure isopropanol and check the performance of the CCO system (CCO-2 or CCO-1, respectively). The oxidized liquid product generated from the oxidation of isopropanol is also analyzed using the in-house GC/MS. The analytical results and DRE (> 99.999%) of isopropanol are always evaluated. When necessary, adjustments or modifications of the system are made prior to oxidation of any waste samples.

(e) Summary of the performance and operating requirements of CCO systems.

When the performance standards, operating requirement, and other monitoring and inspection requirements for a Subtitle C incinerator are applied to the CCO system described above, the CCO system demonstrates that it achieves a measure of performance equivalent to that achieved by a Subtitle C incinerator and meets the applicable technical operating requirements because of the following.

- The CCO system achieves a DRE > 99.99%, as demonstrated by the treatability study sample, which showed a DRE of >99.999%.
- The CCO system does not emit HCl, since the secondary products of the treatability study experiments, such as tritiated water and trace amounts of nitric acid or HCl, are captured in the condenser, cold trap, water bubblers, and silica gel.
- The CCO system does not emit particulate matter, since (a) the organic components of the mixed waste converted to tritiated water are captured in the cold traps, water bubblers, and silica gel filter; and (b) excess oxygen (4 liters/min) is supplied to the CCO system for each oxidation.
- The oxidation temperatures of the oxidation cell and catalytic bed are always high (near or above 500 °C).
- The sample feed rate of mixed waste or nonradioactive surrogate sample is always controlled between 1 to 2 mL/min.
- LBNL staff always monitor combustion temperature, sample feed rate, and the indicator of combustion gas velocity on a continuous basis while oxidizing mixed waste or surrogate samples.
- The CCO system has operating requirements, other monitoring devices, and inspection requirements similar to those described for a Subtitle C incinerator, since the tritiated waste oxidizer has a control system with multiple temperature controllers and has carbon monoxide and residual hydrocarbon monitors.
- The various pieces of CCO system are hard-plumbed to facilitate efficient and safe transfer of material and to prevent release of tritium or tritiated water vapor.
- LBNL staff sample 100% of the mixed waste and nonradioactive surrogate samples and their oxidized liquid products.

- LBNL staff also conduct, on a routine basis, the appropriate system and equipment inspections.

**(C) Demonstration that the CCO is equivalent to the “CMBST” standard: The CCO system is in compliance with federal, state, and local requirements**

Because LBNL’s treatability study is in compliance with the treatability study exemption under 40 CFR Section 261.4(f) and 22 California Code of Regulations (CCR) Section 66261.4 (f), the CCO system is exempt from hazardous waste treatment permitting requirements.

The treatability study is designed to evaluate the effectiveness and efficiency of treating tritiated organic solvent mixed wastes with a catalytic chemical oxidation process in order to meet land disposal restriction treatment standards and generate nonhazardous low-level radioactive waste byproducts. LBNL sent the initial notification on the NTLF treatability study to the California Environmental Protection Agency / Department of Toxic Substances Control (DTSC) on June 5, 1996. Three treatability study annual reports for activities in 1996, 1997, and 1998 have also been submitted to DTSC (see Attachment D).

Also, the CCO unit is exempt from the Bay Area Air Quality Management District (BAAQMD) hazardous waste air permitting requirements, because (1) expected emissions remain well below permit threshold levels for criteria and hazardous air pollutants, and (2) the treatability study experiments showed that the decomposition of the hazardous components is near complete (DRE >99.999%). See Table A-2 for the chemical specific permit threshold limits of BAAQMD Regulation 2-1.

Table A-2. BAAQMD Emission Limits\*

Chemical	BAAQMD Annual Airborne Emission Limit (lb/yr)
acetone	150
acetonitrile	0.67
benzene	6.7
chloroform	36
dimethyl formamide	not BAAQMD listed, but a federal Hazardous Air Pollutant
dioxane	25
ethyl acetate	656,000
isopropanol	444,000
methanol	120,000
methylene chloride	190
pyridine	not BAAQMD listed
tetrahydrofuran	270,000
tetramethyl ethylene diamine	not BAAQMD listed
toluene	38,600
triethylamine	not BAAQMD listed, but a federal HAP

\* BAAQMD regulation 2-1-316, “Toxic Air Contaminant Trigger Levels”

The supporting rationale for BAAQMD permit exemption status uses the following scenario. Assuming 20 liters of process throughput occur annually (since 1997 to

date, LBNL processed 16 liters through the CCO-2 system), and assuming a conservatively large specific density will convert this into 60 pounds of throughput at the stated DRE of >99.999%, this results in about 0.0006 pounds of emissions annually. Therefore, if all of the treated mixture were acetonitrile (which has the lowest BAAQMD TAC limit), it would still not exceed the BAAQMD TAC permitting threshold.

Also, the secondary products of the mixed waste oxidation experiments are water, carbon dioxide, or trace amounts of nitric acid or hydrogen chloride, depending on the composition of mixed waste used in the experiments. The quantity of secondary organic compounds in the final product water is much less than 0.001% (in fact, it is at nondetected level) of the total processed waste streams. The organic components of the waste converted to low-level tritiated water are captured in the cold traps, water bubblers, and a silica gel filter.

**(D) Demonstration that the CCO is equivalent to the “CMBST” standard: The CCO system is protective of human health and the environment**

The CCO system is protective of human health and the environment because the contribution of tritium release from the CCO system, as opposed to incineration, is minimal (less than 0.01% of the sample radioactivity; see Attachment B), in the form of HTO, to the surrounding atmosphere. As discussed above, the environmental emissions of hazardous materials are well within local air standards, and the oxidation products (e.g., CO<sub>2</sub> or NO<sub>x</sub>) would be much less than those from one tank of gasoline from one motor vehicle.

The Department of Energy has built various advanced incineration devices to destroy the organic compounds in mixed waste (e.g. the Mixed Waste Disposal Facility at the Idaho National Engineering and Environmental Laboratory). However, this type of treatment for tritiated mixed waste would result in release of tritium with the incineration emission products (i.e., as tritiated water) rather than retention of the tritium in the treatment residue (in the form of ash). We believe that the combination of the relatively long half-life of tritium and the relatively large amount of tritium that would be released in air emissions during incineration contribute to a treatment option that is not preferred in comparison to the CCO system.

On the other hand, using the CCO system to treat the organic solvent mixed waste and obtaining approval for a delisting would enable the NTLF to land dispose the treatment residues as low-level radioactive waste. The tritiated water generated as a product of the CCO system would meet all waste acceptance criteria for land disposal as low-level radioactive waste. The CCO system, therefore, is protective of human health and the environment.

**(E) Conclusion**

Based on the above analysis, LBNL has shown that the CCO system

- achieves a measure of performance equivalent to that achieved by a Subtitle C incinerator;
- is operated in accordance with applicable technical operating requirements;
- is in compliance with federal, state, and local requirements; and
- is protective of human health and the environment.

Therefore, the CCO treatment method meets the definition of combustion at 40 CFR 268.42 Table 1 or, in accordance with 40 CFR 268.42(b), should be approved as an acceptable alternative to “CMBST” standard, which is specified as the required method for D001 high TOC ignitable wastes at 40 CFR 268.40.