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# Oxidative Decontamination of Tritiated Materials Employing Ozone Gas

by

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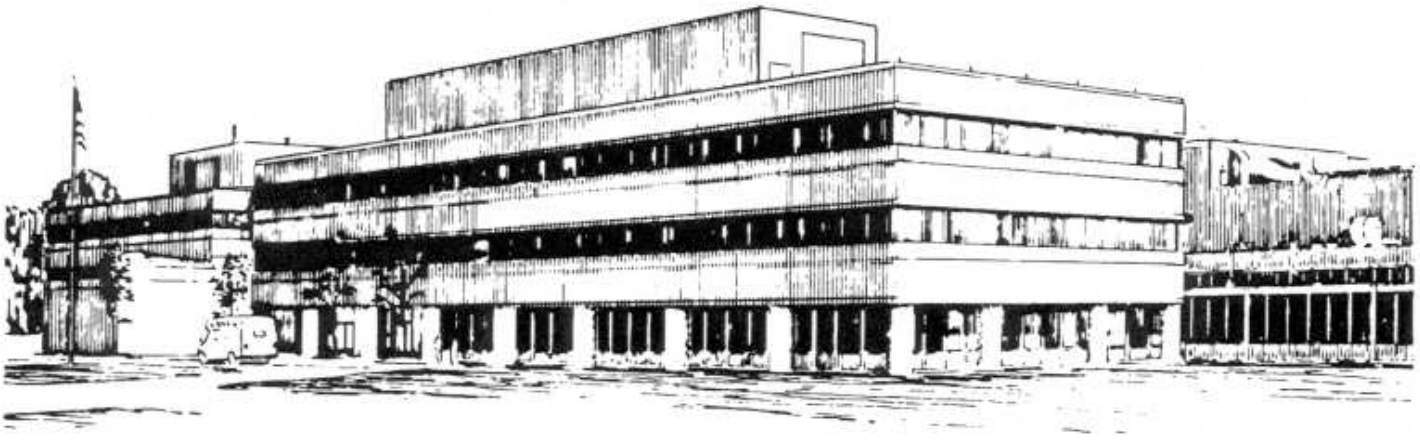

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# OXIDATIVE DECONTAMINATION OF TRITIATED MATERIALS EMPLOYING OZONE GAS

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## ABSTRACT

The Princeton Plasma Physics Laboratory has developed a process by which to significantly reduce surface and near surface tritium contamination from various materials. The Oxidative Tritium Decontamination System (OTDS) reacts gaseous state ozone (accelerated by presence of catalyst), with tritium entrained/deposited on the surface of components (stainless steel, copper, plastics, ceramics, etc.) for the purpose of activity reduction by means of oxidation-reduction chemistry.[1] In addition to removing surface and near surface tritium contamination from (high monetary value) components for re-use in non-tritium environments, the OTDS has the capability of removing tritium from the surfaces of expendable items, which can then be disposed of in a less expensive fashion. The OTDS can be operated in a batch mode by which up to approximately 40 pounds of tritium contaminated (expendable) items can be processed and decontaminated to levels permissible for free release (< 1000 dpm/100cm$^2$). This paper will discuss the OTDS process, the level of tritium surface contamination removed from various materials, and a technique for deep scrubbing tritium from sub-surface layers.

## I. INTRODUCTION

Activities involving tritium/tritiated materials often produce large quantities of contaminated items and mixed low level waste (MLLW). A system has been designed to process these items and waste, in a fashion where these materials can either be re-used or disposed of as non-tritiated waste. This system, the OTDS, employs oxidation-reduction chemistry as a mechanism for surface (and near-surface) tritium removal. Elemental tritium is reacted to tritium oxide, which readily evaporates (can be accelerated by heat application in conjunction with ozone) in the presence of a dry atmosphere.

Implementation of the OTDS can conserve monetary resources by removing tritium from components that could be recycled and consequently not need to be disposed of, or could be disposed of in a less expensive fashion. This technology has the potential to significantly reduce costs associated with the disposal of expendable Personal Protective Equipment (PPE) and other MLLW. In addition, decommissioned tritium fusion reactor components can be decontaminated for re-use in future fusion devices and/or non-radiological environments.

Princeton Plasma Physics Laboratory has conducted similar oxidative decontamination research in the past, involving the use of aqueous hydrogen peroxide ($H_2O_2$). There has been proven success with the application of this technique, as indicated by Table 1. It was discovered that post $H_2O_2$ process activity levels dropped significantly, and that there was no discernable surface regrowth noted after an approximate eight month hold time. This method, however, produces liquid effluent, which must then be disposed of as radiological waste. A gas phase system allows for bulk collection, and/or recycle of tritium, via molecular sieve, gas holding tank, tritium purification (isotope separation), etc.

TABLE 1 $H_2O_2$ Decontamination of TFTR RF Feedthrough Components

| | Date of Survey (MM/DD/YY) | | |
|---|---|---|---|
| RF Feedthrough Survey Location | 8/19/00 dpm/100cm$^2$ | 9/14/00 dpm/100cm$^2$ | 5/02/01 dpm/100cm$^2$ |
| Outside Ctr. Cond. | 1,018,434 | 51 | 7 |
| Inside Ctr. Cond. | 81,351 | 65 | 59 |
| Outside Outer Cond. | 2,698 | 30 | 17 |
| Conductor Area | 928,916 | 48 | 60 |
| Main Body Seal Area | 83,610 | 39 | 13 |

Data represents smear surveys taken from before $H_2O_2$ Process, after $H_2O_2$ Process, and after 8 months in storage.

## II. THEORY

The chemical reaction between ozone and diatomic hydrogen (all isotopic variations) follows an oxidation-reduction (electron transfer) mechanism, by which ozone serves as the oxidizing agent. Due to the high instability of the ozone molecules, the mechanism can occur in the absence of a driving force (i.e. catalytic parameters). The mechanism involves a series of half-reactions, followed by the combination of hydrogen (oxidation number is +1) and

oxygen (oxidation number is -2) ions to form hydrogen oxide (water), or tritium oxide if tritium isotope is involved. Chemical by-product of this reaction mechanism is a diatomic oxygen molecule. The reaction mechanism is given by equation 1 (H represents any isotope of hydrogen present in the system).[2]

$$\text{Reaction:} \quad H_2 + O_3 \rightarrow H_2O + O_2 \qquad (1)$$
$$\text{Mechanism:} \quad H_2 \rightarrow 2H^+ + 2e^-$$
$$O_3 + 2e^- \rightarrow O^{2-} + O_2$$
$$2H^+ + O^{2-} \rightarrow H_2O$$

A series of side (secondary) reactions also can occur, the type and/or extent of which are governed by experimental conditions (i.e. temperature, pressure, etc.) and by material surface composition. These reactions, though secondary in nature with respect to the mechanism shown by equation 1, can often promote additional release of hydrogen isotopes. Examples include oxidation of carbon to carbon dioxide, and degradation of plastics via oxidative dissociation of polymer chains.[3]

Required duration of ozone exposure (adequate system run-time) is heavily dependant upon the concentration of pure ozone in the feed gas and the residence time in the reaction chamber. These parameters can be controlled in various ways, including adjustment of feed gas $O_2$ concentration into the ozone generation unit (via pure oxygen or oxygen/inert gas mixture), adjustment of feed flow rate into reaction chamber, and adjustment of reactor volume. By passing feed gas through a drying agent/desiccant prior to entry into the reaction chamber, evaporation of tritium oxide will more readily occur (relative humidity within chamber is lowered), also shortening system run-time. This drying process also reduces possibility of the formation of hydroxyl radicals, which can hinder the primary reaction mechanism.

## III. SYSTEM CONFIGURATIONS

Specific characteristics of tritium deposition on or within contaminated materials (i.e. quantity, depth, etc.) and the type of material (i.e. metal, plastic, ceramic, etc.) determines design of OTDS. Two systems have been fabricated, and a third system is currently being developed. While these systems employ ozone as an oxidizing (decontamination) agent, other system parameters are applied and/or controlled to achieve desired results.

### A. Rotary System Configuration

A rotary system is implemented for decontamination of light materials (PPE, MLLW). This configuration allows for decontamination of large quantities in relatively short periods of time (up to approximately 40 lbs, or about 3/4 of total fill capacity). An agitation mechanism is applied, which maximizes exposed material surface area (eliminates dead zones within the reaction chamber). Material volume per total reactor volume (1-ε, where ε is void fraction) can consequently be optimized using this configuration.

The key components of the rotary system (Figure 1) are an ozone generation/injection unit; a stainless steel reaction chamber, equipped with baffles for agitation of materials; an open-ended aluminum feed pipe, to allow for permeation of ozone throughout the chamber; a rotary mixer, capable of variable revolutions per minute; and a negative pressure exhaust duct, for release to stack or clean-up process. A stainless steel mesh basket-liner allows for easy loading and unloading of chamber (the baffles mentioned above are riveted to this basket), and a rotating (silicon rubber o-ring) seal provides a means for free rotation of chamber. The unit operates on 120V AC, using a standard three-prong electrical interface. A system schematic is given below.[2]

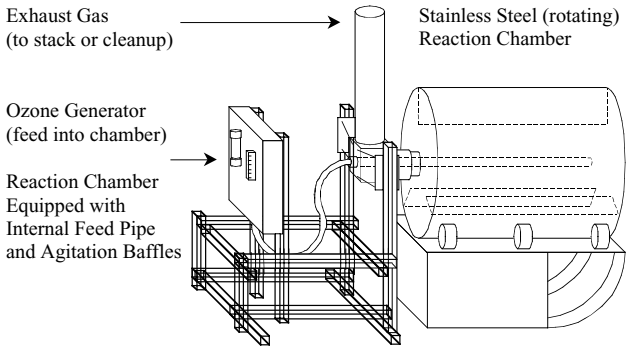


Figure 1 Rotary System Configuration for OTDS

### B. Stationary System Configuration

A stationary system is implemented for decontamination of heavier materials (i.e. tools, diagnostics, etc). The lack of an agitation mechanism allows for decontamination of delicate items. Addition of valve structure to system provides a mechanism for stagnant (no-flow) ozone exposure, which allows for control of residence time within the chamber. Ambient chamber temperature can be maintained below ozone dissociation threshold during heat application (via integrated temperature control).

The key components of the stationary system (Figure 2) are an ozone generation/injection unit; a stainless steel vacuum chamber, equipped with standard Conflat® flange; inlet and outlet manual control valves; and a single tube inlet purge line feed to bottom of chamber. When applying ultraviolet light catalyst, a sapphire window (on Conflat® flange), minimizes ultraviolet light absorption, allowing >70% transmittance through the window.[1] The chamber has the capability of achieving high vacuum or being pressurized to several atmospheres, and has integrated temperature control.[1] Effluent gas is exhausted to the station stack or clean-up process, via ozone resistant tubing. A system schematic is given below.

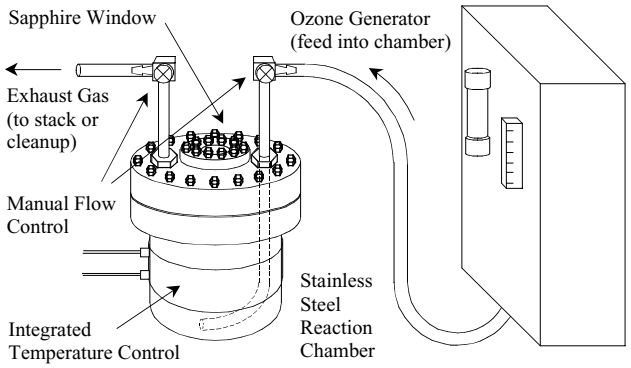


Figure 2 Stationary System Configuration for OTDS

C. PISTON-CYLINDER CONFIGURATION

A system is currently being developed for the decontamination of materials containing tritium deep within their surface (i.e. carbon fiber composites and other porous materials). The proposed design (see Figure 3) will operate via a piston-cylinder mechanism, and will be capable of rapid pressure increases of up to several atmospheres. By applying a piston to the system, reaction chamber volume can be compressed; this, in turn, increases the ozone concentration within the reaction chamber and allows for deeper ozone penetration into the material of concern.

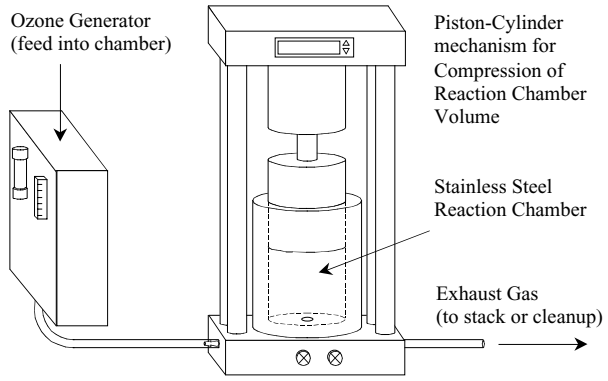


Figure 3 Piston-Cylinder Configuration for OTDS

IV. EXPERIMENTATION

A. Mixed Low Level Waste Experiment

Initial experimentation on the OTDS was performed using the rotary system configuration, in an attempt to decontaminate MLLW. Three sample sets were prepared, each numbered 1-30. Samples were cut into 20cm x 10cm, divided into two 100cm$^2$ areas labeled pre and post liquid scintillation counter (LSC) smear. Materials were as follows: yellow radioactive labeled plastic bag (polyethylene), yellow nuclear grade Herculite¤ (reinforced vinyl laminated fabric), and paper towels reinforced with plastic. The samples were divided into test groups (CONTROL1 = 1-10 of each material, CONTROL2 = 11-20 of each material, EXPERIMENTAL = 21-30 of each material). Numbers 1-5, 11-15, and 21-25 were kept clean (to later assess spreading of contamination during testing). The remaining samples were cross contaminated with tritiated liquid effluent. Samples were dried overnight, and pre smears were taken. CONTROL1 was placed in a sealed bag for 45min, CONTROL2 was placed in rotary system for 45min with an ambient air purge, and EXPERIMENTAL was placed in rotary system for 45min with ozone purge. After run was completed, post smears were taken. Radiological surveys indicated a reduction in the level of tritium on the surface of these materials post ozone exposure, as indicated by Figure 4. Reductions were also noted (to a lesser extent) by the ambient air purge (Figure 4). This is attributed to the evaporation of tritium oxide, a primary constituent of the liquid effluent contamination media.

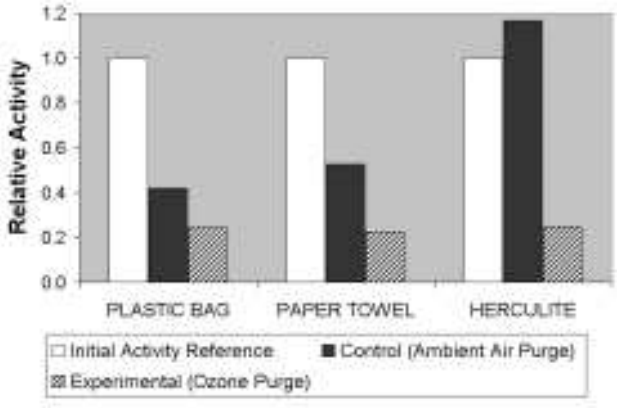


Figure 4 MLLW decontamination via OTDS Rotary System Configuration. Chart displays activity reductions relative to initial activity.

B. Carbon/Graphite Tile Experiments

To date, several experiments have been conducted (using stationary system), involving the use of an RF Tile removed from the TFTR vacuum vessel. These experiments studied reaction time (both static soak and continuous purge), pulsed vs. continuous flow mechanisms, ambient air purge vs. ozone purge, U.V. wavelength introductions into system, etc. Data was gathered through the use of an open-wall ion chamber surface area monitor (microcurie range). There was a total of eight data collection areas etched onto the tile, so that data could be taken from the same area every read attempt. For every data collection area, a total of four assays were recorded to ensure repeatability of ion chamber output. Pre and post collection background readings were also taken to account for minimal error associated with the ion chamber.

It is proposed from experimental data that the extent of tritium removal is in direct correlation to the depth of the co-deposition within the tile surface. Experimental data relating ozone exposure duration to activity reduction indicate that there is no additional removal of tritium from the surface (rate approaches zero) after a few hours of ozone exposure. Tritium entrained in the bulk of the tile cannot react with ozone molecules at or near the surface. At this point, the attractive forces between the ozone molecules and tritium molecules become considerably less than the forces holding the tritium within the lattice of the tile. Only tritium on or within direct proximity of the tile surface will react and/or be released. To resolve this issue, it was found that toggling the ozone purge process with an ambient air purge (approximately 25°C) promotes activity regrowth toward the tile surface. Figure 5 depicts the activity reduction profile of the RF tile during experimentation.[4].

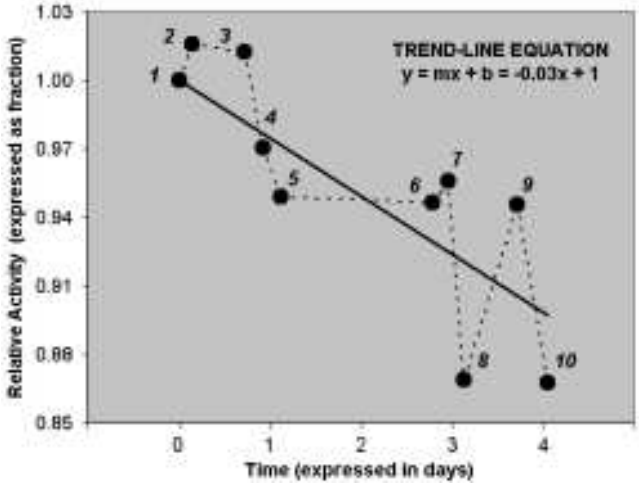


Figure 5 Relative activity of RF tile as a function of time. Positive sloping events (between 1st - 2nd, 6th - 7th, and 8th - 9th points) occur under ozone purge; negative sloping events (between 3rd - 4th, 4th - 5th, 7th - 8th , and 9th - 10th points) occur under ambient air purge. Relatively neutral sloping events (between 2nd - 3rd and 5th - 6th points) indicate stagnant hold times, where RF tile was contained within latex Anti-C glove. Relative activity reduction rate over course of experimentation, as demonstrated by trend-line equation, was approximately 3% per day

Ultraviolet light was added to the system in an effort to catalyze the reaction process. During preliminary experimentation, two wavelengths of ultraviolet light were used, 365nm (UV-A) and 235nm (UV-C), each comprised of two 6W bulbs. Significant activity reductions were seen when the 235nm wavelength was applied (Refer to Figure 6), however, this was not the case with for application of the 365nm wavelength. Ultraviolet light, at wavelengths of about 250nm and below, dissociate ozone gas into diatomic oxygen molecules and oxygen free radicals. Oxygen free radicals are strongly charged and are far more reactive than ozone or diatomic oxygen molecules. Presence of free radicals in the system can substantially affect both the rate and extent of tritium oxidation.[5]

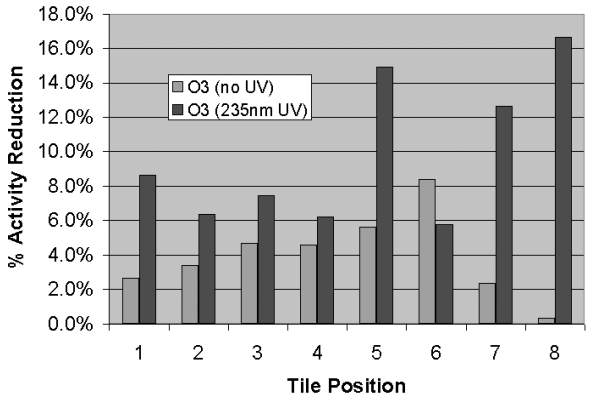


Figure 6 Percent activity reduction at different locations on RF tile. Data series 1 (light gray) represents an ozone exposure under normal experimental conditions (CONTROL group, no ultraviolet radiation present in system). Data series 2 (dark gray) represents an ozone exposure subject to 12W, 235nm ultraviolet radiation (EXPERIMENTAL group). The figure demonstrates that (position 6 is exception) this wavelength of UV stimulus positively affects surface tritium activity reduction.

During experiments, exposure mechanisms were varied to monitor effects on tile surface activity reduction. The two exposure mechanisms which can be applied to the system are continuous purge and static soak. Experimental protocol is underway to determine the best method for tritium removal; however, continuous purge seems to link well with application of 235nm U.V. catalyst, producing approximately 5% - 15% reductions in tile surface activity after approximately 4 hours run-time (Figure 6). This can most likely be attributed to an increase in reaction probability per given time, caused by excess of free radical oxygen present in the system. Static soak coupled with U.V. application is not effective. This is most likely the result of (1) lack of sufficient molecular movement — hence static , and/or (2) ozone approaches full conversion to molecular oxygen after only a short time under ultraviolet catalysis.[4]

C. Metal/Alloy Experiments

Currently, Princeton Plasma Physics Laboratory is in the process of initiating a new series of experiments involving various metals and metal alloys. The objective is to determine oxidation effects (i.e. activity reduction) associated with tritium contaminated metals in the presence of ozone atmosphere, and to observe tritium activity regrowth characteristics following ozone exposure (ambient air purge will be implemented to stimulate potential regrowth process). The lattice structure of metals has few vacancies and/or interstitial spaces, unlike carbon-graphite composites. This greatly limits tritium penetration into the metals during a pore-diffusion process. All tritium contamination will be at or near surface. Therefore, there is a greater chance that there will be no tritium activity regrowth and/or residual following an adequate ozone exposure.

To conduct experiments, coupon samples of varied metals and metal alloys were fabricated for cross-contamination. Metals/Alloys that will be used include: (1) Aluminum, (2) Copper, (3) Stainless Steel, (4) INCONEL¤, and (5) Brass. These samples will be placed in a bake-out furnace chamber along with contaminated carbon-graphite tiles. The chamber is pulled to vacuum and back-filled with an inert gas (i.e. Argon). This back-fill process will limit/prevent any metal oxide or tritium oxide from forming, as the presence of these oxide layers can interfere with the cross-contamination process. The chamber can then be adjusted to pressure and temperature suitable for cross-contamination (via pore diffusion) to occur.

It is predicted that the tritium activity reduction rate during ozone exposure will be slower for metals/alloys, as compared to carbon-graphite composites. The carbon-ozone reaction serves as an additional tritium release mechanism. However, the overall tritium activity reduction rate will be faster for metals/alloys, as compared to carbon-graphite composites. There is limited activity reduction per ozone cycle as a result of subsurface tritium co-deposition. Subsurface co-deposition must be brought to surface via intermittent ambient air purges. The rate of metal/alloy surface decontamination will be relatively continuous, and will be a strong function of time (constant ozone purge -- no need for ambient air purges). Future experimentation will determine whether or not these predictions are valid.

## V. CONCLUSION

The development of an oxidative tritium decontamination system provides a method for the reduction of tritium surface contamination of various components and items. Expendable items can be de-tritiated to levels at or slightly above background, and re-usable items can be de-tritiated for near free release levels, and for use in controlled areas. Initial experimentation employing ozone as a tritium decontamination gas has indicated tritium surface activity reductions by as much as 15% after moderate exposure times (few hours). The cost of the system and its operation are relatively inexpensive, thus making the system an ideal approach to tritium decontamination processes.

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