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# Laser removal of loose uranium compound contamination from metal surfaces

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**Abstract**

Pulsed laser removal of surface contamination of uranyl nitrate and uranium dioxide from stainless steel has been studied. Most of the loosely bound contamination has been removed at fluence levels below 0.5 J $cm^{-2}$, leaving about 5% fixed contamination for uranyl nitrate and 15% for uranium dioxide. Both alpha and beta activities are then sufficiently low that contaminated objects can be taken out of a restricted radiation area for re-use. The ratio of beta to alpha activity is found to be a function of particle size and changes during laser removal. In a separate experiment using technetium-99m, the collection of removed radioactivity in the filter was studied and an inventory made of removed and collected contamination.


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## 1. Introduction

We report studies of the laser removal of radioactive surface contamination from metal substrates. In addition, we have studied collection of the removed radioactive material in a simple extraction and filter system.

The ultimate objective of this work was to develop a simple laser system to remove surface radioactive contamination from mainly metal surfaces. Potential applications exist, for example, in cleaning metal canisters in hot cell complexes and preparation equipment and instrumentation in nuclear fuel production. In the present work we have studied laser removal of uranium compound contamination. This is of specific interest in South Africa due to the development of the pebble bed modular reactor (PBMR) [1] so the compounds studied were uranyl nitrate, the basic feed material for PBMR fuel production, and uranium dioxide, the fissionable material of the fuel element kernels. For convenience, a short lived isotope (technetium-99m) was used for filter retention studies.

Surface contamination that is considered ''loose'' is much easier to remove than contamination that has penetrated into the oxide layer of a metal or into the metal itself. Nevertheless, its removal is an important goal because it can come into contact with the skin, enter the body via ingestion or inhalation, as well as be transported to other, possibly uncontrolled, areas on foot-ware or clothing. Uranium compounds in the body are an internal radiation hazard as well as posing a danger due to chemical toxicity. A sufficient degree of surface decontamination can allow components to be released from restricted areas for re-use.

The scale of the radioactive decontamination problem worldwide is very large [2] and while there is a wide range of decontamination techniques [3] lasers have had very little impact in the field. Nevertheless, the use of lasers in decontamination has been investigated for cutting [4], oxide layer ablation [5,6], concrete surface removal [4,7] and metal surface cleaning [8–11]. There are many ways of removing surface contamination [3] but these normally involve the addition of some other agent such as a chemical or water. The handling of contaminated liquid waste in bulk then poses problems for disposal. The advantage of laser removal is that it is a dry method and in principle only the removed contamination itself needs to be collected. This can ideally be done with an extraction system containing a disposable dry filter.

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Of course, a big disadvantage of a laser technique its high cost. This is particularly so with solid state lamp-pulsed Nd:YAG lasers (as used here) where the wall plug efficiency is only about 1%. However, the relatively recent advent of Q-switched fibre lasers with an order of magnitude increase in efficiency [12] could have a large impact for laser cleaning. Further, the improved efficiency means a much smaller cooling system so the prospect of a compact ''vacuum cleaner'' size laser surface decontamination system becomes feasible.

In the present study we use a short pulse Q-switched laser as this has been shown to be effective at removing tightly bound particles from surfaces, particularly widely studied in applications in the dry laser cleaning (DLC) of microelectronic components [13–22].

## 2. The contaminants

### 2.1. Compounds used

Two forms of uranium contaminant were used, uranyl nitrate hexahydrate, $UO_2(NO_3)_2{\cdot}6H_2O$ and uranium dioxide, $UO_2$. Uranyl nitrate is used for PBMR fuel production and when dried forms characteristic yellow-green crystals. The $UO_2$ was in the form of 500 μm diameter kernels from the PBMR test fuel production facility. Due to licensing restrictions, we used depleted uranium (Table 1). While the adhesion properties should be the same for depleted and enriched uranium, the absolute values of activity differ significantly (Table 2). The Tc-99m for the extraction and filter retention experiments was obtained from the SAFARI reactor at the Nuclear Energy Corporation of South Africa site. It is a by product of Mo-99 production in the form technetium pertechnetate, $TcO_4$. Due to its short half-life (6 h), it is ''washed off'' the Mo-99 only when required.

Since safety criteria differ for alpha, beta and gamma radiation, it is desirable to know the type of activity for uranium. All the main isotopes of depleted uranium, U-238, U-235 and U-234, are radioactive and decay by alpha particle emission (half lives, $\tau_{1/2}$, in parentheses) [23]:

$$_{92}U^{234} \rightarrow {}_{90}Th^{230} + \alpha \quad (2.5 \times 10^5 \text{ years});$$
$$_{92}U^{235} \rightarrow {}_{90}Th^{231} + \alpha \quad (7.1 \times 10^8 \text{ years});$$
$$_{92}U^{238} \rightarrow {}_{90}Th^{234} + \alpha \quad (4.5 \times 10^9 \text{ years})$$

Further decays by beta emission lead to metastable protactinium (Pa-234m) and U-234:

$$_{90}Th^{234} \rightarrow {}_{91}Pa^{234m} + \beta \quad (24.1 \text{ days});$$
$$_{91}Pa^{234m} \rightarrow {}_{92}U^{234} + \beta \quad (1.2 \text{ min})$$

The half-life of U-234 is so long ($2.5 \times 10^5$ years) that the decay chain essentially stops there. Thus, over a time scale ≫24.1 days, a secular equilibrium is setup between U-238 and its daughter products Th-234 and Pa-234m, i.e. if $n$ refers to the density of a given isotope:

$$\left(\frac{n}{\tau_{1/2}}\right)_{\text{U-238}} = \left(\frac{n}{\tau_{1/2}}\right)_{\text{Th-234}} = \left(\frac{n}{\tau_{1/2}}\right)_{\text{Pa-234m}}$$

Table 1
Percentages by weight of different uranium isotopes

| | Natural uranium | Depleted uranium | PBMR uranium |
|---|---|---|---|
| U-238 | 99.28% | 99.78% | 89.31% |
| U-235 | 0.71% | 0.21% | 10.60% |
| U-234 | 0.01% | 0.002% | 0.087% |

Table 2
Representative values of specific activities of uranium (Bq/g)

| Isotope | Natural uranium | Depleted uranium | PBMR uranium | Decay |
|---|---|---|---|---|
| U-238 | 12400 | 12400 | 11100 | α |
| U-235 | 570 | 168 | 8500 | α |
| U-234 | 12200 | 4600 | 200000 | α |
| Th-234 | 12400 | 12400 | 11100 | β |
| Pa-234m | 12400 | 12400 | 11100 | β |
| Total (Bq/g) | 49970 | 41968 | 241800 | |
| Beta/alpha | 0.99 | 1.45 | 0.10 | |

Technetium-99m decays by gamma emission:

$$_{43}Tc^{99m} \rightarrow {}_{43}Tc^{99} + \gamma \quad (6.01 \text{ h})$$

Tc-99 has a half-life of 212 000 years so has a negligible contribution to the activity of the sample.

In order to detect possible contaminants, gamma ray reference spectra were taken of uranyl nitrate and $UO_2$ samples. Counting was done for 16 h using a low background, high resolution (Ge crystal), spectrometer. Most of the emission lines appear in the two energy ranges shown in Fig. 1(a) and (b) for uranyl nitrate. Results for uranium oxide were very similar. All strong emission lines are from U-235 and the daughter products of U-238, Th-234 and Pa-234m. U-238 itself is a very weak gamma emitter and no isolated lines are seen. The samples exhibited no detectable contamination from radio-isotopes outside the uranium chain.

The activity, $A$, of a $UO_2$ kernel can be calculated knowing its size, density and composition from

$$A = \sum -\frac{dn}{dt} = \sum \frac{n \ln 2}{\tau_{1/2}}$$

allowing comparison with measurements and the preparation of test contamination of known activity.

The specific activities of U-234, U-235 and U-238 are $2.3 \times 10^8$, $8.0 \times 10^4$ and $1.24 \times 10^4$ Bq/g, respectively [23]. The absolute activities of these isotopes (Table 2) can then be evaluated using the mass percentages from Table 1. Due to the secular equilibrium, the activities of Th-234 and Pa-234m are the same as U-238 (Table 2). The fractional mass of U in $UO_2$ is 0.881, so for a $UO_2$ kernel of diameter 500 μm and density 10.6 g/cm$^3$ (mass 0.717 mg), the total activity is 30.1 Bq comprising:

$$A_{\text{kernel}} = \begin{cases} 17.8 \text{ Bq (associated with } \beta \text{ emission)} \\ 12.3 \text{ Bq (associated with } \alpha \text{ emission)} \end{cases}$$

This gives a characteristic beta to alpha activity ratio of 1.45 for the depleted uranium.