

Technical note

# Detection of U(VI) on the surface of altered depleted uranium by time-resolved laser-induced fluorescence spectroscopy (TRLFS)

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## Abstract

Time-resolved laser-induced fluorescence spectroscopy (TRLFS) was applied to study the surface of a depleted uranium (DU) disc immersed in a Ca-phosphate solution for 182 days. The weathering solution contained  $2.49 \cdot 10^{-3}$  M calcium and  $1.05 \cdot 10^{-3}$  M phosphate, representing enhanced pore water concentrations of agricultural soils. The TRLFS results clearly show that meta-autunite, a U(VI) phosphate, has formed during low temperature alteration of the DU disc. This secondary U(VI) mineral phase was identified using a fingerprinting procedure by comparing it with TRLFS-spectra from an in-house U(VI) TRLFS database, including U(VI) oxides, U(VI) hydroxides, U(VI) sulphates and U(VI) phosphates. Its TRLFS spectrum is characterized by six fluorescence emission bands at 486, 501, 522, 546, 573, and 601 nm, and two fluorescence life times of  $50 \pm 5$  ns and  $700 \pm 25$  ns. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

Depleted uranium (DU) is a by product in the enrichment of natural uranium during the production of nuclear fuel. Approximately 500,000 t of this material have been stored to date in the USA alone. Because of its high density ( $19.1 \text{ g/cm}^3$ ) and its availability at low cost—it is cheaper than tungsten—it is used as counterweights in aeroplanes, as a shielding material in medical radiotherapy units and in containers for transport of radioactive isotopes (Betti, 2003). In addition, DU is used for military purposes both in projectiles and cladding for armoured vehicles (Giannardi and Dominici,

2001). Besides the USA, DU weapons are owned or under development in various countries, e.g. in Saudi Arabia, France, United Kingdom, Israel, Pakistan, Russia, Thailand, and Turkey (Harley et al., 1999).

DU has received more public attention following the wars in Iraq (1991, 2003), Bosnia (1994), Kosovo and Serbia (1999) in which it was used as ammunition to destroy heavy armoured vehicles. Finely dispersed powder from that ammunition is now widespread in these areas and may cause long-term environmental problems (Durante and Pugliese, 2003). The health consequences for the population and the war veterans are still being studied.

DU contains only about 0.2%  $^{235}\text{U}$  and so has a lower specific activity than natural uranium, which contains approximately 0.7%  $^{235}\text{U}$ . The total radioactivity of DU is therefore only about 60% of the radio-

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activity of natural uranium for the same mass. In addition to its radiotoxicity its chemical toxicity, as with many other heavy metals, has to be considered. The enrichment of uranium in humans is especially marked in the kidneys and bones; it is a known carcinogen (Abu-Qare and Abou-Donia, 2002), and also nephrotoxic (Kurtio et al., 2002). This concern has triggered investigations of its geochemical behaviour including transport and immobilisation in the near-surface environment, studies of its uptake by agricultural plants, incorporation in forage crops and its subsequent transfer through the human food chain. Several reports on the potential effects on human health and the environment from the use of DU have appeared in recent years (Callahan et al., 2004; Craft et al., 2004). However, the long-term effect on groundwater and drinking water as a result of finely dispersed DU projectiles in soil is far from understood. In this study, the weathering of DU in conditions representing agricultural soil, rich in calcium and phosphate, was studied in laboratory experiments. Surface alteration products were identified by time-resolved laser-induced fluorescence spectroscopy (TRLFS).

## 2. Methodology

Discs (25 mm in diameter, 0.5 mm in thickness) were obtained from a pristine British military tank shell (for more details see Trueman et al., 2004). After degreasing, duplicate samples were placed in polypropylene beakers and submerged in a solution containing 100 cm<sup>3</sup> AnalaR grade  $2.49 \cdot 10^{-3}$  M calcium nitrate with  $1.05 \cdot 10^{-3}$  M ammonium phosphate, both reagents supplied by Fisher (Trueman et al., 2003). The pH of this solution was adjusted to an initial value of 6.0 using HNO<sub>3</sub> and NH<sub>4</sub>OH. The samples were kept in an environmental cabinet at a constant temperature (24 °C) and the solution composition monitored at regular

intervals. Samples of the solution (2 cm<sup>3</sup>) were taken for analysis by ICP-MS (U) and ICP-OES (Ca, P), initially twice daily and then at increasing intervals, in each case with stock replacement. The discs were removed weekly for the first 14 weeks, then fortnightly and finally monthly for weighing and surface examination by XRD. After a contact time of 182 days, no further changes in either the solution composition or the discs were apparent and the experiment was stopped.

TRLFS measurements were made on the surface of one of the samples, following drying. The results were compared with measurements under the same conditions (laser energy, starting time) on an unaltered DU disc, which had not been placed in contact with the solution described above.

The TRLFS system consists of a Nd:YAG diode laser with an excitation wavelength of 266 nm. For further details concerning the set-up of the TRLFS equipment and operation modes see Geipel et al. (1996). TRLFS spectra for 15 different spots (3 mm in diameter) on the DU disc were recorded. Metallic U does not emit any fluorescence, whereas U(VI) phases emit characteristic fluorescence signals and are thus detectable (Amayri et al., 2004a,b; Geipel et al., 2000).

## 3. Results

Uranium concentrations in solution rapidly reached a maximum of  $1.5 \pm 0.9 \times 10^{-6}$  mol dm<sup>-3</sup> (360 ppb) and remained at this level for the duration of the experiment. Calcium and phosphate fluctuated only slightly (~10%) from their initial values. However, the pH showed a gradual decrease from  $6.03 \pm 0.30$  at the start of the experiment to  $5.17 \pm 0.15$ .

Other than development of a blue coloration (Fig. 1) the disc remained unchanged throughout the test. There was no evidence of corrosion or of the mass loss observed in parallel experiments conducted in the absence



Fig. 1. Pristine DU sample (left) and the same sample after 182 days in contact with Ca-phosphate solution.

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