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Remediation of soils contaminated with particulate depleted uranium by multi stage chemical extraction☆

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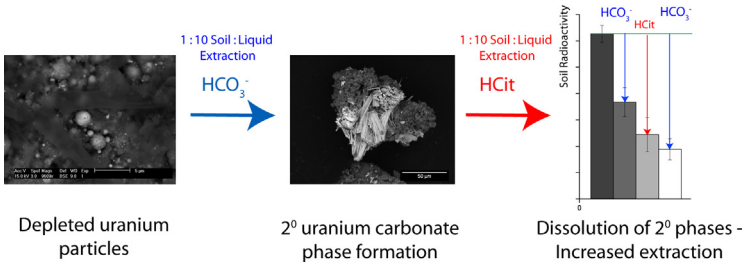
HIGHLIGHTS

- Batch leaching was examined to remediate soils contaminated with munitions depleted uranium.
- Site specific maximum extraction was 42–50% total U in single batch with NH_4HCO_3.
- Analysis of residues revealed partial leaching and secondary carbonate phases.
- Sequential batch leaching alternating between NH_4HCO_3 and citric acid was designed.
- Site specific extraction was increased to 68–87% total U in three batch steps.

GRAPHICAL ABSTRACT



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ABSTRACT

Contamination of soils with depleted uranium (DU) from munitions firing occurs in conflict zones and at test firing sites. This study reports the development of a chemical extraction methodology for remediation of soils contaminated with particulate DU. Uranium phases in soils from two sites at a UK firing range, MOD Eskmeals, were characterised by electron microscopy and sequential extraction. Uranium rich particles with characteristic spherical morphologies were observed in soils, consistent with other instances of DU munitions contamination. Batch extraction efficiencies for aqueous ammonium bicarbonate (42–50% total DU extracted), citric acid (30–42% total DU) and sulphuric acid (13–19% total DU) were evaluated. Characterisation of residues from bicarbonate-treated soils by synchrotron microfocus X-ray diffraction and X-ray absorption spectroscopy revealed partially leached U(IV)-oxide particles and some secondary uranyl-carbonate phases. Based on these data, a multi-stage extraction scheme was developed utilising leaching in ammonium bicarbonate followed by citric acid to dissolve secondary carbonate species. Site specific U extraction was improved to 68–87% total U by the application of this methodology, potentially providing a route to efficient DU decontamination using low cost, environmentally compatible reagents.

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1. Introduction

The development and deployment of armour piercing depleted uranium (DU) munitions has left a legacy of contaminated land in conflict areas and at test sites [1]. These areas may require long-term management and in some cases decontamination could be necessary to release the land for further use, or minimise risks to public health and environmental quality.

When a DU penetrator strikes an armoured target, 10–35% (maximum ~70%) of the mass is converted into aerosol [2] with median aerodynamic diameter of $d < 15\,\mu m$ [3]. Uranium metal used in DU munitions is pyrophoric and oxidation of fragments and aerosols occurs on impact, typically producing UO_2 and U_3O_8 as the dominant species [4–7]. These oxidised particles settle in the surface environment close to DU impact sites, and have been observed in soils from Kosovo and Kuwait [8,9] as well as at test firing ranges [7]. DU is also introduced into the environment as intact penetrators which undergo corrosion [10], and in accidents such as fires [6]. This study focuses on the remediation of soils contaminated with DU impact particles, which due to their prevalence in the near surface represent the most likely route of near-term exposure for populations [11].

The effective remediation of land contaminated with DU particles is an on-going challenge. If contamination is heavy, e.g. at US army firing ranges [12] and some accident sites in Kuwait [6], bulk soil is disposed of as radioactive waste. This involves considerable expense, and methods to decontaminate bulk soils and separate DU contamination into a smaller volume are therefore attractive. Physical separation routes such as sieving have shown to be ineffective due to redistribution of U from weathering processes and agglomeration of DU aerosols [12]. Separation systems based on radioactivity are only useful for large fragments of penetrators due to the low specific activity of DU [13,14]. Chemical extraction could overcome these limitations for aerosol contamination by leaching DU phases from the soil. There are reports of effective chemical leaching of DU munitions contamination [15–17] – however, this has only been applied to a small number of sites and more comprehensive data on the effectiveness of chemical extraction to DU dusts across a range of environments is required. In this study chemical extraction is evaluated as a decontamination approach for two DU laden soils from a UK firing range at Eskmeals [7,18].

Decontamination by soil leaching has its basis in extraction of U from ores, where sulfuric acid or bicarbonate are common leaching agents [17,19]. Additionally, citric acid has been studied due to its strong aqueous complexation of uranyl (UO_2^{2+}) [20], low toxicity, low cost compared to other organic extractants [21], and potential for controlled degradation [22,23]. Under alkaline conditions, bicarbonate is modestly selective for uranium and causes less mobilisation of other metals (e.g. Fe, Zn, Mn) from soils than under acidic conditions [17,22]. Reported efficiencies for carbonate extraction range from 20 to 95% of total soil DU [15,24] depending on the site, demonstrating that local geochemical conditions influence the leaching performance. Site specific DU extraction by citric acid has a comparably wide range in efficiency (25–99% total soil U) [15,22], and sulphuric acid has also shown to be effective across a small number of sites [17].

In this study, the efficiency of chemical extraction for decontamination of DU munitions particulate at two sample sites from a UK firing range was evaluated. The aim was to use microscopic techniques for particle characterisation alongside bulk scale extraction experiments to provide a basis for improving the efficiency of extraction by process modifications. Particles from these sites were characterised prior to treatment by scanning electron microscopy (SEM) and sequential extraction to provide information on the initial geochemical disposition of U at these sites. Following batch extraction, remaining particles were non-destructively characterised by SEM and synchrotron X-ray micro-spectroscopy and micro-diffraction. These techniques were used probe U behaviour in residues, and thus link residue particle properties with extraction efficiency. These data were then used to develop a more effective extraction methodology.

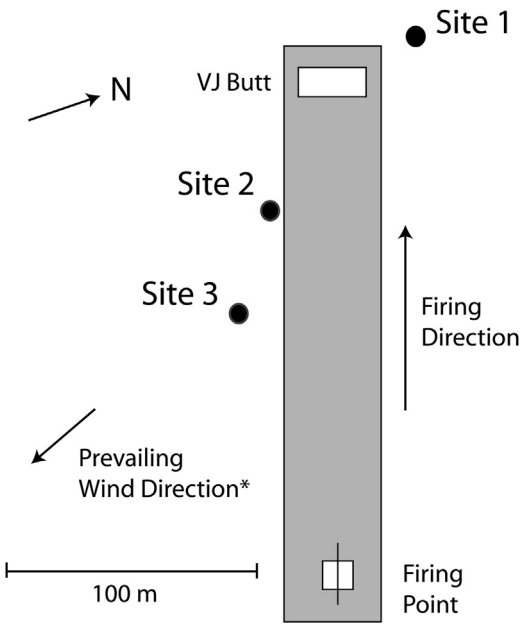

Fig. 1. Schematic of sampling locations within the VJ facility at MOD Eskmeals. The target and firing point are on a concrete apron. *Prevailing wind direction adapted from Oliver et al. [18].

2. Experimental methodology

2.1. Site and soil sampling

Eskmeals in Cumbria, NW England, is a UK Ministry of Defence (MOD) firing range that was used in the development and testing of DU weapons from the 1960s to 1995. The area around the DU firing range (named the VJ facility) was exposed to fragments and aerosols from impacts, and approximately 3 ha is designated as a Controlled Radiation Area [18]. Soils from the site are useful for a remediation case study as contamination at the site has been well characterised, is relatively undisturbed due to restricted access and results from a constant, controlled firing direction [7,18,25].

Samples of soils from within the VJ radiation control area at MOD Eskmeals were collected in November 2011. Sampling was conducted in three areas (Fig. 1); Site 1 is a storage area for contaminated timbers used in the construction of targets, Site 2 is adjacent to a concrete apron area downwind from the target, and Site 3 comprises a spoil heap of disturbed sub-soil from post operational construction at the site. In all cases surface vegetation was removed and soil to a depth of 0.15 m from an area of approximately 0.05 m^2 (total soil volume ~3 L) was sampled into plastic bags, which were sealed for transfer to the laboratory. All samples were air dried at 40 °C and sieved to remove particles above 2 mm. The remaining soil was homogenised by hand, divided into representative portions using the cone and quarter method, and dry stored in sealed containers under ambient conditions. DU particles were localised for spectroscopy and microscopy using a sample splitting technique and autoradiography [7]. Soil pH was measured in 1:5 soil:water extracts shaken for 2 h [18] using a WTW pH 315i (Expotech).