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Source-specific Ecosystem Transfer of Actinides Utilising Advanced Technologies (ADVANCE)

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The ADVANCE project, carried out under the EC's Fifth Framework Programme, was initiated in January 2001 as a co-ordinated effort to investigate the influence of source-term and ecosystem related characteristics on the transfer of actinides in different terrestrial, freshwater and marine ecosystems using state-of-the-art technologies.

The main objectives of the ADVANCE project were to

- (i) identify source- and ecosystem-related characteristics influencing the mobility of actinides in different terrestrial, freshwater and marine ecosystems, using advanced technologies;
- (ii) investigate the effect of source- and ecosystem-related characteristics on the transfer of actinides to biological endpoints (including humans); and
- (iii) significantly strengthen the European scientific competence and analytical technological skills within the field of radioecology.

To achieve these goals, a number of contaminated sites, chosen to represent different source-term and ecosystem characteristics, were systematically studied using a wide range of advanced analytical techniques. The selected study sites included a former nuclear test site (Semipalatinsk, Kazakhstan), sites affected by nuclear accidents involving the disintegration of nuclear weapons (Palomares, Spain; Thule, Greenland), areas affected by releases from reprocessing operations (Sellafield, UK; Mayak PA, Russia) and regions where depleted uranium munitions were used in recent conflicts (Kuwait and Kosovo).

A substantial effort was directed at the identification and characterisation of particles (heterogeneities) in samples collected at each of the selected sites. Particles identified either by sub-sampling and non-destructive gamma spectroscopy or by autoradiography were analysed using electron microscopy techniques. Scanning electron microscopy (SEM) using backscattered electrons provided information on the structure of the particles, as well as on the distribution of high atomic number elements on particle surfaces, while transmission electron microscopy (TEM) was used to identify electron-dense colloidal-sized structures. X-ray microanalysis (XRMA) was also used, in conjunction with electron microscopy techniques, to obtain information on the elemental composition of the particles. A selection of samples of particular interest were subjected to synchrotron-based techniques (μ -XRD, μ -tomography, μ -XANES) to obtain information on elemental distributions, crystallographic structures and oxidation states of actinides on individual micro-sized particles.

In addition, a comprehensive toolbox combining established (low-background alpha, beta and gamma spectroscopy) and novel (ICP-MS, AMS, RIMS) analytical techniques were used, in conjunction with speciation techniques, to identify the distribution, isotopic composition and physico-chemical speciation of actinides in different environmental compartments at each of the study sites. Finally, the bioavailability of actinides was investigated by a series of *in vitro* solubility tests.

The presence of radioactive particles and fragments varying in size, shape, structure, morphology, density, oxidation state distribution and charge was confirmed at all of the sites. Bioavailability and sequential extraction experiments conducted in the course of the project clearly demonstrated that failure to recognise the presence of these particles and their weathering characteristics may lead to analytical inconsistencies, irreproducible results and, ultimately, to erroneous conclusions regarding the mobility of these radionuclides in a given ecosystem.

Moreover, the study makes clear that any realistic assessment of the short- and long-term impact of actinide releases to a particular ecosystem should include, in addition to a programme to evaluate the radionuclide distribution in the ecosystem compartments, a suitable strategy to identify, isolate and characterise radioactive particles present at the site. Information on the physical and chemical characteristics of the particles, and kinetic information on processes influencing particle weathering, mobility and bioavailability of released radionuclide species associated with these particles should also form part of any such assessment.

Characterisation of source-terms, including radioactive particles in the sub-micrometer to micrometer range, certainly represents an analytical challenge. However, as demonstrated in the course of the ADVANCE project, application of emerging, state-of-the-art, advanced technologies in conjunction with more traditional techniques, can undoubtedly provide much of the required information.

It is, thus, proposed that any future assessment of a site contaminated by actinides (or other types of radioactive releases) should include a comprehensive strategy to identify, isolate and characterise radioactive particles present at the site. This strategy might take the following shape:

- Screening of samples to identify radioactive heterogeneities;
- Isolation of individual particles;
- Determination of size distribution;
- Determination of element distribution within individual particles;
- Determination of element or isotopic ratios;
- Determination of crystallographic structures;
- Determination of oxidation states;
- Determination of weathering rates.

The recommended techniques to be used for each of the above steps are briefly described below:

Identification of heterogeneities

Heterogeneities containing localised radioactivity (i.e. hot spots) can be observed in the field using portable Geiger-Muller counters or NaI detectors. To avoid altering the physico-chemical forms of radionuclides in a sample during storage, fractionation techniques should be applied *in situ*, at site or shortly after sampling at the laboratory. When screening solid material such as contaminated soil or sediment samples for heterogeneities, the samples should be dried at room temperature. Autoradiography using digital phosphor imaging is a very convenient way of screening samples for radioactive heterogeneities. This technique allows the production of digital auto-radiographs using a reusable image sensor with 10-100 times higher sensitivity than conventional X-ray or alpha radiation sensitive film. For radionuclides associated with colloids and particles in water, tangential-flow systems applied in the field have proved to be most useful.

Isolation of individual particles

Hot spots identified by autoradiography using digital phosphor imaging can be sub-sampled directly from the sample foils, which have been placed in close contact with the sensitive image plate. Thus, the sample volume is efficiently reduced, and microscopic tools can be utilised for isolation of particles in the obtained sub-sample. Alternatively, splitting a sample in numerous sub-samples followed by gamma measurements has proved to be an efficient mean for detecting and isolating particles, provided that the particles contain gamma emitters.

One of the latest developments within microscopic tools and, in particular, within electron microscopy, is the environmental scanning electron microscope (ESEM), which enables soft, moist and/or electrically insulating materials to be viewed without any pre-treatment. Radioactive particle identification can then be achieved using X-ray microanalysis (XRMA).

Activity concentrations and elemental isotopic ratios

Due to their high sensitivity in comparison with alpha-spectrometry, mass spectrometry techniques such as inductively coupled plasma mass spectrometry (ICP-MS), thermal ionisation mass

spectrometry (TIMS) and AMS have been utilised to determine the activity concentrations and the isotopic ratios of uranium and transuranic elements (e.g. plutonium) in radioactive particles and in samples with low activity concentration (e.g. sediment pore waters). In the case of hot particles, full dissolution is necessary prior to analysis.

Characterisation of colloidal species by transmission electron microscopy (TEM) with X-ray microanalysis (XRMA)

For colloidal radioactive material in water, transmission electron microscopy (TEM) with XRMA can be utilised for structure and element analysis. When droplets of water are transferred to coated grids and carefully dried under an UV-lamp prior to analysis, electron dense structures can be recognised, when compared to the blank (distilled water). Using this method, colloidal material with particle sizes close to 20 nm and pseudocolloids in the range of 100 nm has been identified in Sellafield effluents. XRMA provides information on the element composition, while the distribution of elements is obtained from X-ray mapping.

Determination of particle size distributions, elemental surface distributions and surface structures by SEM with XRMA

Particles isolated using microscopy tools can be further subjected to scanning electron microscopy (SEM) using an instrument interfaced with surface sensitive XRMA (X-ray microanalysis). This technique has proved most useful for obtaining information on particle size distributions, elemental distributions and structures in particles of different origin. Using Backscattered Electron Imaging (BEI) mode, bright areas reflect the presence of high atomic number elements, while the distribution of elements in the upper particle surface layer is obtained using X-ray mapping. XRMA measurements provide information on elemental composition. The structure of particles is characterised from images acquired in Secondary Electron Imaging mode. SEM also serves as a screening technique prior to further detailed studies using Synchrotron Radiation (SR) based X-ray micro-beam techniques.

Determination of 2D and 3D element distributions within individual particles, 2D crystallographic structures and oxidation states by synchrotron radiation based μ -X-ray techniques

Recent developments within synchrotron-based X-ray micro-techniques have proved to be very promising for the determination of 2D and 3D elemental distributions, crystallographic structures and oxidation states of matrix elements. Using monochromatic X-ray micro-beams, microscopic X-ray fluorescence analysis (μ -XRF) and microscopic X-ray absorption (μ -XAS) provide information on the elemental distribution on particle surfaces. Micro-X-ray diffraction (μ -XRD), on the other hand, gives information on the crystallographic structures in microscopic areas of solid particles.

By tuning the energy of the micro-beam source and scanning the energy over an absorption edge of an element of interest, extended X-ray absorption fine structure analysis (EXAFS) provides information on the number of atoms, the atomic number, the distance to neighbouring atoms and co-ordination in the surface of the solid, while X-ray absorption near edge structure spectrometry (XANES) provides information on the oxidation state.

In the laboratory, efficient μ -X-ray sources based on rotating anode tubes equipped with capillary X-ray optics can be usefully applied. However, the third generation synchrotron radiation sources, yielding high intensity and highly monochromatic X-ray micro-beams, have significantly increased the sensitivity and applicability of X-ray microprobe techniques. Using synchrotron (SR) based

XANES, the oxidation states of uranium associated with components in soils and sediments have been well documented.

In the course of the ADVANCE project, different SR-microprobe techniques have been combined by utilising the μ -X-ray beam at the European Synchrotron Radiation Facility (ESRF), France, to study uranium species in μm -sized radioactive particles released from the Chernobyl reactor. In this work, μ -XAS tomography (3D), μ -XRF, μ -XRD and 2D μ -XANES have been utilised to obtain information on distributions, structures and oxidation states. From μ -XRD, different crystalline forms could be identified, while μ -XANES clearly demonstrated differences in oxidation states of U in released UO_2 fuel (apparently reduced U fuel particles were released during the initial explosion and oxidised U_3O_8 particles were released during the fire). Using μ -tomography, internal cavities and channels due to formation of volatiles during normal operations could be observed.

It should be stressed that third generation synchrotrons are not essential for solid speciation of radioactive particles; SR based μ -X-ray Fluorescence (μ -SRXRF) screening of particles using a second generation SR source (e.g. HASYLAB, Germany) has also proved useful, as subsurface hot spot areas of elements of interest can be identified. Furthermore, the μ -XANES technique for uranium particles was developed at ID22, ESRF, though recently a similar approach with lower resolution has become available at beamline L, HASYLAB.

Determination of particle weathering rates

High activity particles can act as a point source when inhaled, ingested, or if deposited on skin (skin dose). Alternatively, radio-nuclides may be mobilised from particles (due to particle weathering) and transferred to man via ecosystem transport. Particle weathering constants depend on particle size, crystallographic structure, and on the oxidation state of the carrying matrix.

To evaluate the mobilisation potential of radionuclides from particles, several leaching procedures have been described in the literature. Moreover, sequential extraction procedures have extensively been used to extract radionuclides from contaminated soils and sediments. However, rather few publications deal with leaching of radionuclides from individual well-characterised particles.

When sequential leaching is applied, it is essential that the first step (i.e. the first extractant), is relevant, and does not interfere with the subsequent steps. Thus, site-specific waters (e.g., soil water, sediment pore water, seawater) reflecting the conditions where particles are deposited should be applied, rather than strong electrolytes (e.g. artificial Ca-solutions), which may aggregate colloidal systems. By gradually decreasing the pH of the extractant solutions, information on pH sensitive phases can be obtained.

Previous studies have demonstrated that weak oxidising reagents (H_2O_2 in HNO_3) are efficient for dissolving oxidised fuel particles from Chernobyl, together with associated radionuclides. However, to evaluate the potential for uptake via the gastro-intestinal tract, rumen liquid (e.g., domestic animals) or simulated stomach juice (e.g., man, 0.16 M HCl) is particularly relevant. In the course of the ADVANCE project, the extraction yield obtained by extraction with simulated stomach juice (0.16 M HCl) varied with particle characteristics, being high for highly oxidised uranium (V, VI) and low for U metal or UO_2 .

Main findings in the study areas of the ADVANCE project

Semipalatinsk (Kazakhstan)

Source-term: nuclear weapons tests

Analyses carried out on soil samples from Ground Zero, Lake Balapan and the Tel'kem experimental sites within the Semipalatinsk NTS showed that these sites are contaminated with significant amounts of transuranium nuclides, as well as fission and activation products. Analyses of plutonium isotopic ratios showed that the plutonium contamination in these areas is mainly due to weapons-grade plutonium. However, considerable differences were observed in the composition of the artificial radioactivity labelling each of the sites.

Radioactive particles with sizes ranging from micrometres to millimetres were identified in soil sampled at each location. Individual particles, especially from Ground Zero, appeared to be vitrified (fused), probably due to the extremely high temperatures involved. The distributions of uranium and plutonium in these particles were well correlated, although no correlation was observed with other major constituents within the particles (e.g. Ca, Fe).

Measurements on the solid partitioning of plutonium at each of the sites showed that a significant proportion of the plutonium contamination is in a highly refractory, non-labile form at the present time. Experimental tests on the availability of ^{241}Am using simulated gastrointestinal fluid on contaminated soils yielded a similar conclusion, with ~ 70-80 % of this radionuclide remaining unextracted even after 168 hours.

Palomares (Spain) and Thule (Greenland)

Source term: nuclear weapons disintegration

Isolated particles from the Palomares accident ranged in size from 1-50 μm , whereas those at Thule were in the range 20-40 μm . As in the case of Semipalatinsk, the distributions of uranium and plutonium within the particles were well correlated. Uranium in Palomares particles was found to be present as UO_2 and U_3O_8 . The absence of metallic uranium suggests the oxidation of uranium during the accident. A similar observation was made in the case of Thule particles. However, here, all the uranium was found to be in the form of UO_2 , with no metallic uranium or U_3O_8 present in any of the particles analysed. It seems that although the oxidation of uranium occurred following both accidents, the degree of oxidation was higher in the case of Palomares.

Plutonium in Palomares and Thule particles was present as a mixture of the relatively soluble Pu(III) and the less soluble Pu(IV). Most impact assessments concerning plutonium contamination at these two sites have been based on the assumption that plutonium is present exclusively in a rather inert form, either as metallic plutonium or as Pu(IV). As Pu(III) is also clearly present, impact assessments should be revised to take into account particle weathering rates and potential remobilisation of Pu(III).

In fact, evidence obtained using sequential extraction in the course of the ADVANCE project suggests a change in the geochemical association of plutonium in Palomares soils as a result of weathering, with a higher proportion of the plutonium present in readily available phases in comparison with previous results. On the other hand, solubility studies carried out on Thule sediments using simulated gastrointestinal fluid suggest that actinides in this area remain rather insoluble, with ~ 90 % of the ^{241}Am unextracted after 70 days.

Chernobyl (Ukraine)

Source-term: nuclear reactor accident

In the course of the ADVANCE project, particles with a variety of sizes, shapes, structures and optical appearance were isolated, ranging from compact, small-sized, single crystalline particles to large amorphous aggregates. Synchrotron radiation X-ray micro-techniques demonstrated that crystalline, inert fuel particles were released during the initial explosion. These particles were characterised by UO_2 -cores surrounded by reduced forms of U (+ 2), probably due to interactions with carbon from the moderator. In contrast, uranium in the UO_2 fuel particles released during the reactor fire was oxidised to U_3O_8 or/and U_2O_5 . These particles were characterised by UO_2 -cores surrounded by a layer of oxidised uranium (in the form of U_2O_5 and U_3O_8).

The weathering rate of fuel particles released during the initial explosion and deposited to the west of the Chernobyl reactor was low (0.04 year^{-1}) compared to that of fuel particles released to the north and south during the subsequent fire (0.4 year^{-1}). The low weathering rates of fuel particles to the west of Chernobyl can be attributed to their inert crystalline structure and presence of reduced forms of uranium, created during high temperature and pressure conditions, without the influence of oxygen. In contrast, the increased weathering rates for particles to the north and south is attributed to the presence of oxidised fuel particles, having UO_2 cores with oxidized U_3O_8 and U_2O_5 layers formed during the subsequent fire.

Although the source term (UO_2 fuel) was the same in both cases, the different release scenarios influenced the characteristics of the uranium particles ejected. Uranium particles released during the initial explosion were inert with low weathering rates and low soil-to-plant transfer, while uranium particles released during the subsequent fire were oxidised with high weathering rates and high soil-to-plant transfer. Thus, differences in crystallographic structure and oxidation state of uranium in fuel particles explain the observed differences in weathering kinetics, mobility and soil-to-vegetation transfer coefficients of radionuclides associated with particles located west and north of the Chernobyl reactor.

Sellafield (UK) and Mayak PA (Russia)

Source-term: reprocessing discharges

Previous studies had shown that a major fraction of the actinide discharge in effluents from reprocessing operations is associated with particles and colloids. In the course of the ADVANCE project, the persistence of these particle and colloidal forms in the terrestrial and freshwater environments surrounding the Mayak PA reprocessing plant, and the marine environment close to the Sellafield reprocessing plant, were thoroughly examined.

In contaminated ground waters from Mayak, about 65 % of the plutonium was found to be associated with particles and colloids. Autoradiography of sediments from Reservoirs 10 and 11 clearly revealed the presence of radioactive particles. However, all attempts to isolate particles containing plutonium or uranium were unsuccessful. Instead, the particles analysed appeared to contain a mixture of other radionuclides as well as heavy metals. Nevertheless, sequential extraction experiments showed that plutonium in these sediments is rather inert, with little (if any) present in a readily available form.

Radioactive particles were also identified throughout a sediment core taken in the muddy sediments close to the Sellafield outfall. Uranium fuel particles originating from Sellafield were also isolated from intertidal sediments collected in the Ravenglass Estuary. Sequential extraction analyses, however, revealed that, in contrast to the plutonium in the Mayak reservoirs, ~ 75 % of the plutonium

in these sediments was associated with relatively mobile phases (including exchangeable, easily oxidisable and acido-soluble phases).

The relatively high mobility and bio-availability of actinide species in contaminated sediments from Sellafield was confirmed in leaching experiments with simulated gastrointestinal fluid. The fraction of ^{241}Am extracted after 168 hours of contact, at ~ 80 %, was much higher than that obtained for samples collected at Thule and Semipalatinsk. Certainly, the remobilisation potential of actinides from contaminated sediments in the Irish Sea should be taken into account in any impact assessment (and modelling) of this particular area. Indeed, a number of studies have shown that it is remobilisation of actinide radionuclides from historically contaminated sediments, rather than direct contemporary discharges, that now constitute the main source of actinides to the waters of the Irish Sea.

Kosovo and Kuwait

Source-term: depleted uranium (DU) ammunition

In the course of the ADVANCE project, radioactive particles were isolated from sites in Kosovo and Kuwait contaminated by depleted uranium. The size distribution of the particles was found to differ depending on the release scenario.

In Kosovo, particles isolated from contaminated soils ranged from sub-micrometers to ~ 30 μm , with an average size of 2 μm . In Kuwait, particles collected from holes in tanks hit by DU ammunition, or from the vicinity of intact DU penetrators, ranged from 2-64 μm (median = 13 μm , $n = 36$). Larger particles, in the range 0.2-1500 μm (median = 44 μm , $n = 43$) were isolated from samples collected at the site of a DU ammunition storage facility destroyed by a fire. These DU particles appeared with a strong yellow colour (typical of uranyl compounds), and were distinctly different to those observed in Kosovo and at target sites within Kuwait. They also differed from uranium particles released during nuclear weapons tests (Semipalatinsk) or following nuclear reactor accidents (Chernobyl).

Measurements carried out on particles from Kosovo and Kuwait yielded a rather constant $^{235}\text{U}/^{238}\text{U}$ atom ratio (0.0020 ± 0.0005), which was in good agreement with previously reported values. In contrast, the $^{236}\text{U}/^{235}\text{U}$ atom ratio measured in DU particles from Kuwait varied depending on the sampling site, with values of ~ 10^{-2} measured in particles associated with the DU ammunition storage facility fire, and values of ~ 10^{-3} measured in particles collected inside disabled tanks. The presence of ^{236}U can only be due either to the use of uranium recycled from spent fuel or to the handling of natural uranium with equipment previously contaminated in the course of recycling operations in the enrichment plants. Variations in the $^{236}\text{U}/^{235}\text{U}$ ratio are thus readily attributable to differences in the nature of the nuclear fuel employed or the history of the enrichment plant producing a particular DU batch.

Speciation experiments conducted on selected, isolated DU particles showed that, in all cases, DU was in an oxidised form. About 50 % of the DU particles from Kosovo were characterised as UO_2 , while the remainder were present as U_3O_8 or a mixture of both oxidised forms (with *ca.* 2/3 UO_2 and 1/3 U_3O_8). Kuwaiti DU particles collected close to DU penetrators or inside disabled tanks (swipes) were similarly characterized as UO_2 , U_3O_8 or a mixture of these oxidized forms. In contrast, DU particles released during a fire in a DU ammunition facility were found to be present in oxidation states + 5 and + 6, similar to solid uranyl standards.

It is clear that, despite having the same origin (DU ammunition), particles formed during the fire were very different from those formed during impact with hard targets, with large, highly oxidised particles characterising the former, and small, less oxidised particles characterising the latter. The weathering behaviour of the two types of particles was also found to differ. Highly oxidised DU associated with particles originating from the fire in the ammunition storage was rapidly dissolved in 0.16 M HCl (84

$\pm 3\%$ after 2 hrs contact time, $n = 3$). The kinetics of the extraction were much slower for less oxidised DU particles originating from DU penetrators impacting with tanks or corrosion of DU penetrators. Furthermore, artificial seawater (pH 8) was able to dissolve large, yellow, highly oxidised DU particles originating from the ammunition storage fire, while DU particles originating from impact on tanks appeared to be relatively inert.

As the particle weathering rate is expected to be higher for U(V)/U(VI) and U_3O_8 than for metallic U or UO_2 , the presence of respiratory $U_3O_8/U_2O_5/UO_3$ /uranyl, their corresponding weathering rates and the subsequent remobilisation of uranium should clearly be included in environmental impact assessments of areas contaminated with DU.

Finally, the ADVANCE project has given rise to approximately 54 quality publications in the international literature, with a number of further publications by members of the consortium anticipated.