



Analytical Division  
Radiochemistry Group

# **14<sup>th</sup> International Symposium on Nuclear and Environmental Radiochemical Analysis**

12-15<sup>th</sup> September 2022  
National Railway Museum  
York UK

## **ABSTRACTS**

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# **ORAL PRESENTATIONS**

## ABSTRACT 1

### USING MOLECULAR CHEMISTRY TO QUANTIFY LANTHANIDE AND ACTINIDE COVALENCY

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Whilst lanthanide and actinide chemical bonding is predominantly electrostatic, these elements exhibit small differences in covalency; an improved understanding of f-block covalency is therefore crucial for efficient recycling and reprocessing of spent nuclear fuel.<sup>1</sup> Covalency can be valence orbital overlap- or valence orbital energy degeneracy-driven, and their relative contributions can be delineated by numerous experimental and theoretical techniques; these include X-ray absorption (XAS), Photoelectron, Mössbauer, Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance (NMR) spectroscopy, and both density functional theory (DFT) and *ab initio* calculations.<sup>2</sup> Molecular chemistry can provide well-defined systems of high purity to perform accurate measurements of covalency, providing transferable data that can be used to inform the design of improved processes to separate lanthanides, and early and late actinides.

Our group and collaborators focus on the synthesis and characterisation of novel molecular lanthanide and actinide compounds that exhibit unusual geometries, oxidation states and bonding regimes. We use a variety of spectroscopic and computational techniques to characterise these compounds, and to assess the amount of covalency in chemical bonds between lanthanide and actinide ions and coordinated ligands. Here we will present some highlights of this work. Firstly we will cover our development of low oxidation state actinide chemistry towards the quantification of covalency in thorium(III) and uranium(III) cyclopentadienyl complexes by pulsed EPR spectroscopy.<sup>3</sup> These results indicate that thorium-carbon bonds are less covalent than those between uranium and carbon, but are surprisingly similar to ytterbium-carbon bonds. Secondly, we present some of our work on molecules that contain structurally authenticated lanthanide- and actinide-silicon bonds, where we have recently used a combination of <sup>29</sup>Si NMR spectroscopy and DFT calculations to measure metal-silicon bond covalency.<sup>4</sup> Calculations indicate that the covalency of metal(II)-silicon linkages is ordered as nobelium(II) > ytterbium(II) > calcium(II) ~ magnesium(II), challenging the traditional view of late actinide chemical bonding being equivalent to the late lanthanides.

We thank the University of Manchester and the Nuclear FiRST CDT for PhD studentships and for access to the Computational Shared Facility. Additional funding was provided by the Engineering and Physical Sciences Research Council (EP/R002605X/1, EP/P001386/1, EP/M027015/1, EP/N022122/1) and European Research Council (CoG-816268, CoG-612724). We thank the EPSRC UK National Electron Paramagnetic Resonance Service for access to the EPR facility and SQUID magnetometer.

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## ABSTRACT 2

### **RAPID RADIOCHEMICAL SEPARATIONS OF AMERICIUM FROM COMPLEX MATRICES USING CUSTOM EXTRACTION CHROMATOGRAPHY RESINS**

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The purification of americium from complex matrices is a great challenge in radiochemical separation science. Separation from the chemically and physically similar lanthanide elements is particularly difficult. The separation of americium from the lanthanide elements has major applications in nuclear fuel reprocessing, environmental monitoring and nuclear forensics.

Extraction chromatography (EXC) is based upon the same principles as solvent extraction (SX) but the separation is carried out using a chromatographic column. The extractant is physically adsorbed or covalently bound onto the surface of a porous support, usually an organic polymer, consisting of bead-like particles.

Benefits of EXC over SX include:

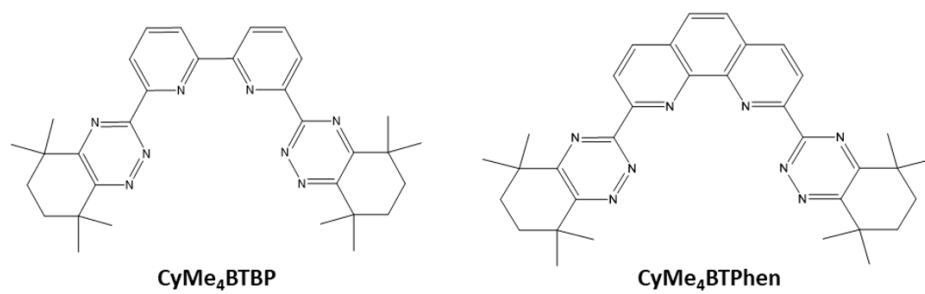
- elimination of the requirement for mixing and phase separation and associated issues of ligand solubility and phase-transfer kinetics,
- removal of the possibility of third phase formation,
- allowance for variable elution profile,
- the reduction, or total absence, of radioactive organic waste streams,
- the potential to recondition and reuse the resin and improve cost effectiveness.

For these reasons EXC is often touted as offering both the high selectivity of SX systems alongside the advantages associated with multi-stage chromatographic techniques and ease of operation of ion-exchange chromatography.

The efficacy of the triazine ligands CyMe<sub>4</sub>BTBP (BTBP) and CyMe<sub>4</sub>BTPhen (BTPhen) in selective solvent extractions of americium for its purification from lanthanides is well documented in the literature with BTBP representing the current European reference ligand for actinide/lanthanide separations.

A handful of attempts have been made to immobilise BTBP and BTPhen onto solid supports to generate an EXC resin capable of selective americium extraction from aqueous media. These methods however all rely upon the generation of a covalent bond between the ligand and support. This work describes the synthesis and characterisation of BTBP and BTPhen EXC resins produced by the solvent impregnation method which provides a simpler, faster and cheaper synthetic route for the production of EXC material.





**Figure 1:** Molecular Structures of CyMe<sub>4</sub>BTBP & CyMe<sub>4</sub>BTPhen.

## ABSTRACT 3

### MEASUREMENT OF CHALLENGING MEDIUM AND LONG-LIVED RADIONUCLIDES USING TANDEM INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Inductively coupled plasma mass spectrometry (ICP-MS) has been increasingly used for measurement of medium and long-lived radionuclides since the first measurements were made in the late 1980's. Compared to alpha and beta counting techniques, ICP-MS offers a high sample throughput, simultaneous measurement of multiple nuclides in a single run, measurement times of several minutes per sample and processing of up to several hundred samples per day.

Accurate measurement is potentially prevented by interferences, namely isobaric, polyatomic and tailing interferences, which must be removed prior to detection.

As ICP-MS sensitivity and interference removal capability has improved, the number of radionuclides measurable has increased and the detection limits achievable reduced. However, there remains a number of radionuclides potentially measurable by ICP-MS that have not been achieved as a result of significant interferences. Detection of such radionuclides would offer expanded measurement options for end users involved in waste characterisation, environmental monitoring, nuclear forensics, and provision of underpinning nuclear decay data.

Inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) has been commercially available for ten years. The instrument layout consists of two quadrupole mass filters separated by a collision-reaction cell. This setup has been proven to offer improved interference removal capability in a range of sectors, including nuclear. This study shows how ICP-MS/MS has been successfully used to expand the number of radionuclides measurable, focusing on those that suffer from significant interferences, in some cases meaning measurement was not previously considered possible. Results are shown for several radionuclides including <sup>36</sup>Cl, <sup>41</sup>Ca, <sup>93</sup>Mo and <sup>79</sup>Se, in each case demonstrating how the ICP-MS/MS setup can be used for interference removal to support offline chemical separation. Consideration is also given to development of traceable standards to enable end users to develop and validate their own methodologies.

## ABSTRACT 4

### FAST AND PSEUDO-QUANTITATIVE ANALYSIS OF ARTIFICIAL RADIONUCLIDES WITH PLASTIC SCINTILLATORS FOR WASTE CHARACTERIZATION

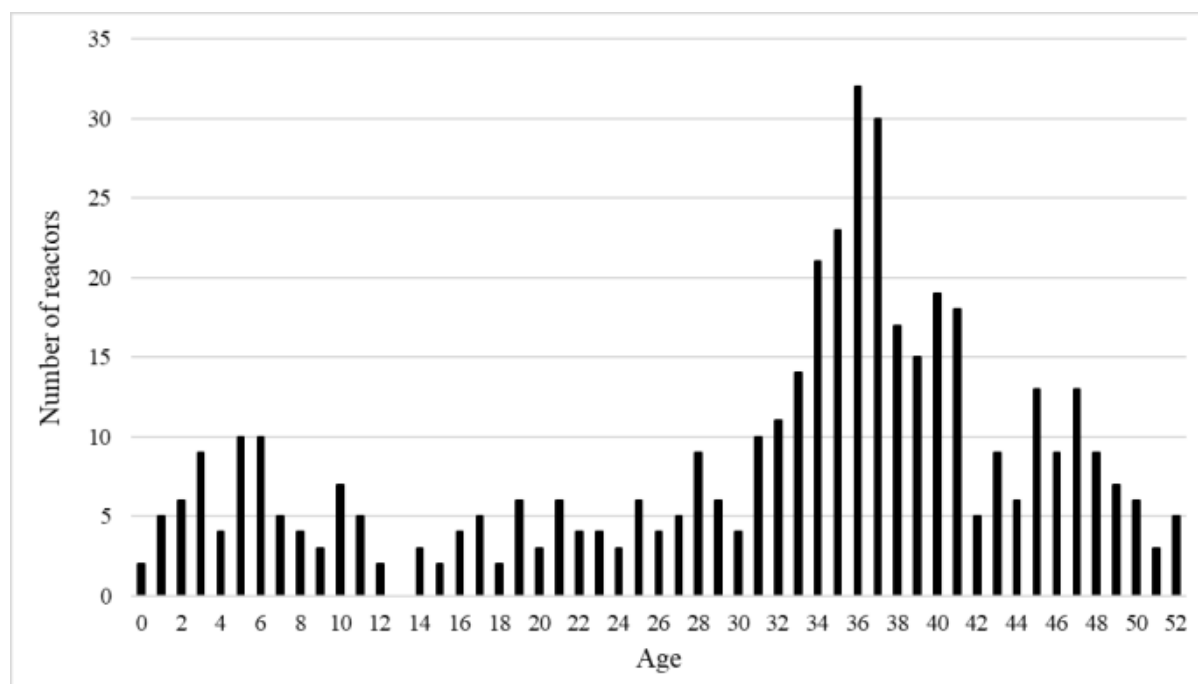
X Mendo<sup>1</sup>, E Antoñanzas<sup>1</sup>, H Bagán<sup>1</sup>; A Tarancón<sup>1,2,3 \*</sup>

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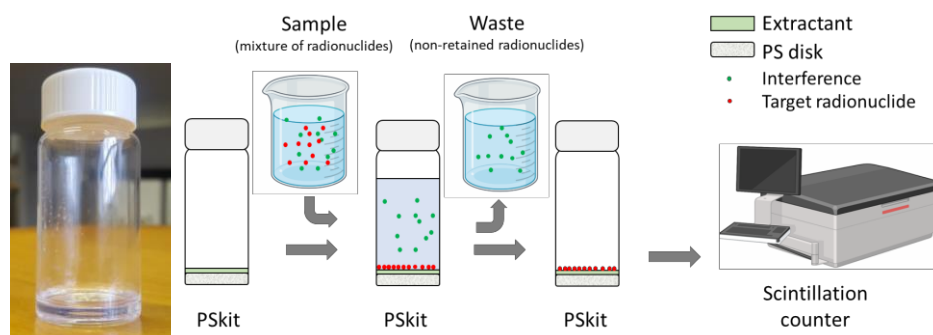
Production of energy in Nuclear Power Plants (NPP) represents, in 2020, 10.1% of the energy generation in the world<sup>1</sup>. This level of production is not expected to change in the future years, despite the need of strict safety requirements and waste management, as NPP do not contribute to greenhouse effect. There are currently 414 (as of May 2022) operating reactors over the globe, while 229 are in permanent shutdown and under decommissioning. If a 40-year average lifetime is assumed, it has been estimated that more than 200 reactors will be shut down by 2030, with Western Europe the most affected region.



Decommissioning of a NPP encompasses several steps and activities and an effective nuclear waste characterization is a vital aspect of the ongoing decommissioning process since it will assist in decisions

on sorting, segregation and decontamination operations<sup>2</sup>. Waste characterization is typically achieved using a combination of in-situ, on-site and off-site (expert laboratory) procedures<sup>3</sup>. However, nowadays, a complex labor-intensive approach is still mainly applied, in particular for those dominant pure alpha and beta emitting radionuclides (i.e.  $^{90}\text{Sr}$ ,  $^{241}\text{Am}$ ). This situation suggests that research and development of more efficient and effective characterization methodologies, especially in on-site and in-situ methods, need to be developed, that could bring significant benefits to current and future decommissioning projects in terms of minimize costs and timescales, improve information and securing workers health<sup>4</sup>. The introduction of novel combined extraction/detection systems would enable more wide-ranging application of on-site characterization.

Combined extraction/detection can be achieved through the use of plastic scintillators as they can be coated with a selective extractant. This strategy has been successfully applied by the authors in plastic scintillators in form of microspheres to a broad variety of radionuclides ( $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ , actinides...)<sup>5-7</sup>. The same concept has been adapted for the development of a PSkit for a selective, ultra-fast and simple strategy of analysis addressed to the on-site analysis of liquid waste from decommissioning of a nuclear installation. A PSkit consist in a 20 mL polyethylene or glass vial used in scintillation measurements with a plastic scintillation disk polymerized and fixed to the bottom of the vial and with a selective extractant coating its surface. The operator simply fills the PSkit with the sample, shake it, empty it, to remove non-retained radionuclides, and measures the radionuclide retained in a scintillation counter. In this approach, potential losses on accuracy, limit of detection and reproducibility, regarding classical strategies, are compensated by its simplicity and possibility to obtain a fast and reliable estimation of the activity of a certain radionuclide in the liquid sample.



PSkits (target radionuclide and extractant used) developed has been:

- $^{99}\text{Tc}$  with Aliquat-336
- $^{90}\text{Sr}$  with 4,4'(5')-di-t-butyl cyclohexano 18-crown-6
- $^{241}\text{Am}$  with bis(trimethylsilylpropyl)methanediphosphonic acid

Optimization of the PSkits design has included several studies: synthesis conditions; cross-linking agent; fluorescent solutes; time and temperature of polymerization; additives effect; amount of PS; stirring method, etc. Finally, two types of designs have been considered for the preparation of PSkits:

- a solid block of PS with the extractant on the surface
- a non-scintillating polymer block with a PS and extractant layer above. This option has been used for  $^{241}\text{Am}$  together with alpha/beta discrimination with the aim to suppress signals from beta emitters and reduce false positive results.

Results obtained for  $^{99}\text{Tc}$  showed that more than 80% of the radionuclide is selectively retained in the PSkit after shaking for 10 min. Detection efficiency is 50% which allows to reach a detection limit of 0.04 Bq/g in 1-hour measurement, which is above the clearance limit for this radionuclide (1 Bq/g). The PSkits were applied to simulated samples of the Hanford site including mixtures of radionuclides ( $^{99}\text{Tc}/^{137}\text{Cs}/^{90}\text{Sr}$  and  $^{99}\text{Tc}/^{63}\text{Ni}/^{238}\text{Pu}/^{236}\text{U}$ ) with satisfactory results in terms of qualitative and pseudo quantitative determination of  $^{99}\text{Tc}$  activity. For the case of  $^{241}\text{Am}$ , retention achieved has been about 82% whereas detection efficiency was of 95%. These results assure that pseudo quantitative determination of  $^{241}\text{Am}$ , or other alpha emitters, can be done at activities lower than the clearance level.

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## ABSTRACT 5

### **RAPID PROTOTYPING LOCS FOR THE FUTURE: A NUMERICAL OPTIMISATION OF BULK OPTICAL PARAMETERS IN MICROFLUIDIC SYSTEMS FOR RADIONUCLIDE DETECTION**

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*In-situ* microfluidic radiochemical analysis has the potential to offer an alternative to traditional manual sampling in industrial and environmental applications. Pure  $\beta$ -emitting radionuclides are typically monitored via discrete manual sampling followed by destructive analysis at an off-site laboratory; which can lead to delays in data availability and response times. The development of an *in-situ* microfluidic “Lab on Chip” (LoC) device capable of detecting pure  $\beta$ -emitting radionuclides presents an alternative to repeated manual sampling and the technical challenges that accompany this method.

A LoC device with an integrated detection system would reduce occupational exposure, lead times for provision of analytical data, and cost of monitoring, whilst providing improved temporal resolution through near real-time data acquisition. Due to the emergent nature of technology in this field, best practices for radioanalytical LoC system development and manufacture has yet to be established. Testing LoC prototype systems with radiogenic analytes is time consuming, requires specialist facilities/equipment, generates wastes, and cannot rapidly evaluate a wide range of configurations. Currently, modelling of designs and testing with non-radioactive substitutes before manufacture is not standardised best practice, so it is essential to explore this approach for prototyping these systems. Pure  $\beta$  emitting radionuclide measurement often relies on counting of photons arising from the Cherenkov Effect (for high energy beta emitters) or via liquid scintillators. Therefore photon transport through a microfluidic system is key area to target for improvement and development to reduce analysis time and achieve best limit of detection.

Here we explored the role of numerical modelling to assess the impact of bulk design features on photon transmission and detection through microfluidic systems; enabling improved designs to realise better efficiency of integrated detectors and overall platform design. Our results demonstrate that theoretical modelling validated by experimentally based radiogenic and non-radiogenic light sources is a viable approach for testing optical properties of a microfluidic system. This method constitutes a proof of concept and the first step towards robust optimisation based numerical modelling approaches for the design of microfluidic LoC systems with integrated detectors for the measurement of pure  $\beta$  emitting radionuclides via scintillation-based detection.

Our work has established the capability to reduce material consumption and requirement for specialist facilities needed for handling radioactive materials during the prototyping process. Our results enable reduced prototyping costs, alleviation of risks arising from working with ionising radiation, a reduction in generation of contaminated waste, and lower prototype development costs and timescales.

*This work was supported by: The Natural Environmental Research Council [grant number NE/N012070/1] as part of the NEXUSS CDT programme and GAU Radioanalytical Laboratories*

## ABSTRACT 6

### ADVANCES IN LOW-LEVEL RADIONUCLIDE DETECTION USING DESOLVATING SAMPLE INTRODUCTION COMBINED WITH ICP-MS/MS

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Inductively coupled plasma mass spectrometry (ICP-MS) measurements are increasingly preferred over alpha spectrometry and liquid scintillation counting techniques for longer-lived radionuclides due to advantages associated with high-volume sample throughput. Examples include Ra-226, U-236 and isotopic ratios including Pu-239/240, increasing applications around nuclear decommissioning, environmental monitoring, nuclear forensics and emergency response scenarios.

Tandem ICP-MS/MS has demonstrated enhanced interference removal for radionuclides with significant isobaric, polyatomic and tailing interferences due to the additional quadrupole mass filter and collision-reaction cell. However, for shorter-lived radionuclides, ICP-MS/MS can struggle to match the detection limits of decay counting techniques. One method for improving the sensitivity of the instrument is through the use of a more efficient sample introduction system.

In this study, ICP-MS/MS has been combined with an APEX Q desolvating sample introduction system. As well as improved sensitivity compared to the standard setup, the APEX Q consumes less sample during analysis, enabling concentration of low-level samples to a smaller volume before measurement. The APEX Q also introduces the sample 'dry', removing the majority of hydrogen and oxygen-based polyatomic interferences. Improvements in the measured sensitivity will be presented for several radionuclides that are challenging to measure by ICP-MS due to their relatively short half-life and significant interferences. Specifically, Ni-63 ( $T_{1/2} = 98.7$  (24) years), Sr-90 ( $T_{1/2} = 28.80$  (7) years) and naturally occurring Pb-210 ( $T_{1/2} = 22.23$  (12) years) and Ra-226 ( $T_{1/2} = 1600$  (7) years).

Results are compared to the 'standard' sample introduction setup. Initial testing was performed using stable analogues where possible, followed by active tests using standards and a range of sample matrices. Results are also compared to those achieved using decay counting techniques.

## ABSTRACT 7

### **RADIONUCLIDES FOR HEALTH UK: IMPROVING UK ACCESS TO RADIONUCLIDES FOR MOLECULAR RADIOTHERAPY**

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Molecular radiotherapy has been identified as a promising treatment for late-stage metastatic cancer and there is significant research and commercial interest in this area (1–3). The Radionuclides for Health UK project was established to advocate for re-establishing a domestic supply of radionuclides to enable molecular radiotherapy research and clinical translation in the UK. A roundtable held was held in 2020 where three key production routes were identified.

- 1- Radionuclides from nuclear legacy material
- 2- Reactor produced radionuclides
- 3- Accelerator produced radionuclides

A collaboration was formed between Radionuclides for Health UK, the National Nuclear Laboratory, the EPSRC MITHRAS program, and the CRUK RadNet City of London Radiation Research Unit to run workshops on each topic. Between July 2021 and March 2022 three workshops were held, each focusing on one of the above production routes. Each workshop included presentations from experts followed by panel discussions. Each was attended by representatives from academia, industry, government (Department for Business Energy and Industrial Strategy, Welsh Government Office for Science), funding bodies, and healthcare professionals. Feedback was collected from the workshop discussions and a follow-up questionnaire. A report was produced on each topic summarising the content of the workshop and the views of the community. These workshops have galvanised the community around the need for domestic radionuclide supply and highlighted routes to making this a reality. A summary of the workshop reports, progress and future directions will be presented. For further information please contact [rad4healthUK@qmul.ac.uk](mailto:rad4healthUK@qmul.ac.uk) or visit our website <https://www.bartscancer.london/radionuclides-for-health-uk/>



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## ABSTRACT 8

### COINCIDENCE AND ANTI-COINCIDENCE GAMMA RAY SPECTROSCOPY IN RADIONUCLIDE IDENTIFICATION

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The two most challenging aspects of gamma ray spectrometry are to achieve spectral free interferences and to achieve the lowest possible detection limits and ultimately low uncertainties. In nuclear forensics isotopic ratios or elemental ratios in environmental analyses need to have the individual results at low uncertainties for meaningful interpretations.

Over the last decades gamma-gamma coincidence and anti-coincidence (Compton suppression) methods have been used for variety radionuclide identifications for passive counting of naturally occurring radioactive material (NORM), special nuclear materials (<sup>239</sup>Pu), fission products and neutron activation analysis (NAA) for environmental, geological, and biological samples. Over the past years at the Nuclear Engineering Teaching Lab these methods have been successfully employed to determine radionuclides in a variety of samples. One real major advantage of these methods is that spectral interferences can be significantly reduced as in the case of Compton suppression or be eliminated as in gamma-gamma coincidence, while also reducing the Compton continuum and decreasing detection limits. For instance, the determination of <sup>137</sup>Cs in soil with Compton suppression can be determined at less than 1 Bq/kg for only a twenty-gram sample. In neutron activation analysis elements such as arsenic and cadmium in biological specimens can be determined with detection limits at the ng/g level, which cannot be determined using traditional NAA methods. Mercury, often hard to determine in environmental samples can be measured virtually interference free.

There are a host of elements determined by NAA that have benefitted using gamma-gamma coincidence and anti-coincidence methods. And in many cases, elements that are seldom or never reported, can now be effectively determined incorporating epithermal neutrons where the resonance integrals for several elements are high. For plutonium in soil samples, gamma-gamma coincidence has proven to be effective in getting good results by almost completely eliminating the background.

An overview of these methods will be delineated with specific examples. As well, a discussion on digital systems will be given showing the unique advantage of having essentially only one module.

## **ABSTRACT 9**

### **DETERMINATION OF SEDIMENTATION RATES IN UK MARINE ENVIRONMENTS USING LEAD-210 AND COMPLEMENTARY FINGERPRINTING TOOLS**

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The fallout of lead-210, present naturally in the atmosphere from the decay of radon gas, is a source of information that is commonly utilised to estimate time-trends of relatively recent environmental changes, variations and pressures recorded in aquatic sediment cores.

Over the last four decades, this geochronological tool has been utilised in diverse environmental research applications. Currently in the UK, there is a particular growing demand from marine scientists interested in further understanding the sequestration rates of natural sources of organic carbon, also known as Blue Carbon, that help mitigate the effect of climate change. It is also of increased interest for environmental research and public organisations concerned by the extent of the impact of legacy chemical releases on sensitive marine habitats.

Between 2019 and 2022, several surveys were undertaken in different UK coastal and offshore regions. These presented an opportunity to test different sample preparative and analytical approaches for measuring lead-210 and radium-226, review the most important challenges and limitations when applying this geochronological tool in UK seas, as well as investigate the forensic options available that could help validate results from lead-210 modelling.

**LEACHING BEHAVIOUR OF CEMENT WITH SUBSTITUTE CLINKER  
MATERIALS IN DEIONISED WATER**

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Clinker substitutes are frequently used in the cement and concrete industries to reduce CO<sub>2</sub> emissions associated with production, improve physico-chemical properties and performance, and reduce costs. Pulverised Fly Ash (PFA), a fine waste residue produced in coal-fired power stations, is the commonly used partial clinker substitute in Ordinary Portland cement (OPC) for cements for the immobilisation of low-level nuclear waste (LLW) <sup>1</sup>. Because of the global trend to shut-down coal-fired power stations, the production of PFA is decreasing and will eventually cease, resulting in increased PFA prices<sup>2</sup>. The UK decided to stop coal-fired power stations in 2024 <sup>3</sup>. Alternative sustainable clinker substitutes can be used must meet strict performance standards for the safe enclosure of LLW for the final disposal. These include physical, chemical, and mechanical properties; performance and suitability for use.

This study investigates the suitability of different materials (natural and anthropogenic) as a substitute of PFA in OPC in LLW immobilisation and compares the behaviour of these substituted cements to those of the current standard. The focus of the study is on the cementing and physico-chemical properties of the cement, and the interaction between groundwater, the cement, and the stored waste.

First the standard, PFA+OPC (samples provided by Low-Level Waste Repository Ltd. (LLWR)), was characterised using X-ray computed tomography (XCT). Here, leaching tests identify the change of the pH of the solvent (deionised water and groundwater) and the release of Ca<sup>2+</sup> ions from PFA+OPC and alternative materials. The samples undergo XCT analysis before and after the treatment to link structural changes due to chemical evolution. Future work will include studying the leaching behaviour in groundwater, the long-term leaching effects and the interaction of the LLW (usage mock waste formulation) with concrete.

These studies will allow us to identify changes to the cement microstructure and physico-chemical properties arising from the PFA substitutes, and the chemical and physical interaction of the cements, especially with groundwater. Such understanding is critical for the adoption of clinker alternatives in LLW encapsulation.

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## ABSTRACT 11

### CORROSION OF NUCLEAR WASTE GLASS IN COMPLEX NATURAL ENVIRONMENTS

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Vitrification in borosilicate glass is commonly used to immobilise high activity waste liquors and is increasingly considered for low and intermediate activity waste streams<sup>1</sup>. Radioactive elements are chemically incorporated in the glass structure and, therefore, will be released at the same rate as the wasteform dissolves. Understanding the long-term behaviour of glass is therefore important in constructing the safety case for its storage and eventual subsurface disposal. Most studies aimed at understanding glass dissolution rates and mechanisms have been conducted at elevated temperatures and under, static, sterile conditions taking no account of changing geochemistry or geomicrobiology<sup>2</sup>. Here, a combination of field and laboratory tests are used to explore the behaviour of glasses in complex natural environments.

Alteration observed on glasses from long-term studies, that have been exposed to environments relevant to the subsurface disposal of radioactive waste, is compared to that observed in short term laboratory based tests. These ongoing field experiments also aim to identify and characterise the unique microbial communities that colonise the interface between nuclear waste type glasses and their environment. Under laboratory conditions, inactive surrogate nuclear waste glasses containing the essential nutrients had a controlling effect on the microbial community that were able to utilize nutrients dissolved from the glass where they were absent in solution. The influence of microbial respiration on the dissolution rate of the glass was more complex with some conditions inducing a pacifying effect whilst other conditions appeared to enhance glass corrosion.

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## ABSTRACT 12

### COMPARATIVE ANALYSIS OF URANIUM (VI) REDUCTION BY A SULFATE- AND AN IRON-REDUCING BACTERIUM

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The safe disposal of high-level radioactive waste represents a significant scientific and societal challenge. According to geological, geochemical, and geophysical properties, clay formations represent a suitable host rock for the long-term storage of this waste. However, for a comprehensive safety assessment, the influence of naturally occurring microorganisms in clay rock and in the backfill material bentonite must be taken into account.

*Desulfosporosinus* species play a crucial role in the community of sulfate-reducing bacteria present in clay rock and bentonite.[1,2] *Desulfosporosinus hippei* DSM 8344<sup>T</sup> is a close relative of the isolated species and was originally found in permafrost soils.[3] *Desulfitobacterium* sp. G1-2 has been isolated from bentonite samples and is an important representative of iron-reducing bacteria. As members of the microbial community from deep geological layers, these strains were selected to get a more profound knowledge about their interactions with U(VI).

During time-dependent experiments in bicarbonate buffer (30 mM, 100  $\mu$ M U(VI)), *Desulfitobacterium* sp. G1-2 showed a removal of up to 80% within 5 days. UV/Vis studies of the dissolved cell pellets verified the formation of U(IV) during the process.

In contrast to these findings, *Desulfosporosinus hippei* DSM 8344<sup>T</sup> was not able to reduce U(VI) in the presence of bicarbonate. Therefore, experiments in artificial Opalinus Clay pore water [4] (100  $\mu$ M U(VI), pH 5.5) were conducted. Determinations of the U concentrations showed a removal of up to 80% of the radionuclide from the supernatants within only 48 h. UV/Vis studies of the dissolved cell pellets provided clear proof of a partial reduction of U(VI) to U(IV), although bands of U(VI) were also still observable. These findings propose a combined association-reduction process as a possible interaction mechanism for this microorganism.

TEM images combined with EDX analysis revealed the presence of two different U-containing aggregates inside cells of *Desulfitobacterium* sp. G1-2. Furthermore, cells of *Desulfosporosinus hippei* DSM 8344<sup>T</sup> released membrane vesicles as a possible defense mechanism against encrustation by U precipitates on the cell surface. However, cells showed almost no uptake of U.

In this study, different analytical methods were used to better understand the U(VI) reduction by sulfate- and iron-reducing bacteria. Significant differences in the occurring mechanisms were evident between both microorganisms, highlighting the importance of studies on the U(VI) interactions of different microorganisms present in clay rock. Moreover, these results contribute to a safety concept for a

nuclear repository in clay formations and for final disposal sites using bentonite as backfill material.

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## ABSTRACT 13

### PORE NETWORK AND FLOW FIELD ANALYSIS TOWARDS IMPROVED PREDICTABILITY OF DIFFUSIVE TRANSPORT IN HOST ROCKS FOR RADIOACTIVE WASTE

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Clay rock formations are considered as host rocks for underground radioactive waste repositories. Reliable predictions of diffusive transport heterogeneity are critical for assessing the sealing capacity of argillaceous rocks. The predictive power of numerical approaches to flow field analysis and radionuclide migration depends on the quality of the underlying pore network geometry. Both sedimentary and diagenetic complexity are controlling factors.

In this study, we demonstrate a cross-scale approach to reconstruct the pore network geometries of the sandy facies of the Opalinus Clay rock, a potential important host rock type. We identified diagenetic and sedimentary subfacies components based on the concentration of diagenetic minerals and grain size variability, and quantified their pore size distributions and pore network geometries. The pore network geometries (length scale: nm to mm), based on focused ion beam scanning electron microscopy (FIB-SEM), mercury intrusion porosity measurements (MIP), scanning electron microscopy (SEM), and elemental analysis (CHNS) of several subfacies components were combined with computer tomography ( $\mu$ -CT) data sets covering the diagenetic and sedimentary heterogeneity of the sandy facies of the Opalinus Clay shale at the core scale.

The resulting generalized pore network geometries are used in digital rock models to calculate effective diffusivities, using a combined upscaling workflow for transport simulations from nanometer to micrometer scales. Positron emission tomography (PET) diffusion experiments validated the simulation results and provided new insight into the heterogeneity of diffusive transport. We introduced a statistical treatment of the PET and  $\mu$ -CT tomographic datasets based on the spatial variability of both PET tracer concentrations and rock density. The analyzed effective diffusivities confirmed the numerical results.

This study illustrates three important steps in migration analysis:

- (i) a workflow of general applicability for cross-scale identification of pore network data in argillaceous rocks,
- (ii) application of the pore network data for the numerical analysis of diffusive transport, and
- (iii) validation of numerical results via combined PET- $\mu$ CT diffusion experiments. Based on the validation of the upscaled numerical results, we propose the use of this combined approach for the analysis of complex diffusive transport patterns.

## ABSTRACT 14

### EXPLORING THE FATE OF URANIUM (VI)-INCORPORATED GOETHITE: IMPACT OF ENVIRONMENTAL PERTURBATIONS

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Uranium is a significant contaminant in the global legacy of radioactive waste and contaminated land, with higher activity wastes destined for deep underground geological disposal, and radioactively contaminated land now being decommissioned. Iron (oxyhydr)oxide phases are expected to be ubiquitous in and around these engineered and natural environments and, given the numerous reports of uranium-incorporated iron (oxyhydr)oxides, these mineral phases may be an additional barrier to the migration of uranium (and other radionuclides) in the environment. However, the long-term stability of these phases under environmental perturbations is largely unknown. Specifically, U-incorporated iron (oxyhydr) oxide phases may interact with aqueous Fe(II) and aqueous sulfide species in the sub-surface. Significant electron transfer may occur between adsorbed Fe(II) and stable iron oxyhydroxides (e.g. goethite), with associated incorporated species released and/or reduced. On exposure to aqueous sulfide, iron (oxyhydr)oxides may also undergo extensive reductive dissolution.

Here, U(VI)-goethite was synthesized, reacted with either aqueous Fe(II) or S<sup>2-</sup>(II), and the system monitored over time using geochemical analysis and X-ray absorption spectroscopy (XAS). Reaction with aqueous Fe(II) resulted in significant electron transfer between Fe(II) and U(VI)-goethite, with up to 52% U(VI) reduced to U(V). XAS analysis revealed that electron transfer only occurred within the outermost atomic layers of goethite, with an enriched U(V)-goethite outer-layer and an unchanged core of U(VI)-goethite formed on reaction with Fe(II). Minimal recrystallisation of goethite (2%) occurred following electron transfer, with both U(VI) and U(V) retained within the mineral structure. Conversely, rapid reductive dissolution of U(VI)-goethite occurred on reaction with aqueous sulfide. Over the first day of sulfidation, a transient release of aqueous U was observed, followed by a progressive reductive scavenging to U(IV), and with solid phase U retained in the long-term as nanocrystalline UO<sub>2</sub>.

Overall, these results further improve our understanding of the long-term behavior of U-incorporated iron (oxyhydr)oxides under environmental perturbations.

## ABSTRACT 15

### APPROACHES TO GROUNDWATER RADIONUCLIDE REMEDIATION AT SELLAFIELD – IN-SITU PHOSPHATE MINERALISATION

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Activities at the Sellafield, UK nuclear licensed site over the last 70+ years have led to discharges of radionuclides to the sub-surface. Resulting in a significant legacy of radioactively contaminated land. Strontium-90 (<sup>90</sup>Sr) is one of the more challenging radionuclides in the sub-surface due to its relatively high mobility in the Sellafield sub-surface. Developing remediation strategies for <sup>90</sup>Sr is therefore important in maintaining the stewardship of the site in the medium to long term. Calcium phosphate minerals such as hydroxyapatite (HAp) have been suggested as promising radionuclide (including <sup>90</sup>Sr) sinks, as they can incorporate a range of radionuclides within their structure. The formation of HAp can be achieved in situ through both biotic and abiotic approaches. In previous studies conducted at the Hanford nuclear site, USA, aqueous injection of HAp-generating solutions have reduced the amount of mobile <sup>90</sup>Sr within contaminated groundwater on both laboratory and field scales.

In this study, prominent biotic (calcium citrate / sodium phosphate, glycerol phosphate) and abiotic (polyphosphate) phosphate amendment techniques were tested using microcosm experiments with the aim of developing a targeted remediation toolkit for <sup>90</sup>Sr remediation at Sellafield. Aqueous geochemical results suggest all three amendment solutions removed Strontium (Sr) from solution at an enhanced rate when compared to the sediment sorption control. Here, the calcium citrate / sodium phosphate amendment was the most effective at Sr removal with the polyphosphate least effective. Scanning electron microscopy in conjunction with energy dispersive x-ray spectroscopy conducted on sediments after treatment with calcium citrate / sodium phosphate and glycerol phosphate amendments showed the presence of strontium containing calcium phosphate phases deposited on the surface of larger sediment grains. Extended x-ray absorption fine structure analysis of these treated sediments is consistent with Sr incorporation into hydroxyapatite. Demonstrating the potential for these techniques to provide remediation strategies at nuclear sites

## ABSTRACT 16

### THE ROLE OF RADIOCHEMISTRY IN THE UK'S ENERGY FUTURE

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The potential role of nuclear energy in the UK has changed in the last few years. While it is nearly 15 years since Government once again entertained new nuclear build<sup>1</sup>, the UK's legally binding commitment to achieving Net Zero by 2050<sup>2</sup>, the 2020 Energy White Paper<sup>3</sup> and the 2022 Energy Security Strategy<sup>4</sup> have given definition to Government's ambitions and we are now attempting to accelerate deployment of new nuclear on a large scale; the 24 GWe target is the equivalent of 18 Hinkley Point C reactors.

However, the well understood, large Light Water Reactor (LWR) technology is not the only one envisaged. Rather, there is a picture of three 'waves' of fission technology- large LWRs; small modular reactors (SMR) probably based on LWR technology; and Advanced Modular Reactors (AMR), where High Temperature Gas-cooled Reactors (HTGR) technology has emerged as the favourite. Water moderated reactors are optimised for production of electricity, whereas HTGR in particular opens up potential new applications. Beyond fission, there is increasing emphasis on the exploitation of fusion technology through the STEP programme.<sup>5</sup>

In this changing environment, the function of the Nuclear Decommissioning Authority (NDA) can also usefully be re-examined.<sup>6</sup> Its structure has already changed, bringing all of its operations together in four operating companies under 'One NDA', with the potential to provide better integration of waste management activities. In addition, as the UK's principal nuclear landowner, has a critical role in the development of new nuclear energy. As exemplified by the transfer of the AGR stations from EDF to NDA at the end of generation, NDA is also evolving from a single focus on the nuclear legacy to taking a wider responsibility for nuclear sites and facilities at the end of commercial activities.

All of these changes open up major opportunities for radiochemistry, defined broadly. With a proposed 60 year design life, even relatively mature LWR technology could benefit from new and improved fuels and structural materials, and from a greater range of sensors to monitor condition and performance. HTGR and fusion will create very challenging operating environments, with intense radiation fields and high heat loads, while HTGR fuels may well be much more highly enriched than conventional LWR fuel- perhaps close to 20%. The development, manufacture, qualification of these fuel materials, and their management once spent, all require work.

In the NDA's remit, geological disposal is progressing, but all four prospective sites offer a sedimentary rock setting, rather than the crystalline rock which has formed the basis of much earlier planning. Implementing geological disposal in sedimentary rock formations will require much research, including the chemistry and geochemistry of radionuclide behaviour. Current plans are for new nuclear power to operate an open fuel cycle, and a 60 year, 24 GW programme will produce many tens of thousands of

tonnes of spent fuel for disposal. This has a major impact on the materials required for packaging and on the footprint of geological disposal. The use of more sustainable materials and development of a heat-tolerant disposal concept could have major impact on the cost of geological disposal.

As decommissioning of the UK's existing legacy progresses, there are opportunities to optimise the management of the wastes and the nuclear materials for which NDA is responsible. A greater range of end points for wastes, for example near surface disposal of suitable Intermediate Level Waste, would open up new options. This, combined with more precise categorisation of waste, would allow the 'right' waste route to be defined for any waste stream, leading to quicker, more cost-effective disposal while still retaining sufficient safety margin. However, this approach will require more detailed safety cases, which will have to be underpinned by better understanding of the whole disposal system, in which radiochemistry will play an important part.

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## ABSTRACT 17

### THE IMPORTANCE OF RADIOCHEMISTRY AND RADIOCHEMISTS IN THE MANAGEMENT OF RADIOACTIVE WASTE

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The management of radioactive waste from all uses of nuclear technology within a country is a complex and involved practice that requires coordination and communication at all levels. Starting at the national regulatory level, an understanding of the behaviour of radionuclides in waste forms and in the environment can help to set informed limits on isotopes. This is extended all the way to the waste generator, who needs a detailed radiochemical inventory of their waste to understand how and where it can be disposed and what obligations, if any, are placed upon it.

The field of radiochemistry, including its techniques and professionals, is a key component in successful radioactive waste management programmes. Radiochemistry is used at all stages of radioactive waste management starting at the legislative level by incorporating science based reasoning and technical information in national policy for regulating radioactive waste; at the research and working levels to develop, characterize and analyse waste forms; and during the disposal planning process to determine the long-term behaviour of waste forms when they are emplaced in repositories. Therefore, knowledge of waste management principles by radiochemistry professionals will help in the long term by ensuring that the individuals making and executing waste programs are knowledgeable about the requirements of the waste lifecycle.

The IAEA also encourages countries to take a holistic approach to waste management by including all relevant stakeholders in decision processes at an early stage. This includes not only the waste generator, treatment facility, and disposal facility but also representation from local communities and addressing security, safety and safeguards concepts. Due to the long times required to create waste acceptance criteria, to develop acceptable waste forms, and to site, then construct, disposal facilities, understanding the possible with respect to waste pathways should be a primary goal as early in the process as possible. Increasing awareness of this diverse set of requirements early should reduce the amount of re-work and corrections needed which reduces the overall cost and increase the efficacy of the radioactive waste management programme.

## ABSTRACT 18

### IMPACT OF GLUCONATE ON THE SOLUBILITY AND REDOX CHEMISTRY OF TECHNETIUM

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Technetium-99 (<sup>99</sup>Tc) is one of the main fission products of <sup>235</sup>U and <sup>239</sup>Pu (~ 6%) in nuclear reactors. Due to its long half-life ( $t_{1/2} \sim 2.1 \cdot 10^5$  a), redox sensitive character and large inventory in spent nuclear fuel, <sup>99</sup>Tc plays an important role in the context of safety assessment of repositories for radioactive waste. Under reducing conditions as those foreseen in underground repositories, Tc is expected to form the sparingly soluble Tc<sup>IV</sup>O<sub>2</sub> (am, hyd) whereas the soluble and mobile pertechnetate anion will form under oxidizing and redox-neutral conditions. Gluconate (GLU) is a polyhydroxycarboxylic acid used as cement additive. GLU is known to form strong complexes with hard Lewis acids such as Ln(III) or An(IV).<sup>[1]</sup> In the case of technetium, previous studies have shown a significant impact of GLU on the solubility of TcO<sub>2</sub>(am, hyd), although so far, no chemical and thermodynamic models are available for this system.<sup>[2]</sup> The present work aims at obtaining a better understanding of the fundamental processes at the molecular level and an improved quantitative thermodynamic model description of the system using the concepts of established solution thermodynamics, novel XAS techniques and quantum chemical calculations.

All experiments were performed at  $t = (22 \pm 2)$  °C in Ar gloveboxes with < 2 ppm O<sub>2</sub>. The impact of GLU on the solubility of Tc was investigated from under- and oversaturation conditions. Solubility samples were prepared in 0.1–5.0M NaCl solutions with  $9 \leq \text{pH}_m \leq 14$  and  $10^{-4} \text{ M} \leq [\text{GLU}]_{\text{tot}} \leq 0.5\text{M}$ . Reducing conditions were chemically set with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, Sn (II), hydrazine or Fe except for a limited number of samples that remained redox-unbuffered. [Tc], pH<sub>m</sub> and E<sub>h</sub> values were monitored at regular time intervals. After attaining equilibrium conditions (constant [Tc] and pH<sub>m</sub>), the redox speciation of Tc in the aqueous phase of selected samples was investigated by L<sub>3</sub> and K-edge XANES measurements.

The presence of gluconate clearly enhances the solubility of TcO<sub>2</sub> (am, hyd) compared to GLU-free conditions, in line with previous solubility data reported by Hess and co-workers.<sup>[2]</sup> L<sub>3</sub>- and K-edge XAFS measurements in combination with ab initio calculations confirm that Tc(IV)-GLU complexes dominate the aqueous speciation of Tc under reducing conditions, whereas Tc(V)-GLU complexes prevail in redox-unbuffered systems. Based on solubility data and speciation information obtained from spectroscopic and theoretical methods, chemical and thermodynamic models are provided for the system Na<sup>+</sup>-Tc(IV)-GLU<sup>-</sup>-Cl<sup>-</sup>-OH<sup>-</sup>-H<sub>2</sub>O(l). These results provide key inputs for source term estimations including the effect of gluconate in a variety of geochemical conditions relevant in the context of nuclear waste disposal.

This work was funded by the BMWK within the VESPA II project (contract number 02 E 11607C).

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## ABSTRACT 19

### COLLOIDAL PARTICULATES IN SPENT NUCLEAR FUEL STORAGE: FROM FUNDAMENTAL PROPERTIES TO EFFLUENT TREATMENT

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Colloids have the potential to mobilise radionuclides in radioactive waste decommissioning and disposal. The legacy ponds and silos complex at the Sellafield nuclear facility contains a range of corroded spent nuclear fuel materials including corroded Magnox sludge (CMS) which contains radionuclides including  $\text{UO}_2$  as well as Mg- and Mg-Al-hydroxides (e.g. hydrotalcite ( $\text{Mg}_4\text{Al}_2(\text{OH})_{16}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$ )). Interestingly, radionuclide behaviour in these systems is thought to be controlled by colloidal processes<sup>1</sup>. Here, we present results from investigations into U colloids under conditions relevant to Sellafield's legacy ponds and silos complex. Experimental results include both laboratory analysis of the fundamental colloidal and structural properties in U(IV) systems, exploration of U interactions with hydrotalcite colloids, and also analysis and characterisation of authentic samples taken from effluent treatment facilities on the Sellafield site. The findings underpin management of the legacy ponds and silos as well as develop the fundamental understanding of radionuclide-colloid properties and environmental mobility of actinides.

Firstly, the properties of intrinsic U(IV) colloids were investigated. Silicate was seen to have a significant role in stabilization of colloidal U(IV), in both core-shell intrinsic U(IV)-silicate particles<sup>2</sup> and colloidal suspension of nano- $\text{UO}_2$  formed via corrosion of metallic uranium<sup>3</sup>. SAXS, TEM and ultrafiltration were used to investigate particle size and colloidal stability, while XAS, XRD and PDF were used to probe particle structure. In both cases, silicate enrichment on the particle surface increased colloidal stability. Intrinsic U(IV)-silicate particles had a  $\text{UO}_2$ -like core (~1 nm) surrounded by a silicate-rich U(IV)-silicate shell making up nanoparticles ~5 nm in size. These particles were stable at circumneutral to alkaline pH, but stability decreased at pH 12 as the silicate content in the particles decreased. The nano- $\text{UO}_2$  particles were not colloidal in the absence of silicate at pH 11, however, when they were exposed to silicate solutions (at pH 11), a detectable fraction of colloidal U developed. Atomic-resolution HR-TEM imaging showed that these colloidal  $\text{UO}_2$  particles had a silicate coating, containing individual U atoms, while EXAFS indicated that the bulk particle structure did not change upon exposure to silicate.

Experiments probing interactions of U(VI) aqueous species and U(IV) nanoparticles with hydrotalcite, which is potentially colloidal and known to be present at Sellafield, illustrated strong interactions between U and hydrotalcite. U(VI) interacted with hydrotalcite via a range of mechanisms depending on U concentration and pH, with ternary U(VI)-carbonate sorption complexes dominating at high pH and low U(VI) loadings, confirmed by EXAFS and TRLS<sup>4</sup>. Interactions between hydrotalcite and nanoparticulate U(IV) phases were also investigated and intrinsic U(IV)-silicate phases had a higher affinity for hydrotalcite than nano-UO<sub>2</sub> and silicate coated nano-UO<sub>2</sub>. This was attributed to the higher colloidal stability, and therefore availability to sorb, for intrinsic U(IV)-silicate nanoparticles. There was, however, evidence from ultrafiltration and TEM studies that all three particle types investigated did interact with hydrotalcite, suggesting that hydrotalcite particles may be a vector for U as a ‘pseudo-colloid’ via sorption of either solution complexes or nanoparticles.

Finally, authentic samples from a Sellafield effluent treatment facility treating effluents from the legacy ponds and silos were analysed. These samples contained stable colloidal U and Mg phases and radionuclides which were analysed by ultrafiltration, TEM and EXAFS for the first time. TEM imaging showed U speciation was dominated by nano-UO<sub>2</sub> particulates often associated with Mg-rich phases including brucite (Mg(OH)<sub>2</sub>) and possibly hydrotalcite. Overall, Mg was present in a range of different phases, with EDX confirming Mg, Al, Si and O in the particle analyses. Alpha analyses on the particle fractions suggested that the actinides were selectively associated with larger particles. Interestingly, EDX analysis showed a range of particle types, including Mg-hydroxides and Fe-(hydr)oxides, had low levels of U even though no U-discrete phases were observed. This was supported by EXAFS measurements on filtrates of the waters, which suggested U was present as both nano-UO<sub>2</sub> and U(VI)-carbonate sorption complexes. These results closely agree with the parallel laboratory investigations with U, and bridging between the real world extreme environments in the ponds and our laboratory simulations. A Pu L<sub>3</sub> edge XANES spectrum taken from an authentic sample was representative of Pu(IV/V) mixed oxidation state speciation, consistent with Pu being associated with UO<sub>2</sub> nanoparticles at trace levels and highlighting the value in obtaining these challenging samples.

Overall, these results illustrate the close relationship that U and Mg phases have in spent nuclear fuel storage. The laboratory studies closely mirror the authentic samples, and, in particular, illustrate the capability of hydrotalcite colloids to mobilize nanoparticulate U(IV) phases – a new type of ‘pseudo-colloid’. This understanding is also of importance for long-term geological disposal of radioactive wastes where alkaline, reducing conditions are also expected.

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## ABSTRACT 20

### RADIOLOGICAL CHARACTERIZATION OF 850 t REACTOR BOILERS AT DUNGENESS A DECOMMISSIONING SITE

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Dungeness-A Decommissioning Site has eight boilers, each 25 m tall and 7.2 m in diameter, that were used throughout the operational life of the site's two Magnox reactors (1965 – 2006). The boilers have subsequently been drained and kept in a passive quiescent state and are now being radiologically characterized in readiness for de-planting and final waste processing. The baseline expectation is that the boilers will be Low Level Waste (LLW) and will be transported to Sweden for smelting, enabling most of the metal to be recycled.

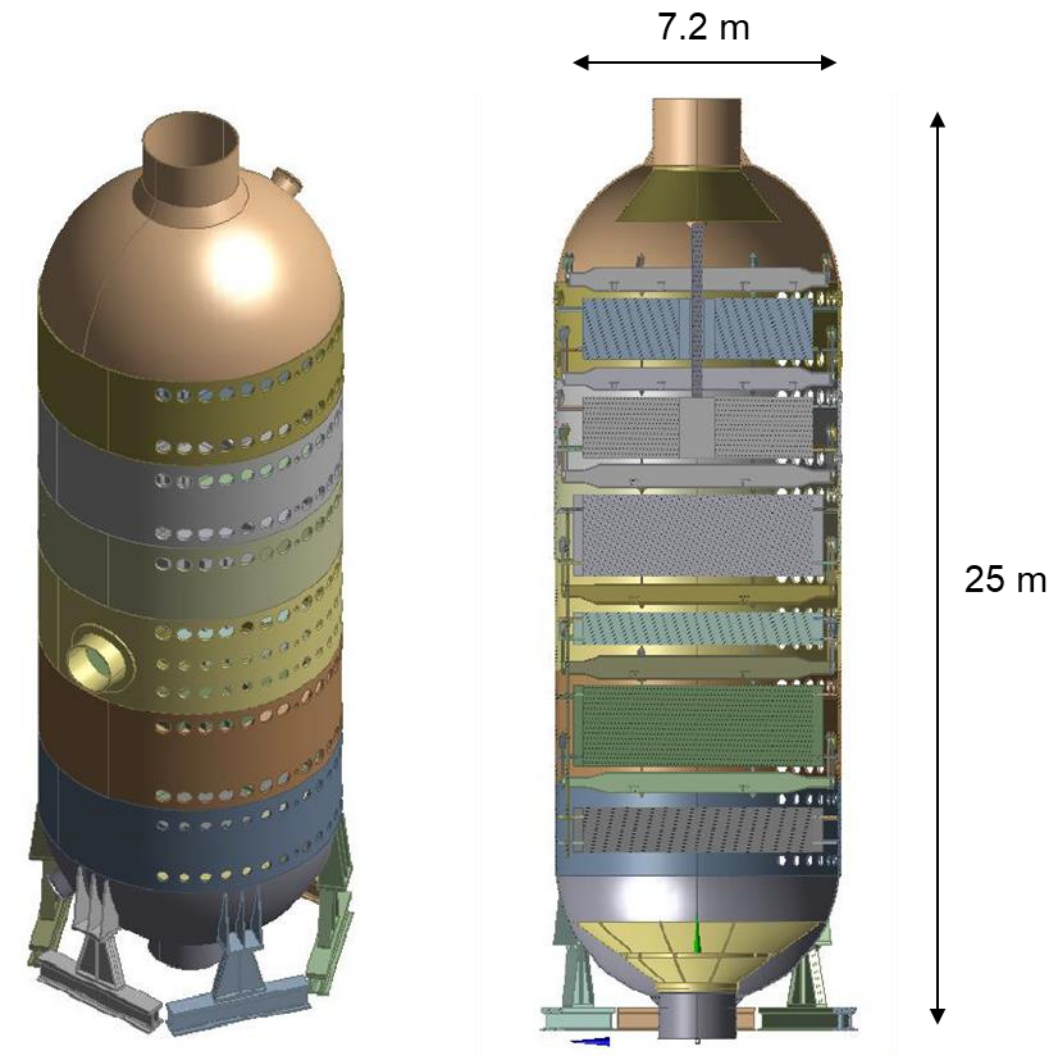
Each boiler weighs 850 t and consists of six tube banks housed within a mild steel shell (Figure 1). Re-circulating carbon dioxide gas was used to transfer heat from the reactors to the boilers where the gas cascaded down through the boilers and was returned to the reactor via the lower gas ducts. As a result, the internal surfaces of the boilers have been exposed to hot radioactive gas carrying particulate and are contaminated. The particles originate from the reactor core (e.g. graphite dust) or in material dislodged from boiler corrosion scale and activated within the core. As tritium was present in the re-circulating gas during operation, diffusion into the steelwork is also possible. The boilers further contain a quantity of loose activated dust, foils and debris which has collected at the base of the boiler as well as on the tube banks. The loose material is potentially Intermediate Level Waste (ILW) and may require removal and separate treatment to the boilers.

Radiological characterisation of the boilers is required to enable them to be transported from site, bound by the IAEA Transport Regulations and be compliant with the acceptance criteria of the institutions that will be receiving the components for processing and disposal. To this end, a range of complementary characterisation approaches are being used, including physical sampling & analysis techniques and *in-situ* assay measurements. A series of full depth cores, ~ 8 cm thick, have been taken from the boiler shell using a cold temperature drilling technique to prevent loss of volatile radionuclides. The inner surfaces of the core samples are to be mechanically removed and analysed to generate a radiological fingerprint for the internal contamination, while the remaining bulk metal will be analysed to assess tritium diffusion and possible neutron activation of the external boiler shell. The loose dust, foils and debris are to be separately sampled and analysed to generate their own separate fingerprint.

In addition, *in-situ* gamma spectroscopy measurements are to be taken using both a Cadmium-Zinc-Telluride (CZT) detector and a High-Purity Germanium (HPGe) detector. These include far-field

measurements external to the boilers and internal measurements through the core sampling holes. These measurements will provide information on the total boiler activity and the activity spatial distribution, including on the extent of debris accumulation on the tube banks. Combined with the sampling data, this will build up a full picture of the radiological profile of the reactor boilers.

This presentation reports the outcomes of the described characterisation programme so far, and discusses the implications for the final deposition of the boiler metal wastes.



**Figure 1:** CAD representation of a Dungeness A boiler (reproduced with permission from Gavin Davidson, Cyclife).

## ABSTRACT 21

### CHARACTERISATION OF MAGNOX REACTOR GRAPHITE

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The decommissioning of existing UK nuclear reactors is estimated to generate around 86,000 tonnes of irradiated graphite requiring to be managed as Intermediate Level Waste (ILW) over the next 100 years<sup>1</sup>. Most of this graphite is associated with Magnox and AGR-type reactor cores where it is used to moderate and reflect neutrons generated through controlled fission of nuclear fuel. Under current government policies, graphite ILW arising in England and Wales is intended to be emplaced within a deep geological repository<sup>2, 3</sup>, however similar waste arising in Scotland shall be managed in purpose-built near-surface near-site facilities<sup>4</sup>. Within the UK the vast majority of reactor core graphite remains *in-situ* until such time as it is feasible to undertake decommissioning (notable exceptions being the Windscale Advanced Gas Reactor (WAGR) and Graphite Low Energy Experimental Pile (GLEEP) which were decommissioned during the 1990's). Facilities to implement policies for the long-term management of ILW have yet to be developed<sup>2, 7, 8, 9</sup>. In the meantime, work is ongoing to identify and examine alternative options for comparison against the baseline position<sup>5, 10</sup> with particular interest in graphite which represents a significant volume of UK ILW.

With the consent of the Nuclear Decommissioning Authority (NDA), Magnox Ltd is developing site-specific strategies to complete decommissioning of reactors across 10 of its 12 sites, starting with the Trawsfynydd site in Snowdonia National Park. This will involve the progressive dismantling of all reactor structures and management of the resulting wastes, plus remediation of land as required. In line with current policy those wastes that require to be managed as ILW shall be packaged into a form that is suitable for long-term management and held securely on site in an environmentally controlled store pending the availability of a UK Geological Disposal Facility (GDF). Experience at Trawsfynydd shall inform the approach to decommissioning the remaining Magnox reactors and dealing with the resulting wastes. This early experience will also benefit decommissioning of the UK's fleet of AGR reactors which are due to cease electricity production from 2022 onwards, noting that Magnox Ltd will assume responsibility for these reactors as each station completes defueling.

Approximately 4,350 tonnes<sup>1</sup> of radioactive graphite will be generated by decommissioning the Trawsfynydd reactors. As part of its early planning, Magnox Ltd is applying the industry-recognised Derived Quality Objectives (DQO) approach<sup>6</sup> to plan characterisation activities that will reveal important information about reactor components and materials, including graphite. Accurate characterisation information is essential to understanding how best to remove and process the graphite safely; identify optimum packaging and conditioning approaches; explore alternative routes for treatment and disposal; and even consider its potential for re-use. Exploratory characterisation work is underway which will inform further activities over the coming years.

This paper describes key activities for the characterisation of irradiated Magnox reactor graphite at Trawsfynydd and how the information obtained supports the development of strategies for decommissioning and onward management of the resulting wastes.

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## ABSTRACT 22

### CHARACTERISATION OF MATERIALS FROM THE HUNTERSTON A SPENT NUCLEAR FUEL STORAGE POND

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Nuclear power plants can become heavily contaminated with fission and corrosion products during their operational lifetime. These contaminated materials give rise to high doses of radiation and heat, increasing risk to workers and the surrounding environment<sup>1</sup>. Rapid identification of radionuclides and the extent of their penetration into nuclear materials could help reduce the volume of intermediate level waste (ILW) produced during decommissioning and minimise the costs of post operation clean out (POCO) procedures<sup>2</sup>. Characterisation of legacy samples provides key insight into the long-term contamination effects of storing nuclear waste and is vital towards developing an appropriate strategy for future decontamination and decommissioning tasks.

A concrete core was obtained during the decommissioning of the Hunterston-A spent fuel storage pond. The core was taken from the middle of the pond wall, where it was exposed to the contaminated pond water. A multi-layered protective coating was applied to the concrete walls during plant operations to prevent uptake of radionuclides. The majority of the activity of the core is due to the presence of <sup>90</sup>Sr, <sup>137</sup>Cs, <sup>241</sup>Pu, and <sup>241</sup>Am, which has been shown to be associated with the painted surface<sup>3</sup>. Autoradiography results have also indicated that some activity may have penetrated through to the bulk concrete. Sorption experiments were completed using concrete coupons in stable Sr, Cs, or Co doped solutions to determine the effects of contamination within the bulk concrete material. Samples were analysed using Laser-Induced Breakdown Spectroscopy (LIBS) to assess its capability as a rapid, multi-elemental characterisation technique within the nuclear industry.

Furthermore, plastic samples were taken from a pontoon which was floated on the pond water and used by workers during decontamination operations to reach the inside of the pond walls. Jet washing of the pond walls caused the wastewater to splash on top and down the sides of the pontoons, contaminating them in the process. Gamma spectroscopy indicated that the radioactivity within the samples is predominantly caused by <sup>137</sup>Cs and <sup>241</sup>Am. Autoradiography was performed on these discs to map the location of the radiation and identify areas of increased contamination for further analysis. Decontamination experiments were also conducted to measure the effect of nitric acid loaded polymer hydrogels for the removal of radionuclide contamination on the plastic disc surfaces.

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## ABSTRACT 23

### RECRYSTALLISATION OF CEMENT PHASES; AN EFFICIENT PROCESS FOR THE IMMOBILISATION OF SILICON-132 AND CALCIUM-41 IN CEMENTITIOUS ENVIRONMENTS

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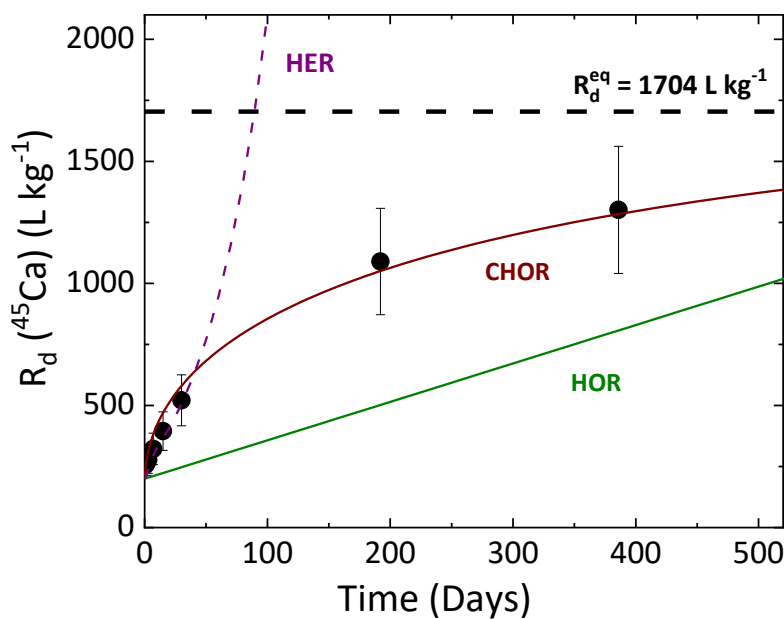
In a recent evaluation, Nagra identified  $^{32}\text{Si}$  and  $^{41}\text{Ca}$  as new dose relevant radionuclides for the safety assessment of a future low and intermediate level (L/ILW) radioactive waste repository in Switzerland.  $^{32}\text{Si}$  results from spallation processes at research facilities while  $^{41}\text{Ca}$  is an activation product generated in nuclear reactors. Little or no research has been published in the literature on the retention of these radionuclides by cementitious materials. The aim of the present study was, on the one hand, to determine  $^{32}\text{Si}$  and  $^{41}\text{Ca}$  sorption values ( $R_d$ ,  $\text{L kg}^{-1}$ ) for the main cement phases and for hardened cement paste, and on the other hand, to gain insight in the geochemical processes controlling the sorption of these radio-nuclides onto cementitious materials. The retention of radionuclides by solids can take place through surface processes such as surface complexation or ion exchange but also by isotopic exchange during dissolution-precipitation (recrystallisation) reactions. The former processes are fast, taking hours to a few days, whereas the latter are much slower, taking up to several years. Recrystallisation processes are likely to have a significant impact on the immobilisation of radionuclides such as  $^{41}\text{Ca}$  and  $^{32}\text{Si}$  by the rather soluble cement minerals such as C-(A)-S-H phases ( $^{41}\text{Ca}$ ,  $^{32}\text{Si}$ ), portlandite ( $^{41}\text{Ca}$ ), ettringite ( $^{41}\text{Ca}$ ) and AFm phases ( $^{41}\text{Ca}$ ).

The sorption kinetics of  $^{32}\text{Si}$ ,  $^{45}\text{Ca}$  (as an analogue for  $^{41}\text{Ca}$ ),  $^{35}\text{SO}_4^{2-}$  and  $^{14}\text{CO}_3^{2-}$  on the above-mentioned cement minerals and on hardened cement paste (HCP) were investigated in batch sorption experiments to evaluate the contribution of recrystallisation processes to the retention of these radionuclides in cementitious environments. Experiments with  $^{35}\text{SO}_4^{2-}$  and  $^{14}\text{CO}_3^{2-}$  have been carried out on AFm phases and ettringite to complete the picture of the recrystallisation behaviour of these cement phases. In all sorption kinetics experiments, a continuous uptake over at least one year was observed. The uptake was initially very fast and decreased continuously with time (e.g., Figure 1). A two-step kinetic behaviour can be recognized. In a first step lasting up to one day contact time, almost instantaneous adsorption was observed. This first step was assigned to a surface adsorption process in which isotope exchange takes place between the mineral surface and the solution. In a second step, sorption slowed down considerably but  $R_d$  values continued to increase for a long period of time of up to 400 days supporting the assumption that  $^{32}\text{Si}$  and  $^{45}\text{Ca}$  uptake is a slow process and that recrystallisation is the driving force.

Three different recrystallisation models combined with instantaneous surface adsorption were applied to describe the experimental sorption results<sup>1,2</sup>, the heterogeneous (HER) and the homogeneous (HOR) recrystallisation model, and a variant of the latter called the continuous homogeneous recrystallisation (CHOR) model.<sup>2</sup> Heterogeneous recrystallisation assumes that at any time during the process only the surface layer of the recrystallised solid is in equilibrium with the aqueous phase, while homogeneous recrystallisation requires the entire recrystallised fraction to be in equilibrium with the fluid. The former produces a zoned tracer distribution in the crystals, while the latter results in spatially uniform tracer

distribution. The CHOR model is a variant of the HOR model, which requires multiple sequential steps of recrystallisation, resulting in considerably slower recrystallisation rates. A constant term was added to the recrystallisation equations to account for the instantaneous surface adsorption of the tracers. Only the CHOR model allowed an adequate description of the experimental isotopic exchange data for  $^{45}\text{Ca}$  and  $^{32}\text{Si}$  as well as for  $^{14}\text{CO}_3^{2-}$  and  $^{35}\text{SO}_4^{2-}$  with time (Figure 1).

For the assessment of the safety of a radioactive waste repository, long-term sorption values for  $^{32}\text{Si}$  and  $^{45}\text{Ca}$  are required. These long-term  $R_d$  values cannot be measured in the lab and have to be estimated from the appropriate recrystallisation models. The CHOR model predicts that  $R_d$  values become constant once isotopic equilibrium between the fully recrystallised cement phase and the liquid phase is reached. These  $R_d$  values at isotopic equilibrium ( $R_d^{\text{eq}}$ ) are selected for inclusion in a sorption database to be used for an assessment of the safety of a cement-based radioactive waste repository.



**Figure 1:**  $^{45}\text{Ca}$  isotopic exchange kinetics on a C-S-H phase with C:S = 0.96. The S:L ratio = 3.9 g L<sup>-1</sup>. Experimental data (●) and curve fits with the help of three different recrystallisation models (HOR, HER and CHOR).  $R_d^{\text{eq}}$  represents the  $R_d$  value at isotopic equilibrium.

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## **ABSTRACT 24**

### **RESEARCH REACTOR SUPPORT FOR NUCLEAR FORENSICS STUDIES AND THE DEVELOPMENT OF A COMPANION GRADUATE COURSE**

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The term nuclear forensics is the detection and analysis of nuclear materials before they are used in a terrorist plot, the analysis of radioactive debris following a nuclear event or the investigation of the pedigree of nuclear materials in nonproliferation. Nuclear forensics typically encompasses these three main broad areas: radiochemistry, chemical instrumentation and non-destructive techniques (typically gamma-ray spectrometry). Research reactors (10 KW – 10 MW) are a great resource to perform research and development in nuclear forensics as well as in the critical need of education. By the sheer fact that reactors can produce isotopes in small or large amounts means that researchers have a unique source of material for nuclear forensics studies. A companion graduate course in nuclear forensics was developed with a grant through the US Department of Homeland Security.

Besides the usual lectures on the basics of nuclear phenomena, a successful effort was made to include a significant amount of historical background. In addition, several guest lecturers from national laboratories and universities were added to the curriculum resulting in a more meaningful and current course. As well due to COVID-19 restrictions, all the laboratories were videotaped and given virtually. These laboratories included half-life measurement, counting statistics, shielding, gamma-ray self-attenuation, gamma ray spectrometry and fission product identification. Lectures included the following topics: Making of the Atomic Bomb, Nuclear Forensics and Attribution, Culture Goes Nuclear, Gamma Ray Spectroscopy Software, How Nukes Work, Alpha Decay Beta Decay, Decay and Equilibrium, Decay Schemes, Interaction of Radiation with Matter - Alphas and Betas, Interactions of Radiation with Matter – Photons, Interactions of Radiation with Matter – Neutrons, Counting Statistics, Robotics and Radiation Detection, Gamma- Ray Self Attenuation, Gamma Ray Self Attenuation, History and Effects of Radiological Weapons, Radiation Portal Monitors, Chemistry of the Actinides and Fission Products, Chemical Equilibria, Chemical Separations Chemical Separations, Nuclear Fuel Cycle, Nuclear Fuel Reprocessing, Air Dispersion, New Scintillators and their Integration into Detector Systems, Rapid Characterization of Fresh Nuclear Fallout using Full-Spectrum Inverse Transport Methods, Measurement of Uranium Isotope Ratios in Keratinous Materials, Materials Analysis for Nuclear Forensics, Solid-state U Chemistry in the Nuclear Fuel Cycle. Various Applications of Machine Learning/Data Analytics for Nonproliferation Neutron Interrogation (Cole Thompson LANL).

An overview of the research performed at the Nuclear Engineering Teaching Lab in nuclear forensics and the development of a graduate course in this area will be given

## ABSTRACT 25

### RECENT ANALYTICAL DEVELOPMENTS IN RADIO-CHRONOMETRIC AGE DATING AT THE ATOMIC WEAPONS ESTABLISHMENT (AWE)

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In the event of a nuclear material being interdicted, detailed characterisation of impurities and isotopes can provide information on its source and origin. One possible suite of measurements, termed radiochronometry, enables the determination of the age and/or processing history of a nuclear material. Therefore, a radiochronometry project has been established to develop the required measurements in support of this objective.

Developments in radiochronometry were first established by geologists and archaeologists in order to date specimens of rocks, fossils and historical artefacts. There are a multitude of different radioactive isotopes that can be used to date a material. However, the longevity of the isotope half-life will determine the time period it will be suitable for and the error or precision of the calculated age.

The same basic principles can be applied to nuclear forensics, enabling precise age dating of nuclear material that is found outside of regulatory control. The measurement of radioactive chronometers found in both uranium and plutonium provide an important nuclear forensic signature, assisting the final provenance assessment. This is done by accurately measuring the ratio of a parent isotope (e.g.  $^{235}\text{U}$ ) to the amount of radiogenic daughter product (e.g.  $^{231}\text{Pa}$ ), and applying a mathematical model known as the Bateman equation. Multiple chronometers can be established using different isotope pairs for the same material. Chronometer concordance can be used to further validate and add confidence to the analysis. Discordant chronometer pairs can also be a useful forensic signature and provide information on processing history.

Current methods can provide age estimates with a demonstratable range of months to the oldest anthropogenic nuclear material, with <2% combined standard uncertainty ( $K=2$ ). This presentation briefly explains the fundamentals of radiochronometry, the requirement for a radio chronometric capability, and the methodology that the Atomic Weapons Establishment use to achieve this objective.

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## DETERMINATION OF TRANSURANIUM ELEMENTS PRODUCED BY THE CASTLE BRAVO EXPLOSION

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### Introduction

Thermonuclear explosions offered a possibility for investigating the production of transuranium elements. The thermonuclear test “Mike”<sup>1</sup>, fired at Enewetak (Marshall Islands) and “Barbel”<sup>2, 3</sup> and “Par”<sup>3</sup>, at Nevada test site (USA), were among the most investigated ones. Little information has been reported for other important tests such as the “Castle Bravo” explosion. This thermonuclear test was fired by USA on 1 March 1954 at Bikini Atoll (Marshall Islands) and produced the largest yield (15 MT) of the entire series in the Pacific Proving Grounds (PPG), about 1000 times more powerful than the atomic bomb dropped on Hiroshima in 1945. Apart from the analysis of the so-called “Bikini ash” debris<sup>4</sup> and marine sediment samples collected at Bikini<sup>5</sup>, little has been published about the production of transuranium elements in this thermonuclear explosion. In this study, we aimed at determining the yield of long-lived transuranium radionuclides (e.g. <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Pu, <sup>242</sup>Pu, <sup>244</sup>Pu, <sup>241</sup>Am, <sup>243</sup>Am and <sup>245</sup>Cm) produced by the “Castle Bravo” thermonuclear explosion. We based our study on the analysis of surface soil samples collected at Bikar, Marshall Islands, an atoll that was contaminated predominantly with radioactive fallout debris from the “Castle Bravo” explosion<sup>6, 7</sup>. The results of the radionuclide activity concentrations and ratios are discussed in view of the production process.

### Results

The activity concentrations of the lighter <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Pu and <sup>241</sup>Am radionuclides was found to be in the order of a few Bq kg<sup>-1</sup>. The heavier <sup>242</sup>Pu, <sup>243</sup>Am and <sup>245</sup>Cm radionuclides showed much lower activity concentrations in the order of a few mBq kg<sup>-1</sup>. <sup>244</sup>Pu was also detected at ultra-trace levels, in the range of a few μBq kg<sup>-1</sup>.

The mean <sup>240</sup>Pu/<sup>239</sup>Pu, <sup>241</sup>/<sup>239</sup>Pu, <sup>242</sup>Pu/<sup>239</sup>Pu and <sup>244</sup>Pu/<sup>239</sup>Pu atom ratios are equal to  $0.261 \pm 0.005$ ,  $(1.2 \pm 0.2) \times 10^{-3}$ ,  $(9.5 \pm 0.5) \times 10^{-3}$  and  $(2.8 \pm 0.6) \times 10^{-4}$ , respectively. Low variability of Pu atom ratios confirms a similar source (Castle Bravo) for the radioactive contamination found in all the soil samples from Bikar. <sup>243</sup>Am/<sup>241</sup>Am atom ratios varying between  $2.87 \times 10^{-2}$  and  $3.49 \times 10^{-2}$ , with a mean value of  $(3.2 \pm 0.3) \times 10^{-2}$ , were measured in soil from Bikar (decay corrected for 19.10.2019). Mean <sup>241</sup>Am/<sup>239</sup>Pu and <sup>243</sup>Am/<sup>239</sup>Pu atom ratios of  $(2.5 \pm 0.3) \times 10^{-2}$  and  $(8 \pm 1) \times 10^{-4}$ , respectively, were calculated.

The mean normalized isotope ratios in soil from Bikar are plotted as function of the mass in Figure 1. For comparison, the isotope ratios for the Ivy Mike and the Anacostia nuclear tests, and the ones found

in an Irish Sea sediment (IAEA-135), are also shown. Overall, we observe a rapid decrease of the normalized isotope ratios with the mass of the isotope (Fig. 1), as observed in other studies. The relative abundances of the transuranium radionuclides produced by the Castle Bravo test are described by two smooth curves, one for the even-massed abundances that lies uniformly above that for the odd-massed abundances (Fig. 1a).

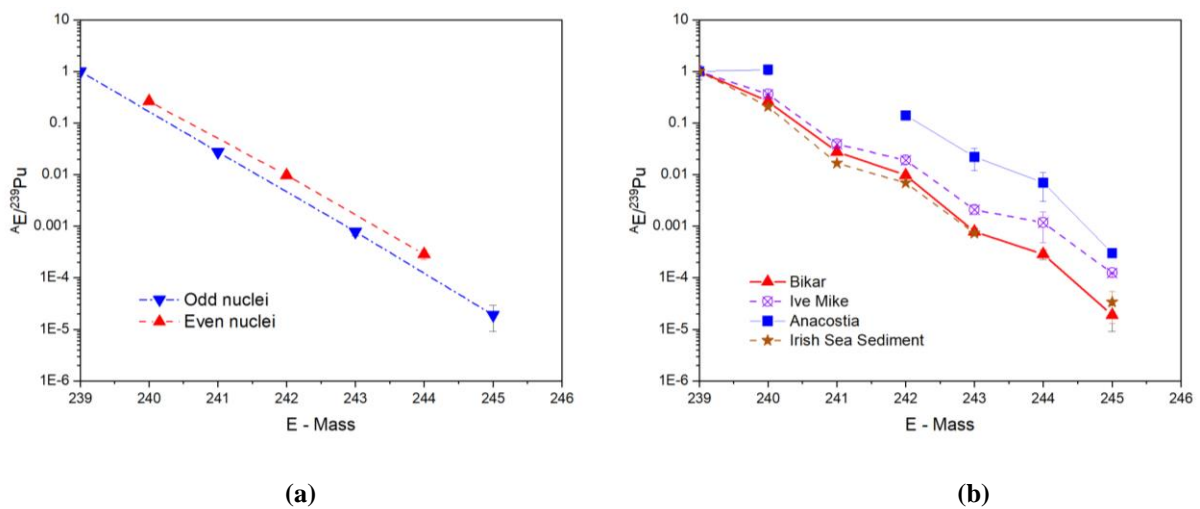
According to previous studies<sup>6, 8</sup>, at time zero after the explosion, it is expected that the ratio between mass 241 and 239 will be related to that between mass 242 and 240 as:

$$\left(\frac{{}^{241}\text{Pu}}{{}^{239}\text{Pu}}\right)_0 = 0.7412 \cdot \left(\frac{{}^{242}\text{Pu}}{{}^{240}\text{Pu}}\right)$$

Where the factor 0.7412 is derived from the odd-even effect. After a certain time, this relationship will vary according to the decay of  ${}^{241}\text{Pu}$  ( $T_{1/2}$  of 14.4 yrs). The time  $T$  since the thermonuclear explosion can then be calculated only from the relationship of different Pu isotopes<sup>8</sup> as:

$$T = \frac{T_{1/2}}{\ln 2} \cdot \ln \left( \frac{\frac{{}^{241}\text{Pu}}{{}^{239}\text{Pu}}}{\frac{{}^{242}\text{Pu}}{{}^{240}\text{Pu}}} \right)$$

Based on the Pu ratios measured in Bikar soil, the date of contamination was estimated to be  $1954 \pm 3$  yrs. This result agrees remarkably well with the year of the Castle Bravo explosion in 1954.



**Figure 1.** a) Mean relative abundances of the transuranium isotopes (in log scale), normalized to  ${}^{239}\text{Pu}$ , in soil samples from Bikar Atoll. The even-odd effect is clearly observed. b) Comparison with data reported in other studies (debris from the Ivy Mike and Anacostia explosions, and sediment from the Irish Sea).

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## ABSTRACT 27

### DETERMINATION OF PLUTONIUM-241 AND AMERICIUM-242m IN GLOBAL FALLOUT AND CHERNOBYL SAMPLES BY DECAY PRODUCTS INGROWN METHOD APPLIED TO OLD ALPHA SOURCES

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The alpha emitters like  $^{239,240,238}\text{Pu}$  or  $^{241}\text{Am}$  in nuclear fallouts (like global or Chernobyl) were accompanied by beta emitting long lived isotopes, namely  $^{241}\text{Pu}$  and  $^{242\text{m}}\text{Am}$ , respectively. The direct measurement of them, especially that of  $^{242\text{m}}\text{Am}$  ( $T_{1/2}=141$  years) faces many difficulties. However the method used often in determination of  $^{241}\text{Pu}$ , based on the ingrown of decay product found in old alpha sources can be adopted to measure  $^{242\text{m}}\text{Am}$  in old americium sources [1]. This radionuclide decays to  $^{242}\text{Am}$  ( $T_{1/2}=16$  h) followed by beta minus decay to  $^{242}\text{Cm}$  ( $T_{1/2}=163$  d) which then decays to the  $^{238}\text{Pu}$  ( $T_{1/2}=88$  a). So in case of  $^{241}\text{Pu}$  the ingrown  $^{241}\text{Am}$  in old Pu fraction sources is subject of studies, whereas in case of  $^{242\text{m}}\text{Am}$  it is the  $^{238}\text{Pu}$  ingrown in old americium sources. In our previous attempt to measure  $^{242\text{m}}\text{Am}$  [1] we were only able to give upper limits due to unknown amount of  $^{242\text{m}}\text{Am}$  in the tracer solution. Since 13 years have elapsed from that study we were able to undertake an attempt with the next set of old sources for which also tracer samples survived. In laboratory we have numerous alpha sources of Am or Pu fractions obtained by the  $\text{NdF}_3$  method, prepared in 2001-2003, so about 20 years ago in projects conducted those years on different locations of Poland affected with fallouts: global, Chernobyl or mix of both.

Selected sources of Pu or Am were dissolved (only the membrane filters with  $\text{NdF}_3$  microcrystals separated from metallic support discs) using 4M  $\text{HNO}_3$  with addition of  $\text{H}_3\text{BO}_3$ . In case of Am sources the spike of  $^{242}\text{Pu}$  was added, whereas in case of Pu sources it was  $^{243}\text{Am}$  added (tracers produced by NIST). Samples were evaporated to dryness and the boric salts were removed by their conversion into volatile boron-methyl compounds by adding  $\text{HCl}$  and  $\text{CH}_3\text{OH}$ . The remains of filters material are then destructed by hot  $\text{HClO}_4$ . The remaining invisible residue is dissolved in 1M  $\text{HNO}_3$ . The Pu oxidation step was adjusted as +IV by using hydrazine and  $\text{NaNO}_2$ . Pu and Am were separated using TEVA resin. Americium fraction passes the column without retention from 4M  $\text{HNO}_3$ , whereas Pu was eluted using mix of diluted acids solution (0.1M  $\text{HCl}$  +0.1M  $\text{HF}$ ). Both Am and Pu alpha sources were prepared using again  $\text{NdF}_3$  co-precipitation method and spectra were measured. Calculated ingrown activities (for  $^{238}\text{Pu}$  in case of original Am sources and  $^{241}\text{Am}$  in original Pu sources) allows to calculate the original ratios of  $^{241}\text{Pu}$  and  $^{242\text{m}}\text{Am}$  in studied fallouts. Project is ongoing during writing this abstract so final results will be presented at the Conference.

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## ABSTRACT 28

### ESTABLISHING DISCORDANCE AS A RADIOCHRONOMETRIC SIGNATURE FOR NUCLEAR FORENSIC INVESTIGATIONS: A MULTI-LABORATORY INTERCOMPARISON EXERCISE

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Joanna S. Denton<sup>2</sup>, James A. Dunne<sup>1</sup>, Mark A. Edwards<sup>2</sup>, Charlotte. Eng<sup>3</sup>, Amy M. Gaffney<sup>3</sup>,  
Chris R. D. Gilligan<sup>1</sup>, Maya N. Morris<sup>3</sup>, John M. Rolison<sup>3</sup>, Matthew E. Sanborn<sup>2</sup>, Allison M. Wende<sup>2</sup>

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The model age of a nuclear material is an important tool in nuclear forensic analysis. Recent studies illustrated the need for controlled experiments on the behavior of decay products during uranium casting to provide a foundation for interpretation. This talk will give an overview of a laboratory intercomparison study.

A variety of uranium metal and alloy samples cast under known conditions were analysed by three laboratories by mass spectrometry techniques. This is the first multi-laboratory study of its kind to explore these fractionation effects. The inter-comparison approach allowed for capability demonstration and method development on real samples and provided data to add to our understanding of the behavior of decay progeny in these complex systems

**‘HOT’ PARTICLE DETECTION WITH REAL-TIME AUTORADIOGRAPHY**

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Radioactive ‘hot’ particles constitute a significant fraction of radionuclides released by nuclear events to the environment<sup>1</sup>. They can be deposited as a result of nuclear weapons testing, nuclear accidents (e.g., Chernobyl, Fukushima), illicit activities, mining, and/or nuclear waste disposal. Information on the characteristics of these ‘hot’ particles, such as size distribution, composition, and chemical form, is essential for making assessments of their potential impact. However, it is challenging to locate and isolate the particles for characterisation due to their small size. Current techniques, screening, and sample splitting using phosphor screen autoradiography and gamma spectroscopy<sup>2</sup>, are often laborious. In this talk, we propose the use of BeaQuant™, a micro-pattern gas detector (MPGD) incorporating a parallel ionisation multiplier that provides real-time autoradiography<sup>3</sup>, for the imaging and detection of ‘hot’ particles.

Thus far, MPGD has been extensively used in radiopharmaceutical and geological applications. With its high sensitivity (0.0005 cpm/mm<sup>2</sup>) and radioactivity range (linearity over 5 order of magnitudes), MPGD can be used to differentiate hotspots from a heterogeneously distributed radioactive sample, which is relevant to environmental samples. For example, soil samples in the vicinity of the Fukushima Daiichi Nuclear Power Plant contain highly radioactive caesium-rich microparticles in a less radioactive caesium-labelled clay<sup>4</sup>. Hence, it is advantageous to develop a method to prepare environmental samples suitable for the MPGD. To optimise the MPGD for ‘hot’ particle detection, considerations such as sample thickness, spatial resolution, and artefact contribution must be made. This presentation will provide an overview of the sample preparation process of MPGD analysis and address the above considerations with the help of Monte Carlo simulation and analysis with the BeaQuant™ system (data acquisition and image reconstruction) for particles containing either radiocaesium or uranium.

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## ABSTRACT 30

### RETROSPECTIVE DETERMINATION OF $^{236}\text{U}/^{238}\text{U}$ AND $^{240}\text{Pu}/^{239}\text{Pu}$ ATOM RATIOS IN AEROSOLS AND LUNG ASHES FROM VIENNA, AUSTRIA

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Already in the frame of the first scientific project sponsored by the IAEA with the title “Factors controlling the distribution of fission products in the biosphere” in the early 1960’s of the last century, air filters and lung autopsy samples from people, who had been living in Vienna, Austria, were collected and investigated with regard to short-lived fission products from the nuclear weapons tests.

The organs were ashed and then measured with a well-type NaI(Tl) crystal to quantify  $^{141}\text{Ce}+^{144}\text{Ce}$ ,  $^{103}\text{Ru}$ , and  $^{95}\text{Zr}+^{95}\text{Nb}$  contamination of humans. Later on (after decay of these rather short-lived radionuclides) also  $^{137}\text{Cs}$  was determined. From a part of the ash samples Pu was separated and the sum activity of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  was measured by alpha-spectrometry. Corresponding investigations were also performed with air filters.

In the last years we investigated some of the remaining air filters and lung ash samples with Accelerator Mass Spectrometry (AMS) with regard to  $^{236}\text{U}$  (half-life  $2.3 \cdot 10^7$  years) which is mainly produced via the reactions  $^{235}\text{U}(n,\gamma)^{236}\text{U}$  and  $^{238}\text{U}(n,3n)^{236}\text{U}$ . Additionally, the Pu isotopes  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  were measured to obtain an improved data set with reduced uncertainties compared to the earlier study.

The samples were dissolved in half-concentrated nitric acid, a defined amount of  $^{233}\text{U}$  was added as a spike and uranium was then separated by anion exchange (UTEVA) and co-precipitated with  $\text{Fe}(\text{OH})_3$ . Pu was separated with DOWEX 1x2, here a  $^{242}\text{Pu}$  spike was used. After calcination the samples were analysed by AMS at the VERA laboratory (university of Vienna).

The results of our lung measurements will be compared to the corresponding filter results. Possible explanations of the discrepancies will be discussed.

## ABSTRACT 31

### WHAT SINGLE HOT PARTICLES TELL US: FROM NUCLEAR FORENSICS TO BIOAVAILABILITY

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When on April 26, 1986 the reactor of the Chernobyl nuclear power plant exploded, nuclear fuel was in part released as microscopic solid particles. Structurally intact hot particles pose a risk to humans mainly by the (unlikely) path of inhalation. However, over the decades, weathering may lead to considerable release of radionuclides that subsequently can enter the human food chain. Since hot particles differ strongly with respect to morphology, chemical composition and stability, investigations need to be performed on single particles, rather than on bulk samples.

We separate and extract the micrometer sized particles from the environmental matrix in a scanning electron microscope (SEM) equipped with a micro manipulator. Subsequently, the particles are fixed by SEM glue on in-house made tungsten needles. Element composition is imaged by EDX-measurements and radioactive isotopes are detected by gamma spectrometry. To selectively image the elemental and isotopic composition at below 100 nm spatial resolution, we combine secondary-ion mass spectrometry with resonant laser ionization. Identification of actinide elements and fission products including Am-242m and Cm at ultra-trace levels is possible. Isobaric interferences, particularly U-238/Pu-238 and Pu-241/Am-241, are suppressed by up to five orders of magnitude. In contrast to most mass-spectrometric techniques, only negligible mass is consumed, leaving the particle intact for further studies: Selected individual particles were sequentially leached in ammonium acetate solution, hydrochloric acid, oxalic acid, nitric acid and aqua regia. The solutions are then measured via gamma spectrometry and ICP-MS to analyze their uranium content and the amounts of leached fission and breeding products. Fuel particles from the Chernobyl accident are usually classified according to their appearance, dissolution rates and oxidation state: the further oxidized and brittle  $\text{UO}_{2+z}$ , non-oxidized  $\text{UO}_2$  and zirconium merged bearing  $\text{U}_x\text{-Zr}_y\text{-O}_z$  particles, of which we investigated at least one particle each.

The first leaching steps did not attack the structure of the particles, and only small fractions of Am-241 and Cs-137 were leached under mild conditions, indicating a low bioavailability. Leaching behaviors were mostly in line with the predictions based on the visually assigned classes and oxidation states. From these data, conclusions on potential risks to human health and environment are drawn. Beyond that, the technique is applicable to almost all elements and opens up new scientific applications also apart from the nuclear field.

## ABSTRACT 32

### IS IT POSSIBLE TO MEASURE STRONTIUM-90 IN RADIOACTIVE WASTE WITHOUT HARMFUL CHEMICAL REAGENTS?

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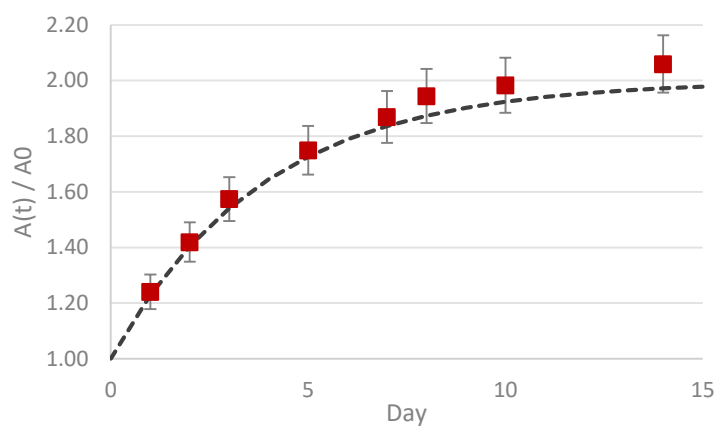
Strontium-90 (Sr-90) is, with caesium-137 (Cs-137), one of the main radioactive fission product occurring in nuclear power plants in terms of abundance proportion. This radionuclide can thus be present in significant amount in spent nuclear fuel or in radioactive waste from nuclear reactors. In the context of the increase of the number of decommissioning and dismantling operations in nuclear facilities, a reliable and rapid determination of Sr-90 is of prime interest for the characterization of all types of radioactive waste (effluent, ion exchange resin, concrete, sludge, etc.).

Sr-90 has a half-life of 28.8 years and emits beta particles of relatively high energy (maximum energy of 546 keV). It disintegrates into Y-90 which is also a pure  $\beta$ -emitter (maximum energy of 2280 keV) with a half-life of 2.67 days. Sr-90 needs to be purified from interfering analytes through selective radiochemical separations before any reliable detection. It can be directly measured or indirectly evaluated from Y-90 growth. Both radionuclides are often measured by gas flow proportional counting and liquid scintillation counting (LSC). The separation yield is determined from stable strontium carrier by inductively coupled plasma (ICP) techniques or gravimetry.

Two main radiochemical methods for Sr-90 determination are generally implemented<sup>1</sup>: Sr precipitation in highly concentrated nitric acid or extraction chromatography on Sr-resin<sup>®</sup>. Both procedures are robust and selective to provide accurate measurement of Sr-90 in radioactive samples. However, they involve the use of harmful chemical substances, respectively fuming nitric acid and liquid scintillation cocktails for LSC detection. Both reagents are in the scope of European REACH regulation and have to be removed from use as much as possible.

The purpose of this presentation is to demonstrate the feasibility of accurate Sr-90 measurement in radioactive waste without the use of toxic chemical reagents. The presentation will first focus on the optimization of a precipitation method by applying a design of experiments methodology<sup>2</sup>. The implemented strategy induces the replacement of fuming nitric acid (above 82 % concentration) by concentrated nitric acid (69 % concentration) while maintaining high separation yield and improving the selectivity towards calcium which is the main interfering analyte of this method. Secondly, the presentation will deal with the implementation of plastic scintillation resin<sup>3</sup> (noted PS resin) to avoid the use of liquid scintillation cocktails. A method based on a PS resin selective towards Sr was optimized so as to achieve high decontamination factors towards interfering radionuclides, in particular

Pu-241  $\beta$ -emitter. For both developed purification methods, the validation step is performed by comparing the results obtained on different types of radioactive waste (effluents, concretes and sludges) with the ones obtained with the reference method of the laboratory based on fuming nitric acid. The selectivity of both methods is also evaluated by checking Y-90 growth (see Figure 1).



**Figure 1:** Y-90 growth curve from Sr-90 obtained with plastic scintillation resin selective towards Sr

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## ABSTRACT 33

### FAST AMERICIUM, PLUTONIUM AND STRONTIUM SEPARATION AFTER AUTOMATED FUSION OF HIGHLY DENSE BARITE CONCRETE

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In the context of dismantling nuclear facilities, fast total dissolution, separation, and determination of various radionuclides simultaneously is important for decommissioning.

Highly dense barite concrete samples were fused with an automated fusion instrument (Claisse LeNeo), Si was flocculated with PEG-6000, and samples were separated with the four loose resins UTEVA-TEVA-DGA-Sr-Resin (Triskem international). Inactive barite concrete ( $n = 4$ ) was fused with three different flux materials  $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$  (F1: 80% / 20%),  $\text{LiBO}_2 / \text{Li}_2\text{B}_4\text{O}_7 / \text{LiBr}$  (F2: 49.5% / 49.5% / 1%), and  $\text{LiBO}_2/\text{LiBr}$  (F3: 98.5% / 1.5%). Best recoveries were found applying F1,  $93\% \pm 4\%$  and  $78\% \pm 6\%$  for Am-243 and Sr-85, respectively. For Pu-242 however, best recoveries were found applying F3,  $91\% \pm 6\%$ , compared to F1:  $76\% \pm 7\%$ . As most promising, flux material F1 was used to fuse and separate 6 inactive barite concrete samples each with the loose resins, the cartridges in series, and a different separation technique, published in <sup>1</sup>Jäggi et al.

Best results were found using the cartridges UTEVA-TEVA-DGA-SR-Resin, giving recoveries for Am-243 of  $88\% \pm 7\%$ , for Pu-242 of  $83\% \pm 3\%$ , and for Sr-85 of  $75\% \pm 16\%$ . Due to the new separation technique, the overall preparation time was reduced from 5.5 days<sup>1</sup> to 3.5 days for 4 samples with one single slot automated fusion instrument.

Furthermore, to reduce the limits of detection for Am, Pu, and Sr, the parameter-file of the automated fusion instrument Claisse LeNeo was adapted to fuse 3 g of material, containing 18.5 mg Sr. A two-step filtration was applied to reduce Sr-85 loss and Sr was separated with 2.5 g of loose Sr-Resin, thus resulting in a maximum recovery of  $74\% \pm 2\%$  ( $n = 2$ ). Over all 8 ( $n = 2$ ) optimization steps the averaged recoveries were  $94\% \pm 6\%$  ( $n = 13$ ) for Am-243 and  $81\% \pm 5\%$  ( $n = 15$ ) for Pu-242, respectively.

## References

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## ABSTRACT 34

### INFLUENCE OF POTENTIAL COMPLEXING AND DECORPORATION AGENTS ON THE SPECIATION OF RADIUM IN THE HUMAN DIGESTIVE SYSTEM

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Radionuclides pose a potential radio- and chemotoxic hazard to humans when ingested. Knowledge of radionuclide interaction in the digestive tract at the molecular and cellular level is necessary for risk assessment and to contribute to an element-specific decontamination strategy.

Synthetic biofluids prepared according to the UBM protocol (BARGE)<sup>1</sup> are used to investigate the speciation of radium in the human digestive tract. The biofluids are analyzed in the presence and absence of Ra(II)/Ba(II) by mass spectrometry using electrospray ionization (ESI-MS). Here, Barium serves as a non-radioactive homolog to Ra(II). The identification of barium-containing species takes place via isotope pattern signatures. Algorithms specifically tailored to the evaluation of complex mass spectra are used. For comparative purposes, Ra(II)/Ba(II) containing complexes and reference compounds are synthesized and subsequently characterized by ESI-MS and other spectroscopic methods.

In addition, the influence of different decorporation and complexing agents on the speciation of Ra(II)/Ba(II) in the simulated digestive process is studied. This way, element-specific decorporation strategies are investigated for their potential efficacy after oral ingestion of radium.

This work is funded by the German Federal Ministry of Education and Research (BMBF) under grant number 02NUK057C and is part of the joint project RADEKOR.

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**RADIOACTIVE COSMETICS**

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The discovery of Radium and Polonium by Maria Skłodowska – Curie and her husband Pierre Curie in 1898 opened a new chapter in the history of the good and bad uses of radioactive products. The use of radioactive elements in various products was observed all over Europe in the 20<sup>th</sup> century, particularly in the beauty and cosmetic industry. One of the most well-known products that incorporated the use of radioactive elements were Dr Alfred Curie and pharmacist Alexis Moussalli's "Tho-Radia" face powders and creams.

The main experimental objective of this project was to obtain data about the presence of naturally occurring decay series radionuclides in radioactive quack products. Face powder samples from the 1930s, the early years of production, as well as the later versions from the 1950s, were analysed qualitatively and quantitatively by destructive and non-destructive assay. Various types of non-destructive analysis, including Scanning Electron Microscopy and Powder X-Ray Diffraction, were used to determine the bulk composition of both samples. High-Resolution Gamma Spectroscopy (HRGS) were used to determine the presence of radionuclides. Destructive assays included Microwave Assisted Acid Digestion for further Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analysis and Liquid Scintillation Counting. These were also used to determine the presence of radionuclides both qualitatively and quantitatively.

Data obtained to this date suggest that traceable amounts of  $^{232}\text{Th}$  were detected in the earliest "Tho-Radia" powder sample. HRGS data revealed that the major gamma emission lines for daughter isotopes used for the analysis of the parent radionuclide  $^{232}\text{Th}$  were detected. ICP-MS analysis further confirmed the quantitative presence of  $^{232}\text{Th}$ .

# LUMINESCENCE SPECTROSCOPIC INVESTIGATIONS OF URANIUM (VI) COMPLEXATION WITH AQUEOUS SILICATES UNDER (HYPER) ALKALINE CONDITIONS

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Uranium is one of the main constituents in spent nuclear fuel (SNF), and thus will be present in large inventories in underground repositories for the disposal of high-level radioactive waste. The migration of uranium in the near-field of a repository is governed by the surrounding environment parameters such as temperature, pH, Eh, chemical composition, etc. Thus, complete and reliable thermodynamic data for uranium solid phases and aqueous complexes are required to model the retention of uranium in the repository and its possible mobilisation into the biosphere. The ubiquitous presence of silicon in the environment in different forms of monomeric, polymeric or colloidal silicate species has been the focus of radionuclide research relevant in the context of clay formations as well as for repository concepts involving cementitious materials, in which calcium silicate hydrate (C-S-H) phases are one of the main components. In vitrified wastes, the dissolution of borosilicate glasses is as an additional source of silicon interacting with the radionuclides. Orthosilicic acid,  $\text{H}_4\text{SiO}_4$ , is known to dominate the aqueous speciation of Si over a wide pH range below  $\text{pH} \approx 9$ . Above this pH, the formation of  $\text{H}_3\text{SiO}_4^-$ ,  $\text{H}_2\text{SiO}_4^{2-}$  and (to some extent) polynuclear species leads to an increased silicate solubility. Although the predominance of anionic silicate species may trigger the formation of stable complexes with U(VI), the aqueous speciation of the system  $\text{UO}_2^{2+}$  -  $\text{H}_2\text{SiO}_4$  -  $\text{H}_2\text{O(l)}$  in alkaline conditions remains poorly understood.

The formation of the complex  $\text{UO}_2\text{OSi(OH)}_3^+$  has been reported in acidic pH conditions, and the corresponding thermodynamic properties have been determined using different experimental methods. In alkaline to hyperalkaline systems, the interaction of U(VI) with  $\text{H}_3\text{SiO}_4^-$  and  $\text{H}_2\text{SiO}_4^{2-}$  may result in the formation of further complexes of the type  $\text{UO}_2(\text{OH})_x\text{OSi(OH)}_3^{1-x}$  or  $\text{UO}_2(\text{OH})_y\text{O}_2\text{Si(OH)}_2^{-y}$ , which are rarely studied in the literature.

In this work, the complexation of U(VI) with silicate is investigated between  $\text{pH} \approx 9$  and 13.5 by laser-induced fluorescence spectroscopy. The TRLFS measurements were collected with a pulsed laser Nd:YAG of energy around 3mJ at a repetition rate of 10 Hz to excite uranium at 266nm. Fluorescence spectra are recorded in the 425-650nm range using the 300 lines per mm grating of the spectrograph. The U(VI) concentration was fixed at either  $1 \times 10^{-7}$  M or  $1 \times 10^{-6}$  M, the silicon concentration was varied within  $1 \times 10^{-4}$  M – 0.1M (below the solubility limit of amorphous silica at varying pH values) and the ionic strength was kept constant at 0.05 or 0.5M  $\text{NaNO}_3$ . The molybdate-method and ultrafiltration with 10 kD filters were used to quantify oligomeric and colloidal Si species. Based on thermodynamic calculations, experiments were designed to avoid the precipitation of any U(VI) solid phase (e.g. boltwoodite, weeksite, or  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}_{(\text{cr})}$ ), but possible interferences caused by the formation of

secondary phases were evaluated by means of ultrafiltration and ICP-MS. Preliminary results showed a continuous bathochromic shift of the emission spectra with increasing silicate concentration and pH values. Additional measurements for other luminescence characteristics including lifetimes are in progress. The identification of pure component spectra of the individual species will be attempted after peak deconvolution. The SIT approach is considered for the extrapolation of the conditional equilibrium constants to infinite dilution.

This work is partly funded by the BMWK within the GraZ II project (contract number 02E11860C)

## ABSTRACT 37

### ACCELERATOR MASS SPECTROMETRY – NNUF LANCASTER; AN EXAMPLE OF HOW SUCH A CAPABILITY CAN BE APPLIED TO NUCLEAR SITE REMEDIATION AND ENVIRONMENTAL CLEAN-UP

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Multi-Isotope Low-Energy AMS allows measurement of trace amounts of isotopes of interest such as <sup>10</sup>Be, <sup>14</sup>C, <sup>26</sup>Al, <sup>41</sup>Ca, <sup>129</sup>I, U, Pu and other actinides. The Lancaster National Nuclear Facility AMS is initially targeting ultra-trace isotope research and environmental contamination, particularly trace actinide assay for land quality applications.

Previous AMS work provided an example of how such capability can be applied in assessing local and global trace plutonium contributions in legacy soils on a fast breeder reactor site.

Trace-level plutonium in the environment often comprises local and global contributions, and is usually anthropogenic in origin. We determined estimates of local and global contributions to trace-level plutonium in soil from a former, fast-breeder reactor site. The measured <sup>240</sup>Pu/<sup>239</sup>Pu ratio is anomalously low, as per the reduced <sup>240</sup>Pu yield expected in plutonium bred with fast neutrons. Anomalies in plutonium concentration and isotopic ratio suggest forensic insight into specific activities on site, such as clean-up or structural change. Local and global <sup>239</sup>Pu contributions on-site are estimated at (34 ± 1)% and (66 ± 3)%, respectively, with mass concentrations of (183 ± 6) fg g<sup>-1</sup> and (362 ± 13) fg g<sup>-1</sup>. The latter is consistent with levels at undisturbed and distant sites, (384 ± 44) fg g<sup>-1</sup>, where no local contribution is expected. The <sup>240</sup>Pu/<sup>239</sup>Pu ratio for site-derived material is estimated at 0.05 ± 0.04. The study demonstrates the multi-faceted potential of trace plutonium assay to inform clean-up strategies of fast breeder legacies

Nature Communications 12, Article 1381 (2021)

**ANALYTICAL REQUIREMENTS FOR FUSION FUEL CYCLE**

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There are many challenges to achieving fusion energy, all of which must be overcome in order to accomplish our goal of clean energy. When looking at Tritium Analytics we must consider four key areas: process control, environmental protection, safety, and non-proliferation.

The current state-of-the-art methods employed on a research scale, such as the Active Gas Handling System for JET, are not suitable for commercialisation for two reasons. Firstly, using Pressure Volume Concentration Temperature (PVTc) measurements means pulling all the free tritium back to a single vessel, and is not suitable in continuous operation. Secondly, with the larger inventories required for commercial plants, it is unlikely that pulling tritium back to one place will be deemed safe.

Continuous operation also raises challenges from a process control perspective, as process performance and therefore the plant efficiency and ultimately the viability, will be dependent on precisely managed inventories and flow rates. Real-time measurements of process fluids will be required, in a wide range of conditions. Temperatures are expected to vary from liquid hydrogen through to liquid lithium or lithium lead (~20 – 700K). Pressures will vary from very high vacuum up to ~10 bar, and flow rates may vary from 0 to >1000 m<sup>3</sup>/hr. There is also a need to measure tritium, or a mixture of hydrogen isotopologues, in a variety of materials.

The best measurement techniques currently commercially available to separate out the 6 hydrogen isotopologues – such as Mass Spectroscopy or Gas Chromatography – can provide a measurement results every 90-120 s. It is expected that fuel cycle process controls will need ~1 Hz response times. Clearly, this is a big step forward from the current state-of-the-art, and will be required for the first demonstration plants, planned for the 2030s and 40s.

In order to tackle this problem, a number of laboratories around the world are investigating new measurement techniques. At UKAEA, the Tritium Analytics Program team are designing an experimental rig to allow the characterisation of the performance of different measurement instruments under the most common fuel cycle conditions. This rig will be operational later in 2023 and will assess techniques in stages.

Firstly, the instrument can be assessed with a hydrogen isotopologues mixture to confirm the technique is appropriate for separating out the hydrogen isotopologues. Secondly, the continuous accountancy capability will be assessed using the concentration measurement from the instrument under test in combination with a flow meter and comparing the results to a static PVTc measurement. Thirdly, the response rate of the test instrument can be assessed by introducing a step change in concentrations to the gas flow. And finally, any memory effects of the instrument can be assessed via recirculation mode and running the gas mixture through the rig for longer periods.

## ABSTRACT 39

### DEVELOPMENT OF SINGLE PARTICLE ICP-MS FOR NUCLEAR APPLICATIONS.

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The growing use of inorganic nanoparticles has led to a need for robust characterisation tools which allow for increased measurement confidence. One such tool is inductively coupled plasma mass spectrometry (ICP-MS), which enables for the determination of the bulk concentration of dissolved inorganic nanoparticles in sample matrices relevant for nuclear application. For example, in radiation dosimetry for assessing the specificity of nanoparticles as radiosensitisers [1].

More recently, developments made in ICP-MS has led to single particle ICP-MS (spICP-MS) increasingly being adopted. In addition to bulk nanoparticle concentration, spICP-MS enables for the time-resolved detection of single nanoparticle events. This in turn allows for additional sample information, such as particle size and particle number concentration of inorganic nanoparticles to be determined in a single batch run.

In this work, a spICP-MS method was developed and validated on two tandem ICP-MS/MS instruments. Initial studies were focused on developing a measurement method for Au standard nanoparticle suspensions to determine an optimal instrument setup and sample preparation procedure. Lastly, data is presented to show the role spICP-MS can play in rapid identification and monitoring of the uptake mechanism of several inorganic nanoparticles, focusing on applications in radiation dosimetry and monitoring of air filters for industrially sourced nanoparticles.

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# **POSTER PRESENTATIONS**

## ABSTRACT 40

### THE BEHAVIOUR OF GROUP 13 ELEMENTS ON TK400 RESIN

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Group 13 elements are of interest in the radiochemical analysis of solid matrix samples. Aluminium has a crustal abundance of around 8%<sup>1</sup> and thus is a major matrix component of any solid sample. Ion exchange and extraction chromatography resins can become saturated with matrix elements, which will result in them not behaving in the intended way. Removal of matrix elements is thus a priority when analysing complex matrix samples. We have investigated the use of TK400 as a “filter” to remove these matrix components before separation, to remove the need for precipitation steps. The others in the group are primarily of interest because of their radionuclides, which are encountered in various processes at AWE.

TK400 resin consists of 1-octanol adsorbed on an inert base<sup>2</sup> and has several potential uses, including separation of Fe, Ga and Pa. Literature indicates that most elements show little adsorption on the resin.<sup>2</sup> Recently we studied the use of the resin with samples equivalent to 1 g of crustal material or more. This would significantly reduce the solid content of the sample before separation, allowing a more robust method for complex matrix samples. Fe is adsorbed very well in strong HCl, there was no data on Al. Ga is adsorbed in strong HCl<sup>3</sup> and so we believed that the other group 13 elements may adsorb as well.

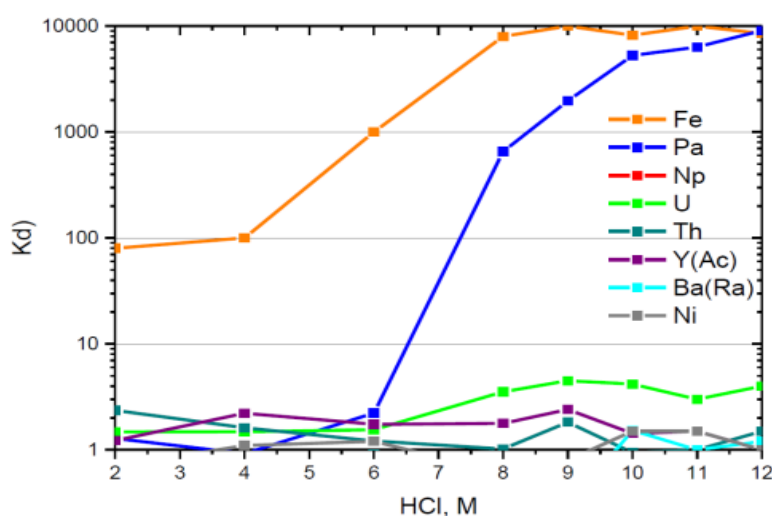


Figure 2: Distribution coefficients of elements on TK400<sup>2</sup>



Experiments were conducted to determine the distribution coefficient of group 13 elements from B to Tl, in HCl concentrations from 0.1M to 12M. These were carried out both with stable isotopes and radioactive standards. The results of these experiments are presented.

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## ABSTRACT 41

### SOLUBILITY AND AQUEOUS SPECIATION OF URANIUM (VI) IN ALKALINE TO HYPERALKALINE SYSTEMS CONTAINING SILICATE

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Uranium is the main element in the nuclear fuel cycle and accordingly contributes with a very large inventory to nuclear waste. In the reducing conditions expected to develop in deep underground repositories, uranium will mostly prevail in the +IV oxidation state. However, in alkaline to hyperalkaline conditions, the stability field of U(VI) expands and the redox borderline between U(VI) and U(IV) is shifted to significantly reducing conditions, *i.e.*  $(pe + pH) \approx 2-3$ . Silicon (in the form of silicates) is the most abundant element in the earth's crust and is a relevant component in mineral phases found in different host rocks. Silicate is also one of the main components of cement, which is widely used for construction purposes and for the stabilization of the waste especially in repositories for low and intermediate level waste (L/ILW). The solubility limit imposed by amorphous silica, SiO<sub>2</sub> (am), limits the concentration of dissolved Si to  $\approx 2$  mM from acidic to weakly alkaline conditions. Above pH  $\approx 9$ , the subsequent formation of anionic species like SiO(OH)<sub>3</sub><sup>-</sup> and SiO<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup> leads to a significant increase in the solubility of SiO<sub>2</sub>(am). The enhanced Si concentration together with the predominance of anionic silicate species may compete with U(VI) hydrolysis and accordingly may result in the formation of U(VI)-SiO<sub>4</sub> complexes potentially increasing solubility. In spite of the relevance of hyperalkaline systems in cementitious environments, most of the available studies investigating U(VI)-SiO<sub>4</sub> complexes have focused on acidic conditions. The present study aims at obtaining a better description of the U(VI)-SiO<sub>4</sub> system in the alkaline to hyperalkaline conditions relevant in cementitious systems using the concepts of established solution thermodynamics. This study extends from dilute to intermediate ionic strength conditions, the latter being representative of Cretaceous argillites in Northern Germany.

All experiments are performed under Ar-atmosphere. The solubility of U(VI) is investigated from undersaturation conditions using a step-wise approach. In a first step, the solubility of synthetic Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O (cr) and commercial SiO<sub>2</sub> (am) is separately investigated in 0.1 and 1.0M NaCl-NaOH solutions with  $8 \leq pH_m \leq 11.5$  (U) and  $8 \leq pH_m \leq 11.5$  (Si). Three experimental series are defined for the investigation of the U(VI)-SiO<sub>4</sub> interaction in 0.1 and 1.0M NaCl-NaOH systems: (i) solubility of Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O (cr) in the presence of SiO<sub>2</sub> (am), with  $8 \leq pH_m \leq 11.5$ ; (ii) solubility of Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O (cr) in the presence [Si] = constant = 1.5–0.1mM (*i.e.* below solubility limit of SiO<sub>2</sub> (am)) and  $8 \leq pH_m \leq 11.5$ . The possible formation of polynuclear silicate species is evaluated using the molybdate-method. Solid phases of selected samples after completing the solubility experiments will be characterized by different spectroscopic techniques, with focus on the possible formation of U(VI)-silicate secondary phases, *e.g.* Na-boltwoodite. Preliminary results of this on-going study will be presented.

*This work is funded by the BMWK within the GraZ II project (contract number 02E11860C).*

## ABSTRACT 42

### ADVANCES IN TRACEABILITY AND MEASUREMENT CAPABILITIES FOR CHALLENGING RADIONUCLIDES

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Accurate, traceable measurement of radionuclides with long half-lives is critical for a multitude of applications including geological dating, environmental monitoring, and de-commissioning. Hence improving the precision of half-life measurements and providing traceable standards of long lived radionuclides will allow for great advances and improved confidence in measurement across several research areas. This ongoing study focuses on producing traceable standards of difficult to measure, long lived radionuclides produced by fast and thermal neutron activation that are important across multiple applications.

Firstly, a cosmogenic isotope of chlorine,  $^{36}\text{Cl}$ , decays via  $\beta^-$  to the ground state of  $^{36}\text{Ar}$  (branching ratio 98.1%) or via electron capture to the ground state of  $^{36}\text{S}$  (branching ratio 1.9%).  $^{93}\text{Zr}$  ( $1.61(6) \cdot 10^6$  a) and  $^{93}\text{Mo}$  ( $4.0(8) \cdot 10^3$  a) both decay to stable  $^{93}\text{Nb}$ ;  $^{93}\text{Zr}$  decays via  $\beta^-$  and  $^{93}\text{Mo}$  decays via electron capture. As  $\beta^-$  and electron capture emitters, the above radionuclides are typically assayed via liquid scintillation counting (LSC). There are advantages to additional measurement using inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) as an independent validation technique, which also offers measurement times of several minutes per sample, benefitting applications where high volume sample throughput is required.

ICP-MS/MS is a rapid method that offers online interference removal that can reduce or eliminate the need for offline chemical separation, further improving the sample throughput. Best suited for the measurements of long lived radioisotopes, ICP-MS/MS has been shown to advance capabilities for medium and long lived radionuclides. To validate the newly available ICP-MS/MS results, standardised solutions, which were standardised by the efficiency tracing (CIEMAT/NIST) technique using  $^3\text{H}$  as a tracer. Additionally, a commercial LSC with 2 PMTs was used along with the MICELLE code from PTB. This unique combination of the primary counting and mass spectrometry offers improved confidence in measurement for long lived radionuclides, with the standardised material produced enabling a range of end users to develop and validate their own decay counting and mass spectrometric methods.

## ABSTRACT 43

### ASSESSMENT OF LIKELY DOSES FROM RADIUM-226 RELEASED FROM A DEEP GEOLOGICAL REPOSITORY FOR SPENT FUEL: LOOKING AT NATURE

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#### Introduction

Recent safety cases<sup>1</sup> for the geological disposal of spent nuclear fuel (SF) place emphasis on the long-term behaviour of <sup>226</sup>Ra as it is likely to contribute significantly to likely releases and doses from the repository. Corrosion of SF will release <sup>226</sup>Ra and, due to the limited thermodynamic databases for solid Ra phases, it is generally assumed that its solubility is limited by precipitation of pure RaSO<sub>4(s)</sub> (and then only at rather high Ra concentrations). In contrast to the limited knowledge on Ra behaviour, the current thermodynamic databases for solid Ba phases are much more extensive<sup>2</sup>. Here, experimental studies indicate that barium isotopes which may be released as decay products of Cs fission products from the waste matrix, will combine with groundwater sulphates to form baryte (BaSO<sub>4(s)</sub>) in both the repository engineered barrier system (EBS) and the repository host rock. In addition, extensive laboratory studies<sup>3</sup> indicate that Ra is likely to co-precipitate with the baryte and that the presence of Sr-rich solutions can increase Ra uptake into a (Ba, Sr, Ra)SO<sub>4</sub> solid.

It is clear from the above brief introduction that significant progress has been made recently on better understanding Ra retardation in the EBS and host rock of a repository. However, it is also clear that, even at the long timescales (*for laboratory experiments*) noted in several of the studies, full equilibrium between Ra and the solid phases examined has not yet been attained. As such, it is clear that these laboratory studies require further support, one which will address the both the temporal scale missing in the laboratory, but also utilising a methodology which more closely represents the conditions in and around a repository for SF.

The approach adopted here is basically a natural analogue. As noted in<sup>4</sup>, “Argumentation by use of analogy is well established in many fields including philosophy, biology, linguistics and law (Petit 1992), and most earth scientists are familiar with this approach and will have used it at some point in their career.

“For the case of radioactive waste disposal, the main inaccessible features are:

- The very long time it will take for long lived waste to decay to safe levels – how can anyone know how the materials which are used to contain the wastes will behave over thousands to millions of years?
- The large spatial scales which cannot be directly addressed in a laboratory – how can the migration of radionuclides through several hundred metres of host rock from the repository to the earth’s surface be studied and modelled?

- The heterogeneity and structural complexity of the geological environment which will host the repository – how can this ever be approached in a laboratory or modelled on a computer?”

Here, the focus of any study should be on the first and third point noted above – the very long timescales (to address the inherent shortcomings of laboratory experiments) and the heterogeneity and complexity of the repository environment. To address these points, there should be two areas of focus in any such study:

At a site of commercial extraction of bentonite for industrial uses (including in the EBS for SF), the partitioning of  $^{226}\text{Ra}$  (along with parent and daughter isotopes in the  $^{238}\text{U}$  decay chain) between groundwater, porewater and the bentonite would be studied and compared to blind predictions of  $^{226}\text{Ra}$  speciation and solubility. The potential role of clays (smectite in the EBS bentonite) and accessory sulphate and carbonate phases in  $^{226}\text{Ra}$  retardation could thus be assessed

The distribution of  $^{226}\text{Ra}$  in the groundwater, porewater and rock of a potential repository host rock would be studied to provide direct evidence of the likely sites and mechanisms of  $^{226}\text{Ra}$  retardation at the actual repository site itself. This regional analogue approach examines the actual repository host rock and groundwater at a site nearby the repository and has the clear advantage that the processes and mechanisms controlling  $^{226}\text{Ra}$  retardation at the regional analogue will be the exact same as those at the repository site itself

## Summary

Although significant improvements in the understanding of  $^{226}\text{Ra}$  retardation processes have been made in the past few years, it is clear that the short-term laboratory experiments (and the associated modelling studies) require additional support from NA studies to provide data of direct relevance to a repository safety case. This presentation will look at the most recent laboratory data and modelling output on  $^{226}\text{Ra}$  behaviour and compare them with the reality of  $^{226}\text{Ra}$  processes in natural systems which closely resemble those expected in a deep geological repository for SF (cf.<sup>5</sup>). In this way, it is intended to significantly improve the accuracy (and hence confidence in) of the output of the dose calculations for  $^{226}\text{Ra}$ .

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## ABSTRACT 44

### THE EUROPEAN NUCLEAR EDUCATION NETWORK (ENEN) ASSOCIATION

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The European Nuclear Education Network (ENEN) is the largest education and training (E&T) network in Europe.

Founded in 2003, it operates for the preservation and the further development of expertise in the nuclear fields by higher Education and Training. This objective should be realized through the co-operation between universities, research organisations, regulatory bodies, the industry and any other organisations involved in the application of nuclear science and ionising radiation.

Today ENEN has 88 members from 25 countries, including full members: universities, research centres, industries, TSO from the European Union; International members: beyond European Union borders, and international Partnerships with whom ENEN signed a Memorandum of Understanding.

ENEN main activities consist in the management of European Commission funded education and training projects with a focus on the set-up of E and T activities; dissemination and communication and management of travel funds to grant mobility for students, researchers and professional in the nuclear field.

ENEN also has also some specific activities such as the EMSNE Certification and the ENEN PhD Event and Prize. The European Master of Science in Nuclear Engineering (EMSNE) is a Certificate delivered by ENEN, with the endorsement of all its members, in order to certify the highest quality standards of Nuclear Engineering Education and the European dimension pursued achieved by the EMSNE laureate. The **ENEN PhD Event & Prize** is an action of ENEN to support the Research and Science in the nuclear fields promoting the works of the young scientists and researchers who start their careers finishing their PhD. It takes place on a yearly basis in the framework of the international congress in the field of nuclear science.

# FIRST RESULTS WITH THE REAL TIME TESLA RADON DETECTOR

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Indoor measurement of radon-222 (Rn-222) suffers from a few practical drawbacks. Generally, sampling and measurement takes a long time and gives an average Rn-222 concentration without details during the sampling period.

Tesla ([www.tesla.cz](http://www.tesla.cz)) has developed an active and real-time Rn-222 detector, *Radon Probe TSR3DNM* (Fig. 1). Radon gas diffuses into the detector and the charged daughters polonium-208 (Po-218) and polonium-214 (Po-214) are electrostatically drawn to the photodiode surface. The detection principle is an alpha-particle sensitive diode enabling energy discrimination between the alpha energy of Po-218 (6.0 MeV) and Po-214 (7.7 MeV). A display shows the current radon-222 activity concentration. Data can be downloaded from the detector via USB to a laptop: activity concentrations are measured every hour, and alpha spectrum data are given every 12 hours.

## Test results

In this paper the test results of the Tesla Radon detector are described. Analytical data, such as sensitivity and detection limit, are described; the detection limit is  $< 20 \text{ Bq.m}^{-3}$  in 24 h. The selectivity of detectors is verified in a radon chamber where a known concentration of Rn-222 and Rn-220 can be established. The results for both Rn isotopes will be discussed.

Practical application in drinking water production. The first practical application of radon-detectors is described. In the basement of a drinking water producing company, where raw water is aerated for oxidation purposes, the release of Rn-222 is monitored. See Fig. 2.

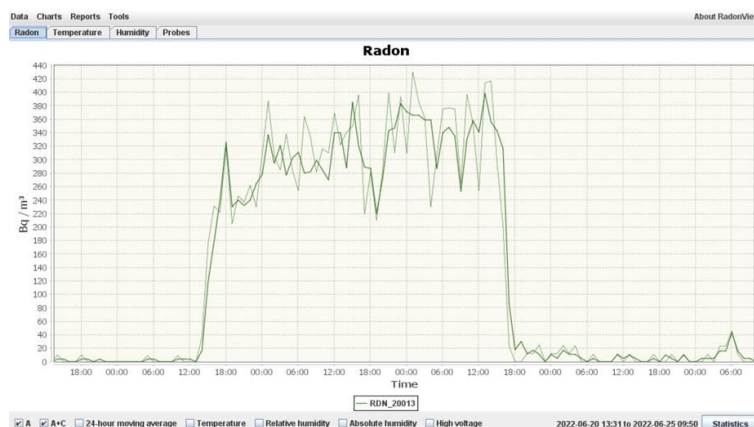


Fig1 (left)

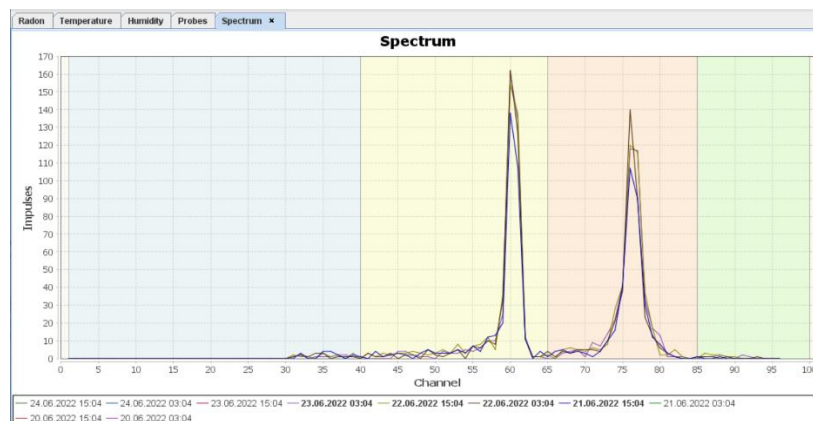
The Tesla radon detector with display (dimensions 8 x 18 cm).

Fig 2 (right)

Rn-222 activity concentration in a basement for drinking water treatment

### Alpha-spectrum resolution.

An interesting characteristic of this detector is that even in ambient air the photodiode can discriminate between the alpha energy of Po-218 (6.0 MeV) and Po-214 (7.7 MeV). See Figure 3.



**Figure 3** Alpha spectrum of Rn-222 daughters Po-218 (yellow window) and Po-214 (orange window). Channel number 100 coincides with 10 MeV.

### Conclusions

The first results of the Tesla Radon detector are very promising. This detector offers a number of advantages:

- Detection limit for Rn-222 of  $< 20 \text{ Bq.m}^{-3}$  in 24 hr measuring period
- Real-time data on a display; data available on an hourly frequency
- Data downloadable during measurement with USB-connection
- Alpha spectrum resolution for identification of Rn-222 or Rn-220 daughters.
- Simple application in the field
- Long battery life ( $\sim 1$  year) and large memory data storage

A correction for the measurement of Rn-222 is necessary in the presence of Rn-220, because of a (low) spill into the Rn-222 window. This correction needs further investigation.



## ABSTRACT 46

### COMPLEXANTS MONITORING AT THE LOW LEVEL WASTE REPOSITORY

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The Low Level Waste Repository (LLWR) is the UK's principal facility for disposal of low-level radioactive waste (LLW). Waste is currently disposed in purpose-built concrete-lined vaults. Prior to construction of the first vault in 1988, waste was tumble-tipped into a series of clay-lined trenches.

Certain complexants are potentially of concern because of their capacity to solubilise and mobilise otherwise surface-bound radionuclides making them more liable for transport out of the repository near field and into the geosphere. Such complexants may occur in the repository near field because they are present in waste consignments or because they are generated in situ as degradation products of other materials.

Complexants of potential concern include organic carboxylic acids such as citrate, picolinate, oxalate, formate, and inorganic compounds such as tri-polyphosphates. These are examples of Category 1 materials. These complexants are expected to biodegrade or degrade by chemical or other processes in the near field. They cannot be disposed in bulk quantities, but no overall site capacity is defined.

Aminopolycarboxylic acid complexants (APCAs), such as ethylenediaminetetraacetic acid (EDTA), commonly occur in radioactive waste because of their use in decontamination agents. They are expected to persist in the repository near field because they are chemically resistant and do not biodegrade under repository conditions. APCAs are classified as Category 2 materials. They may have an effect on radionuclide migration and therefore they are subject to a maximum repository capacity.

Assessment calculations are used to determine the risk the repository presents to the environment. The level of risk informs the remaining site capacity for a range of radionuclides. APCAs affect the risk so their impact, determined by the concentration in which they are present, must be accounted for. In recent assessment calculations, we have estimated EDTA concentrations in the trenches on the basis of measured concentrations and in the vaults on the basis of the estimated EDTA content of disposed wastes. EDTA is taken to be representative of the effects of APCAs in assessment modelling because it is the most commonly occurring species.

The LLWR is regulated by the Environment Agency, who require that further sampling of trench leachate is undertaken. A specialist method to detect APCAs in environmental samples based on reverse-phase high-performance liquid chromatography (RP-HPLC) was developed and tested at the University of Manchester in 2019<sup>1</sup>. The results of this analysis suggest that EDTA concentration of is present in the trenches at an average concentration of about 0.5µM.

The LLWR Complexants Monitoring Strategy was issued in 2021<sup>2</sup>. The strategy refers to the previous trench leachate analyses and identifies a number of uncertainties. These include issues related to sample preservation and the use of different sampling locations and methodologies.

Here we report on the future complexants monitoring strategy, designed to mitigate these uncertainties. The strategy undertakes that EDTA analysis will be carried out on an annual basis. Samples from probe holes are preferable to samples from drainage points because they are highly representative of in situ anaerobic conditions. Samples are to be immediately acidified in the field using sulphuric acid to mitigate the potential for biodegradation. The oxidation-reduction potential of samples should be monitored to ensure continued anaerobic conditions and exposure to light should be minimised to limit photolysis of the photoactive Fe(III)-EDTA coordination complex.

We also report on the results from the first round of sampling and analysis carried out by a commercial laboratory in May 2022. The detection method was based on the RP-HPLC method developed at the University of Manchester. The EDTA concentration was found to be below the limit of detection (0.1µM) in samples from nine of fifteen probe-hole locations tested. Concentrations less than 0.5µM were reported in five of the remaining locations and an EDTA concentration of 1.0µM was reported in the final remaining location. Further rounds of sampling and analysis are required to provide further confidence.

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## ABSTRACT 47

### AN INTER-LABORATORY COMPARISON EXERCISE TO ASSESS THE PERFORMANCE OF DIFFERENT METHODOLOGIES USED FOR MEASURING LEAD-210 IN AQUATIC SEDIMENT MATERIALS

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Variation of unsupported fraction of lead-210 (<sup>210</sup>Pb) in aquatic sediment cores from atmospheric fallout is used to provide constraints on sedimentation and accumulation rates, fate of contaminants and much more [1,2,3]. However, the determination of this naturally occurring radionuclide's activity remains a challenge for many radioanalytical laboratories because of specific issues with available radiometric techniques.

Lead-210 is commonly measured by gamma spectrometry, preferably using detectors optimised for low energy sensitivity to accommodate its weak gamma-ray emission at 46.5 keV, which is attenuated by heavy elements. The interpretation of gamma spectra can be challenging when sediments of interest have different bulk densities or contain elevated concentration of other radionuclides also emitting at low energy such as <sup>210</sup>Pb.

In 2021, Cefas instigated an inter-laboratory comparison (ILC) exercise with partners across the UK and Europe that focused on the direct measurement of low levels of <sup>210</sup>Pb in several aquatic sediments with different mineralogical and chemical profiles by gamma spectrometry. The ILC exercise also presented an opportunity to trial a recent chromatographic resin capable of preconcentrating <sup>210</sup>Pb prior to gamma counting and mass spectrometry analysis. The performance of these new approaches was compared with more conventional radiometric methodologies, including alpha spectrometric protocols used to measure polonium-210, a decay product of <sup>210</sup>Pb, and assuming secular equilibrium.

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**ESTABLISHING A PRAGMATIC APPROACH TO OBTAINING A  
REPRESENTATIVE FINGERPRINT FOR 1,400 SLUDGE CANS AT BERKELEY  
POWER STATION**

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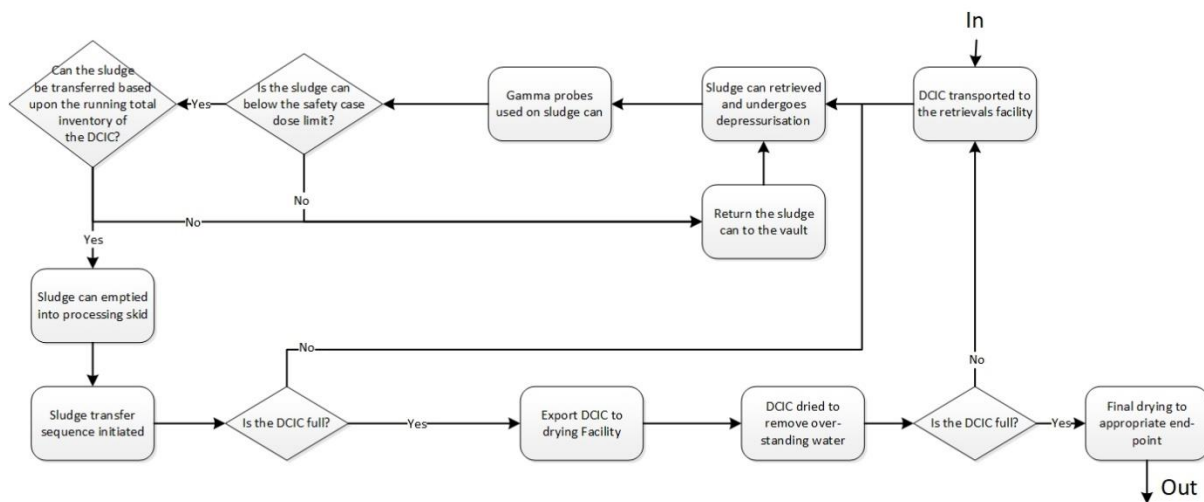
Magnox Ltd, Magnox Hub (Bristol), Almondsbury Business Park, Great Park Rd, Bradley Stoke,  
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Berkeley Power Station has approximately 1,400 sludge cans housed within a subterranean vault that need to be characterised. The contents of the cans will be retrieved into ductile cast iron containers (DCICs) and go through a fill-dry process, see figure 1, until the DCIC is filled with dried sludge, approximately 300 cans per DCIC.

The cans are welded shut and may be pressurised due to evolution of the waste – it is known that there is high variability of the cans' contents. Some of the cans contain asbestos fibres, oils, acids and microbial populations, some have low activities, and some have high actinide contents; but it is impossible to assign contents to any individual can with certainty. A methodology to minimise the risk of producing non-compliant packages has been developed to negate the need to sample the sludge until it is packaged within the DCIC.

Magnox Ltd. (MxL) will demonstrate that the methodology will provide assurance that all waste packages produced meet the requirements associated with the transport regulations and Nuclear Waste Service's (NWS) requirements for disposal. A fingerprint for the waste is available but the data primarily comes from two limited sampling campaigns: samples from the 1978 pond clear-out campaign and samples from six drums from the top of the vault accessed more recently. A representative fingerprint is required to estimate the DCICs contents as reversal of the packaging process would be problematic. This will be done by measuring the  $^{137}\text{Cs}$  content of the cans using two gamma monitors. The system will have a factor applied to account for the uncertainty associated with the fingerprint. Once the packages are produced additional sampling will be required to confirm the nature of the waste.

Different options were considered with regards to how to achieve a representative fingerprint, these ranged from sampling all 1,400 cans during retrievals to not doing any sampling and apply the extant fingerprint. Working closely with NWS, MxL have been able to agree a sampling strategy which involves core sampling two DCICs, the first and the last, prior to final drying. Given how the fill-dry process operates, each DCIC will contain materials from a diverse, but representative range of sludge cans. Once the new fingerprint has been obtained, it will be retrospectively applied to all DCICs using the same methodology as that used to apply the current fingerprint, i.e. scaling to the measured  $^{137}\text{Cs}$  inventory.



**Figure 3.** High-level overview of the sludge retrievals system

**THERMODYNAMIC STUDY OF EUROPIUM (III) IN DILUTE TO CONCENTRATED NITRATE AND SULFATE SYSTEMS: EXPERIMENTAL AND (SIT, PITZER) ACTIVITY MODELS**

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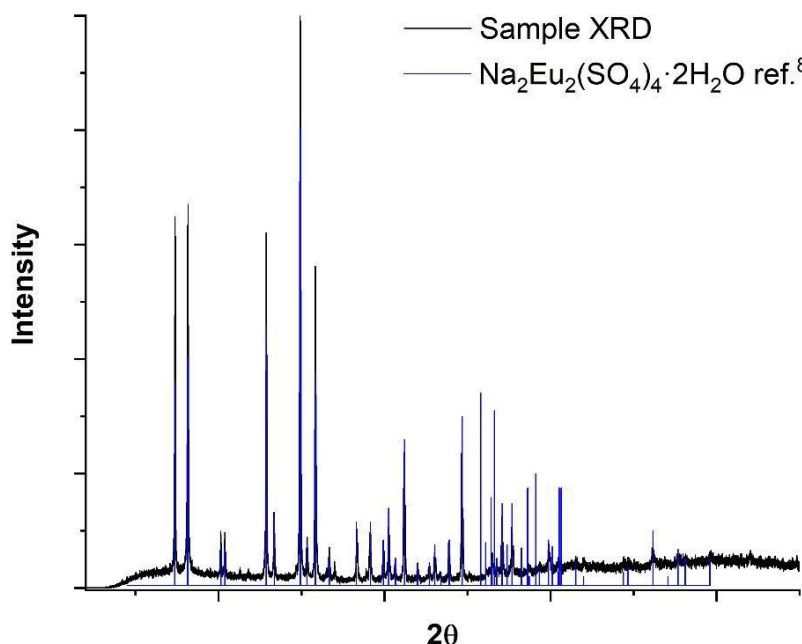
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High inventories of nitrate are expected in specific waste streams in the context of nuclear waste disposal of low and intermediate level waste. Sulfate naturally occurs in the pore water of clay systems, in brines possibly forming in rock salt formations, and as a component in some cement phases (ettringite, monosulfate). Based on the similar ionic radii and equal charge, Eu(III) is often considered as inactive, redox-stable analogue of trivalent actinides expected in the waste, e.g. Pu(III) and Am(III). Thermodynamic and activity models describing the solubility and ion interaction processes of Eu(III) in dilute to concentrated nitrate and sulfate solutions can provide relevant inputs for the description of trivalent actinides under repository-relevant conditions<sup>1,2</sup>. In this study, solubility data determined for the Eu-Na-Mg-SO<sub>4</sub>-NO<sub>3</sub> system are combined with spectroscopic methods (TRLFS) and iso-water activity (IWA) measurements with the aim of deriving thermodynamic and (SIT, Pitzer) activity model parameters of these systems.

Diluted to concentrated aqueous solutions containing Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, MgSO<sub>4</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> were prepared and contacted with the binary, well characterized solid phases Eu<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O(cr) and Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O(cr). Solubility samples were continuously stirred, and the concentration of Eu(III) in the liquid phase was monitored by ICP-OES until attaining equilibrium conditions. Solid phases were characterized by XRD analysis for identification after terminating the solubility experiments. Indeed, literature available for other lanthanides previously reported the formation of some double salts<sup>3,4</sup>.

The new experimental data obtained in this study for the system Eu-Na-Mg-SO<sub>4</sub>-NO<sub>3</sub>, in combination with previously reported solubility and isopiestic data are considered to derive the thermodynamic and (SIT, Pitzer) activity model parameters for these systems. The optimization routine is implemented in PEST<sup>5</sup>, an optimization software, and chemical equilibria are calculated using the PhreeSCALE software<sup>6</sup> and the dedicated database. The ThermoChimie database is considered as basis for the development of the SIT models<sup>7</sup>.

The present work was jointly performed by BRGM and KIT-INE and financially supported by ANDRA.



**Figure 1** - XRD pattern of the double salt  $\text{Na}_2\text{Eu}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$  (cr) recovered from solubility experiments.

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## ABSTRACT 50

### ANAEROBIC BIODEGRADATION OF CITRIC ACID IN THE PRESENCE OF NICKEL AND URANIUM AT ALKALINE PH; IMPACT ON METAL FATE AND SPECIATION

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Citrate is a key decontaminant in the nuclear industry and here we explore its biogeochemical fate in the presence of Ni and U under conditions relevant to low level radioactive waste (LLW) disposal. Ni(II) and U(VI) were selected for this study as they are significant contaminants in radioactive wastes. The environmental mobility of Ni and U may be affected by organic ligands, such as citrate, which are also present in wastes. Citrate is expected to increase Ni solubility via complexation, even under alkaline pH levels expected in cementitious repositories for L/ILW. By contrast, U-citrate complexes are unlikely to form at elevated pH, however citrate can be utilised as an electron donor to fuel microbial reduction reactions. Microbial metabolism may influence the speciation and oxidation state of U, and it turn its solubility. Accordingly, understanding the fate of Ni and U in the presence of citrate informs radioactive waste management practices.

The biodegradation/biotransformation of Ni-citrate and U-citrate complexes has been studied previously under neutral pH and/or aerobic conditions. However, to date, there has been little focus on the biogeochemical behaviour of Ni and U in systems containing citrate under alkaline conditions relevant to expected L/ILW waste disposal conditions. Enrichment and resting cell experiments were used to explore citrate biodegradation in the presence of Ni and U under nitrate- and sulfate-reducing conditions at pH 9-10.

Here, citrate (1mM) was supplied as both a metal ion complexant and electron donor and three concentrations of Ni or U were tested in incubation experiments: 0.01, 0.1 or 1 mM. Nitrate- or sulfate-reducing inocula were used in experiments; these were enriched from alkaline sediments obtained from high pH lime-working sediments. A multi-technique approach was adopted to characterise the aqueous geochemistry (pH, IC, ICP-MS, and ESI-MS), solid phase mineralogy (SEM/TEM with EDS/SAED), and bacterial communities (16S rRNA gene sequencing) in each system. In the Ni incubations [Ni(Cit)]<sup>-</sup>

was the dominant Ni species, and, in the inoculated 0.01mM Ni systems this complex was fully biodegraded under both nitrate- and sulfate-reducing conditions in less than 15 days. In the sulfate-reducing experiment, 50 % of aqueous Ni was removed from solution over 100 days and black precipitates formed; electron microscopy suggested this was a nickel sulfide phase. In the U experiments, citrate was biodegraded within 55 days in all systems except the 1 mM U/nitrate-reducing incubations. By day 55, a dark-coloured precipitate formed in all U/sulfate-reducing experiments. In the 0.01mM U and 0.1mM U systems 83-98 % of the added U(VI) was removed from solution by day 15, and substantial U(VI) removal (between 50-70%), was also observed by day 55 in the 1 mM U experiment.

The XAS analysis of pelleted samples indicated that the solids contained a mix of nanocrystalline uraninite and non-crystalline U(IV)-phosphate. Microbial community analysis identified bacteria affiliated with genera that have known nitrate- and sulfate-reducing members, in the relevant systems. Overall, findings suggest microbial degradation of citrate occurs under repository relevant conditions with Ni and U present (0.01-0.1 mM). Significantly, the work suggests that citrate will degrade and can support the development of Ni sulfides and / or development of reducing conditions which facilitate reductive scavenging from U(VI) to poorly soluble U(IV) phases under conditions relevant to LLW disposal and thereby promotes the biogeochemical immobilisation of metals into the solid phase

## ABSTRACT 51

### UPTAKE AND BIOACCUMULATION OF NANOPLASTICS IN MUSSELS USING CARBON-14 LABELLED PARTICLES

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Up until now, only a few studies have addressed the effects of nano-plastics (NPs) on marine biota, mainly owing to the analytical challenges associated with the tracking of ultrafine particles in organisms. This highlighted a need for developing an innovative approach that could help better understand their fate and role as vector of transport for other hazardous substances of concern. (Al-Sid-Cheikh et al., 2018; Lanctôt et al., 2018).

In this study, a novel radiolabelling technique was applied to two different sizes of NPs (<sup>14</sup>C-polystyrene; 20 and 250nm diameter). Mussel samples (*Mytilus edulis* and *Mytilus galloprovincialis*) were selected and used as reference biota. The mussels were first acclimated for approximately 2 months and fed with *Isochrysis galbana* (Haptophyta) at a density of 10,000 cells /ml, prior to exposing them to a known concentration of <sup>14</sup>C-NPs for studying uptake, depuration rates and assessing potential bioaccumulation effects. The measurements of <sup>14</sup>C in seawater and mussels were performed at Weymouth and Lowestoft, respectively, using validated radioanalytical methods.

The methods and results from these initial exposure experiments are presented in this poster as well as images of the distribution of <sup>14</sup>C-NPs in mussel tissues obtained from micro-autoradiography analysis undertaken at the University of Surrey.

**ULTRA-LOW NOISE MULTIPLE ION COUNTING FOR HIGH  
PRECISION ISOTOPE RATIO MEASUREMENT OF LOW  
ABUNDANCE ACTINIDES**

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When measuring very small ion signals ( $<10,000\text{cps}$ ), in sub picogram samples of actinides, ion counting detectors are necessary due to their low noise compared to that of a Faraday detector. Ion counters however, still have a non-zero noise associated with them, known as the dark noise, which is typically several counts per minute. Additionally, there are sources of measurement error present that are not of concern with Faraday detectors, such as dead-time/linearity, peak flatness, and gain stability. The challenge in determining the relative gain of an ion counter presents a significant challenge in acquiring high quality data at low count rates.

In this presentation, the performance characteristics of the Isotopx Phoenix ATONA equipped with 10 channels of upgraded Isotopx Ion Counting (IIC) power supply and counting electronics is evaluated. The ion counters are conversion dynode multipliers, whereby the ion beam strikes a conversion dynode, and the released electrons are detected using a Sputs multiplier aligned at  $90^\circ$  relative to the ion beam.

Furthermore, the performance of the ATONA Faraday system for these small samples is also considered. Ultimately, we describe the ideal ion signal value at which it would be benefit the measurement precision to change from using ATONA Faraday detectors to the Phoenix multiple ion counting system.



The Phoenix Thermal Ionisation Mass Spectrometer

**DEVELOPMENT OF RADIOCHEMICAL ANALYSIS TECHNIQUES TO  
UNDERPIN THE SAFETY CASE FOR A GDF IN LOWER STRENGTH  
SEDIMENTARY ROCK**

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Transport in groundwater is a potential pathway by which radionuclides and non-radiological species released from wastes disposed to a geological disposal facility (GDF) could migrate through the geosphere. An understanding of the behaviour of radionuclides and non-radiological species in groundwater, as well as their partitioning to available surfaces, is fundamental to the delivery of an Environmental Safety Case (ESC) for a GDF.

To date, as Nuclear Waste Services (NWS) has progressed its ongoing GDF siting programme, environmental radiochemistry research has focused on illustrative geological environments and, coupled with progress internationally, has fostered a robust, generic understanding of radionuclide behaviour in the geosphere<sup>1</sup>.

However, the focus of radionuclide behaviour research is anticipated to shift significantly in the coming years as NWS focuses its technical programme on site-specific needs, guided by those communities that have expressed an interest in hosting a GDF. Given the nuanced behaviour of species dissolved in groundwater (sorption, solubility, and diffusion), it is anticipated that significant work will be required to underpin a future site-specific ESC. Once a site, or subset of sites, is selected, intrusive activities (i.e., borehole drilling) will generate samples for radiochemical analysis. NWS needs to demonstrate adequate preparedness for the receipt of drill-core samples.

Methodologies for measuring parameters that describe radionuclide sorption and diffusion in geological materials were developed as part of the Nirex Safety Assessment Research Programme (NSARP) in support of site characterisation activities undertaken by Nirex between 1984 and 2000. Here, the viability of these techniques for characterising the performance of a sedimentary host rock has been tested, in order to understand areas for continued development.

Since no site-specific samples are yet available in the UK, samples of Opalinus Clay were obtained from the underground research laboratory (URL) at Mont Terri in Switzerland. Samples of the shaley facies (clay and carbonate-rich layers) and sandy facies (clay and sandy, carbonate-rich layers) were

explored for measurements of the intrinsic diffusion coefficient ( $D_i$ ), sorption distribution ratio/coefficient ( $RD/K_d$ ), solute accessible porosity ( $\phi$ ), beta factor ( $\beta$ ) and anion-exclusion factors. The work demonstrates that the sorption and diffusion methodologies employed are well developed for a swelling sedimentary rock such as the shaley facies, giving values for  $D_i$  and  $RD$  that were comparable to those reported in the literature. However, it was demonstrated that some methodologies require further development for use with non- or poorly-swelling clay rocks such as the sandy facies, and that challenges remain associated with assessing radionuclide sorption under variant chemical conditions.

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## DFT + U STUDY OF URANIUM DIOXIDE AND PLUTONIUM DIOXIDE WITH OCCUPATION MATRIX CONTROL

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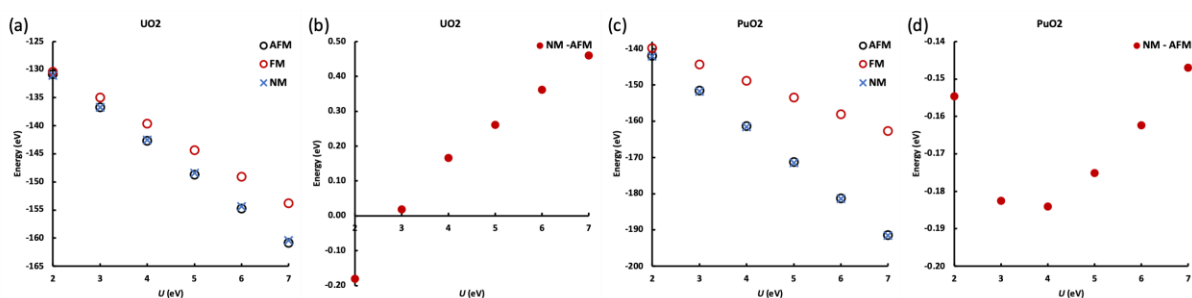
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In the actinide series of elements, many of the chemical and physical properties display a turning point at plutonium. The actinide dioxides, which are the subject of this work, change from Mott-Hubbard insulators to charge transfer insulators at  $\text{PuO}_2$ .<sup>1,2</sup>  $\text{UO}_2$  and  $\text{NpO}_2$  have antiferromagnetic (AFM) ground states,<sup>3,4</sup> while a nonmagnetic (NM) ground state, which has been established by various experiments over a wide temperature range (4 - 1000K),<sup>5,8</sup> is found for  $\text{PuO}_2$ . However, previous DFT + U simulations have predicted an AFM ground state for  $\text{PuO}_2$ .<sup>9</sup> The inconsistency between experiment and DFT + U simulation over the correct magnetic ground state of  $\text{PuO}_2$  needs to be clarified. As  $\text{PuO}_2$  is a product of the recycling of spent  $\text{UO}_2$  nuclear fuel, detailed understanding of  $\text{PuO}_2$  is clearly essential not just at a fundamental level, but also to inform its safe current and long-term storage.

There are typically many different ways in which the actinide f orbitals may be populated, and use of the Hubbard U parameter in DFT calculations can lead to the location of meta-stable states arising from those electronic configurations.<sup>10</sup> The occupation matrix control (OMC) method in VASP, developed by Dorado et al, is able to impose initial occupation matrices (OMs) on the orbitals of interest.<sup>11,12</sup> By considering all possible occupations of the actinide 5f orbitals, the true ground state is the OM state with lowest energy. There are  $C_7^2 = 21$  OMs for FM and 1k colinear AFM  $\text{UO}_2$ ,  $C_7^1 = 7$  OMs for NM  $\text{UO}_2$ ,  $C_7^4 = 35$  OMs for FM and 1k colinear AFM  $\text{PuO}_2$ , and  $C_7^2 = 21$  OMs for NM  $\text{PuO}_2$ .

We initially tested the OMC on  $\text{UO}_2$  bulk, as  $\text{UO}_2$  is much better studied than  $\text{PuO}_2$ , with a wide range of U values (0.0 – 7.0 eV in 0.5 eV steps). When the U value not too small ( $\geq 2.0$  eV), the [0000101], [00000101] and [0000200] OMs are always found to be the lowest energy state of AFM, FM and NM  $\text{UO}_2$ , while the AFM ground state is found for  $\text{UO}_2$  with  $U > 2.0$  eV. After locating the ground state of  $\text{UO}_2$ , various properties (lattice parameter, magnetic moment, band gap and densities of states) have been compared over a wide range of U.

We conclude that  $3.0 \text{ eV} \leq U \leq 5.0 \text{ eV}$  gives a good overall balance of agreement with experiments, with the best value being 4.0 eV. Similar to  $\text{UO}_2$ , when U is not too small ( $> 2.0$  eV), the same OM states of  $\text{PuO}_2$  are found to have the lowest energy for the AFM, FM and NM states, these are [1010101], [1010101] and [0000202], respectively. The NM ground state is found for  $\text{PuO}_2$  with  $U > 2.0$  eV for the first time, in agreement with experimental results. We suggest  $4.0 \text{ eV} \leq U \leq 5.0 \text{ eV}$  with 4.5 eV and 4.0 eV being the best values for the simulation of NM and AFM  $\text{PuO}_2$  bulk, respectively.



**Figure 1** (a) energy of the most stable AFM, FM and NM OM state of  $\text{UO}_2$  (b) energy difference between the most stable AFM and NM state of  $\text{UO}_2$  (c) energy of the most stable AFM, FM and NM OM state of  $\text{PuO}_2$  and (d) energy difference between the most stable AFM and NM state of  $\text{PuO}_2$ .

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## ABSTRACT 55

### STUDIES ON DISTRIBUTION OF POLONIUM-210 AND LEAD -210 ACTIVITY AND PHYSICO CHEMICAL EFFECTS OF UNDISTURBED ALLUVIAL CLAY SOIL IN BELAGAVI DISTRICT, KARNATAKA, INDIA

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The paper discusses the activity of polonium-210 ( $^{210}\text{Po}$ ) and lead-210 ( $^{210}\text{Pb}$ ) and physico chemical effects on undisturbed alluvial clay soil in Belagavi district of Karnataka, India. The activity of  $^{210}\text{Pb}$  was estimated through  $^{210}\text{Po}$  by radiochemical separation and subsequent deposition on a silver disc. The  $\alpha$ -activity was then counted using a ZnS(Ag) counter of 30% efficiency, and the activity was calculated.

The average of  $^{210}\text{Po}$  activity in soil samples ranged from 9.45 to 31.75 Bq kg<sup>-1</sup>, with an average of 16.76 Bq kg<sup>-1</sup>. Whereas, the  $^{210}\text{Pb}$  activity range from 17.58 to 78.52 Bq kg<sup>-1</sup>, with an average value of 37.89 Bq kg<sup>-1</sup>.  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  activity ratio range from 0.39 to 0.54 Bq kg<sup>-1</sup>, with an average value of 0.46 Bq kg<sup>-1</sup>.

The low activity of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  was observed in the dissolved phase due to the removal of these reactive radionuclides from solution. The granulometric contents (silt, clay, and sand), organic matter and pH contents were measured in soil, respectively. Using IBM SPSS software, a good correlation with correlation coefficient was found between the activity  $^{210}\text{Po}$ , and  $^{210}\text{Pb}$  with organic matter percentage and clay. The Surfer software version 8, kriging interpolation method, 3D map is used to predict the value of a random variable over a spatial

# **RADIOMETRIC MEASUREMENT METHODS TO OBTAIN REALISTIC KD VALUES FOR RADIUM-226 ON BIOTITE**

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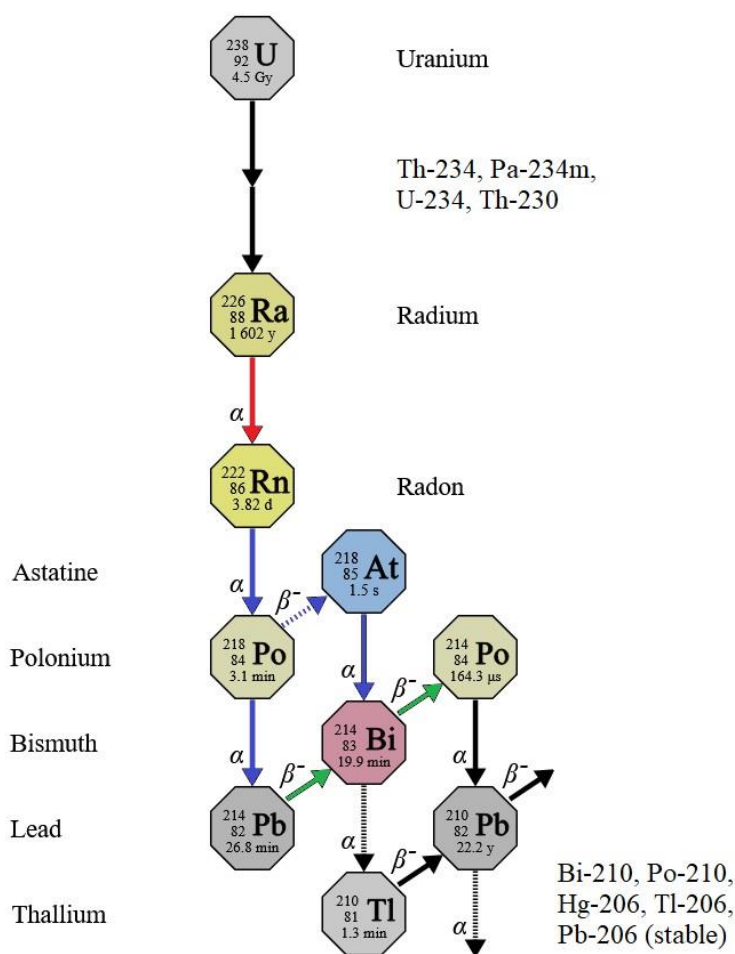
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The spent nuclear fuel of Finnish nuclear power plants will be permanently disposed of in a deep geological facility at the depth of 450 m, starting in the 2020s<sup>1</sup>. The final barrier retarding the spread of waste radionuclides in the event of a containment failure is the bedrock surrounding the facility<sup>1</sup>. The transport properties of the spent nuclear fuel-borne radionuclides will need to be considered in the long-term safety case calculations of the disposal plant. In this study, the sorption properties of <sup>226</sup>Ra, from the decay chain of the spent fuel-dominating <sup>238</sup>U, were examined in the form of distribution coefficient determinations with various radiometric measurement methods for batch sorption<sup>2</sup> and thin section biotite samples (Fig. 1).

In the Ra batch sorption experiments on biotite, the activity of <sup>226</sup>Ra tracer (Eckert & Ziegler) was measured through its gamma emission (186.2 keV, 3.64%) with High Purity Germanium (HPGe) gamma detector (Canberra Semiconductor Detector, GX8021). To control the accuracy of the low intensity gamma emission measurements with <sup>226</sup>Ra (MDA ~ 0.2 Bq ml<sup>-1</sup>), its decay daughters <sup>214</sup>Pb and <sup>214</sup>Bi were let to achieve secular equilibrium with parent, and were subsequently measured through their most intensive gamma emissions of 295.2 keV (18.47%) and 351.9 keV (35.72%), and 609.3 keV (45.44%), respectively<sup>2</sup>. Liquid Scintillation Counting (LSC, on Quantulus 1220) was used to confirm <sup>226</sup>Ra activity gamma measurements. LSC measurements and alpha/beta separation are based on the alpha and beta emissions of <sup>226</sup>Ra (α 4784.3 keV, 93.84%) and relevant daughters, such as <sup>222</sup>Rn (α 5489.5 keV, 99.92%). Additionally, <sup>226</sup>Ra and daughters' alpha emissions were studied with alpha-particle spectroscopy equipment (ALPHA-KINGTM) and multi-channel analyzer software (MAESTRO by ORTEC).

Site and mineral specific/heterogeneous sorption of <sup>226</sup>Ra on biotite was further studied with rock thin section samples in digital autoradiography using both phosphor imaging plate technique (Fuji 5100) and micromesh-based gas detector BeaQuantTM (Ai4r)<sup>3</sup>. To quantitatively determine the sorption of Ra on biotite mineral in whole rock sample autoradiography, <sup>226</sup>Ra tracer standard series (5-100 Bq ml<sup>-1</sup>) were devised by polymerizing concentrated aqueous <sup>226</sup>Ra with 1:3 volume ratio mixture of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA). Sorption studies on rock thin section samples can be used to upscale distribution coefficients from crushed pure mineral samples to intact rock. The experimental data of this study can be used to optimize radiation detection and measurement in Ra site and mineral specific sorption experiments and geochemical modelling.



**Fig. 1.** Truncated  $^{238}\text{U}$  decay chain, with the most  $^{226}\text{Ra}$  measurement-relevant radioactive decays color-coded as such: red - autoradiography and liquid scintillation counting ( $\alpha$  and  $\beta$ ), and gamma detection ( $\gamma$ ); blue - liquid scintillation counting ( $\alpha$  and  $\beta$ ); green - liquid scintillation counting ( $\alpha$  and  $\beta$ ) and gamma detection ( $\gamma$ ).

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**PREPARATION AND IMPREGNATION OF METHACRYLATE BASED POROUS MONOLITH FOR RADIOCHEMICAL SEPARATION AND RECOVERY FOR MICROFLUIDIC SYSTEMS**

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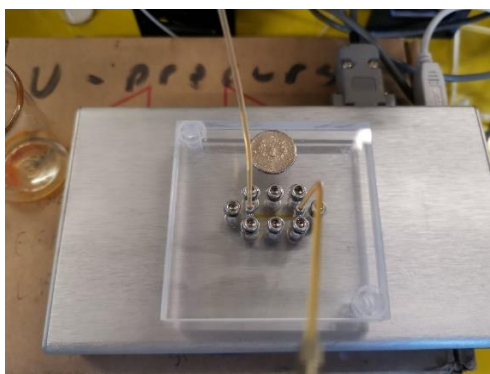
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Advancement in analytical device miniaturisation through microfluidic technology offers an alternative approach towards radiochemical analysis. When compared to traditional macroscale analytical process, microfluidics devices manipulate and process fluid samples typically in the microlitre range, which provides benefits in terms of more efficient mixing and precise conditions control that are not feasible in macroscopic systems.

Microfluidic extraction devices are fabricated using PMMA (figure 1) and packed with commercial UTEVA chromatographic resin have already been produced and tested for molybdenum and uranium separation from acidic media. Initial assessment of microfluidic device functionalisation with commercial particulate resins have proven to be difficult and inconsistent.

Exploration into either light or thermally initiated methacrylate-based monolith materials as solid phase support for radiochemical separation under harsh conditions are investigated. Using variety of differing methacrylate functional monomers such as allyl methacrylate, methyl methacrylate and butyl methacrylate, functionalised by impregnation of TBP. Functionalised monoliths are produced and tested for its stability, functional capacity and cyclability under exposure to concentrated nitric acid (>8M).

These monoliths may be produced via ex-situ or in-situ fabrication methods and reincorporated into desired microfluidic channels.



**Figure 1.** An assembled 20 microlitre extraction device, unpacked, compared to a UK five pence coin, 18mm in diameter.

**EVALUATION OF ICAP ICP-TQMS (THERMOFISHER SCIENTIFIC) FOR THE MEASUREMENT OF RADIOISOTOPES IN VARIOUS MATRICES**

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In the last thirty years inductively coupled plasma - mass spectrometry (ICP-MS) technology has started to become a very interesting analytical option for measuring some radioelements in environmental matrices as it presents much shorter counting times in comparison with more traditional radiometric techniques. Initially, it was applied to long-lived and heavy radionuclides presenting a low specific activity. Recent ICP-MS instrumental advances as well as the development of engineered state-of-the-art sample introduction and detecting interfaces have expanded the possibility of measuring a wider range of radioelements with greater sensitivities.

The Inductively Coupled, Plasma, Triple Quadrupole Mass Spectrometer manufactured by ThermoFisher Scientific (iCAP ICP-TQMS) presents specific configurations in comparison with other ICP-MS technologies available on the market. For example, it has a unique orthogonal deflection lens (Right-Angle Positive-Ion Deflection - 'RAPID') system instead of a linear system commonly provided by other manufacturers. The sensitivity, resolution, and robustness of the iCAP ICP-TQMS is presented in this poster. Several optimisation parameters were also tested for measuring low levels of strontium-90 (<sup>90</sup>Sr), iodine-129 (<sup>129</sup>I), radium-226 (<sup>226</sup>Ra), plutonium-239 (<sup>239</sup>Pu) and <sup>240</sup>Pu present in a wide range of environmental matrices.

**SOLUBILITY AND STRUCTURAL CHARACTERIZATION OF ZIRCONIUM (IV)  
HYDROUS OXIDES**

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**INTRODUCTION:**

Besides their strong hydrolysis, M(IV) (e.g. actinides, Zr, Tc) ions form sparingly soluble amorphous hydrous oxides, MO<sub>2</sub>(am, hyd), controlling M(IV) solubility over a broad range of pH. Ageing or exposure to elevated temperatures expectedly results in a transformation into thermodynamically more stable crystalline phases and thus in a decreased solubility in aqueous systems [1, 2].

Zirconium alloys (Zircaloy) are used as cladding material for nuclear fuel, especially in water reactors. Zr-93 (t<sub>1/2</sub> = 1.53x10<sup>6</sup> a) is produced by nuclear fission of U-235 as well as by neutron activation of the cladding. ZrO<sub>2</sub>(s) has been identified as possible solid phase controlling the solubility of Zr under repository conditions.

The present study systematically investigates the impact of temperature on the crystallinity and water content of ZrO<sub>2</sub>(s, hyd) solid phases, and further the solubility and thermodynamic properties of these solid phases in hyperalkaline conditions. For this purpose, a combination of solubility batch experiments and comprehensive solid phase characterization methods is used. As overarching objective, this work intends to shed light on the mechanisms for the potential transformation of amorphous hydrous oxides into thermodynamically more stable crystalline phases of Zr(IV) relevant in the context of nuclear waste disposal.

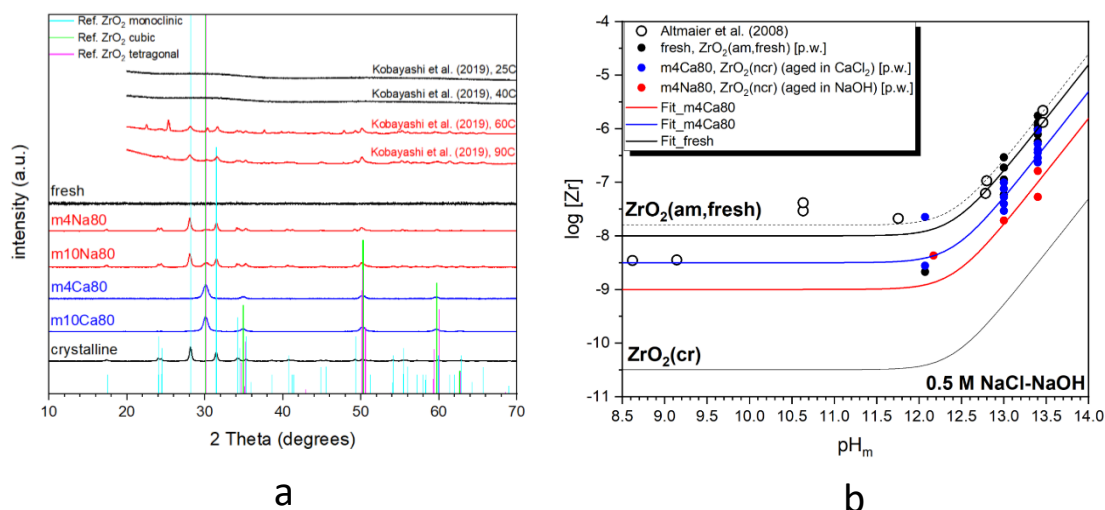
**DESCRIPTION OF THE WORK:**

The starting solid phase used in this study, ZrO<sub>2</sub>(am, hyd, fresh), was prepared by slow titration of a  $\approx$  0.02M ZrOCl<sub>2</sub> solution with 0.1M NaOH. Independent aliquots of the starting solid phase were equilibrated at T = 80°C in 0.02M CaCl<sub>2</sub>-Ca(OH)<sub>2</sub>, 0.2M CaCl<sub>2</sub>-Ca(OH)<sub>2</sub> or 0.001M NaOH solutions at pH<sub>m</sub> = 11.0 for 4, 10 and 18 months. Afterwards, the sample solutions were cooled down and the solid phases were separated from the supernatant solution, washed 2–3 times with water and characterized with various methods including XRD, TG-DTA, SEM-EDX, XPS, XAFS, IR-ATR, BET, TEM, SAXS and zeta potential measurements. Experiments approaching solubility equilibrium from undersaturation conditions were performed with 5–20 mg of the fresh and aged ZrO<sub>2</sub>(s, hyd) solid phases, equilibrated at T = 22°C with solutions of 0.02M CaCl<sub>2</sub>-Ca(OH)<sub>2</sub>, 0.2M CaCl<sub>2</sub>-Ca(OH)<sub>2</sub> or

0.5M NaCl-NaOH solutions at  $10 \leq \text{pH}_m \leq 13.4$ . The concentration of Zr in the aqueous phase was quantified by ICP-MS after ultrafiltration with 3 kD filters.

## RESULTS AND DISCUSSION:

XRD (Figure 1a), SEM-EDX and TEM confirm the amorphous character of the fresh  $\text{ZrO}_2(\text{am}, \text{hyd}, \text{fresh})$ . Solid phases aged at  $T = 80^\circ\text{C}$  in 0.001M NaOH solutions resulted in monoclinic  $\text{ZrO}_2$  (size of crystal domains: 23-27 nm, Scherrer analysis) with a small fraction of cubic/tetragonal  $\text{ZrO}_2$ , in agreement with XRD data reported by Kobayashi et al. [3]. In contrast, samples aged at  $T = 80^\circ\text{C}$  in presence of 0.2M or 0.02M  $\text{CaCl}_2\text{-Ca(OH)}_2$  led to the formation of nanocrystals with cubic/tetragonal structure and a size of 11-14 nm. The weight loss determined by TG-DTA was correlated with the higher water content of the amorphous solids, qualitatively confirmed by IR spectroscopy. All these observations underpin the key role of  $\text{OH}^-$  and  $\text{H}_2\text{O}$  in the ageing / crystallization process of  $\text{ZrO}_2(\text{s})$ , which is described more accurately as  $\text{ZrO}_x(\text{OH})_{4-2x} \cdot n\text{H}_2\text{O}(\text{s})$ . These results highlight also the stabilization of the cubic/tetragonal structure induced by Ca at a concentration level expected in specific repository concepts. Figure 1b exemplarily shows solubility data of Zr(IV) collected in 0.5M NaCl-NaOH for a fresh solid as well as for solid phases aged in 0.2M  $\text{CaCl}_2\text{-Ca(OH)}_2$  and 0.001M NaOH solutions at  $T = 80^\circ\text{C}$ . A preliminary evaluation of the  $\log K_{s,0}^\circ$  of these solid phases was conducted for the most alkaline samples, considering the predominance of the  $\text{Zr(OH)}_6^{2-}$  (in NaCl) and  $\text{Ca}_x\text{Zr(OH)}_6^{2x-2}$  (in  $\text{CaCl}_2$ ) aqueous complexes as reported in the NEA-TDB[4] and Altmaier et al.[5]. Further results from on-going experiments will be discussed in this contribution.



**Fig. 1.** (a). XRD patterns collected for  $\text{ZrO}_2(\text{s})$  solid phases aged in NaOH (red) for 4 months (m4Na80) and 10 months (m10Na80) and  $\text{CaCl}_2$  (blue) for 4 months (m4Ca80) and 10 months (m10Ca80), as compared to data reported by Kobayashi et al.[3] and reference patterns available for  $\text{ZrO}_2(\text{cr})$  in the JCPDS database; (b). Solubility data determined for fresh and aged phases ( $T = 80^\circ\text{C}$ , NaOH and  $\text{CaCl}_2\text{-Ca(OH)}_2$ ) equilibrated at  $T = 22^\circ\text{C}$  in 0.5M NaCl-NaOH. Solid lines show solubility calculations for  $\text{ZrO}_2(\text{am}, \text{fresh})$  and  $\text{ZrO}_2(\text{cr})$  [4,5], as well as preliminary model calculations for the systems investigated in this work.

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## ABSTRACT 60

### IMPROVEMENTS IN THE ESTIMATION OF INGESTED DOSE FROM NATURAL RADIOACTIVITY IN THE IRISH DIET

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In 2014, the Radiological Protection Institute of Ireland estimated the radiation doses received by the Irish population. It was estimated that the annual effective dose from the ingestion of food and water was 267  $\mu\text{Sv}$  per year<sup>1</sup>. This ingestion dose accounts for approximately 6.5 % of the estimated average annual effective dose to members of the public in Ireland. It was estimated that 98 % of the radioactivity ingested in the Irish diet is as a result of natural radioactivity, highlighting the importance of natural radionuclides in the determination of ingestion doses. UNSCEAR have provided an estimated worldwide average ingestion dose of 260  $\mu\text{Sv}$  per year for the annual effective dose for the ingestion of radioactivity in food<sup>2</sup>, which is consistent the Irish dose report. However, in a more recent publication by the IAEA, it is estimated that the ingestion dose is estimated to be 319  $\mu\text{Sv}$  per year<sup>3</sup> (when including K-40).

The goal of this study was to provide an updated assessment of the ingestion dose to the Irish public through an improved duplicate diet sampling survey and the development of radioanalytical methods for specific natural radionuclides of interest.

The radioanalytical methods in the laboratory were developed with the aim of improving detection limits to enable the measurement of low levels of natural radioactivity in food and to minimise the time required to conduct the analyses and assess activity concentrations. The radionuclides analysed were Po-210 by spontaneous deposition and measured by alpha spectrometry, Pb-210 by extraction chromatography and measuring the Bi-210 daughter using Gas Proportional Counting and finally, C-14 using a Pyrolyser Furnace and measured by Liquid Scintillation counting. Additionally, Ra-226, Ra-228, U-238, Th-232 and Th-230 were measured by gamma spectrometry to provide a broader overview of natural radionuclides in food that could contribute to the overall assessment of the ingestion dose to the Irish population.

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**VALIDATION OF RADIOANALYTICAL METHODS VIA INTERCOMPARISON EXERCISES WITHIN NORDIC NUCLEAR RESEARCH COMMUNITY**

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Analysis of difficult to measure (DTM) radionuclides often require lengthy radiochemical separation and purification methods, whereas gamma radionuclides (easy to measure, ETM) can be determined using non-destructive gamma spectrometric analysis without pre-treatment. In both cases, however, the analysis methods need to be validated. In general, for example in analytical chemistry, method validation can be carried out using reference materials. Unfortunately, reference materials for DTM analysis in decommissioning or radioactive wastes are not commercially available. Therefore, a need for method validation via intercomparison exercises was realised in 2019 when a three year project within Nordic Nuclear Safety Research (NKS) community was launched. The studied materials were activated steel in 2019 [1], activated concrete in 2020 [2] and spent ion exchange resin in 2021 [3] focusing on beta DTMs, such as H-3, C-14, Fe-55, Ni-63, and Sr-90. Additionally, ETMs were analysed and actually, ETMs were included in the main radionuclides list in 2021 when the studied material was spent ion exchange resin containing variety of gamma emitters. The reported results were analysed according to ISO 13528 standard [4]. The involved Radioanalytical laboratories were from both Nordic countries (i.e., Finland, Sweden, Denmark and Norway) and outside (i.e., France, Taiwan) providing either analytical services or building up their competences in DTM and ETM analyses in radioactive waste. Currently, another intercomparison exercise, namely RESINA project, is been carried out for the same spent ion exchange resin as studied in 2021 but the focus is on alpha emitters.

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# INVESTIGATING URANYL (VI) SPECIATION IN CEMENT USING LUMINESCENCE SPECTROSCOPY

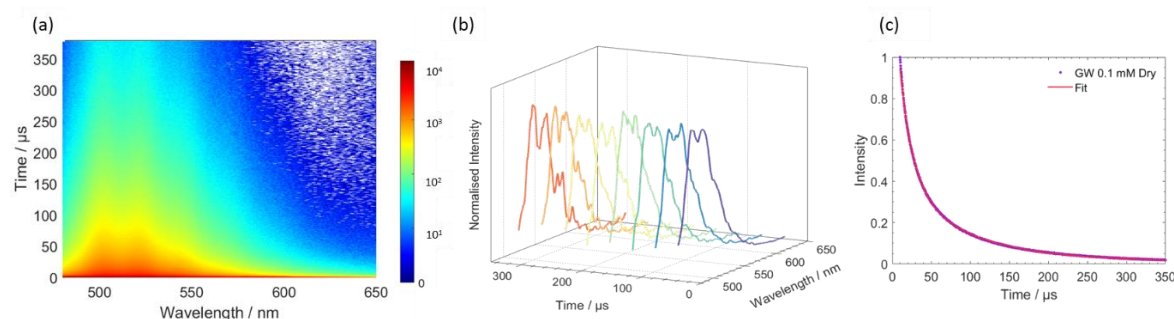
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As a key element in the nuclear fuel cycle, uranium is a major component of nuclear waste and understanding its fate in the environment is essential to ensure appropriate safety cases can be made for the safe disposal of nuclear waste. Fundamental understanding of the speciation of uranyl in the presence of relevant natural and engineered materials is crucial and the characteristic luminescence signal of uranyl (VI) can provide important information regarding its speciation and coordination environment.<sup>1,2</sup> Steady state and time resolved luminescence techniques can be used in conjunction with signal enhancement methods to resolve the speciation of uranyl on a sample of cement. Preliminary bulk studies focusing on the behaviour of uranyl (VI) (0.05 - 0.1 mM) with aged cement in in atmospheric conditions, suggest two emissive species are present. The existence of multiple uranyl species is supported by previous studies by Tits et al.<sup>3-5</sup> under a nitrogen atmosphere and demonstrates the inherent potential of luminescence spectroscopy to be used in the elucidation of the speciation of uranyl (VI) in relevant systems. Furthermore, the findings from this bulk study illustrate the complexity of the system at a macroscopic level and create a good starting point for the use of lifetime image mapping to ascertain the bonding and speciation of uranyl (VI) at a microscopic level.



**Figure 1** (a) Time resolved emission spectrum (TRES) ( $\lambda_{\text{ex}}$  250 nm) of U (VI) (0.1 mM) on cement (b) Sliced spectrum showing improvement of peak resolution over time (c) Lifetime fitting obtained from TRES data between 480 and 550 nm, fitted with a double exponential.

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## ABSTRACT 63

### MICROBIAL IMPACTS ON COLLOID-RADIONUCLIDE INTERACTIONS IN SPENT NUCLEAR FUEL PONDS

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The legacy spent nuclear fuel ponds (SNFPs) and silos at Sellafield house a diverse inventory of waste from the early Magnox reactors which used uranium metal as a fuel encased in a magnesium non-oxide cladding. Corrosion of the cladding results in the release of radionuclides, primarily uranium, and the formation of brucite ( $\text{Mg}(\text{OH})_2$ ) phases which are present both in the corroded Magnox sludge (CMS) at the base of the pond and suspended in the water column as colloids<sup>1</sup>. The legacy ponds are maintained at high pH to minimise corrosion of the Magnox cladding, however significant corrosion has still occurred. Colloids have the potential to significantly enhance radionuclide mobility providing an important pathway for radionuclide migration in the environment.

Despite the seemingly inhospitable conditions in SNFPs, numerous studies have found microorganisms capable of surviving in SNFPs<sup>2,3,4</sup>.

Previous work has also demonstrated increased abiotic sorption of strontium to brucite in the presence of natural organic matter derived from the cyanobacterium *Pseudanabaena catenata* 5, which dominates algal blooms in the Magnox storage pond. In this study we focus on uranium interactions with colloidal brucite in the presence of metabolically active microbes adapted to high pH environments under conditions relevant to the legacy facilities at Sellafield. Data will be presented that have been collected using a range of geochemical and spectroscopic techniques, including luminescence and lifetime analysis.

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**HELIUM DIFFUSION IN PLUTONIUM DIOXIDE**

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Until the UK Government arrives at a decision regarding the final treatment and disposition of Pu, the NDA remain responsible for the “safe and secure storage” of PuO<sub>2</sub> currently in inert steel cans at Sellafield.<sup>1</sup> Radiogenic helium gas generation naturally occurs in the ageing of PuO<sub>2</sub> due to the spontaneous alpha decay of Pu isotopes, creating self-radiation damage to the lattice. The risk of helium gas pressurisation is a safety concern for long-term storage of Pu oxides. Hence, fundamental understanding of helium behaviour, including its generation, incorporation and release, is needed.<sup>2</sup> Atomistic simulation techniques are ideally suited to provide fundamental insight into the behaviour helium in PuO<sub>2</sub>.

Molecular dynamics has been used to investigate helium diffusion through the lattice for a range of temperatures and defect concentrations for 5 ns. In defect free PuO<sub>2</sub>, He exhibits limited diffusive behaviour until the temperature exceeds 1500 K. However, when vacancies are present within the lattice, the He diffusion energy barrier is significantly reduced and He atoms exhibit diffusive behaviour at lower temperatures. Therefore, whilst the storage of PuO<sub>2</sub> will be at temperatures below 1500 K, due to the presence of defects within the lattice helium may be mobile during storage. The main He diffusion mechanism proposed is oxygen vacancy assisted inter-site hops with helium and oxygen having comparable diffusion rates.

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## **ABSTRACT 65**

### **DETERMINATION OF PLUTONIUM ISOTOPES IN RADIOACTIVE WASTE CONTAMINATED WITH URANIUM AND THORIUM**

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The waste characterization carried out by Nucleco SpA includes a large variety of radionuclides belonging to the gamma, beta and alpha emitter families. The determination of Uranium and Plutonium isotopes plays a key role in the waste characterization.

Nucleco SpA has distinguished itself in characterizations of radioactive waste in complex and nuclear plant matrices. These matrices have large amounts of alpha emitters, in particular isotopes of Uranium, Thorium and Plutonium. A significant presence of U-238 results in such a large amount of Th-234 (and daughters) that interferes with the determination of Pu-241. Hence, the need of finding a pre-treatment, extraction and subsequent purification technique that would allow Th-234 to be detached and thus Pu-241 to be determined in complex high-activity matrices.

The above elements are extracted using chromatography columns. An isotope of the element to be analysed, with known activity, is added at the beginning of the process to determine the extraction yield. Before being eluted into the column, the sample undergoes a series of treatments in order to be purified of any interferents. The method developed by Nucleco involves the oxidation of Pu at valence +6 and the subsequent precipitation, in fluorides form, of the elements with valence +4 and +3 (i.e. Th-234).

Pu-241 is then measured by LSC, while the other isotopes are measured by alpha spectrometry after electrodeposition on a metal plate.



## **ABSTRACT 66**

### **LOW LEVEL MULTI ION COUNTING FOR URANIUM ON NuTIMS FROM Nu-INSTRUMENTS**

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Low level signals and low abundance isotopes may benefit from the detector configurations possible on the NuTIMS instrument. Thanks to its different detector configurations the NuTIMS from Nu Instruments presents clear advantages when measuring low level signals and low abundance isotopes. The mass spectrometer utilizes a zoom lens system, allowing the detector to be equipped with multiple full size ion counters ideal for extremely low signal measurements. In this work we present some low level (1cps or less) data run in both static and dynamic routines, showing the possibility for low sample sizes or extremely low abundance <sup>236</sup> measurements.

## **ABSTRACT 67**

### **MULTISTATIC NEGATIVE ION MEASUREMENTS INSTRUMENTS**

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The Nu TIMS instrument allows ultimate peak alignment of all isotopes thanks to its unique Zoom Lens system. With 16 faradays present multistatic routines can be used to collect all isotopes on each magnet position. The collection of all isotopes on each measurement line allows for a reduced error when measuring small signals for online oxide corrections. Here we present some high precision data for (Mo, W) using negative ions in MultiStatic routines.

## **ABSTRACT 68**

### **DETERMINATION OF EDTA IN LOW LEVEL WASTE TRENCH LEACHATE MATRIXES BY ION-PAIRING REVERSE PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (IP-RP-HPLC)**

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The aminopolycarboxylic acid (APCA), ethylenediaminetetraacetic acid (EDTA) is commonly used throughout the nuclear industry in processes such as decommissioning, as a decontamination agent. EDTA poses risks to the environment and health through the residuals of decontamination processes ending up in waste streams which can lead to mobilisation of radionuclides due to its chelating properties. Levels of EDTA within waste transported to repositories are subject to acceptance limits and therefore require to be determined and monitored. Metal-EDTA complex formation has been widely used for the measurement of EDTA by HPLC with UV detection.

Iron(III)-EDTA and Co(III)-EDTA were selected as the measurement species due to iron's high abundance in nature and its high stability constant. Co(III)-EDTA must be measured as it cannot be readily dissociated and converted to Fe(III)-EDTA due to its higher stability constant. Full chromatographic separation of the metal EDTA complexes was achieved through the use of tandem RP column application and without the requirement of significant expenditure on specialist deconvolution software as previously reported in literature.

Trench leachate samples from a licensed nuclear waste facility were analysed within development stages and highlighted sample matrix interference issues, ICP-MS analysis of the sample matrix showed presence in varying amounts of alkaline earth and transition metals, predominantly calcium and magnesium, previously shown in recorded methods to have interfering effects. Further development showed the use of sodium form cation exchange filters within sample preparative steps greatly reduced matrix interferences and increased recovery of EDTA in target complex form. This method has been demonstrated to be suitable for characterising levels of EDTA in low level waste leachate matrixes, and therefore increasing knowledge of the potential for radionuclide mobilisation within waste repositories.

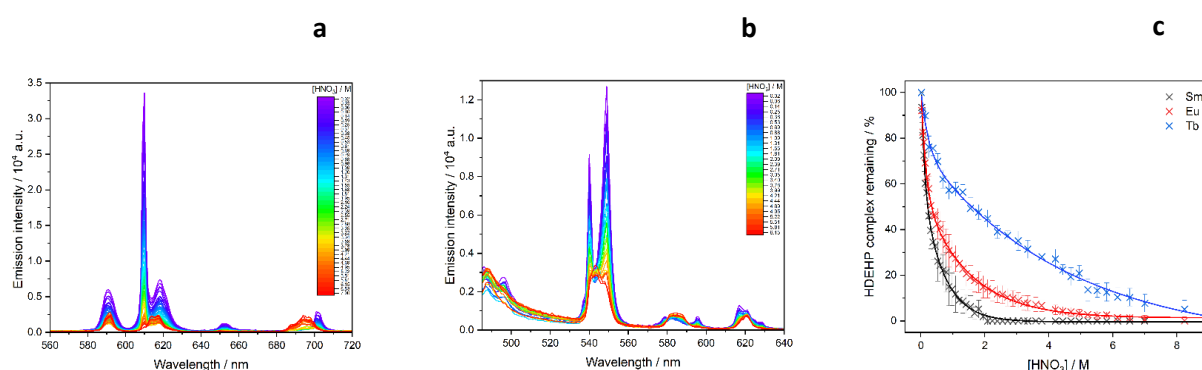
## IMPROVED QUANTIFICATION OF F-ELEMENT FISSION PRODUCTS.

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Isotopes of rare earth elements (lanthanides and yttrium) are products from the fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ , making them important in the characterisation of nuclear wastes.<sup>1</sup> While some isotopes can be quantified directly through gamma spectroscopy, other isotopes such as  $^{151}\text{Sm}$  and  $^{161}\text{Tb}$  must be separated before detection.<sup>2</sup> Chemical separation of the lanthanides has in the past been performed using ion exchange chromatography with 2-hydroxybutyric acid as an eluent. Insufficient separation of  $^{161}\text{Tb}$  has led to interest in the use of the commercial TrisKem Lanthanide (LN) resin (di-(2-ethylhexyl) phosphoric acid (HDEHP) on a polymer support) as an alternative separation system. Although improved resolution and separation time can be obtained, in complex radiochemical samples co-elution of the lighter lanthanides (Sm and Eu) occurs when Tb and Y are present. It is thought that this is an effect of complex solution speciation which must be characterised in order to explain the separation behaviour.

We have therefore been investigating the solution complexation behaviour of HDEHP with the trivalent lanthanides. Initial investigations using emission spectroscopy have shown a change in the splitting of the lanthanide f-f transitions when HDEHP is added in solution and that stoichiometry is unaffected by HDEHP ligand concentration. Nitric acid concentration affects lanthanide speciation (Figure 1).



**Figure 1.** Luminescence emission spectra of (a)  $\text{Eu}^{\text{III}}(\text{H}(\text{DEHP})_2)_3$ , (b)  $\text{Tb}^{\text{III}}(\text{H}(\text{DEHP})_2)_3$  with 0.01 – 7.00M nitric acid at a dodecane: water interface. (c) Percentage of Eu(III), Tb(III) and Sm(III) complexed at a given nitric acid concentration.

The percentage lanthanide complexed with HDEHP was quantified from changes in peak height or area; the calculated elution behaviour closely matched experimental elution behaviour for each lanthanide. The elution behaviour of mixed lanthanide solutions will be compared using luminescence and speciation changes validated by  $^{31}\text{P}$  NMR spectroscopy.

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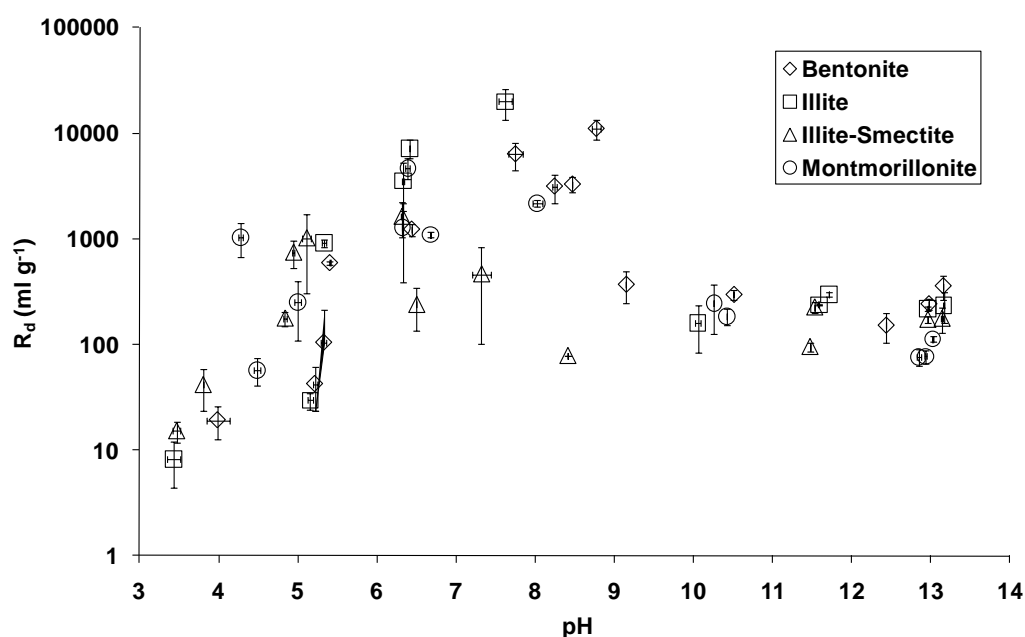
# THE SORPTION OF TECHNETIUM (IV) TO SOME CLAY MINERALS WITH REFERENCE TO RADIOACTIVE WASTE DISPOSAL

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Technetium-99 (Tc-99) is one of the most important isotopes likely to be disposed of in the proposed UK Geological Disposal Facility for higher-activity radioactive wastes, due to its long half-life, high fission yield and ability to migrate through the geosphere as the pertechnetate ion. However, much of the technetium is likely to be in the lower oxidation state of Tc(IV) due to the low Eh in the near field. Batch sorption experiments across the pH range have been performed on Tc(IV) using Tc-95m as a spike in the presence of some representative clay minerals (bentonite, smectite, kaolininte, montmorillonite and illite). Tc(IV) solutions were used at trace concentrations to avoid precipitation as technetium dioxide. Values for the partition coefficient ( $R_d$ ) were found to range from 7 to  $2 \times 10^5$  mL  $g^{-1}$ .  $R_d$  was heavily dependent on pH in all cases, with the highest values being found in the circumneutral area. These data will inform the performance assessment for the behaviour of technetium in the near-field of the UK's planned higher-activity wastes GDF. Surface complexation modelling of the data has been performed.



**Figure 1.**  $R_d$  as a function of pH for Tc(IV) sorption to 4 sample clays.

## ABSTRACT 71

### DEVELOPMENT OF A SIMPLE AND FAST COMBINATION METHOD FOR THE DETERMINATION OF STRONTIUM-90, AMERICIUM-241, AND PLUTONIUM ISOTOPES IN ENVIRONMENTAL SAMPLES

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For laboratories in the scope of environmental radioactivity monitoring with high sample volume, it is important to have a quick and robust radiochemical method for routine measurements. This method should consist of as few steps as necessary and still provide accurate results. Additionally the radiochemical separation should be simple in order to minimize sources of error.

According to this, the aim of this project was to develop a simple method for the determination of  $^{90}\text{Sr}$ ,  $^{241}\text{Am}$  and Pu-isotopes for environmental samples like soil and vegetation. As in Austria the content of thorium in soil samples is quite high, it was also important to handle thorium-related interferences. The method used so far based on the consecutive separation with an ion-exchanger (DOWEX 1 x 8) followed by extraction chromatography (Sr-Resin by Eichrom®). Recently the separation of Th and its daughters was not sufficient. Therefore, we developed a method that fitted our requirements.

Nowadays the usage of extraction chromatographic resins for radiochemical separation is state-of-the-art. Based on Horwitz<sup>1</sup> we chose a combined approach using Sr, DGA and TEVA® Resins by Eichrom®. After the first separation step, we obtained the element pure fractions of Pu and Sr. Whereas the Am fraction needed another purification step using DGA and TEVA® Resin filled cartridges and the vacuum box system by Eichrom®. In the end, the Pu- and Am- isotopes were measured via alpha spectroscopy. Whereas the activity concentration of  $^{90}\text{Sr}$  was determined via LSC. The chemical recovery of the analytes was monitored by using  $^{236}\text{Pu}$  and  $^{243}\text{Am}$  as tracers for the alpha emitting nuclides. Additionally natural  $^{86/88}\text{Sr}$  was added to the samples and measured via ICP-MS just before the LSC-measurement.

In order to verify the accuracy of the method's results we analysed spiked samples during an internal laboratory exercise ( $^{241}\text{Am}$ ,  $^{239}\text{Pu}$  and  $^{90}\text{Sr}$ ) and participated in intercomparison exercises (for  $^{239}\text{Pu}$ ). Altogether high chemical yields and good accordance to internal and external reference values were achieved. Furthermore, using this method we managed to generate Th-free Pu alpha spectra. Hence, the presented method is suitable for various environmental sample types like soil, vegetation, vegetables or sediments. This method will be presented as a poster at ERA14.

#### References

1 Horwitz, et al, "A Novel Strontium-Selective Extraction Chromatographic Resin", Solvent Extraction and Ion Exchange, 1991, 10, 313-336

**FORMATION OF ALKALINE EARTH/URANIUM/CARBONATE COMPLEXES.  
THERMODYNAMIC DATA AND THEIR INFLUENCE ON URANIUM  
SPECIATION AND SOLUBILITY IN GEOCHEMICAL ENVIRONMENTS**

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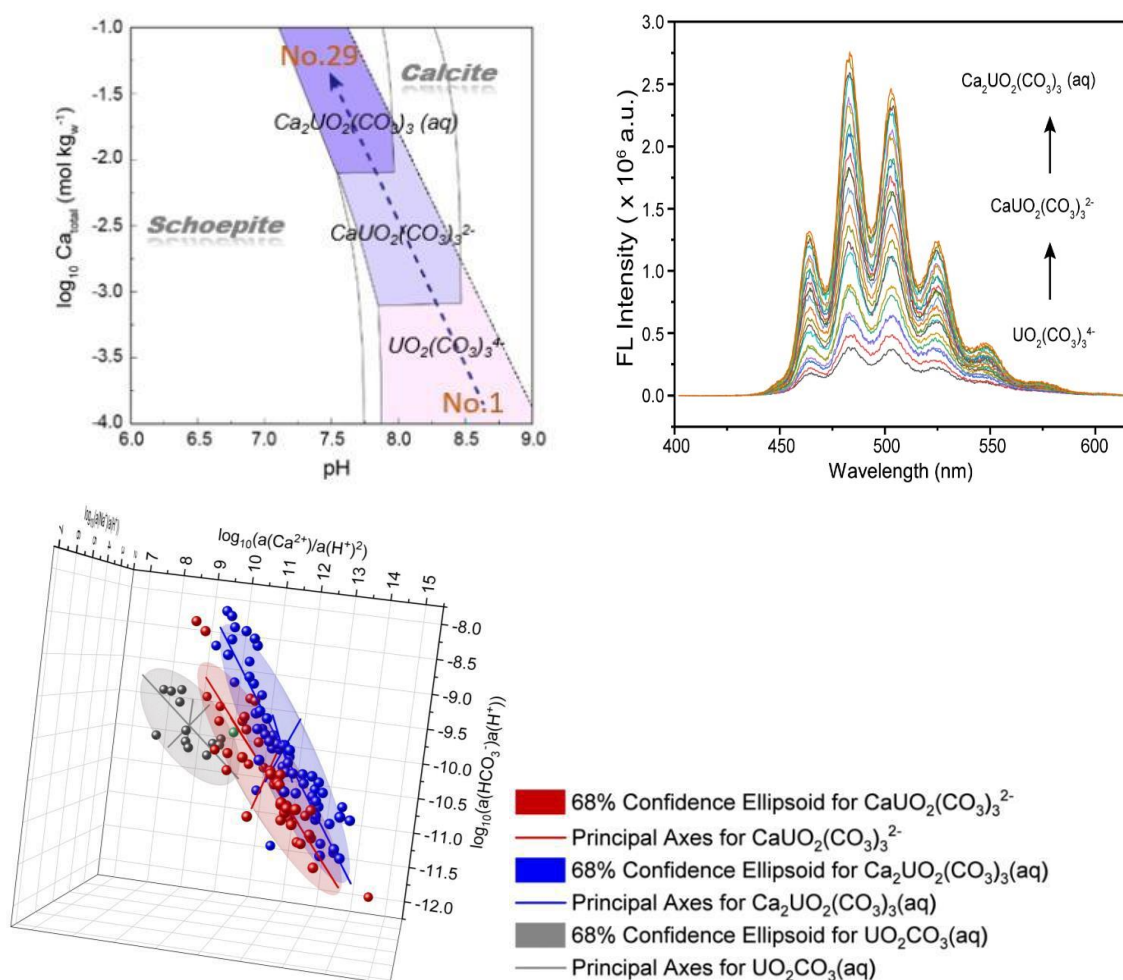
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The formation of carbonato complexes of uranyl (VI) is of great importance for the understanding of the chemistry and transport of uranium. The ternary alkaline-earth triscarbonato-uranyl complexes,  $(\text{Mg/Ca})_n[\text{UO}_2(\text{CO}_3)_3]_{(4-2n)}^-$  ( $\text{M} = \text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ), evidenced in the late 1990's, can control the uranium chemistry and its solubility and adsorption properties in various environments, including deep geological disposal, surface waters, and seawater. However, thermodynamic data for these ternary complexes are still a matter of debate. In addition of alkaline-earths, the influence of alkaline cations is not clearly settled between the ionic strength effect and the influence on the structure of complexes. The aim of this research is to clarify the existence domains of  $(\text{Mg/Ca})_n[\text{UO}_2(\text{CO}_3)_3]_{(4-2n)}^-$  complexes as a function of ionic strength by studying the additional influence of alkali ions. Time-resolved laser spectrofluorimetry (TRLFS), a highly sensitive technique to probe the characteristic features of uranium species, was chosen as the analytical technique. The quantification of  $(\text{Mg/Ca})_n[\text{UO}_2(\text{CO}_3)_3]_{(4-2n)}^-$  complexes from luminescence measurements was done for laboratory analysis. The presence of the studied complexes in the synthetic samples can be verified by their characteristic bands and decay times.

In this work, the thermodynamic data with respect to temperature and ionic strength for the  $(\text{Mg/Ca})_n\text{UO}_2(\text{CO}_3)_3$  complexes in NaCl et NaClO<sub>4</sub> media are very useful for estimating the effects of temperature and salinity on the speciation of U(VI), especially in nuclear waste repositories, and for filling in the gaps in the thermodynamic database for these complexes. We also examined the main species in the natural water compositions linked to radioactive waste management (RWM), uranium mining activity, and of other more general interest related to natural uranium with the newly determined thermodynamic data for  $(\text{Mg/Ca})_n[\text{UO}_2(\text{CO}_3)_3]_{(4-2n)}^-$  complexes. Based on the repartition of major uranium species obtained in the speciation calculations for the selected water compositions, three ellipsoidal predominance regions of  $(\text{Ca})_n\text{UO}_2(\text{CO}_3)_3$  complexes were constructed from the sample point-clouds in  $\log_{10}(\text{a}(\text{Ca}^{2+})/\text{a}(\text{H}^+)^2) - \log_{10}(\text{a}(\text{Na}^+)/\text{a}(\text{H}^+)) - \log_{10}(\text{a}(\text{HCO}_3^-)/\text{a}(\text{H}^+))$  three-dimension space. The determination of ellipsoids for  $(\text{Ca})_n\text{UO}_2(\text{CO}_3)_3$  complexes allows a quick identification of the major (calcium) uranyl carbonate species for a given natural water sample once its chemical composition is available. Thermodynamic calculations and TRLFS analyses were performed for two water samples collected from the Lodève site. The calculated dominant species

corroborates well the experimental observations in terms of important luminescence characteristics: band positions and decay time. The measured luminescent properties for  $(\text{Mg/Ca})_n[\text{UO}_2(\text{CO}_3)_3]^{(4-2n)-}$  complexes under different conditions type of electrolyte, ionic strength, and temperature detailed in preceding paragraphs and partly verified by the in-situ samples, surely enrich the reference catalogue of Mg/Ca- $\text{UO}_2\text{-CO}_3$  luminescence spectral fingerprints.





## **ABSTRACT 73**

### **PCM RE-CHARACTERISATION PROJECT**

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This poster presents an overview of the Plutonium Contaminated Material (PCM) Re-Characterisation Project, whereby a new method for re-characterising drummed waste using the Antech Universal Drum Assay Sort and Segregation System (UDASS) has been deployed on the Low Level Waste Repository (LLWR) Site to assess drummed waste previously characterised as PCM. The project has yielded a >99% conversion rate from PCM to Low Level Waste (LLW), with the majority of the waste being reclassified as Low-Activity Low Level Waste (LA-LLW) and Very Low Level Waste (VLLW) resulting in cost savings in excess of £9 million (through cost avoidance of consigning the waste to the Engineered Drum Store (EDS) pending disposal in the Geological Disposal Facility (GDF)).

This continuous improvement project, led by Nuclear Waste Services, NSG Environmental and Antech, has been recognised as a “beacon” project by the Nuclear Decommissioning Authority (NDA) and has been presented at the Asset Management Summit as well as achieving the Value for Money award at the NDA Group Employee Awards (2022).

## ABSTRACT 74

### MICROSCALE LOCALISATION OF RADIO-CAESIUM IN LICHEN THALLI

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Lichens are well known for their ability to accumulate radiocaesium discharged into atmosphere in the thallus via wet and dry deposition over long periods of time. Therefore, lichens are often used as biomonitors for radiocaesium contamination levels [1]. However, the exact location and chemical form of radiocaesium (ionic and/or particulate) in the thalli of lichen, are still unknown. By combining autoradiography, electron microscopy and quantum chemical calculation, we demonstrate the microscale localisation of radiocaesium within lichen thallus tissues.

Two samples of radiocaesium contaminated lichen, *Parmotrema tinctorum*, were used in this study. The samples were collected within Okuma town (between 1 and 4 km from the FDNPP) two and six years after the accident [2-3]. Both samples had similar <sup>137</sup>Cs activity concentrations (ca. 1130 Bq g<sup>-1</sup>) and were taken from the same substrate (the trunk of *Cerasus* sp.). An initial screening analysis was performed by autoradiography to distinguish any radiocaesium distribution patterns, e.g. broad distribution or spot distribution. This was because previous studies [4-5] had shown that radiocaesium uptake in ionic form can exhibit broad distribution patterns, whilst deposition of radiocaesium in particulate form, can present as spot distributions. Samples containing each type of distribution pattern were fragmented into smaller pieces, before tissue fixation and resin embedding were performed. The sample fragments were then sliced into 5 µm-thick sections, after which autoradiogram images were obtained. The detailed location of radiocaesium distribution in the samples was determined using a digital microscope and on samples where a spot distribution was observed, an electron microscope was used.

In the samples exhibiting a broad distribution, the radiocaesium was found to be concentrated in brown pigmented parts of the lower cortex tissues and this was the case for both samples (collected two and six years after the accident). These brown pigments are known to be “melanin-like substances”. By using the same methodology as used in a previous study [6], quantum chemical calculations showed that Cs<sup>+</sup> ions can chelate functional group present within melanin. These findings suggest that radiocaesium ions may be stably retained in melanin-like substances for at least six years after the

FDNPP accident. In the samples exhibiting a spot distribution, radiocaesium containing particles were observed (using electron microscopy and autoradiography) on/in the lichen upper cortex and also around the medullary layer. In addition, electron microscopy showed the presence of other micron-sized particles on thallus surface tissues, similar in size to those of the radiocaesium containing particles. These results suggest that radiocaesium particles deposited on thallus surface tissues were retained by development of the adhesive layer in the upper cortex, and not just by physical retention in either the upper cortex or the medullary layers.

In this study, microscale localisation of particulate and ionic radiocaesium within lichen thallus tissues was determined. Our novel approach presented here is expected to contribute to future studies on the mechanisms radiocaesium accumulation in other biological organisms such as wild vegetables and mushrooms.

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## ABSTRACT 75

### CHARACTERIZATION OF NEW CROWN-ETHER CONTAINING TK102 RESIN FOR THE SEPARATION OF STRONTIUM, LEAD AND BARIUM/RADIUM

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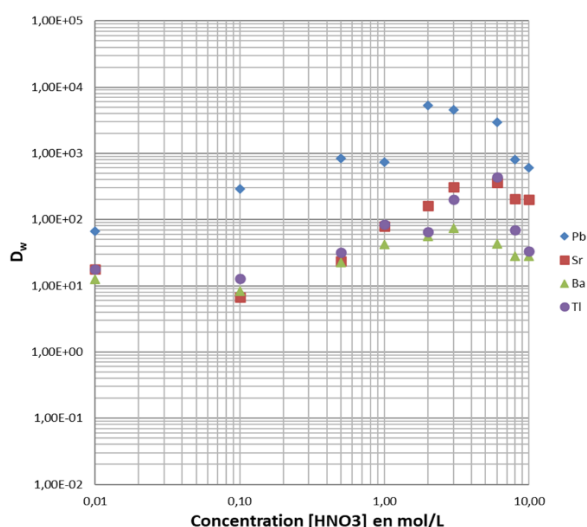
Rapid and accurate low-level measurement of <sup>90</sup>Sr, <sup>210</sup>Pb and <sup>226</sup>Ra activities in environmental, decommissioning and waste samples remain a challenge for analytical laboratories, accordingly there is elevated interest in improving separation materials and methods. The purpose of this work is to characterize a new extraction-chromatographic resin based on 4,4'(5')-di-t-butylcyclohexano-18-crown-6 dissolved in a fluorinated alcohol (TK102 Resin) with respect to its selectivity and capacity, and to evaluate its suitability in this context.

Weight distribution ratios (DW values) of a range of elements on TK102 Resin were determined experimentally using multicomponent solutions of varying HNO<sub>3</sub> and HCl concentrations. The influence of increasing amounts of Ca, Na and K on Sr retention from 3M HNO<sub>3</sub> was also determined. Based on the obtained DW values several elution studies were performed with the aim of evaluating the separation performance of the TK102 Resin. Further the capacity of the sorbent for selected elements has been determined.

Most of the studied elements (e.g. transition metals, lanthanides, and selected actinides) are not retained on TK102 Resin from HNO<sub>3</sub>, highest distribution coefficients were observed for Sr, Pb and Tl. The DW values showed a maximum at 2M HNO<sub>3</sub> for Pb, and 6M for Sr and Tl. The maximum values of the distribution coefficients of Pb are an order of magnitude higher than those of Sr. It is worth noting that TK102 shows distribution coefficients for Sr that are up to 50% higher than for SR Resin, making it potentially interesting for the analysis of samples with more complex matrix. While Ba retention was distinctively lower than for Pb or Sr, it was still sufficiently high to be of interest for considering its use for the separation of Ba from Ra, a very important step e.g. before Ra measurement by ICP-MS and the preparation of sources for alpha-spectrometry.

In HCl solutions, Pb showed high retention at concentrations between 0.5M HCl and 2M HCl. At higher HCl concentrations its retention decreases, similar to the SR Resin, which should allow for its elution with HCl of high concentrations. At high HCl concentrations mainly elements forming anionic species with HCl, such as Tl, Sb, Sn, Ga, Nb, Mo and U are well retained.

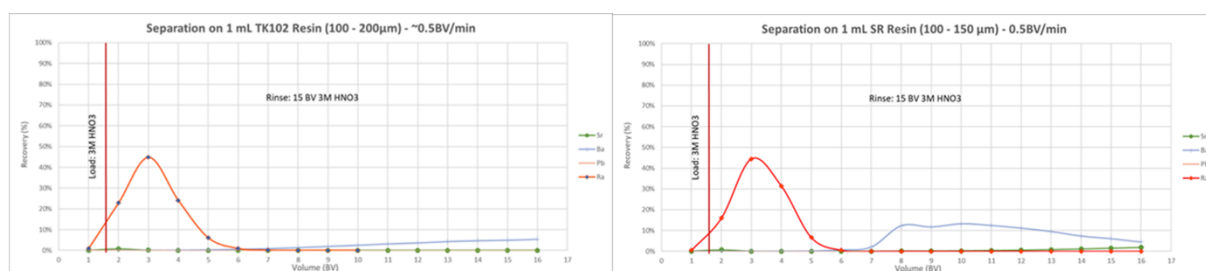
The value of the total dynamic capacity for Sr and Pb on TK102 Resin is near 90% of maximum theoretical for Sr (45.5 mg/g) and Pb (106.9 mg/g), total capacity for Ba is much lower than theoretical, near 30%.



**Figure 4:** DW values for selected elements on TK102 in HNO<sub>3</sub>

Elution studies were performed for separation of Sr, and of Pb, from multi-element mixture using columns and gravimetric flow. As expected, from 2M HCl most of the studied elements (including Sr, actinides, lanthanides, etc) were not retained by the TK102 Resin, only Sn, Tl and Pb are strongly sorbed from 2M HCl. Sn and Tl could be removed with dilute HNO<sub>3</sub>, allowing for recovering a clean Pb fraction with dilute ammonium citrate. Sr and Pb were well retained from 3M HNO<sub>3</sub>. Like for the SR Resin other elements (incl. Ba) could be eluted from the column using 3M HNO<sub>3</sub>/0.05M oxalic and 8M HNO<sub>3</sub>. Sr was then eluted using dilute HNO<sub>3</sub>, while Pb remains retained under these conditions.

In additional elution studies the Ba and Ra retention of TK102 and SR Resins was compared. It could be shown that TK102 Resin retains Ba stronger than SR Resin, while letting Ra pass equally fast, making it very interesting for Ra/Ba separation.



**Figure 5:** Ra / Ba elution studies. Load and rinse 3M HNO<sub>3</sub>. Left: TK102 Resin. Right: SR Resin

The new TK102 Resin shows promise for use in the radioanalytical determination of <sup>90</sup>Sr, <sup>210</sup>Pb and other radionuclides such as <sup>226</sup>Ra in environmental, decommissioning and waste samples. It has up to near 50% higher Sr distribution coefficients than SR Resin in HNO<sub>3</sub>, and high dynamic capacity for stable Sr (>40 mg·g<sup>-1</sup>) and Pb (>90 mg·g<sup>-1</sup>). It further allows improved Ba removal from Ra.

**STRONTIUM BEHAVIOUR IN RADIOACTIVELY CONTAMINATED LAND  
UNDERPINNING OPTIONS FOR IN-SITU DISPOSAL**

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Decommissioning and site clearance activities at nuclear sites are expected to produce large volumes of lightly radioactively contaminated concrete and rubble from building demolition that will require management. Disposal of these wastes on site ‘in-situ disposal’ is a potentially new approach which offers the potential for reduced disposal and transport costs while also optimising inventory at existing disposal sites. The safety case for in-situ disposal is currently being developed and will be underpinned by further understanding of the speciation and mobility of radionuclide contaminants in the environment around these structures.

Sediment and concrete relevant to potential disposal scenarios at the Sellafield Nuclear licensed site have been sampled for use in sorption studies and analysed by a range of x-ray, solid phase and wet chemistry techniques. The sediment was found to contain mostly quartz and a small amount of non-swelling clays and goethite, which have previously been identified as potential sinks for radionuclides. Crushed concrete contained portlandite whereas the surface of the original concrete blocks showed significant carbonation had occurred during storage. Initial batch sorption experiments found that strontium sorption to the sediment fit to a Langmuir model, suggesting that sorption is occurring at energetically equivalent sites on the sediment. This data will inform future work investigating the fate of strontium and other radionuclides in the environment around buried concrete structures.

## **ABSTRACT 77**

### **THE USE OF FIDLER PROBES FOR SAMPLE SCREENING**

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Analytical Services at Sellafield analyse Plutonium Dioxide product for a number of species. Whilst some analysis is performed on powder or dissolved material it is safe to analyse very highly diluted material in fumehoods. This does leave a residual risk; the dilution may not have been performed correctly or a “high” sample is mis-labelled and sent to a fumehood for analysis.

The FIDLER (Field Instrument for the Detection of Low Energy Radiation) probe used was sourced from Pycko Scientific and is a thin Sodium Iodide detector (5.0"x 0.063" NaI(Tl) mounted on a quartz light pipe) designed to enable high efficiency measurement of low energy gammas, with reduced interference and Compton Scatter from higher energy emitters such as Cs-137. The detector is specifically tuned for Am-241 and the challenge was to determine the ability of the detector to distinguish between samples bound for fumehood work, i.e. low alpha active, and those bound for glovebox work i.e. high alpha active. The detector should be operable by individuals with no knowledge of gamma spectrometry.

The challenge is complicated by the fact that the samples are dispensed in a number of different bottle shapes and sizes. The sample volumes and dilutions themselves are variable and the positioning of bottles and the amount of PVC shielding is also variable.

Early work determined a threshold limit and this was validated by sample trials. On each occasion the FIDLER probe successfully discriminated between glovebox and fumehood samples. It was demonstrated that the detector efficiency for Am-241 was 10X higher than the efficiency for Cs-137.

Future work will consider refinements to the process and whether or not the detector can be used to identify rogue alpha activity in all samples, i.e. include samples with other significant gamma emitters present. This will likely necessitate the use of a CZT or other gamma detector to help understand Cs-137 impact.

## ABSTRACT 78

### THE USE OF THERMO GRAVIMETRIC ANALYSIS MASS SPECTROMETRY (TGA-MS) FOR NUCLEAR ANALYSIS

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Analytical Services at Sellafield analyse Plutonium Dioxide powder for impurities as part of its commitment to meet customer product specifications. The analysis involves volatilisation and measurement of evolved gases. Whilst this analysis has been successfully carried out for many years it does involve a number of bespoke techniques. Going forward, Sellafield Limited is looking to deliver this requirement more efficiently.

Thermo Gravimetric Analysis – Mass Spectrometry (TGA-MS) has the potential to deliver the optimal solution whereby the four key requirements (Loss on Heat, moisture, chloride and carbon) are analysed in a single protocol without the use of oxygen. This is safer than techniques requiring oxygen and also far cheaper in terms of capital and operational costs. Direct analysis of evolved gases also produces virtually no waste products.

For TGA-MS to deliver this analysis a protocol and temperature profile must be developed that delivers sharp discrete mass spectrometry peaks for species identification. The quantitative element of the analysis is determined in the TGA. Development work is ongoing with NNL. The preferred carrier gas is argon/CO<sub>2</sub>. The CO<sub>2</sub> is reduced by carbon in the sample to produce CO which is measurable by Mass Spectrometry and proportionate to carbon in the sample. This is the Boudouard reaction.



It is possible that we may need to employ more than one protocol to deliver this work scope. There are also opportunities to expand the scope to different matrices and analytes, such as volatile radionuclide species. This technology is flexible and could be used on environmental or Highly Active samples, whilst sensor detection technology could be used instead of, or in series with Mass Spectrometry.



## ABSTRACT 79

### AUTOMATED RADIOCHEMICAL SEPARATIONS USING A NIV SEPARATOR

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Analytical Services at Sellafield Limited currently analyse 20-40 samples per week for Sr-90. The current separation method takes a day to prepare a 22 sample batch and the counting protocol takes 3 days. However, a customer requires shorter turnaround for Sr-90 so these samples will be analysed daily rather than weekly. Utilising the current approach would be very inefficient as small batches take almost as long to prepare as large ones.

NNL and Microlab Devices Limited Sellafield have jointly designed and built the NiV Separation System. This instrument performs automatic radiometric separations to isolate specific radionuclides from the species interfering with detection and measurement. The instrument fits into a standard fumehood and replaces current wet chemistry and manually performed ion exchange separation techniques. The chemistry is performed within a disposable cartridge with up to 4 separations per cartridge.

A single system can perform numerous types of radiochemical separations dependent on the software and the cartridge used. Sellafield have received 2 NiV separator with cartridges for Sr-90 separations. Four separations can be performed in two hours with minimal operator input. This is ideal for short turnaround work. There are plans for the same instruments to perform Pu separations also. This technology is also baseline for the Replacement Analytical Project in the re-fitted NNL analytical facility where the Niv's flexibility is highly prized. Sellafield Limited and NNL have confidence that this instrument will offer a number of advantages over the current manual separation techniques:

- Reduced liquid and solid waste
- Reduced chemical handling and hazard
- Reduced radiation dose to operators
- Significant reduction in operational time
- Reduce scope for human error and inter-operator variability leading to improved analytical reproducibility
- Reduced training requirements; very simple interface
- Reduced infrastructure and footprint requirements (one instrument in a single enclosure can be used for multiple separation protocols e.g. Sr, Pu, Am/Cm etc.)
- Two cartridge system fits into a standard fumehood enclosure
- Efficient small batch analysis
- Chemistry is performed within cartridges so there is minimal cross contamination potential
- Significant capital and operational cost savings

Potential to use in-situ if detection techniques are available

## **ABSTRACT 80**

### **AUGMENTED COOPERATION IN EDUCATION AND TRAINING IN NUCLEAR AND RADIOCHEMISTRY**

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Expertise in nuclear and radiochemistry (NRC) is of strategic relevance to the whole nuclear energy sector, and in parallel it ranges from life sciences, e.g., nuclear medicine and radiology - through dating in geology and archaeology to (nuclear) forensics and safeguards, radiation protection, and radioecology. The A-CINCH project primarily addresses the young generation's loss of interest for nuclear knowledge by focusing on secondary education, using a "Learn through Play" concept to engage with students and teachers.

The overall objective of the project is to set up the CINCH Hub platform. The platform incorporates all previous CINCH results and completes it with newly developed courses and tools. It also implements a highly innovative Virtual Laboratory and wraps it all up into a user-friendly and easy-to-navigate single page interface. Utilising a well balanced mix of e-learning and traditional teaching methods in nuclear and radiochemistry education aims to increase the number of students and trainees in the field. To address the new target groups directly and efficiently attract the attention of secondary school students, new didactical tools, suitable for today's youth, are used.

The project receives funding from the EURATOM Research and Training programme under grant agreement N° 945301.

**CHARACTERISATION OF SKIPS FROM THE PILE FUEL STORAGE POND  
USING DESTRUCTIVE AND NON-DESTRUCTIVE ANALYSIS**

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The Pile Fuel Storage Pond (PFSP) was constructed in the 1950's and became operational in the early 1960's. PFSP is a vast re-enforced concrete structure ca, 106m x 24m x 5.5m deep, with twelve adjoining concrete withdrawal bays.

PFSP's primary function was to store, cool and decan irradiated fuel from the two Windscale pile reactors. Transfer of fuel from the pile reactors to the pond was via underwater ducts using open top skips. The plant remained operational until the shutdown of the pile reactors; decanning operations ceased in the early 1970's. The decision to decommission the facility was made in the early 1980's with a programme of works to remove pond inventory prior to it being dewatered as a precursor to final demolition.

In total there was approximately 200 PFSP skips identified for retrieval and disposal via an appropriate Best Available Technique (BAT) routing option. The PFSP skips are constructed from an open top Alclad (aluminium alloy) box held within a mild steel frame. This box itself is approximately 2.1 meters long by 1.8 meters wide by 1.5 metres high. The mild steel frame is approximately 2.4 meters long by 2.1 meters wide by 1.6 meters high.

The baseline routing option for the PFSP skips was Low Level Waste, and a characterisation plan was developed to underpin and enact a disposal route.

The onsite characterisation team derived a characterisation plan following a Data Quality Objective process. A data acquisition strategy was identified, and a targeted destructive sampling and analytical programme of work was established to confirm:

- The radiological fingerprint of the metallic substrate for both the Alclad box and mild steel frame.
- If the pond skips were activated.
- Determine the potential for decontamination for both the steel and aluminum material.
- Estimate the average activity associated with a retrieved pond skip to underpin the baseline routing option.
- Information to justify or discount the use of the existing contamination radiological fingerprint derived for the facility for an alternative substrate.

The targeted sample approach included taking metal coupons of the Alclad box and mild steel frame. Coupon sizes were dictated to enable the required analysis to be performed. The analytical programme included analysis on leachate and the coupon by pyrolysis.

The analysis regime comprised of:

- HRGS on both faces of the coupons as-received.
- Leaching of the coupons and repeat HRGS on both faces of the coupons.

Leachate analysed for: Gross alpha and beta activity, HRGS, Am-241, Cm-252, Cm-243/244, Np-237, Pu-238, Pu-239, Pu-240, Pu-242, Ra-226, Th-228, Th-229, Th-232, Th-234, U-232, U-233, U-235, U-238, Fe-55, Ni-63, Pm-147, Pu-241, Sm-151, Sr-90, Tc-99).

- C-14 and H-3 analysis by pyrolysis.
- Full dissolution of the coupon.

Digest analysed for: Gross alpha and beta activity, HRGS, Fe-55, Ni-63, Pm-147, Sm-151.

Data showed that

- The radiological fingerprint for both the metallic substrates were comparable with existing contamination fingerprint derived for the facility, further substantiating the PFSP radiological fingerprint.
- The pond skips were not activated, with contamination being predominantly Cs-137 and Sr-90.
- Targeted decontamination for both the steel and aluminum material is plausible however, further consideration would be needed to implement such a process on site.
- The average activity associated with a retrieved pond skip was shown to meet the Low Level Waste Criteria therefore underpinning the baseline routing option.

The characterisation activity has enabled a radioactive metals recycling route to be initiated.

Since the development of the radiological fingerprint there has been an opportunity to gather further data to substantiate the PFSP radiological fingerprint. During the skip retrieval process, non-destructive analysis and testing was implemented. This characterisation approach was adopted to ensure the retrieval delivery schedule could be maintained in line with the programme.

With the assistance of the sites radiometric group and supply chain, In-Situ Object Counting System (ISOCS) using a HRGS detector established the key gamma radionuclides associated with the skips. The ratios of detectable gammas were used as a comparison data set for the PFSP radiological fingerprint PFSP. The non-destructive analysis showed good agreement, demonstrating the original sampling campaign was fit for purpose and valid for solid waste sentencing from PFSP.

This project demonstrates that both characterisation approaches have a place in the characterisation tool bank. To enact a sound radiological fingerprint, a degree of destructive analysis is required to meet the characterisation objectives where no other information can be obtained. Non-destructive analysis is a reasonable tool to deploy in field to provide re-assurance that the radiological fingerprint is fit for purpose. Its role in waste sentencing can only be enacted with a sound radiological fingerprint.

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### CHARACTERISATION OF FILTER BED MATERIAL FROM THE FLOC STORAGE TANKS.

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The historical function of the Floc Storage Tanks (FST) facility, which was constructed in the 1950's, was to provide settling and storage of alumino-ferric flocs produced from the treatment of liquid effluents arising from reprocessing operations. The facility contains ten fully enclosed cylindrical concrete tanks comprising of: seven Primary Sludge (PS) tanks, two sea tanks (ST) and one buffer tank. The tanks are 15m in diameter and 10m tall. They have a filter bed made up from sand and gravel which was used to provide filtration of the effluent and floc. The tanks are currently undergoing floc retrievals with the floc/supernatant being transferred to the Enhanced Actinide Removal Plant (EARP) for processing.

The baseline disposal option for the filter bed material from these tanks is Intermediate Level Waste (ILW). Characterisation of the filter bed material was/is required to underpin decommissioning strategies and waste disposal options, including information to build a Local Encapsulation Plant (LEP).

A Data Quality Objectives study was carried out with sampling and appropriate analysis required to provide:

- the radiological classification of the filter bed material
- information on the effects of washing the material in water, weak acid and strong acid
- an estimate of the different size ranges of material

Several challenges exist for this project which include:

- Access to the tank from the operations floor which is 14m above the filter bed
- Access is only available to directly below the pump access port
- The settled/remaining floc on top of the filter bed has a consistency of clay
- There is a head of water above the filter bed in some of the tanks
- Alpha dominated fingerprint

Trials were carried out to determine the BAT for collecting the samples. This tool was successful in the first tank sampled however unsuccessful for the following two. The site innovation team was tasked with developing an appropriate sampling tool. Inactive trials have been carried out on the developed tools with active trials planned for the near future.

Analysis of the samples from the first tank included the following:

- Estimate and proportion of size fractions
- Gamma scan as received (Bq/g)
- Split for water, weak acid (0.1M HNO<sub>3</sub>) and strong acid (1M HNO<sub>3</sub>) washes
- Gamma scan prior to washing of solids (Bq/g)
- Gamma scan of solids following washing (Bq/g)
- Liquor – alpha, beta and gamma scan (Bq/ml) – with weight of portion washed and volume of liquor used)

Results showed that the filter bed material was Low Level Waste without any washing. Washing showed an increasing reduction in alpha activity with increasing concentration of acid. However, there was no reduction in the beta activity from washing. These samples mainly consisted of solid material <5mm in size.

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### NNUF RADioactive waste disposal & Environmental Remediation (RADER)

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Embedded within the Williamson Research Centre in the Department of Earth and Environmental Sciences, the NNUF RADER user facility supports research into characterising and understanding the behaviour of radioactive species in natural and engineered environments. This science base is crucial for underpinning large parts of the UK's >100 year, >£130 billion nuclear decommissioning, clean-up and waste management programmes. The newly refurbished laboratories support radiological counting facilities, specialist experimental equipment, aqueous and colloid analysis instruments and instruments for solids characterization including specialist labs for:

- Radiometrics
- Instrumental analysis
- Column throughflow studies
- Wet chemistry
- Sample preparation, including cutting and polishing
- These join our two existing labs, specialising in U/Th experiments, and higher activity lab where other radioisotopes are handled

Applications are open for the NNUF funded user access scheme for RADER. We are open for research for external academic and industry users. Visit <https://www.nnuf.ac.uk/rader> or email for more information.



**Figure 1.** Nanoparticle tracking analysis, DLS size and zeta potential measurements

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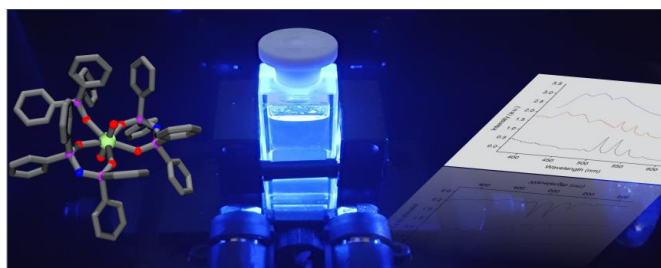
### The Centre for Radiochemistry Research National Nuclear User Facility

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The Centre for Radiochemistry Research (CRR), due for completion in 2023, will be an accessible ‘one-stop-shop’ for making and studying compounds of relevance to academic and industrial radiochemistry and other nuclear-related research, enabling new generations of researchers to overcome the barriers that have long prevented discovery, analysis, and synthesis in this area. Activities will range from fundamental coordination and organometallic chemistry to the study of colloids, immobilised glasses and concrete materials, and to challenges in nuclear waste management and its environmental impact. The refurbished CRR will feature a range of capabilities, especially to underpin medium-activity level work, including:

- Single crystal X-ray diffraction with Mo and Cu K $\alpha$  sources.
- 400 MHz NMR spectroscopy with multi-nuclear and variable temperature capability.
- SQUID 7 Tesla Magnetometry with variable temperature, VSM, and AC susceptibility.
- Low-pressure glove boxes for handling, synthesising, and recycling of transuranics.
- Alpha and gamma counters, Liquid scintillation.
- Fluorescence spectroscopy, confocal microscopy, lifetime image mapping.
- Multi-Photon spectroscopy, microscopy, lifetime image mapping.
- Laser-induced breakdown spectroscopy.
- Attenuated total reflectance infrared spectroscopy.
- Ultra-violet, visible, and near infrared spectroscopy.
- Ball -milling, Centrifugation.
- Stocks of various actinides and other radioisotopes.



**Figure 1.** Emission spectroscopy of neptunyl(VI) complexes in organic solution.

**Reference** S.D. Woodall, A.N. Swinburne, N.L. Banik, A. Kerridge, P. Di Pietro, C. Adam, P. Kaden, L.S. Natrajan, *Chem. Commun.*, 2015, **51**, 5402-5405.





