

Programme and Abstracts

# Frontiers in Environmental Radioactivity

Organised by the STFC Env-Rad-Net  
and the RSC Radiochemistry Group

January 6<sup>th</sup> and 7<sup>th</sup> 2016  
London

MANCHESTER  
1824  
The University of Manchester



Environmental  
Radioactivity  
Network



Science & Technology  
Facilities Council

**Wednesday 6<sup>th</sup>****Thursday 7<sup>th</sup>**

09:00	Coffee & Registration	08:30	Tea & Coffee
09:45	Welcome	09:00	Annie Kersting
10:00	Thorsten Stumpf	09:40	Ian Burke
10:40	Dominik Weiss	10:05	Johannes Raff
11:05	Break	10:30	Break
11:30	Robert Baker	10:55	Louise Natrajan
11:50	Kath Morris	11:35	Nick Smith
12:30	Stephanie Handley-Sidhu	11:55	Thomas Scott
12:55	Lunch	12:20	Lunch
14:00	Carolyn Pearce	13:20	Rizlan Bernier-Latmani
14:25	Aislinn Boylan	14:00	Roy Wogelius
14:45	Nik Kaltsoyannis	14:25	Phil Warwick
15:25	Break	14:45	Kevin Rosso
15:50	Steve Conradson	15:25	Env-Rad-Net 2: Announcement of Opportunities
16:30	Claire Corkhill		
16:55	Pieter Bots		
17:15	Session Close		
18:00	Poster Session		
19:30	Dinner		

**Keynote****Invited****Abstract Submitted****ORGANISED BY**

'Frontiers in Environmental Radioactivity' is organised by the STFC Env-Rad-Net and the RSC Radiochemistry Group



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**COMMITTEE**

Gareth Law (University of Manchester)  
 Sam Shaw (University of Manchester)  
 Oliver Street (University of Manchester)  
 Joanna Renshaw (University of Strathclyde)  
 Ian Burke (University of Leeds)

## 6<sup>TH</sup> JANUARY 2016

09:00	TEA/COFFEE & REGISTRATION	
09:45	<b>WELCOME</b> <i>S. Shaw, G. Law</i>	
10:00	<b>UNDERSTANDING ACTINIDE REACTIVITY AT THE WATER-MINERAL INTERFACE</b> <i>T. Stumpf, M. Schmidt, S. Hofmann, S.E. Hellebrandt (Keynote)</i>	A1
10:40	<b>URANIUM ADSORPTION ON MINERAL SURFACES AT HIGH pH AND I</b> <i>D. Weiss (Invited)</i>	A2
11:05	<b>BREAK</b>	
11:30	<b>URANYL MINERALS AS MODELS FOR STORAGE OF SPENT NUCLEAR FUELS</b> <i>R.J. Baker, A. Walshe, S. Biswas, E.D. Spain, T.A. Keys, R.A. Forster T. Prüßman, I. Pidchenko, T. Vitova</i>	A3
11:50	<b>BIOGEOCHEMICAL GRADIENTS AND RADIONUCLIDE TRANSPORT: CLEAN-UP &amp; DISPOSAL OF OUR NUCLEAR LEGACY</b> <i>K. Morris (Keynote)</i>	A4
12:30	<b>BIOGENIC SORBENT REMEDIATION MATERIALS: MODELLING HYDROXYAPATITE FORMATION USING SMALL ANGLE NEUTRON SCATTERING</b> <i>S. Handley-Sidhu, S. King, B. Stolpe, Y. Sidhu, M.O. Cuthbert, L.E. Macaskie (Invited)</i>	A5
12:55	<b>LUNCH</b>	
14:00	<b>INFLUENCE OF RADIATION DAMAGE ON REDOX REACTIVITY AND SCORPTION CAPACITY OF PHYLLOSILICATES IN A GDF ENVIRONMENT</b> <i>C.I. Pearce, W.R. Bower, A. Yorkshire, A.P. Sims, J.F.W. Mosselmans, A.D. Smith, P. Cubillas, K. Morris, K.M. Rosso, S.M. Pimblott, A. Qaisar, R.A.D. Patrick (Invited)</i>	A6
14:25	<b>UNDERSTANDING THE BEHAVIOUR OF ORGANIC CARBON-14 COMPOUNDS IN CONTAMINATED GROUNDWATER</b> <i>A.A. Boylan, D.I. Stewart, J. Graham, I.T. Burke</i>	A7
14:45	<b>WATER ADSORPTION ON AnO<sub>2</sub> (An = U, Np, Pu) SURFACES</b> <i>N. Kaltsoyannis, J.P. Wellington, A. Kerridge (Keynote)</i>	A8
15:25	<b>BREAK</b>	
15:50	<b>STRUCTURAL CHEMISTRY OF U, Np AND Pu OXIDES</b> <i>S.D. Conradson (Keynote)</i>	A9

16:30	<b>UNDERSTANDING GEOLOGICAL DISPOSAL FACILITY MATERIAL PERFORMANCE USING X-RAY SYNCHROTRON TECHNIQUES</b> <i>C. Corkhill D.Bailey, J. Vigor, B. Ravel, C. Murray, C. Tang, D. Crean, X. Xiao, R. Tappero, M. Stennett, S. Bernal, J. Provis, N. Hyatt (Invited)</i>	<b>A10</b>
16:55	<b>CONTROLS ON THE FATE AND SPECIATION OF Np(V) DURING IRON (OXYHYDR) OXIDE CRYSTALLISATION</b> <i>P. Bots, S. Shaw, G.T.W. Law, T.A. Marshall, J.F.W. Mosselmans, K. Morris</i>	<b>A11</b>
17:15	<b>SESSION CLOSE</b>	
18:00	<b>POSTER SESSION &amp; DRINKS RECEPTION</b>	
19:30	<b>DINNER</b>	
<b>7<sup>TH</sup> JANUARY 2016</b>		
08:30	<b>TEA &amp; COFFEE</b>	
09:00	<b>BIOGEOCHEMICAL PROCESSES CONTROLLING THE BEHAVIOR OF PLUTONIUM IN THE ENVIRONMENT</b> <i>A.B .Kersting (Keynote)</i>	<b>A12</b>
09:40	<b>SORPTION AND INCORPORATION OF CAESIUM TO SEDIMENTS AND ILLITE CLAY: A MACRO TO MOLECULAR SCALE INVESTIGATION</b> <i>I. Burke (Invited)</i>	<b>A13</b>
10:05	<b>BACTERIAL S-LAYER PROTEINS AND THEIR INTERACTION WITH RADIONUCLIDES</b> <i>J. Raff, M. Vogel, B. Drobot, C. Schmoock, H. Moll, A. Barkleit, H. Börnick, E. Worch, T. Stumpf</i>	<b>A14</b>
10:30	<b>BREAK</b>	
10:55	<b>OPTICAL IMAGING OF URANYL IN THE ENVIRONMENT: FROM FIRST PRINCIPLES TO APPLICATIONS</b> <i>L.S. Natrajan, M.B. Andrews, D.L. Jones, M.A. Williams, A.N. Swinburne, J.R. Lloyd, S. Shaw, S.W. Batchway, A.D. Ward (Keynote)</i>	<b>A15</b>
11:35	<b>PHLAME: PHOTONICS AND LASER ANALYSIS OF MATERIALS AND ENVIRONMENTS: IN-SITU STAND-OFF CHARACTERIZATION OF EXTREME LOCATIONS</b> <i>N. Smith D. Trivedi, L. Li, D. Whitehouse, O. Horsfall, C. Lennon, D. Hodgetts, W. Head (Invited)</i>	<b>A16</b>
11:55	<b>FORENSICALLY UNDERSTANDING FUKUSHIMA – THE STORY NEARLY 5 YEARS ON</b> <i>T.B. Scott (Invited)</i>	<b>A17</b>

12:20	<b>LUNCH</b>	
13:20	<b>THE CHALLENGES OF REMEDIATING URANIUM CONTAMINATION IN THE SUBSURFACE</b> <i>R. Bernier-Latmani (Keynote)</i>	<b>A18</b>
14:00	<b>SURFACE AND TIME RESOLVED SPECTROSCOPY OF RADIONUCLIDE ADSORPTION</b> <i>R.A. Wogelius, A.van Veelen, J.F.W. Mosselmans, K. Morris, G.T.W. Law, J.R. Bargar, G.E. Brown Jr (Invited)</i>	<b>A19</b>
14:25	<b>ADVANCES IN ENVIRONMENTAL RADIOACTIVITY STUDIES – APPLICATION OF ICP-QQQ MASS SPECTROMETRY</b> <i>P.E. Warwick, I.W. Croudace</i>	<b>A20</b>
14:45	<b>FUNDAMENTAL PROCESSES IN THE REDOX-DRIVEN INCORPORATION OF RADIONUCLIDES IN IRON OXIDES</b> <i>K.M. Rosso, M. Sassi, V. Alexandrov, S. Kerisit, P. Zarzycki, A.M. Chaka, S.D. Taylor, E.S. Ilton, C.I. Pearce, J. Liu, R.N. Collins (Keynote)</i>	<b>A21</b>
15:25	<b>ENV-RAD-NET 2: ANNOUNCEMENT OF OPPORTUNITIES</b> <i>S. Shaw, G. Law</i>	

## POSTERS

<b>P1</b>	<b>COUPLED EFFECTS OF HEAT AND GAMMA RADIATION ON CLAY BARRIER PERFORMANCE IN A GEOLOGICAL DISPOSAL FACILITY (GDF)</b> <i>A.P. Sims, J.M. Devine, K. Morris, R.A.D. Pattrick, C.I. Pearce</i>
<b>P2</b>	<b>CO-TREATMENT OF MIXED RADIONUCLIDES IN LARGE VOLUMES OF CONTAMINATED WATER BY CARBONATE PRECIPITATION REACTIONS</b> <i>D.J. Hodgkin r, D.I. Stewart, J.T. Graham, I.T. Burke</i>
<b>P3</b>	<b>RADIONUCLIDE UPTAKE DURING IRON (OXYHYDR)OXIDE FLOC FORMATION: APPLICATION TO THE ENHANCEDACTINIDE REMOVAL PLANT (EARP) PROCESS</b> <i>E. Winstanley, S. Shaw, K. Morris</i>
<b>P4</b>	<b>IRON OXYHYDROXIDE FORMATION IN THE ENHANCED ACTINIDE REMOVAL PLANT (EARP)</b> <i>J. Weatherill, K. Morris, P. Bots, T. Stawski, A. Janssen, R. Blackham, L. Abrahamsen, S. Shaw</i>
<b>P5</b>	<b>RADIOACTIVE EXPERIMENTS AND FACILITIES AT THE DIAMOND LIGHT SOURCE</b> <i>F. Mosselmans, S. Parry, R. Doul</i>
<b>P6</b>	<b>THE EFFECT OF ORGANIC MATTER ON Co SORPTION TO SOIL MINERALS</b> <i>G. Woodward, C. Peacock, O. Thompson, G. Law, I. Burke</i>

- P7** INVESTIGATION OF THE FATE OF THE RADIONUCLIDE COMPLEXING COMPOUND ISOSACCHARINIC ACID  
G. Kuippers, N. Bryan, J.R. Lloyd
- P8** URANIUM INCORPORATION INTO MAGNETITE WITH VARYING Fe(II)/Fe(III) AND U CONCENTRATION AT DIAMOND LIGHT SOURCE  
H. Roberts, K. Morris, G. Law, F. Mosselmans, P. Bots, S. Shaw
- P9** URANIUM SPECIATION AND MIGRATION AT AN ABANDONED URANIUM MINE IN CORNWALL, UK  
J. Kulaszewska, D. Kosmidis, C. Kirk, N. Evans
- P10** LONG-TERM IMMOBILIZATION OF TECHNETIUM VIA BIOREMEDIATION WITH PROPRIETARY ELECTRON DONORS  
L. Newsome, A. Cleary, K. Morris, J.R. Lloyd
- P11** OPTIMISATION OF UREASE CONCENTRATION ON HYDROXYAPATITE  
L. Dackombe, E. Carter, S. Handley-Sidhu
- P12** INVESTIGATING U(VI) – MINERAL INTERACTIONS USING LUMINESCENCE LIFETIME IMAGE MAPPING  
M. Williams, L. Natrajan, S. Shaw
- P13** CAN MICROBES HELP STABILISE RADIOACTIVE WASTE IN THE SUBSURFACE?  
N.M. Bassil, J.R. Lloyd
- P14** LONG-TERM BIOGEOCHEMICAL REDOXCYCLING OF TECHNETIUM  
N. Masters-Waage, K. Morris, J.R. Lloyd, F.R. Livens, J.F.M. Mosselmans, P. Bots, C. Boothman, G.T.W. Law
- P15** THE STABILITY OF COLLOIDAL U(VI) NANOPARTICLES UNDER ALKALINE IN THE PRESENCE OF BIOTITE, QUARTZ, ORTHOCLASE AND CEMENT PHASES  
R. Hibberd, G.T.W. Law, N.D. Bryan, P. Bots, T.A. Marshall, S. Shaw, K. Morris
- P16** THE STABILITY AND COMPOSITION OF URANIUM (IV)-SILICATE COLLOIDS IN ALKALINE SYSTEMS  
T. Neil, K. Morris, C. Pearce, Z. Maher, S. Shaw
- P17** ENVIRONMENTAL STUDIES AT THE STFC, CENTRAL LASER FACILITY  
A. Ward
- P18** RADIONUCLIDE SCIENCE AT THE KITC SYNCHROTRON FACILITY ANKA – THE INE-BEAMLINE AND THE NEW ACT EXPERIMENTAL STATION  
K. Dardenne, J. Rothe, T. Pruessmann, M. Vespa, T. Vitova, H. Geckeis

## Understanding actinide reactivity at the water-mineral interface

*Thorsten Stumpf, Moritz Schmidt, Sascha Hofmann, Sophia E. Hellebrandt*

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The behaviour of radionuclides in the environment is determined by interfacial reactions such as adsorption, ion exchange and incorporation processes. In literature such processes are often described by operational solid-liquid distribution ratios (Rd values). Distribution ratios are defined as the ratio of the quantity of a radionuclide sorbed per solid mass and the equilibrium concentration of the radionuclide. They are macroscopic parameters which are strictly valid only for the mineral and solute combination in the experimental system. For reliable and trustworthy long-term predictions of radionuclide transport behaviour, interaction mechanisms and processes occurring at the solid-water interface, they need to be understood at the molecular level. This can only be achieved by the application of spectroscopic methods.

In the talk a multi-spectroscopic approach will be presented. We used a combination of microscopy, laser and X-ray based techniques to gain process understanding on a molecular level of the interaction of actinides with mineral surfaces. Of key interest are sorption and incorporation reactions at the  $\text{CaCO}_3$  (calcite, aragonite, vaterite) – water interface. In addition reactions observed on clay and microbial surfaces will be presented.

### References

- [1] Charge compensation in solid solutions  
Moritz Schmidt, Thorsten Stumpf, Maria Marques Fernandes, Clemens Walther, Thomas Fanghänel  
Angew. Chem. Int. Ed., 2008, 47, 5846-5850.
- [2] Site-selective time resolved laser fluorescence spectroscopy of Eu and Cm doped  $\text{LaPO}_4$   
Kiel Holliday, Carole Babelot, Clemens Walther, Dirk Bosbach, Thorsten Stumpf  
Radiochim. Acta, 2012, 100, 189-194.
- [3] Trace concentration - Huge impact: Nitrate in the calcite/Eu(III) system  
Sascha Hofmann, Kislou Voitchovsky, Moritz Schmidt, Thorsten Stumpf  
Geochim. Cosmochim. Acta 2014, 125, 528-538.
- [4] Surface-Mediated Formation of Pu(IV) Nanoparticles at the Muscovite-Electrolyte Interface  
Moritz Schmidt, Sang Soo Lee, Richard E. Wilson, Karah E. Knope, Francesco Bellucci, Peter J. Eng, Joanne E. Stubbs, Lynne Soderholm, Paul Fenter  
Environmental Science & Technology 2013, 47, 14178-14184.

## Adsorption of U from alkaline solutions on geo-materials relevant to possible UK radioactive waste sites – Preliminary results from laboratory experiments

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The success of establishing a nuclear waste facilities hinges arresting waste migration in engineered primary barriers and secondary natural barriers. In the case of repositories located in silicate basement rocks, quartz ( $\text{SiO}_2$ ) is the dominant rock-forming and fracture sealing mineral. The canisters holding the cement-fixed radioactive waste will eventually fail and groundwater will enter the canisters. Cement will dissolve in several stages: (i) calcium hydroxide of the cement will dissolve and the pH will be buffered around 12.5; (ii) dissolution of CSH gel buffers the pH at 10.5, and (iii) dissolution of the remaining cement minerals, which should offer no pH buffering to the system. The pH will likely remain above 10.5 for several hundred thousand years. Groundwater passing through the cement will have a high ionic strength and carbonate content. Adsorption of U to quartz is well studied in the pH range between 3 and 10, with the majority of adsorption occurring at neutral pH values and only little adsorption at pH values closer to 3 or 10, with the specific adsorption edge depending on surface area, U concentration, and ionic strength. Even though adsorption is low at pH 3, we know that U still adsorbs to silica via an inner-sphere, mononuclear, bidentate surface complex whereas at pH 6, U forms an oligometric surface complex or precipitate at the quartz surface.

Our knowledge, however, is limited on uranium sorption and resulting species at the quartz-water interface under alkaline (pH >10), high carbonate conditions (2mM). The high pH values are expected to immobilize U via precipitation. However, recent studies have shown that at pH 13, U is precipitated as U-nanoparticles, which may remain significantly more mobile. Therefore, understanding the speciation of U in solution and at the mineral-water interface in high pH and ionic strength solutions is critical to predicting the mobility of such actinides in the subsurface.

To this end, we report here results from a series of preliminary experiments developing a reliable electrochemical technique for the determination of low U concentrations in alkaline solution and testing U sorption at high pH and ionic strength on quartz, with and without carbonate. At pH 12 in the carbonate free system, we find little U removed from solution and no difference in filtered vs unfiltered samples despite the system thermodynamically supersaturated with respect to sodium diuranate ( $\text{Na}_2\text{U}_2\text{O}_7$ )(s). This is suggesting that U is either dissolved in solution or suspended as colloids. When carbonate is present, U is sorbed with increasing pH until pH 11.3. U removal may be via adsorption to the quartz or precipitated. Adsorption, despite electrostatic repulsion between the negatively charged U-carbonate solution species ( $\text{UO}_2(\text{CO}_3)_3^{4-}$ ) and the quartz mineral surface, could be due to chemisorption overcoming the repulsion at high pH values. This process is known to operate for cations adsorption on iron oxides. At pH 12, similar to the carbonate-free system, U sorption decreases significantly. The carbonate solution is supersaturated with respect to  $\text{Na}_2\text{U}_2\text{O}_7$ (s) at pH values >10 and may then be present as a precipitate on the quartz surface. Previous work found 1-10 nm sodium uranate crystalline colloids produced at pH 13 for 4.2-252  $\mu\text{M}$  U(VI) solution.



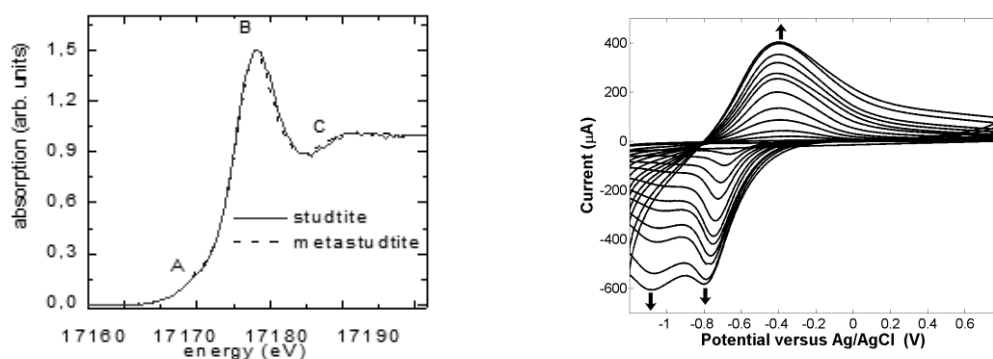
## Uranyl Minerals as Models for Storage of Spent Nuclear Fuels

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The favoured method of disposal of Spent Nuclear Fuels (SNF) is in a geological repository. Under moist oxidising conditions,  $\text{UO}_2$  will oxidise to uranyl compounds via a number of phase changes. These have been characterised on the weathering of uranium ores and on the surface of  $\text{UO}_2$  and SNF [1]. These phases can sorb radionuclides such as neptunium and therefore alter the migration rates. We present our recent work on the characterisation of the unusual mineral studtite,  $[\text{UO}_2(\eta^2\text{-O}_2)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , using solid-state electrochemistry [2] and XAS spectroscopy [3] (Figure). We have expanded our electrochemical study to selected uranyl (oxy)hydroxides, phosphates and carbonates, and these results suggest that uranyl minerals are redox non-innocent. We will also discuss  $\text{Eu(III)}$  and  $^{241}\text{Am(III)}$  sorption onto the surface of selected minerals using emission spectroscopy, and the reactions of  $^{237}\text{Np(V)}$  with selected mineral phases, studied by XAS spectroscopy.



**Figure.** U L<sub>3</sub>-edge HR-XANES spectrum (left) and solid state cyclic voltammogram (right) of studtite.

In conclusion we have spectroscopic information on the behaviour of environmentally relevant uranyl phases that may influence migration of transuranic ions in a nuclear waste disposal facility.

### References

- [1] R. J. Baker (2014). Uranium Minerals and their Relevance to Long Term Storage of Nuclear Fuels. *Coord. Chem. Rev.*, **266-267**, 123-136.
- [2] C. Mallon, A. Walshe, R. J. Forster, T. E. Keyes, and R. J. Baker (2012). The Physical Characterization and Reactivity of the Uranyl Peroxide  $[\text{UO}_2(\eta^2\text{-O}_2)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ : Implications for Storage of Spent Nuclear Fuels. *Inorg. Chem.*, **51**, 8509-8515.
- [3] A. Walshe, T. Prüßman, T. Vitova, R. J. Baker, (2014). An EXAFS and HR-XANES Study of the Uranyl Peroxides  $[\text{UO}_2(\eta^2\text{-O}_2)(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$  ( $n = 0, 2$ ) and Uranyl (Oxy)hydroxide  $[(\text{UO}_2)_4\text{O}(\text{OH})_6] \cdot 6\text{H}_2\text{O}$ . *Dalton. Trans.*, **43**, 4400-4407.

## **Biogeochemical Gradients and Radionuclide Transport: Clean-up & Disposal of Our Nuclear Legacy.**

Kath Morris

The University of Manchester

Globally, there is a significant legacy of defunct nuclear plant and facilities; these represent some of the most hazardous sites in the world and their decommissioning and management is of critical concern. Additionally, the common route identified by Government for management of the wastes generated from the nuclear fuel cycle is via deep geological disposal. Finally, many countries see new nuclear power as a critical part of their long term decarbonisation energy mix. These factors have resulted in a new focus on environmental radioactivity over the past few years. Our work has applied synchrotron based techniques coupled to radiochemistry, biogeochemistry, electron microscopy and geochemistry approaches to complex environmental systems. These approaches have highlighted that biogeochemical processes can have a profound effect on the mobility of radionuclides in natural and engineered environments. I will present data demonstrating our molecular environmental science understanding of the speciation, fate and biogeochemical cycling of radionuclides in systems relevant to radioactive waste disposal and radioactively contaminated land and demonstrate how these processes will help in underpinning the safe management and disposal of our nuclear legacy.

## Biogenic Sorbent Remediation Materials: Modelling hydroxyapatite formation using Small Angle Neutron Scattering.

*Handley-Sidhu S<sup>(1)</sup>, S. King<sup>(2)</sup>, B. Stolpe<sup>(1)</sup>, Y. Sidhu<sup>(3)</sup>, M.O. Cuthbert<sup>(1)</sup>, L.E. Macaskie<sup>(1)</sup>*

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Apatites are suitable materials for radioactive waste cleanup, storage and disposal because they can incorporate radionuclides within their structures, are very stable in the geosphere and are resistant to radiation damage [1-3]. *Serratia* sp. cells contain high levels of an atypical phosphatase; this enzyme cleaves inorganic  $\text{PO}_4^{3-}$  from the glycerol 2-phosphate (G2P) substrate and, in the presence of  $\text{Ca}^{2+}$ , the solution becomes supersaturated, producing an amorphous calcium phosphate biomineral (BHAP) [4,5], which is mainly composed of hydroxyapatite (HAP), cell biomass and  $\beta$ -tricalcium phosphate ( $\beta$ -TCP). BHAP is a promising remediation material with higher sorption capacities for Sr(II) and Co(II) (~ 15 times higher) than that of commercially produced HAP; the specific morphology (i.e. Smaller crystallite size (< 50 nm), amorphous content, high specific surface area (> 70 m<sup>2</sup> g<sup>-1</sup>)) and calcium deficient properties was shown to underlie these advantages [6,7]. Evidence suggests that the growth of BHAP is controlled within spatial localisation of the biological space and in close proximity to cells [2-4]. Images from transmission electron microscopy and atomic force microscopy show a network around the bacteria, consisting of EPS template and BHAP. Small angle neutron scattering (SANS) was carried out to examine size, shape, internal structure and spatial arrangement of bio-nanomaterial growth over time. SANS measurements were conducted on the SANS2D time of- flight small-angle diffractometer at the ISIS Pulsed Neutron Source (STFC Rutherford Appleton Laboratory, Didcot, UK) [8,9]. Biomineral formation over time was measured in solutions containing four varying concentrations of bacteria (0.05 to 1 optical density measured at 600nm) and biomineralisation solutions (tris-HCl buffer, 40 mM  $\text{Ca}^{2+}$  and 100 mM G2P). Model interpretations of the SANS data will be presented.

References: [1] Oelkers EH & Montel JM (2008) *Elements* 4:113-116. [2] Handley-Sidhu S, (2011) *Biotechnol. Lett.* 33:79-87. [3] Simon FG (2004) *Sci. Total Environ.* 326:249-256. [4] Macaskie LE & Dean ACR (1984) *J. Gen. Microbiol.* 130:1855-1867. [5] Thackray AC (2004) *J. Mater. Sci. Mater. Med.* 15:403-406. [6] Handley-Sidhu S, et al. (2011) *Environ. Sci. Technol.* 45:6985–6990. [7] Handley-Sidhu et al (2014) *Environ. Sci. Technol.* 48, 6891-6898. [8] <http://www.isis.stfc.ac.uk>. [9] Heenan, R.K. et al. (2011) *Neutron News*. 22, 19-21.

## Influence of Radiation Damage on Redox Reactivity and Sorption

### Capacity of Phyllosilicates in a GDF Environment

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Phyllosilicates will be exposed to  $\alpha$ -particle doses from high level radioactive waste contained in a geological disposal facility (GDF) for tens of thousands of years, both as engineered clay barriers around high level waste canisters, and in the far-field where clays and micas will be reactive constituents of the host lithology [1]. For any GDF safety case, it must be understood how physical effects of  $\alpha$ -particle damage will influence the ability of phyllosilicates to perform their long-term safety function of limiting radionuclide transport

We used controlled  $\alpha$ -particle irradiation coupled with microfocus XAS/XRD to obtain an understanding of radiation damage effects in model phyllosilicates [2]. Analysis of  $\alpha$ -irradiated biotite revealed interlayer distortion, with both dilation and contraction of the tetrahedral-octahedral-tetrahedral sheets and localised redistribution of interlayer potassium, as well as increased point defect density and formation of randomly oriented crystallites with more available reactive 'edge' sites. Redox changes due to  $\alpha$ -particle damage varied with depth of penetration; electrons were stripped by  $\text{He}^{2+}$  ions at the surface, but overall electron density increased over the 18 $\mu\text{m}$  damage track due to liberation of reducing species by OH- group radiolysis [3] and creation of oxygen vacancies by displacement [2]. Experiments with the problematic anionic radionuclide  $\text{TcO}_2^-$  demonstrated that radiation damaged phyllosilicates would continue to perform their safety function of limiting radionuclide transport due to their increased sorption capacity.

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## Understanding the behaviour of organic carbon-14 compounds in contaminated groundwater

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<sup>14</sup>C containing organic compounds can be formed by oxidation of carbides and impurities within nuclear fuel cladding[1]. The aim of this study is to determine the fate of the four most common such compounds (formate; acetate; formaldehyde and methanol) in subsurface environments. Experiments used sediment representative of the subsurface at Sellafield, UK, with synthetic groundwater[2] to study the behaviour of <sup>14</sup>C organic contaminants under aerobic conditions. <sup>14</sup>C movements were tracked in each phase: aqueous (liquid scintillation counting); gaseous (by CO<sub>2</sub> capture); inorganic solid (acidification to release gaseous CO<sub>2</sub>) and organic solid (oxidation of acidified sample to release gaseous CO<sub>2</sub>). The results for open systems show that only ~5% of initial <sup>14</sup>C remained in solution at the end of the experiments (~300 hours). Loss of formate and acetate can be attributed primarily to microbial metabolism within the sediment. For methanol and formaldehyde partial loss by volatilisation may also occur.

Organic <sup>14</sup>C contaminants are not retained in the aqueous phase. It is hypothesised that most are transformed to CO<sub>2</sub> by dissimilatory metabolism. In subsurface environments this will lead to an increase in aqueous carbonate species which may precipitate as solid carbonate or isotopically exchange with solid or gaseous phases.

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## Water adsorption on $\text{AnO}_2$ (An = U, Np, Pu) surfaces

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Over 100 tonnes of separated Pu are stored at Sellafield in the UK as  $\text{PuO}_2$  powder in sealed steel cans. Under certain circumstances, gas generation may occur in these cans, with consequent pressurization. Many routes to gas production have been suggested, several of which involve complex, inter-connected and poorly understood  $\text{PuO}_2/\text{H}_2\text{O}$  interactions.

We have recently begun a computational study of the interaction of  $\text{AnO}_2$  (An = U, Np, Pu) surfaces with water. Standard periodic boundary condition (PBC) implementations of Density Functional Theory (DFT) using generalized gradient approximation (GGA) functionals can fail to reproduce key features of actinide solids, *e.g.* predicting metallic properties in systems known to be insulating. This failure stems from incorrect description of the strongly correlated 5f electrons, which are overly delocalized by the GGA, and the standard solution to this problem is to correct the GGA functionals with an onsite Coulomb repulsion term known as the Hubbard  $U$ .

A more elegant solution is to employ hybrid DFT, in which some of the exact exchange energy of Hartree Fock theory is incorporated into the Hamiltonian. Such functionals typically produce more localized 5f electrons, and recover insulator behaviour. They are, however, extremely expensive to employ in PBC calculations, and hence are rarely used. We have therefore sought a model which allows the routine use of hybrid DFT in  $\text{AnO}_2$ /water systems, and have adopted the periodic electrostatic embedded cluster method, in which a quantum mechanically treated cluster is embedded in an infinite 1-, 2- or 3-dimensional array of point charges. We treat a cluster of  $\text{AnO}_2$  and adsorbing water molecules using hybrid DFT (PBE0) whilst the long-range electrostatic interactions with the bulk are modelled via the embedding of charges. Early results are promising; the technique correctly predicts the insulating behaviour of  $\text{UO}_2$ ,  $\text{NpO}_2$  and  $\text{PuO}_2$ , and shows good agreement with recent GGA+ $U$  studies of the adsorption of water onto  $\text{UO}_2$  [1].

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## Structural Chemistry of U, Np, and Pu Oxides

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Because of their chemical and thermodynamic properties, the oxyhydroxides of U, Np, and Pu in the forms of both isolated compounds and surface complexes on other minerals will be important determinants of their environmental chemistry. Fifteen years ago this was relatively straightforward, the species of interest were the  $\text{AnO}_2$  fluorites,  $\text{U}_3\text{O}_8$ , and schoepite-like phases. This has since been complicated first by the confirmation of  $\text{PuO}_{2+x}$  [1], with subsequent EXAFS experiments showing additional complexity as a distinction between heated and precipitated materials [2] and the incorporation of other cations [3], and now our recent identification of  $\text{NpO}_{2+x}$  [4]. It has also, however, moved from complicated to bizarre with the finding by EXAFS [5] – and for  $\text{UO}_{2+x}$  a large number of other experimental probes [6, 7] – that the An speciation in the  $\text{AnO}_{2+x}$  compounds is U(VI)-oxo and Np/Pu(V)-oxo, with the planar geometry that is incompatible with the fluorite structure stabilized by the formation of a dynamical polaronic condensate. Regardless of the structure and mechanism the challenge for environmental chemistry remains the same, what are the effects of the speciation on solubility and transport? The original report on  $\text{PuO}_{2+x}$  included the warning that the presence of Pu(V) would increase the solubility, but there has been no evidence for this. The unusual physics may modify the chemistry so that the properties coupled to the valences of molecular complexes do not transfer to these solids.

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## Understanding geological disposal facility material performance using X-ray synchrotron techniques

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The final disposal of nuclear wastes in a geological disposal facility represents a significant engineering challenge. The proposed design for a UK disposal facility, in common with several other facilities planned or operating worldwide, will utilise a multi-barrier concept, where several materials will be used to build layers of containment, mitigating the infiltration of water and the release of radionuclides to the geosphere. These materials include the wasteform itself, the container, and the backfill.

We describe here three examples of how synchrotron X-ray facilities are supporting research into the development of nuclear waste and geological disposal facility backfill materials, including an understanding of their long-term performance. Firstly, uranium XANES data obtained at the NSLS are used to understand charge balancing mechanisms in novel brannerite materials developed as robust immobilisation matrices for mixed oxide fuel residues. Results from the world's first long duration synchrotron X-ray experiment at the Diamond Light Source are used to describe the *in-situ* hydration kinetics of cement materials used to backfill intermediate level radioactive wastes, over a two-year period. Combined with complementary *in-situ*  $\mu$ -XCT experiments performed at the APS, these data are providing the first insight to the rate of formation of secondary cement phases capable of sorbing radionuclides over extended timescales, as well as providing crucial information for predictive radionuclide transport modelling. Finally,  $\mu$ -XAS measurements taken at the NSLS have been used to support the development of novel cement barrier materials by elucidating mechanisms of radionuclide sorption.



## Controls on the fate and speciation of Np(V) during iron (oxyhydr)oxide crystallisation

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Neptunium-237 (Np) is a transuranic isotope produced in the nuclear fuel cycle (half-life =  $2.13 \times 10^6$  yr) and will be present in radioactive wastes. Under oxic conditions, it dominantly exists as neptunyl ( $\text{Np(V)O}_2^+$ ), potentially the most mobile actinide species at nuclear legacy sites and in geodisposal systems. To date, studies have reported  $\text{NpO}_2^+$  interactions with mineral surfaces [e.g. 1], however recent work has shown that actinyl species (e.g.  $\text{UO}_2^{2+}$ ) can incorporate into iron oxides [2]. This study aims to characterize  $\text{NpO}_2^+$  interaction with, and incorporation into iron oxides during crystallisation. In particular, for this study we focus on the alkaline geochemical conditions persistent at nuclear legacy sites, and relevant to intermediate level radioactive waste geodisposal.

We performed experiments to determine the interaction of  $\text{NpO}_2^+$  with the crystallisation of ferrihydrite to hematite and goethite at pH = 9.5 – 13 [2]. We applied chemical extraction, solid phase characterization (TEM, XRD) and synchrotron based X-ray absorption spectroscopy (XAS) to identify and characterize the fate and local coordination environment of  $\text{NpO}_2^+$  during the crystallisation. When  $\text{NpO}_2^+$  was added to systems prior to ferrihydrite crystallisation and pH  $\leq 11$ , both the chemical extraction and XAS data showed the Np was incorporated in the mineral particles. Specifically, the EXAFS indicated that  $\text{NpO}_2^+$  was directly substituted for Fe in the hematite (and goethite). Conversely, at pH = 13, chemical extractions suggested  $\text{NpO}_2^+$  was weakly bound to goethite, and EXAFS suggested it was surface associated presumably as an adsorbed species or surface precipitate. These results indicate that the changes in speciation of Np(V) during ferrihydrite crystallisation will limit the mobility of  $\text{NpO}_2^+$  in natural and engineered environments.

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## **Biogeochemical processes controlling the behavior of plutonium in the environment**

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There is an acute need to expedite progress toward a permanent storage facility that can safely isolate long-lived actinides and fission products from the biosphere. Significant uncertainty remains on how to safely store long-lived radionuclides that will make up the majority of the dose after a few hundred years.

Plutonium (Pu) is of particular interest because of its high toxicity and long half-life ( $t_{1/2}$   $^{239}\text{Pu}$   $2.4 \times 10^4$  yrs). The chemical interactions of Pu are dependent on its oxidation state, which in turn control its stability and solubility. Understanding the interplay (the bio-geo-chemistry) between Pu and the repository environment is necessary to predict the conditions for which Pu will either migrate or remain immobile. A mechanistic understanding of the surface structure and reactivity of coupled Pu–mineral, Pu–organic ligand, and Pu–microbe, interfacial processes is needed to advance our understanding. To elucidate the mechanisms controlling Pu transport, we have investigated Pu sorption and desorption rates from mineral, organic and microbe surfaces over a range of concentrations found in the environment. Field and laboratory experiments show that the both inorganic and organic matter play an important role in stabilizing Pu in solution and on mineral surfaces. I will present an overview of our present understanding of the behaviour of Pu in an effort to develop a conceptual model of Pu subsurface behavior.

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## Sorption and incorporation of caesium to sediments and illite clay: a macro to molecular scale investigation

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Contamination of land with radiocaesium ( $^{137}\text{Cs}$ ), is a serious environmental problem and an enduring legacy of accidental and authorised releases. The mobility of Cs in the environment is governed by its sorption to charged mineral sites within soils and sediments. Sorption experiments using illite-mica containing sediments representative of glacial outwash sands underlying the UK Sellafield nuclear site were used to investigate the potential for Cs mobility. At low Cs concentrations, sorption was dominated by interaction with highly selective sites present at relatively low abundance. Sorption to these sites was not affected by changes in solution pH or low concentrations of competing ions. Selective Cs sorption can explain the lack of observed Cs mobility occurring after past leaks at Sellafield. At intermediate Cs concentrations, sorption is controlled by interaction with amphoteric sites (i.e. low sorption observed at low pH) which are affected by competing ions. Therefore, we can predict that, if leaked to ground, the  $^{137}\text{Cs}$  associated with acidic high level liquid wastes would (in contrast to previous experiences) likely be very mobile and not be quickly sorbed to sediments. The long term interaction of Cs with illite was investigated using HRTEM, DFT modelling and EXAFS analysis to investigate the physical nature of the selective sorption site. After initial sorption onto the frayed edges, Cs migrates into the illite interlayer, becoming incorporated within the mineral structure. Cs initially exchanges with hydrated Ca at the expanded interlayer edges. This causes the frayed interlayer edges to collapse forming a Cs-enriched illite region at the edge of the K interlayer. Cs held in the collapsed interlayers is not exchangeable with Ca. During longer term experiments Cs did not remain at the edge of the illite crystal, but migrated into the collapsed interlayer through exchange with K. Once Cs has diffused away from the illite edges, these sites are able to sorb more Cs, facilitating its continued uptake from solution. These results help to explain both the well documented irreversibility of Cs sorption to the illite interlayer sites and the ability of illite to sorb Cs over extended time periods without reaching saturation. Caesium cannot be easily remobilised from such interlayer regions, and therefore, any effective remediation measures must either separate or degrade the clay fraction.

## Bacterial S-layer proteins and their interaction with radionuclides

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Bacterial surface-layer (S-layer) proteins form the outermost cell envelope of many bacteria and all archaea. These proteins are able to self-assemble in highly regular layers forming an oblique, square or hexagonal lattice on the entire cell. This layer protects especially bacteria living in extreme habitats against diverse harmful environmental influences. In case of uranium mining waste pile isolates belonging to the genera *Lysinibacillus* and *Bacillus* it was proven that the S-layers act as scavenger for reactive oxygen species probably formed by either radiolysis of water or Fenton reaction. The inactivation of the radicals is achieved by intermolecular crosslinking of tyrosine residues of the protein monomers. Furthermore, these S-layers have a variety of free functional groups such as carboxyl, hydroxyl and amino groups determined by potentiometric titration. These groups form at least two different calcium binding sites being important for the self-assembly of the protein and are responsible for the selective binding of toxic elements. Additionally, S-layer proteins are posttranslationally modified with sugar residues, phosphate, sulfate or sulfoxide groups. While hexavalent uranium is bound by several surface exposed functional groups, it is easily released at acidic pH and thusly do not affect strongly cell metabolism. However, the trivalent curium substitutes calcium and is only released at pH 2.0 or below. Interestingly, metabolism relevant metals such as Mn, Fe, Co, Ni, Cu, Zn were not bound by the proteins. These examples demonstrate that radionuclides can specifically interact with the biosphere affecting significantly their behaviour even in natural environments.

## Optical Imaging of Uranyl in the Environment: From First Principles to Applications

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The world currently holds a substantial nuclear legacy arising from fission activities, with a large proportion of high activity wastes that pose a radiological threat to natural and engineered environments. The decision to dispose of these wastes (following separation) in a suitable geological disposal facility (GDF) has provided some of the most demanding technical, and environmental challenges facing the world today. To help address these issues, we have begun a programme of work to establish a comprehensive understanding of the electronic properties and physical and chemical properties of the radioactive actinide metals using state of the art optical techniques to probe actinide speciation *in situ* at sub micron resolution.[1]

Here, we will discuss the potential to use the inherent fluorescence properties of the uranyl cation to study redox speciation in uranium-containing environmental samples by one and two-photon confocal fluorescence and phosphorescence microscopy and lifetime image mapping (Figure 1). Although previous studies carried out on crystalline samples have shown that uranyl species are capable of experiencing two-photon excitation, extrapolation into the solution phase has enabled us to study uranyl species in solution at room temperature for the first time. We will present fundamental two photon properties of uranyl coordination complexes including two-photon excitation and emission spectra and two-photon cross sections. These capabilities are then applied to confocal fluorescence microscopy of uranyl in a range of bacterial and mineral samples, to both study and map potentially useful process in (bio)remediation strategies including incorporation, biosorption and the *in situ* enzymatic reduction of uranyl.[2]

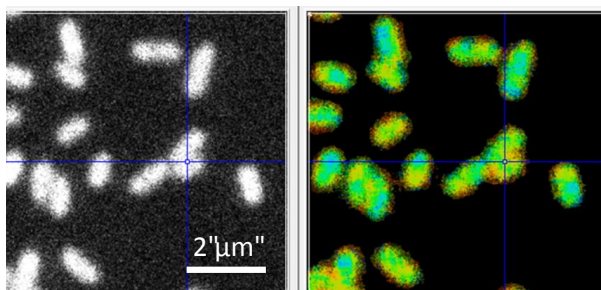


Figure 1. Two-photon confocal brightfield and fluorescence lifetime image microscopy map of *Geobacter sulfurreducens* undergoing bioreduction with uranyl(VI).

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## **PHLAME: Photonics and Laser Analysis of Materials and Environments: in-situ stand-off characterization of extreme locations**

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The nuclear industry presents a huge variety of locations that often comprise extreme environments that often provide a home for a myriad of potentially dangerous solid, liquid and gaseous materials. These environments range from deep geological disposal facilities (GDFs) to operating nuclear plants, and surface waste storage sites to legacy plants that are in the process of being decommissioned. All are typified by having human access restrictions and restrictions on the extraction of samples for analysis, which is the usual way of characterising unknown materials in nuclear industry environments, prior to build, operation, decommissioning or waste disposal.

The new National Nuclear Laboratory / University of Manchester Photonics and Laser Analysis of Materials and Environments (PHLAME) Research Group brings together researchers who are exploring the use of photonics-based spectroscopy techniques and 3D laser and photogrammetry-based geometrical characterisation techniques in characterisation of extreme environments and materials in the nuclear and other industries.

We have investigated the use of LIBS and Raman probe spectroscopy to quickly characterise materials from the aerospace and atomic weapons arenas, whilst other members have investigated the use of LIBS in the fingerprinting of different forms of stainless steel, and its use in the characterisation of radioactive contamination of stainless steels, including depth profiling of Caesium and Strontium contamination. We have also designed and constructed telescopic-based prototype stand-off Raman instruments in order to test the feasibility of in-situ Raman spectroscopy deployment in extreme environments.

This presentation describes current results and findings and their potential impact on the nuclear industry.

## Forensically understanding Fukushima – The story nearly 5 years on.

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In March 2011, an earthquake and tsunami of unprecedented scale hit the eastern coast of Japan, exacting a deadly toll on coastal areas. The Fukushima Daiichi nuclear power plant (FDNPP) was severely stricken by the tsunami, and a catalogue of containment failures caused Units 1-4 to contaminate the environment with a significant atmospheric release of radioactive material by a variety of mechanisms that are yet not fully understood. A fallout inventory of some 890 PBq of radiocaesium is estimated<sup>[i]</sup> with most of this material removed from the atmosphere by a combination of wet and dry deposition to contaminate a large area of land extending up to 200 km from the site. Currently, the chemical state, mobility and fate of the fallout material are poorly understood. It is well-recognised that the mobility of the principal components of the radiation for the next decades will be determined by the transport of fine-grained particulates, especially pulses of redistribution via suspended sediments in river systems stimulated by periodic typhoon events<sup>[ii]</sup>. But, it has been unclear as to exactly what the fallout contained in terms of radionuclides and their chemical speciation. This is a key question because modelling the remobilisation depends critically on the host material of all sources of radioactivity.

The current talk presents new information relating to the characteristics of the Fukushima fallout collected from different areas within 30km of the site. Using advanced laboratory and synchrotron-based analytical techniques we demonstrate the presence of uranium in a selection of samples, suggesting that some areas received fallout of spent fuel particulates.

[i] MEXT: Ministry of Education, Culture, Sports and Technology in Japan, Results of the Fourth Airborne Monitoring Survey by MEXT. Official press release of December 16, 2011. [http://radioactivity.nsr.go.jp/en/contents/4000/3179/24/1270\\_1216.pdf](http://radioactivity.nsr.go.jp/en/contents/4000/3179/24/1270_1216.pdf) (accessed 28 September 2013).

[ii] Y. Yamashiki et al. (2014) Scientific Reports 4, 3714.

## The challenges of remediating uranium contamination in the subsurface

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Uranium contamination in the subsurface is a salient issue in countries where uranium mining, milling, or processing took place or where accidental spills of uranium occurred. The major challenge associated with this type of contamination is that the hexavalent form of uranium (U(VI)) is highly mobile, resulting in the rapid spread of this contaminant in aquifers. A strategy for remediation involves the reduction of U(VI) to U(IV) (tetravalent uranium), that, in contrast to the oxidized valence state, is insoluble and expected to precipitate out in most settings. Sediment microorganisms can catalyze this reduction either directly or indirectly and have been shown to do so effectively when stimulated with an electron donor. The speciation of U(IV) is a key parameter to determine whether this strategy is viable in the long-term. In particular, two major categories of species have been identified in laboratory and field investigations. The nanocrystalline U(IV) oxide (UO<sub>2</sub>, uraninite) is largely favored as a remediation product due to its low solubility, and high stability, particularly in the presence of iron sulfide minerals produced as a result of sulfate reduction. The second, less well-defined, product is non-crystalline U(IV). This product represents a family of compounds in which U(IV) is coordinated to phosphate, organic carbon, or carbonate ligands, depending on the formation environment. This species was shown to be more labile than UO<sub>2</sub> with respect to oxidation, making it a less desirable product. Unfortunately, several studies show that it is the most abundant *in situ* product. The mechanism of formation of this family of products involves the presence of ligands that preclude the precipitation of U(IV) by binding the ion and likely forming polymeric chains. One of the drivers for the formation of non-crystalline U(IV) in the environment is the presence of microbial biofilms. Thus, much of the current work in this field is focused on these non-crystalline species, their formation mechanism, and their potential persistence in subsurface environments.



## Surface and time resolved spectroscopy of radionuclide adsorption

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Here, we will discuss the development and application of surface sensitive EXAFS and XRF analyses of critically important radionuclides that have adsorbed onto mineral surfaces characteristic of contaminated land, engineered barrier systems for geological disposal, and effluent treatment materials. These experiments have determined, in real-time, the adsorbate configurations of uranium on portlandite, magnesite, brucite, magnetite, and biotite under conditions representative of a near-field geological disposal facility. We will also present results obtained from analogue experiments (with non-radioactive Sr) constraining the mode of <sup>90</sup>Sr attachment onto surfaces representative of treatment columns and structural concrete at Fukushima. Polarization dependent EXAFS analyses of uranyl adsorbed onto single crystal surfaces of high-Mg phases present in Magnox cooling ponds have also been obtained and will be compared to both our *in situ* experiments and to computational results. This set of time-resolved and surface-resolved experiments provides unequivocal data on the dominant reactive surfaces of key mineral phases under a range of nuclear legacy relevant scenarios. Our development of *in situ* glancing incidence capabilities is providing an improvement in our fundamental knowledge of adsorbate behaviour and will ultimately feed into GDF safety case development and effluent treatment methodologies.

## **Advances in environmental radioactivity studies – application of ICP-QQQ mass spectrometry**

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ICP-QQQ mass spectrometry (uniquely providing MS-MS capability) offers many advantages over conventional ICPMS for the measurement of radionuclides in environmental matrices. The ICP-QQQ comprises an octopole collision / reaction cell between two quadrupole mass spectrometers. The reaction / collision cell can be used to remove polyatomic interferences through the introduction of He. In addition, reactive gases can be introduced to react with either the analyte of interest or a potential isobaric interference, permitting separation of these species by the second quadrupole (e.g. for distinguishing  $^{90}\text{Sr}$  from  $^{90}\text{Zr}$  or  $^{238}\text{Pu}$  from  $^{238}\text{U}$ ). The installation of a quadrupole mass spectrometer prior to the reaction cell is unique and permits only those ions of the selected mass to enter the reaction cell, resulting in significant reduction in interference. The combination of two quadrupoles also significantly reduces the abundance sensitivity of the system permitting the measurement of low abundance radionuclides in the presence of high abundance stable isotopes (e.g.  $^{59}\text{Ni}$  in the presence of  $^{60}\text{Ni}$ ). The key features of the ICP-QQQ, their characterisation and the potential application of ICP-QQQ in environmental studies are discussed.

## Fundamental processes in the redox-driven incorporation of radionuclides in iron oxides

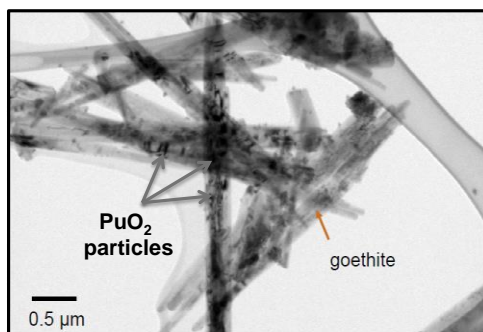
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The behaviour of many actinides and fission products in soils and sediments is controlled by strong interaction with select mineral phases. Examples include interlayer incorporation of radiocaesium and strontium in phyllosilicates, and sorption of uranium, technetium, and plutonium to various iron oxides. Understanding the fundamental chemical basis for these associations as well as their durability under changing biogeochemical conditions and accumulating radiation damage and isotope transmutation effects is central to accurately forecasting fate and transport over long periods of time. In this presentation we will overview some recent advances and challenges in this science area at the nanoscale.

In particular, the strong association of the redox-active radionuclides U, Tc and Pu by iron oxides under sub-oxic conditions appears to derive not just from their reductive sorption but also structural incorporation into the mineral lattice (Fig. 1). [1] Fe(II)-catalyzed recrystallization that transforms, for example, less crystalline ferrihydrite to more crystalline goethite, hematite, and magnetite, is a key pathway for incorporation. Important but poorly understood aspects of this redox-driven process under experimental and computational study include the structure of intrinsically nanophase ferrihydrite, rates and products of homogeneous versus heterogeneous Fe(II)/U(VI)/Tc(VII)/Pu(III) electron transfer, interfacial Fe(II)/Fe(III) electron exchange and associated mechanisms of recrystallization, and the local structure of charge-balanced U/Tc/Pu lattice defects. A range of surface-sensitive x-ray spectroscopic and scattering probes combined with computational molecular simulation is shedding important new light on these basic processes, highlighting the importance of interfacial Fe(II)/Fe(III) electron exchange, and ultimately progressing toward an improved conceptual model of redox-coupled Fe/U/Tc/Pu association, retention, and fate in the environment.



**Figure 1.** TEM image of Pu(IV) particles embedded in recrystallized goethite after exposure to Fe(II) solution.

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## Coupled effects of heat and gamma radiation on clay barrier performance in a Geological Disposal Facility (GDF)

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Clay will form an integral part of the Engineered Barrier System (EBS) in many proposed GDFs for heat generating radioactive waste disposal. The clay selected for this purpose will need to have the necessary physical and chemical properties to perform safety functions of protecting the waste container against corrosion and limiting release of radionuclides after container failure, in spite of challenges from heat and irradiation.

Here, the effect of heating a clay (montmorillonite) to 90, 160, and 500 °C followed by a  $\gamma$ -irradiation (2 - 5 MGy), two of the primary challenges faced by the buffer after disposal, are investigated. Heating showed little structural alteration of the clay up to 160 °C by x-ray diffraction (XRD) and infra-red spectroscopy (IR). Above 160 °C water content was reduced and long range order was affected. Subsequent  $\gamma$ -irradiation produced atomic-scale changes observed using extended x-ray absorption fine structure (EXAFS) and electron paramagnetic resonance (EPR), showing distortion of interlayer cations and an increase in defect concentration within the clays, respectively [1,2,3]. Colloidal suspensions produced before and after irradiation showed that  $\gamma$ -radiation had little effect on particle size but produced a more negative effective charge as determined by zeta potential (ZP) measurements, suggesting the possibility of increased colloid stabilisation in solution [4]. In contrast to previous studies showing annealing effects of heating after  $\gamma$ -irradiation, this study shows that heating prior to  $\gamma$ -irradiation changes the nature of the radiation induced defects [5].

This study demonstrates that, although heating to ~160 °C followed by  $\gamma$ -irradiation had limited effects on long range structure and water/hydroxyl content, changes at the atomic- and electronic-level may affect clay sorption properties and the potential for colloid formation, which are of relevance to barrier performance in a GDF.

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## Co-treatment of mixed radionuclides in large volumes of contaminated water by carbonate precipitation reactions

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Treatment of radioactive effluents and groundwaters containing  $^{90}\text{Sr}$  at low molar concentrations is traditionally achieved by cation exchange [1]. However, the effectiveness of the process is reduced by competing ions present in groundwaters [2] (e.g.  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ) and anionic radionuclides are not removed ( $^{99}\text{Tc}$ ,  $^{14}\text{C}$ ). Inorganic precipitation of  $^{90}\text{Sr}$  and  $^{14}\text{C}$  as insoluble carbonate offers a lower cost alternative, producing a solid residue that is readily grouted in cement wastefoms. Work has been carried out to understand the importance of initial concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  and crystallization pathways on the removal of Sr and  $^{14}\text{C}$  from solution.

The crystallization pathways occurring between aqueous ions of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ , and thermodynamically stable calcite appear to be an important control on the removal of  $^{14}\text{C}$  from solution. If the precipitate undergoes recrystallization  $^{14}\text{C}$  and  $^{90}\text{Sr}$  will become remobilized to the solution. This is of minimal importance for the Sr, which is reprecipitated into the newly formed crystal lattice.  $^{14}\text{C}$  however undergoes mixing with  $^{12}\text{C}$  derived from  $\text{CO}_2$  in-gassing and becomes diluted, reducing its removal efficiency. Solution  $\text{Ca}:\text{CO}_3$  ratios were found to be important for  $^{14}\text{C}$  removal, due to the effects of dilution by excess  $\text{CO}_3^{2-}$ . Sr removal however was not significantly affected, as atmospheric  $\text{CO}_2$  in-gassing was able to provide sufficient  $\text{CO}_3^{2-}$  for full  $\text{Ca}^{2+}$ , and thus  $\text{Sr}^{2+}$  removal.

Future work for this project will involve researching the importance of groundwater ionic composition and seed crystal concentration on the removal of  $^{14}\text{C}$  and  $^{90}\text{Sr}$ . The project will also seek scale up the most promising reaction conditions to column scale to develop methods applicable to flowing systems and large volume treatment. A full cost-benefit analysis will also be performed for an installed engineered treatment system versus likely alternative methods.

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## Radionuclide Uptake during Iron (Oxyhydr)oxide Floc Formation: Application to the Enhanced Actinide Removal Plant (EARP) Process.

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The Sellafield site in the North West of the UK reprocesses nuclear fuel from UK and overseas power stations in both the Magnox Reprocessing and Thermal Oxide Reprocessing Plant (THORP) and is transitioning from commercial operations to decommissioning. The Enhanced Actinide Removal Process (EARP) plant processes medium activity aqueous effluent from reprocessing, using iron(III) hydrolysis to remove radionuclides from the aqueous phase. As reprocessing transitions from operations to post-operational clean-out (POCO), the composition of effluents treated by EARP will change, requiring an expansion of the feed envelope. A clear understanding of the EARP process and the mechanisms by which radionuclides are removed from solution is required in order to predict and prepare for the future.

Iron hydrolysis can be induced by raising the pH of an acidic solution containing aqueous Fe(III) causing the precipitation of a solid ferrihydrite floc. Any radionuclides present (such as U<sup>238</sup>, Sr<sup>90</sup> and Np<sup>237</sup>) will adsorb to the solid ferrihydrite due to its high surface reactivity and large specific surface area (>200m<sup>2</sup>/g) which allow it to be an extremely effective adsorbent of many trace metals<sup>1</sup>.

This investigation focuses on the behaviour of uranium(VI) within a laboratory system which mimics the EARP process. Various spectroscopic methods including ICP-MS and EXAFS analysis have been utilised to determine the behaviour of U(VI) in this system over the course of the hydrolysis reaction. Our results indicate that any uranium present in solution is adsorbed to the surface of ferrihydrite, forming a bidentate, inner-sphere complex. Future work will investigate the effect of various anions on this behaviour, and will also investigate the behaviour of other relevant radionuclides.

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## Iron Oxyhydroxide Formation in the Enhanced Actinide Removal Plant (EARP)

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The formation of iron (oxyhydr)oxide (FeOx) nanoparticles is a key process in many industrial effluent treatment processes and is also important in natural systems. The high adsorptive capacity of FeOx, and their ability to co-precipitate aqueous metal ions makes them effective industrial decontaminants of key radionuclides in effluent streams from fuel reprocessing operations. The Enhanced Actinide Removal Plant (EARP) at Sellafield, UK is one such facility where radionuclides are removed from acidic effluent streams by inducing FeOx precipitation via NaOH addition. In order to better understand this crucial radioactive effluent treatment process, this study aims to elucidate the fundamental process of FeOx nucleation growth and aggregation during base hydrolysis of an acidic iron (III) nitrate solution of the type applied in effluent treatment at EARP.

The EARP treatment process was replicated in the lab using an automated small volume reactor. Here, a 1 M nitric acid ferric nitrate solution (400 ppm Fe) was raised to pH 9 by the addition of NaOH over approximately 45 mins. Further experiments were performed with sulfate, phosphate and boron, present in some effluents, to investigate their effect on particle formation. To characterise these processes, *in situ* and time resolved Small Angle X-ray Scattering (SAXS) measurements were performed at the Diamond Light Source, in conjunction with ATR-FTIR and transmission electron microscopy.

Results show that 2-line ferrihydrite was precipitated as an end product in all systems. SAXS data showed the formation of ~ 1 nm diameter colloidal particles/clusters in solution from pH 0.15 when the solution is undersaturated with respect to ferrihydrite. Comparison with simulated scattering curves suggest that these clusters represent the Fe<sub>13</sub> Keggin clusters reported by Sadeghi *et al.* (2015). The clusters are persistent below ~ pH 1.0, and between pH 1.0 and 3.5 aggregation to form ferrihydrite dominates. The results of ATR-FTIR analysis provide further insight into the mechanisms of phosphate, borate and sulfate interactions during the hydrolysis process, with both inner and outer sphere complexation observed for different systems. These results highlight the complexity of particle formation in this system and underpin management of the EARP process effluents for the future.

## **Radioactive Experiments and facilities at the Diamond Light Source**

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Diamond Light Source is the UK national synchrotron light source. Active sample experiments have taken place there since 2009. The beamlines used include: I18 and B18 to obtain X-ray absorption data, I22 for small angle scattering, I12 and I13 tomography and diffraction based imaging. Commonly, B18 is used to collect XANES and EXAFS of samples at the Tc K-edge and the L-edges of U, Th and Np. I18 has been used to look at small U containing particles, I22 has been used to study U colloid chemistry. I12 and I13 have been used to study materials relating to nuclear power and solid waste.

There is a small radiochemistry lab for handling low activity samples. This is equipped with bench space, centrifuges, fridges and an anaerobic glovebox for storage and manipulation of samples that cannot be prepared off line. More active samples currently need to come on site in containment suitable for their intended beamline use. Diamond is in the process of seeking funding to build a laboratory to handle a wide variety of active samples offline and thus to simplify the study of more active materials especially in experiments as opposed to straightforward measurements.

Diamond is keen to encourage its use in the study of active materials and welcomes discussions about what can be done at the facility.



## The Effect of Organic Matter on Co Sorption to Soil Minerals

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Cobalt-60 is a common radionuclide used extensively in industry. Understanding Co interactions with soil constituents is important to determine the best remediation methods should it be released into an urban environment by accident or through terrorist activities.

Batch sorption experiments were carried out to study how Co sorption onto ferrihydrite and kaolinite changes with pH, ionic strength, Co concentration, and the presence of humic acid (HA). In both the ferrihydrite and kaolinite systems, Co sorption increased with pH with a sorption pH edge for the ferrihydrite system between pH 6 and 7. The kaolinite system had two increases in sorption: one between pH 3 and 5.5, and the other between pH 7 and 8.5. Co sorption to ferrihydrite was not affected by a change in ionic strength. In the kaolinite system, increasing the ionic strength reduced sorption below pH 7. Increasing the initial Co concentration resulted in less Co sorbed at low pH values, but above pH 7 this effect was not apparent. The presence of HA in the ferrihydrite and kaolinite systems increased the amount of Co sorbed in the acidic pH range where there was negligible sorption to the pure mineral.

To summarise, Co sorption to ferrihydrite and kaolinite is a function of pH, initial Co concentration and the presence of HA, but only sorption to kaolinite is affected by ionic strength. Other studies also support the conclusion that the presence of organic matter significantly enhances metal sorption in the low-mid pH regime.

## Investigation of the fate of the radionuclide complexing compound isosaccharinic acid

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It is UK Government policy to dispose of higher activity radioactive waste through geological disposal into an engineered deep underground geological disposal facility (GDF). Low-level (LLW) and intermediate-level (ILW) radioactive wastes are very heterogeneous, containing significant amounts of cellulosic material. After closure of the GDF, eventual resaturation with groundwater will result in the development of a hyperalkaline environment within the cementitious backfill. Under these high pH conditions, cellulose is unstable and will be degraded chemically, forming water-soluble isosaccharinic acid (ISA). As ISA is known to form stable, soluble complexes with a range of radionuclides, in particular Am(III), Eu(III), Np(IV) and U(IV) and other metals, such as Ni(II), the impact of microbial metabolism on this organic substrate was investigated, to help determine the role of microorganisms in moderating the transport of radionuclides and metals from a cementitious GDF.

In this study we focused on circumneutral conditions representative of the geosphere surrounding a GDF. Here we report the fate of ISA in circumneutral microcosms poised under aerobic and anaerobic conditions; the latter with nitrate, Fe(III) or sulfate added as electron acceptors. Data are presented confirming the metabolism of ISA under these conditions, including the direct oxidation of ISA under aerobic and nitrate-reducing conditions and the fermentation of ISA to acetate, propionate and butyrate prior to utilization of these acids during Fe(III) and sulfate reduction. The microbial communities associated with these processes were characterised using 16S rRNA gene pyrosequencing are also presented. Methane production was also quantified in these experiments, and the added electron acceptors were shown to play a significant role in minimizing methanogenesis from ISA and its breakdown products, thus minimising gas production in situ (of concern during GDF evolution).

Since Fe(III) is a common electron acceptor in soils and concentrations are also elevated, due to the steel used in the construction of a GDF and to encapsulate the wastes, further investigation of ISA metabolism under Fe(III)-reducing conditions was performed. Transmission electron microscopy (TEM) and environmental scanning electron microscopy (ESEM) were applied to obtain insight in the microbial role of mineral formation. Based on this outcome, the impact of ISA degradation on metal solubility, and hence mobility, will be also assessed in future experiments.

## Uranium incorporation into magnetite with varying Fe(II)/Fe(III) and U concentration at Diamond Light Source

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The nuclear fuel cycle has left a significant legacy of contaminated land and radioactive waste. Many nations currently plan to dispose of their higher activity radioactive wastes within deep geological disposal facilities. However, it is predicted that over long timescales (1000's – 10,000's years), steel containers that encase the waste will undergo anaerobic corrosion, potentially leading to the release of radionuclides, including uranium. This process will result in the formation of a number of solid phases, including the iron oxide magnetite ( $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$ ). Uranium is known to sorb to magnetite via various mechanisms, including surface mediated reduction to U(IV), and incorporation within the mineral structure. These sorption processes may significantly limit the migration of U within the repository system. Despite this importance, the mechanism(s) of U incorporation into magnetite, and the impact of U concentration and magnetite stoichiometry, are poorly understood.

Magnetite was synthesised under anaerobic conditions via a direct precipitation process in the presence of U(VI). The concentration of U(VI) (0.3–20wt %) and the magnetite stoichiometry (Fe(II)/Fe(III) ratio,  $x=0.5 - 0.8$ ) were varied during the reaction. A range of synchrotron techniques were used to characterise the mineral phase and to understand the fundamental mechanisms occurring. X-ray absorption spectroscopy indicated that with increasing Fe(II)/Fe(III) ratio, an increasing fraction of U becomes directly incorporated into magnetite. Upon increasing uranium, high resolution powder diffraction showed the formation of uraninite. These data suggest that U incorporation or precipitation with magnetite may have an important impact on the mobility of U in an engineered geological disposal facility.

## Uranium Speciation and Migration at an Abandoned Uranium Mine in Cornwall, UK

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Cornwall has a rich history of mining activities, but from a radiological point of view, South Terras is the most significant. Abandoned for nearly a century, it was the only mine worked primarily for uranium. The spoil heaps discarded by the miners has been left largely untouched; much of it retaining significant levels of activity. Previous studies indicated that these spoil heaps do not provide a significant source of contamination to the River Fal, which runs through the site. The work presented here used batch and column experiments to investigate the role of humic acid, which is known to form complexes with radionuclides (including uranium) that can aid mobility in the environment. It was found that humic acid extracted from South Terras soils, can form complexes with uranium, however these complexes do not seem to be mobile as no breakthrough was observed in the column experiments.

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## Long-term immobilization of technetium via bioremediation with proprietary electron donors

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Technetium groundwater contamination is an issue at a number of nuclear sites such as Sellafield and Hanford, particularly due to its environmental mobility and its biological availability as a sulfate analogue. In oxic waters technetium is present as aqueous and mobile pertechnetate  $\text{Tc(VII)O}_4^-$ , but under reducing conditions it can precipitate from solution as  $\text{Tc(IV)}$  mineral phases. Biostimulation of sediment microbial communities via the addition of electron donor can lead to the removal of  $\text{Tc(VII)}$  from groundwater as  $\text{Tc(IV)}$ , driven by the microbially-mediated formation of  $\text{Fe(II)}$ .

Here we investigated the potential for different slow-release proprietary electron donors to stimulate technetium bioremediation using sediments collected from a UK nuclear site. These included a poly-lactate substrate (HRC<sup>®</sup>), a poly-lactate substrate containing a sulfur moiety (MRC<sup>®</sup>) and a plant material mixed with zero valent iron (EHC<sup>®</sup>). Sediment microcosms were supplemented with a proprietary electron donor and then monitored for changes in aqueous and solid phase geochemistry over three months.

Results revealed that  $\text{Tc(VII)}$  was removed from solution following biostimulation with each proprietary electron donor. It was precipitated as a  $\text{Tc(IV)O}_2$ -like phase with HRC<sup>®</sup> and EHC<sup>®</sup>. MRC<sup>®</sup> produced a phase similar to  $\text{Tc(IV)S}_2$ . The  $\text{Tc(IV)}$  phases were then exposed to air to assess their sensitivity to oxidative remobilisation; negligible quantities of technetium were re-released to solution under these highly oxidising conditions.

In summary, we have demonstrated that targeted treatments can be used to stimulate the *in situ* formation of recalcitrant  $\text{Tc(IV)}$  biominerals, and therefore could be effective in the long-term remediation of technetium-contaminated groundwater.

## Optimisation of Urease Concentration on Hydroxyapatite

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Conceptually, it was anticipated that successful immobilization of urease enzymes onto hydroxyapatite could be achieved and that this composite material would then exhibit dual mechanisms, of sorption and calcite precipitation facilitation, that would both contribute to the uptake and stabilisation of Sr<sup>2+</sup> contaminated groundwaters.

Hydroxyapatite-urease (HAP-urease) was successfully produced using urease-active jack bean meal, a readily available and cost-effective source of urease.

The concentration of jack bean meal solution required to produce an optimum concentration of protein in the filtered solution was established. Additionally, the rate of ureolysis ( $k_{urea}$ ), which drives calcite precipitation, was determined for the composite by measuring the NH<sub>4</sub><sup>+</sup> produced. This allowed for a direct comparison to jack bean meal ureolysis rates reported in the literature.

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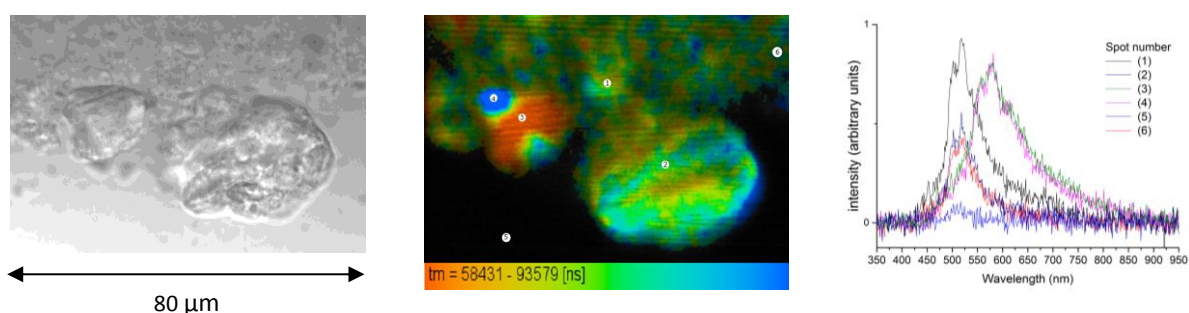
## Investigating U(VI) – mineral interactions using luminescence lifetime image mapping.

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The luminescence profile of uranyl(VI) sorbed to montmorillonite clay suspended within an aqueous solution under controlled carbonate conditions has been studied by fluorescence and phosphorescence lifetime image mapping over a range of pH values. Spectra collected of the imaged clay aggregates provide a new level of detail. The sorption of uranyl(VI) onto the aluminosilicate minerals, montmorillonite and muscovite and simpler silica and alumina will also be presented. Sorption isotherms, elemental characterisation and batch sorption experiments were performed to determine the uptake and kinetics of uranyl(VI)-clay interactions in salt solution (0.1 M, NaNO<sub>3</sub>) within natural groundwater pH ranges. Geochemical modelling in PHREEQC has been used to aid speciation analysis, as well as highlighting the effect of carbonate, pH and ionic strength.



*From left to right: brightfield confocal optical image of wet montmorillonite clay at pH 6.78 loaded with 1000 ppm uranyl(VI) under carbonate free conditions; phosphorescence lifetime image map of the same image; steady state uranyl(VI) emission spectra collected at different locations, corresponding to numbered spots on the centre image.*

This investigation highlights the variation in speciation across simple uranium-mineral systems and that a combination of steady-state luminescence spectroscopy, confocal microscopy and lifetime image mapping greatly aids in the assignment of uranyl(VI) speciation on these mineral surfaces. It is anticipated that work in this field could expand our understanding of radionuclide-mineral interactions at the sub-micron scale and at low, geologically relevant, uranium concentrations.

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## Can microbes help stabilise radioactive waste in the subsurface?

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Intermediate-level radioactive waste from the nuclear fuel cycle, will be disposed of via a deep geological disposal facility (GDF). This wasteform is highly heterogeneous and is expected to contain cellulosic material and other materials encapsulated in cement. Under high pH conditions imposed by the cement, cellulose will be chemically hydrolysed to short chain organic acids, the most abundant being isosaccharinic acid (ISA). ISA can bind to various radionuclides and increase their mobility, thereby increasing the probability of their release from the GDF.

As ISA is an organic molecule, there is the potential for its degradation by microorganisms and the subsequent mitigation of ISA promoted radionuclide mobility. Enrichment cultures prepared at pH 10 and inoculated using sediments from a high pH limekiln site, showed that alkaliphilic bacteria can degrade ISA under aerobic and anaerobic conditions [1]. A novel obligate alkaliphile belonging to the *Bacillus* genus was isolated from these cultures and was able to degrade ISA under aerobic and anaerobic conditions. *Bacillus sp.* growth also led to the precipitation of U(VI) from solution. Further work, including genome and transcriptome sequencing, TEM and XAS is helping identify the mechanisms of ISA degradation and U(VI) precipitation by this novel *Bacillus* species. Similar processes in or around the GDF may potentially stabilise radioactive waste in the subsurface.

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## Long-term Biogeochemical Redox Cycling of Technetium

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Technetium is a  $\beta$ -emitting fission product whose solubility is largely determined by its oxidation state. The highly soluble pertechnetate ion ( $\text{TcO}_4^-$ ) predominates under oxic conditions, sorbing poorly to geomedial. Conversely, poorly soluble Tc(IV) (as  $\text{TcO}_2$ ,  $\text{TcS}_2$  or sorbed Tc(IV) [1]) is formed under reducing conditions promoted by microbial processes [2, 3]. Currently, our understanding of Tc behaviour is focused on one bioreduction cycle. However, environmentally relevant radionuclides released into the subsurface will likely see numerous changes in their local redox environment. Here, we have investigated the fate of Tc in sediments over multiple reduction and oxidation cycles. Tc-spiked microcosms were 'cycled' between reducing and oxidising conditions three times and regular monitoring revealed that Tc remobilisation to solution decreased with subsequent oxidation cycles. This observation is reinforced by chemical extraction data, where resistance to acid extraction increased as redox cycles progressed. Data from X-ray Absorption Spectroscopy (XAS) experiments showed Tc was present as hydrous  $\text{TcO}_2$  like chains throughout multiple cycles, and that the chain length shortened as a result of redox cycling. We suggest that the shortening of the Tc-Tc chain is a cause for Tc recalcitrance, as Tc-Tc bonds are preferentially broken during oxidation events compared to the Tc-solid bond. Further, we hypothesise that protective 'Fe(II)/(III) rinds' inhibit the remobilisation of Tc species in sediments. In conclusion, this research provides insight to the long-term redox stability of Tc in sediment systems relevant to the UK nuclear legacy.

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## The Stability of Colloidal U(VI) Nanoparticles Under Alkaline in the Presence of Biotite, Quartz, Orthoclase and Cement Phases

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Colloidal U(VI) nanoparticles have been observed and fully characterised in high pH (pH > 13.1) synthetic cement leachate [1]. Thermodynamic modelling and X-ray absorption spectroscopy analysis shows these systems are supersaturated with respect to a number of calcium and sodium uranate phases. This study investigates the stability of U(VI) colloids in a range of single minerals and cement sorption experiments run under extremely high pH conditions relevant to disposal of intermediate level radioactive wastes in engineered barrier systems containing cement. The U(VI) colloids were found to be stable and remained in solution in the presence of biotite, quartz, and orthoclase for periods of at least 2.5 years. By contrast, when contacted with a disposal relevant cement phase, significant (> 95 %) of the added uranium was retained on solids after 1 month. X-ray absorption spectroscopy of the cement system where significant U was removed confirmed the formation of a uranate-like phase associated with the solids. Interestingly, after one month of reaction with the cement system, U(VI) was present at levels which were supersaturated with respect to a number of U(VI) phases according to solubility calculations. This suggests that intrinsic U(VI) colloids are poorly reactive with pure mineral phases, but that significant reactivity occurs with disposal relevant cement phases.

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## The Stability and Composition of Uranium (IV)-Silicate Colloids in Alkaline Systems

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Uranium(IV) colloids have the potential to greatly enhance the mobility of uranium and other radionuclides in anaerobic systems, including geodisposal environments and radioactive waste storage facilities[1]. Recent studies have shown that the presence of silicate has the potential to stabilise U(IV) in a colloidal form at near neutral pH[2]. This study investigates the chemical conditions under which U(IV) silicate colloids form and their long term behaviour.

Uranium (IV) silicate colloids produced under a variety of silicate concentrations and pH have been analysed using synchrotron based small angle X-ray scattering (SAXS), ultrafiltration-ICP-MS/AES and TEM analysis has indicated the primary particle size is less than 20 nm with some aggregates present both above and below 200 nm in size with the colloids stable over months and with differences between different colloidal systems: higher silicate concentrations in the initial experiments result in greater long term colloidal stability. EXAFS data suggest a local U(IV) coordination environment similar to coffinite (USiO<sub>4</sub>), however there is little long range structure.

This results of investigations into the size and stability of U(IV) silicate colloids has produced colloids that are stable under alkaline conditions over long periods of time.

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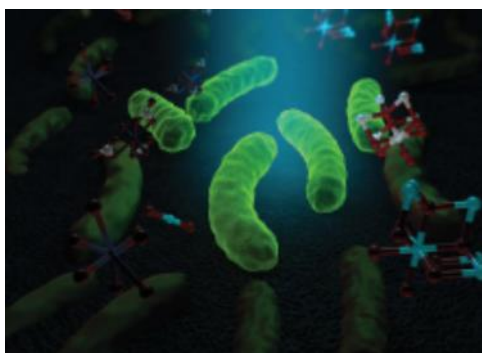
## Environmental Studies at the STFC, Central Laser Facility

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The Central Laser Facility (CLF) at the STFC Rutherford Appleton Laboratory is one of the world's leading laser facilities providing scientists from the UK and Europe with an unparalleled range of state-of-the-art technology. The applications range from high power laser installations that recreate the conditions inside stars to super-resolution microscopy for imaging biological cells. The specialised laser equipment can be applied to a broad range of experiments in physics, chemistry and biology. Here we show case experiments, from previous visitors to the facility, using laser-based imaging microscopy, optical trapping and spectroscopy techniques to perform environmental studies. If you have any interest in using these techniques for your research please feel free to come and discuss how you can access the Central Laser Facility.



Targeting bacteria: Representation of the fluorescence lifetime microscopy imaging of *Geobacter sulfurreducens* microbes containing uranyl acetate. Experimental work from CLF facility access, led by Dr Louise Natrajan, University of Manchester. (Reproduced from *Chemical Science*, 2015, 6, 5133 with permission of authors, copyright Royal Society of Chemistry)

## Radionuclide science at the KIT synchrotron facility ANKA – the INE-Beamline and the new ACT experimental station

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Synchrotron radiation based techniques have become key speciation methods in radionuclide and actinide research. This is partially driven by the need to assess (geo)chemical processes determinant in the mobilization or immobilization of long-lived actinide nuclides and fission products possibly released from a future nuclear waste repository. Moreover, the increasing need to understand degradation processes of nuclear waste forms such as discharged reactor fuel and vitrified reprocessing residues during extended interim storage demands the development of speciation methods capable of the direct characterization of highly radioactive samples with a minimum of pre-treatment. In this context standard XAS (X-ray Absorption Spectroscopy) and advanced HRXES (High energy Resolution X-ray Emission Spectroscopy) techniques have been recently shown to be well suited to study the chemical state and electronic structure of radionuclides in various matrices [1-3] - a prerequisite to predict their reactivity.

As one of a few research institutes in the world KIT-INE operates beamline laboratories at a synchrotron light source (the ANKA facility at KIT Campus North) dedicated for the spectroscopic investigation of radioactive materials. With a license to investigate radioisotopes up to 1E+06 times the exemption limit, the new ACT-Station at the ANKA CAT-ACT beamline, together with the existing INE-Beamline and the direct proximity of the radionuclide laboratories of both INE and the European Commission's Institute for Transuranium Elements (JRC-ITU), is recognized as presenting unique possibilities for safety research relevant for nuclear waste disposal at the European level. These facilities are available to both the national and international user community within the HGF NUSAFE program and via strategic research cooperation.

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