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The DISTINCTIVE University Consortium: Legacy Ponds and Silo Wastes

J. A. Hriljac[a],* C. Boxall[b], F. J. Currell[c], J. Day[d], M. Fairweather[e], D. Harbottle[e], R. Holdich[f], T. Hunter[e], N. C. Hyatt[g], N. Kaltsoyannis[h], A. Kerridge[i], W. E. Lee[j], B. Lennox[k], R. J. Lunn[l], S. M. Pimblott[h,**], D. Read[m], M. Ryan[j], T. B. Scott[d], L. Tovey[e], L. J. Vandeperre[j]

[a]School of Chemistry, University of Birmingham, Birmingham B15 2TT, UK
[b]Dept. of Engineering, Lancaster University, Lancaster LA1 4YR, UK
[c]School of Mathematics and Physics, Queen's University Belfast, Belfast BT7 1NN, UK
[d]School of Physics, University of Bristol, Bristol BS8 1TL, UK
[e]School of Chemical & Process Engineering, University of Leeds, Leeds LS2 9JT, UK
[f]Department of Chemical Engineering, Loughborough University, Loughborough LE11 3TU, UK
[g]Dept. of Materials Science & Engineering, University of Sheffield, Sheffield S1 3JD, UK
[h]School of Chemistry, University of Manchester, Manchester M13 9PL, UK
[i]Dept. of Chemistry, Lancaster University, Lancaster LA1 4YB, UK
[j]Dept. of Materials, Imperial College London, London SW7 2AZ, UK
[k]School of Electrical & Electronic Engineering, University of Manchester, Manchester M13 9PL, UK
[l]Dept. of Civil & Environmental Engineering, University of Strathclyde, Glasgow G1 1XQ, UK
[m]Department of Chemistry, University of Surrey, Guildford GU2 7XH, UK

ABSTRACT
The EPSRC sponsored DISTINCTIVE consortium (Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories) is undertaking 22 science and engineering projects across 11 universities related to the decommissioning of the Legacy Ponds and Silos at Sellafield. These are grouped into three work packages that focus on wasteform durability, effluent treatment and pond & silo sludges. Specific challenges include understanding the durability of ILW glass-ceramic wasteforms, studying thermally treated Pu-containing materials, producing and testing new inorganic ion exchange materials including derivatised magnetic nanoparticles for Cs, Sr and U removal from effluent, developing micro- and ultra-filtration methods, providing improved modelling and simulation of sludge disturbance, mobilisation and transport, developing a better understanding of gas hold-up in sludges, exploring methods for sludge characterisation including the use of acoustic backscatter and quartz crystal microbalance techniques and Raman spectroscopy and computer modelling of the interaction of cations with brucite surfaces.

INTRODUCTION
Legacy Ponds and Silo Wastes
Site restoration is a key part of the UK Nuclear Decommissioning Authority (NDA) mission and the clean-up of the Legacy Ponds and Silos (LP&S) at Sellafield are a major part of the challenge [1]. They comprise four main plants which were used historically for fuel reprocessing or waste storage. It currently costs £70M per annum to maintain the LP&S in their basic condition and prevent leakages, and they represent 22% of all Sellafield site programmes, 35% of total site costs and 77% of major project costs over the next few years. Their decommissioning and clean-up remains one the UK's top priority engineering programmes. The objectives of the NDA's LP&S strategy includes acceleration of high hazard and high risk reduction, reduction or mitigation of the impact of the risk of a loss of containment, preparation of facilities for retrieval operations, and subsequent waste retrieval and immobilisation. One of the four DISTINCTIVE themes was therefore set up to undertake basic science and engineering research that could provide sound technical advances to underpin the efforts to decommission the LP&S. The projects in this theme provide understanding of key aspects of the Sellafield programme, focussing on the characterisation, mobilisation, transport, conditioning and immobilisation of waste.

* *Corresponding author, e-mail:j.a.hriljac@bham.ac.uk*
** *Present address: Idaho National Laboratory, Idaho Falls, ID, USA*

The main aim of this theme is therefore to develop innovative technical approaches to clean up UK legacy wastes. The objectives are:

- To understand the durability of heterogeneous intermediate level waste glass-ceramic wasteforms from LP&S wastestreams.
- To develop improved ways to remove radionuclides from solution, using both novel inorganic ion exchange solids and tailored binding superparamagnetic nanoparticles, to treat complex and variable effluents.
- To develop new micro- and ultra-filtration methods for use with sludges.
- To provide three-dimensional modelling and simulation for sludge disturbance, mobilisation and transport, with supportive experimental studies, and manipulation planning for removing corroding nuclear materials.
- To develop a better understanding of gas hold-up in sludges.
- To develop improved techniques for remote monitoring of sludges and heterogeneous wastes.

These objectives are being met by 22 linked projects in three work packages, the details of which are given in Table I.

TABLE I. Projects, researcher type, researchers and university undertaking work in the legacy ponds and silo wastes theme, organised by work package ([a]indicates associated PhD).

Project Title	**Type**	**Researcher(s) & Supervisor(s)**	**University**
Wasteform Durability			
Durability of heterogeneous ILW glass/ceramic wasteforms from complex wastestreams	PDRA	Dr. Paul Fossati Prof. Bill Lee	Imperial
Microstructures and Corrosion of Intermediate Level Wasteforms Fabricated Using Novel Thermal Techniques	PhD[a]	Mr. Charles Hutchison Prof. Bill Lee	Imperial
Glass composite materials for Fukushima ILW immobilisation	PhD[a]	Mr. Dimitri Pletser Prof. Bill Lee	Imperial
Thermal treatment of Pu-contaminated materials and ILW	PhD[a]	Mr. Luke Boast Prof. Neil Hyatt	Sheffield
Assessment of the behaviour of metallic uranium during encapsulated product evolution	PhD[a]	Mr. Charilaos Paraskevoulakos Prof. Tom Scott	Bristol
Computational investigation of the interactions of solvated Sr^{2+} complexes with the hydrated brucite (0001) surface	PhD[a]	Ms. Eszter Makkos Prof. Nik Kaltsoyannis)	UCL /Manchester
Novel ceramic wasteforms for Cs and Sr encapsulation	PhD[a]	Mr. George Day Dr. Joe Hriljac	Birmingham
Corrosion of uranium in water and hydrogen	PhD[a]	Mr. Antonis Banos Prof. Tom Scott	Bristol
Effluent Treatment and Analysis			
Novel ion exchange materials	PDRA	Dr. T.-Y. Chen Dr J.A. Hriljac	Birmingham
New ion exchange materials for effluent clean-up	PhD[a]	Mr. Ryan George Dr. Joe Hriljac	Birmingham
Magnetic nanoparticles for waste separation or sequestration	PhD	Ms. Eleonora Cali Prof. Mary Ryan	Imperial

		Dr. Luc Vandeperre	
Shear enhanced micro and ultrafiltration	PhD	Mr. Keith Schou Prof. Richard Holdich	Loughborough
Pond and Silo Sludges			
Measurement and modelling of sludge mobilisation and transport	PDRA	Dr. Derrick Njobuenwu Prof. Mike Fairweather	Leeds
In-line rheometry and flow characterisation of dense slurries in pipe flow using acoustic methods	PDRA	Dr. Hugh Rice Prof. Mike Fairweather Dr. Tim Hunter Dr. David Harbottle	Leeds
Gas retention and release from nuclear legacy waste	PhD	Mr. Michael Johnson Dr. David Harbottle Dr. Tim Hunter	Leeds
Characterisation of flocculated waste suspensions with acoustic backscatter	PhD	Mr. Alastair Tonge Dr. Tim Hunter	Leeds
Quartz crystal microbalance as a tool to measure complex suspension Rheology	PhD[a]	Mr. Andre Botha Dr. David Harbottle	Leeds
In-Situ Monitoring of the Legacy Ponds and Silos at Sellafield	PhD	Mr. Olusola Ayoola Prof. Barry Lennox	Manchester
Development of Raman spectroscopy techniques for the remote analysis of nuclear wastes in storage	PhD	Ms. Kate Wyness Dr. John Day	Bristol
Computational simulations of storage pond sludge disturbance	PhD	Ms. Olivia Lynes Dr. Andy Kerridge	Lancaster
Modelling hydrogen generation from radioactive sludges	PhD[a]	Mr. Conrad Johnston Prof. Fred Currell	Queen's Univ. Belfast
Irradiated sludges, a joint theoretical/experimental study	PhD[a]	Mr. Mel O'Leary Prof. Fred Currell	Queen's Univ. Belfast

Notable achievements in this theme to date include the development of a non-intrusive acoustic backscatter measurement technique for monitoring suspended sediment particles which is being installed on plant at Sellafield, allowing the improved design of waste processing options. Other work on slurry transport and deposition has also provided input to process design. According to Sellafield, the technology being developed could accelerate a 7 year hazard reduction programme (emptying of tanks) by more than 1 year, with multi-£M savings. As a result of the work undertaken, technical advice has also been given regarding the design of a new SIXEP Contingency Plant for waste slurry discharges based on the slurry modelling and experimental work performed, with studies of gas hold-up in sludges informing operational planning at Sellafield for raw waste storage, with follow-on work planned. This work is seen as fundamental to maximising store capacity pending geological disposal and underpins waste monitoring strategy, and has the potential to avoid the generation of several hundred waste packages. Image recognition techniques developed are being considered as a possible method for the (partial) characterisation of mixed waste as it is being retrieved or while in pond storage. If successful this would significantly reduce the effort required to catalogue the inventories of thousands of waste boxes. Improved understanding of the corrosion behaviour of partially immersed glass wasteforms, and of glass-crystal composite wasteforms, has been developed through experimental and modelling work. Successful knowledge transfer of slag formulation development for the treatment of Pu-contaminated materials, and validation of vitrified products from pilot scale melter experiments, has also been completed. Lastly, new non-zeolite inorganic ion exchange materials for Cs and Sr removal from effluent, with high capacity and direct conversion routes to ceramic wasteforms, have been developed.

DISCUSSION

Further details of the outputs from each project in this theme are summarised below and organised by work package.

WP1 - Wasteform Durability

Durability of Heterogeneous ILW Glass/Ceramic Wasteforms from Complex Wastestreams. (Paul Fossati, Bill Lee)

This project is investigating issues and phenomena related to heterogeneities in glass/crystal waste forms using atomistic modelling techniques by considering a simplified Glass/Crystal Composite (GCC) material, in which the crystalline phase is TiO_2 with a rutile structure, and the glass phase is amorphous $(Na_2O)_x(SiO_2)_{1-x}$. The simulations are based on classical Molecular Dynamics (MD) techniques, using potentials which have been shown to accurately predict properties of $(Na_2O)_x(SiO_2)_{1-x}$ glasses. The simulated system is a succession of crystal and glass layers as shown in **Error! Reference source not found.**. Dependence on glass composition and crystalline orientation of the interface was considered by simulating three glass compositions (with 20 wt%, 10 wt% and 0 wt% Na_2O) and the 12 possible interface planes with crystallographic indices ≤ 2.

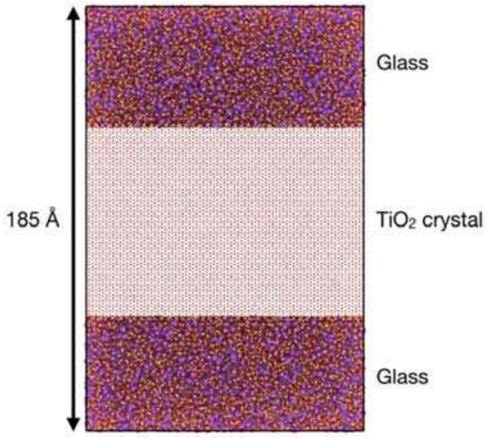

Figure 1: Simulation setup for glass-crystal interface simulations. The middle layer is a rutile TiO_2 crystal, and the other layers are $(Na_2O)_x(SiO_2)_{1-x}$ glass. This particular example is a (100) interface.

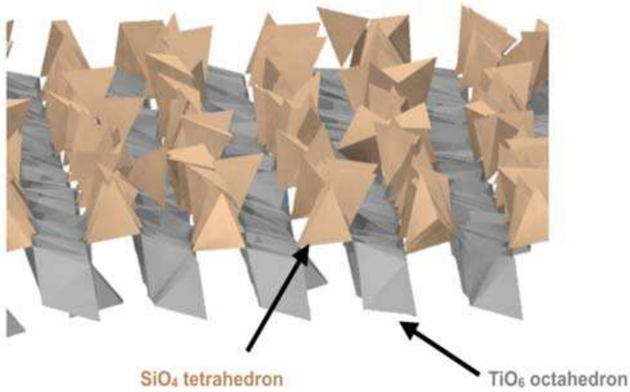

Figure 2. First SiO_2 glass layer in contact with a (100) rutile TiO_2 surface, showing aligned SiO_4 tetrahedra.

The calculations showed the presence of partially ordered glass layers close to some of the interfaces, with preferential orientations for SiO_4 tetrahedra. In particular, the first silicate layer in contact with the crystal tended to be highly-structured, with Si ions occupying well-defined positions that depend on interface orientation, and showing 2-dimensional ordering depending on glass composition. This is particularly visible in some interfaces such as (100), which is shown in Figure 2.

A structured interface layer in turn restricts the conformational freedom of the SiO_4 units that are connected to it. This creates 3-dimensional structures such as the rings connected to the crystal structure that are observed on the same (100) interfaces and shown in Figure 3. These rings tend to be aligned because of the regular spacing between the tetrahedra of the first layer. When present, sodium ions tend to occupy the resulting channels, thus forming elongated Na clusters on the interface plane, along specific crystalline directions. The effect of these interface structures on ion

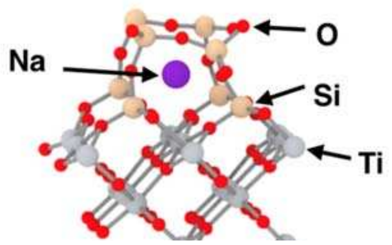

Figure 3. Interface rings on a (100) interface with $(Na_2O)_x(SiO_2)_{1-x}$ glass with 10 wt% Na_2O.

transport, and ultimately chemical durability of the composite will be the subject of the next step of this project.

Microstructures and Corrosion of Intermediate Level Wasteforms Fabricated Using Novel Thermal Techniques (Charles Hutchison, Bill Lee)

Simulant intermediate level waste materials received from Sellafield, three produced using Joule heating techniques and three from plasma furnace methods, were characterised and subjected to leaching tests for up to 14 weeks to assess their potential as a waste matrix. Each wasteform was used to simulate a combination of waste surrogates such as plutonium contaminated material, site ion exchange plant waste, high metal content waste, Magnox sludge, asbestos, or pile fuel cladding. Five samples were characterised as glass composite materials, containing a crystalline and glassy portion, with the sixth being characterised as a glass. XRD and EDX analysis were used to identify the crystalline components, revealing a wide array of phases over the six samples such as pigeonite, anorthite, diopside, cerium-lanthanum silicate, proto and clino hypersthene, augite, and two glasses from liquid-liquid phase separation. ICP-OES analysis and pH were used to analyse the leachant, and SEM-EDX surface scans and depth profiles for analysis of the wasteform, post corrosion. Several of the wasteforms made via Joule heating were suitably durable for safe disposal, showing protective corrosion layers or durable crystalline components. However, not all wasteforms were suitable; in particular glass encapsulated metals made by plasma melting (Figure 4) should not be used as a waste matrix due to the susceptibility of the metal/metal oxide portion to chemical attack [2].

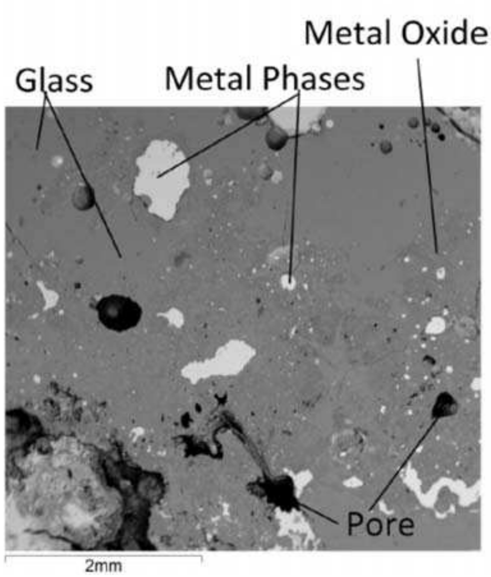

Figure 4. SEM image of as-received plasma furnace high metal surrogate sample showing Al,Mg alloy metal in glass and ceramic matrix.

Glass composite materials for Fukushima ILW immobilisation (Dimitri Pletser, Bill Lee)

The clean-up of the Fukushima Daiichi site continues to generate large volumes of spent adsorbents which need to be disposed of permanently. A low temperature immobilisation process is needed to avoid volatilising the adsorbed Cs and Sr. Detailed radionuclide volatilisation experiments were performed at Hitachi Research Laboratories in Japan and showed Cs volatilisation from a used adsorbent was negligible below 600ºC, with volatilisation starting at 700 ºC and strongly increasing above 800ºC. Hence a glass based waste form that can be sintered below 600 ºC is desirable and two have been developed: one system uses a lead borosilicate (PBS) and sinters fully at 500 ºC, see Figure 5, while an alternative system based on lead borate (PB) sinters fully at 400 ºC. Full encapsulation of the model waste was achieved for waste loadings up to 50 wt.% in PBS and 40 wt.% in PB, with both systems showing dense microstructures. The sintering behaviour was shown to be independent of Cs waste loading of the adsorbent, but was strongly influenced by thermal profile of the sintering treatment.

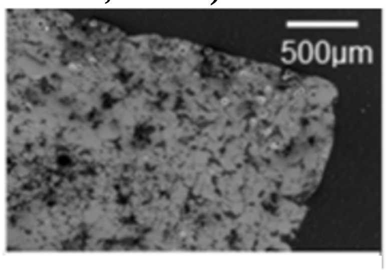

Figure 5. SEM micrograph of a PBS waste form after sintering

Thermal Treatment of Pu Contaminated Material (PCM) Waste (Luke Boast, Neil Hyatt)

This project follows on from previous work which provided proof of concept studies for thermally treating PCM waste. This work uses a soda lime silica (SLS) glass cullet as the glass forming additive to aid with vitrification, providing substantial benefits in terms of costs savings compared to previous work. The thermal treatment experiments showed no violent reactions between the waste simulant and the glass additives. The Ce (acting as a Pu surrogate) was effectively partitioned within the slag fractions of the waste form, with crystalline regions present in certain waste forms. The Ce was found as trivalent species, providing confidence that the slag component of the wasteforms developed here could incorporate Pu at the concentrations expected from treatment of PCM wastes. The materials produced here are broadly comparable, in terms of durability, to other simulant UK ILW glass products considered potentially suitable for geological disposal. The project will support the NDA's commitment to "generate credible and preferred strategic option for the estate-wide use of thermal technologies", by developing the necessary skills, capability, fundamental knowledge and understanding, required to support timely insertion of thermal treatment technologies and develop national expertise in this subject.

This project has already demonstrated non-academic impact. From February to June 2016 a placement was organised in Kurion. During this period a number of samples were acquired from full scale thermal treatment operations. The research performed on characterising and assessing the performance of the vitrified products, using the facilities at The University of Sheffield, enabled Kurion Inc to build a strong safety case in terms of treating and disposing of problematic ILW streams.

Assessment of the Behaviour of Metallic Uranium During Encapsulated Product Evolution (Charilaos (Haris) Paraskevoulakos, Tom Scott)

Metallic ILW is grouted and stored in stainless steel canisters. Corrosion of the encapsulated waste occurs throughout years of storage, followed by a volumetric expansion which threatens the package integrity. This research project has explored the mechanical degradation of these packages in conjunction with the magnitude of the internal corrosion of the metallic ILW using experimental and modelling techniques. Grout, which is supposed to offer a monolithic bonding with the encapsulated waste and keep it fully constrained, has been observed to fail at very primary corrosion stages. The steel liner was found suitable to accommodate the volume expansion without failing thanks to its hardening behaviour. This piece of work was actually the first dealing with the problem of the durability of UK ILW packages since the actual problem in the industry was spotted only some years ago.

Computational Investigation of the Interactions of Solvated Sr^{2+} Complexes with the Hydrated Brucite (0001) Surface (Eszter Makkos, Nik Kaltsoyannis)

The aim of this project was to develop a computational model for the brucite surface and the solvated ions, which allow atomic scale insight into possible adsorption mechanisms between the two. During the course of the research an approach was developed and optimised to describe Sr complexes in the bulk solvent (water) as well as in the vicinity of a hydrated brucite surface. The interaction between Sr hydroxide complexes and brucite was unfavoured at neutral pH conditions which are line with the experimental results. The developed computational model is reliable and its computational requirements are relatively modest compared to other type of calculations involving solid surfaces.

WP2 - Effluent Treatment and Analysis

Novel Ion Exchange Materials (Tzu-Yu Chen, Ryan George, Joe Hriljac)

The aim of this research was to find new materials that could be used as a replacement for, or adjunct to, the Mud Hills clinoptilolite used in SIXEP at Sellafield to remove caesium and strontium radioisotopes from effluent. Synthetic materials are preferred as this allows better control of properties and ensures the ability to replenish stocks when necessary. It is also desirable that materials are found that work over a large pH range and are selective to the many possible competing cations including sodium, potassium, magnesium and calcium. Early attempts indicated systems such as those denoted AV-3 and AV-7, which are synthetic silicates of formulae $Na_5Zr_2Si_6O_{18}(Cl,OH)\cdot 2H_2O$ and $Na_{0.5}K_{1.5}SnSi_3O_9\cdot H_2O$ and have the petarasite and kostylevite structures, respectively, [3, 4] can remove Sr^{2+} from solution but are inferior to Mud Hills clinoptilolite or IONSIV [5]. More recent work has focussed on materials with the umbite structure, Figure 6, which are polytypes of kostylevite with the same formula of $M_2M'T_3O_9 \cdot H_2O$ where M is typically an alkali metal such as Na^+ or K^+, M′ is a tetravalent octahedral metal such as Ti^{4+}, Zr^{4+} or Sn^{4+} and T is a tetravalent tetrahedral metal such as Si^{4+} or Ge^{4+}. The zirconosilicate system has been extensively studied and shown to be good for removal of Cs^+ [6].

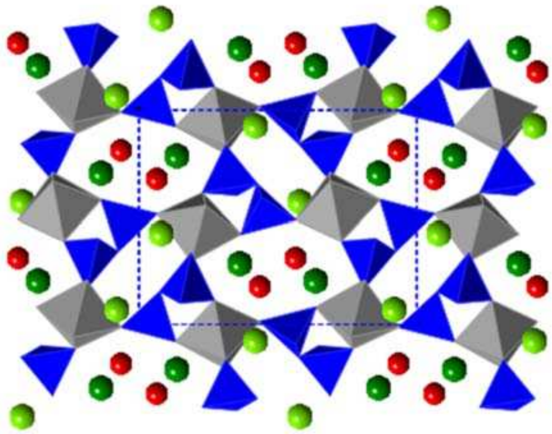

Figure 6. Representation of the umbite structure showing the tetrahedral (blue) and octahedral (grey) metal framework, with two cation sites (green) and water oxygen positions (red) in the

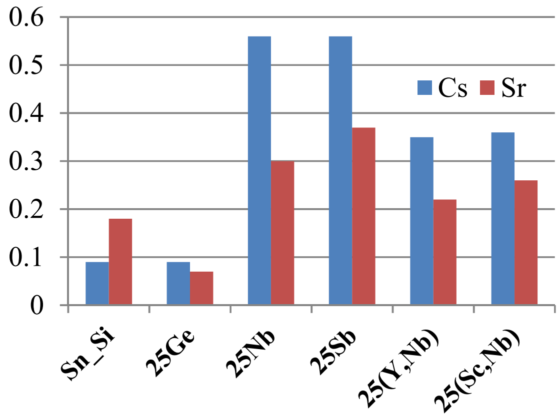

Figure 7. Uptake of Cs^+ or Sr^{2+} from solution for the parent (Sn_Si) and doped systems (the number is the atomic % doping). The uptake is molar relative to the octahedral metal.

The stannosilicate form of umbite, $K_2SnSi_3O_9 \cdot H_2O$, was first reported by Lin and co-workers and given the designation AV-6 [7]. Through careful control of chemical synthesis conditions we have produced a series of doped samples that involve either substitution of some of the Sn^{4+} on the octahedral site (by Nb^{5+}, Sb^{5+}, Y^{3+} and Sc^{3+}) or some of the Si^{4+} on the tetrahedral site (by Ge^{4+}). Static batch ion exchange testing of these systems with 0.1N Cs^+ or Sr^{2+} solutions using a volume/mass ratio of 100 $cm^3 \cdot g^{-1}$ for 1 day at room temperature led to some uptake. However, this was markedly improved by substitution of metals on the octahedral site as measured by X-ray fluorescence spectroscopy and shown in Figure 7. We have collected powder neutron diffraction data on these systems and are currently analysing these to look for systematic changes in the occupancies of the exchangeable intrapore cations to explain this improved performance.

We have also tested the removal of Cs^+ or Sr^{2+} over a wide pH range (pH 1-14) or in the presence of high concentrations of relevant competing cations (e.g. Na^+, Mg^{2+} and Ca^{2+}). All of the pentavalent element (e.g. Nb^{5+} and Sb^{5+}) doped materials have shown excellent Cs/Sr removal as well as great chemical stability in extremely acidic or basic conditions. These key findings are important, because they demonstrate that not only are the stannosilicate umbites more chemically stable compared to natural zeolites, which are currently used in the industry, but also work well over a wide pH range. In addition, it is known that some umbite materials can be thermally converted to a dense ceramic wadeite structure [8] and we are investigating if this is the case for these systems. Denser wadeite materials have much more strongly bonded cations and these should be better retained if the solid is in contact with an aqueous solution of high ionic strength, if that is the case then these materials will also have a simple and convenient route to a good wasteform as we have already demonstrated for IONSIV [9, 10].

In a parallel project, studies have been made of the preparation and ion exchange of zirconium germanium umbites of general formula $K_{2-x}(Zr_{1-x}Nb_x)Ge_3O_9 \cdot H_2O$ with x = 0 to 0.3 [11]. X-ray powder diffraction studies confirm single phase products and X-ray fluorescence spectroscopy the level of doping. When these materials are exposed to a 0.1 N caesium solution for 24 hours at room temperature there is a clear improvement of the uptake with increased Nb-doping as shown in Table II. Analysis of laboratory powder X-ray diffraction data shows there are no significant changes in the unit cells as a function of the Nb content, we are currently analysing synchrotron X-ray powder diffraction data to determine the relative changes in the occupancies of the two crystallographically distinct potassium sites to see if those correlate to the ion exchange behaviour. We believe this improved ion exchange is due to the creation of cation vacancies in the pores and subsequent increased mobility that therefore allows caesium uptake.

TABLE II. Atomic molar ratios normalised to Ge based on XRF results

	0% Nb		**10% Nb**		**20% Nb**		**30% Nb**	
Element	As-made	Cs-exchanged	As-made	Cs-exchanged	As-made	Cs-exchanged	As-made	Cs-exchanged
Cs		0.02		0.29		0.37		0.63
K	0.60	0.55	0.62	0.38	0.65	0.32	0.68	0.25
Zr	0.50	0.46	0.39	0.37	0.35	0.33	0.32	0.30
Nb			0.04	0.04	0.08	0.08	0.12	0.11

Magnetic Nanoparticles for Waste Separation or Sequestration (Eleonora Cali, Mary Ryan, Luc Vandeperre)

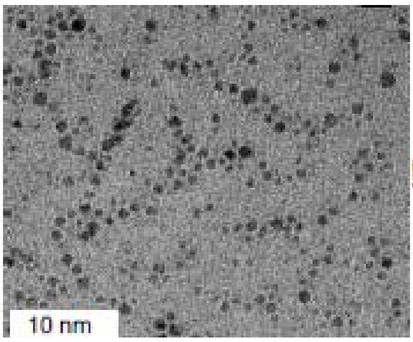

Figure 8. TEM micrograph of the magnetite nanoparticles

Magnetic nanoparticles functionalised with surface groups for sorption of specific species are advantageous over other sorption methods because a magnetic field can easily separate them from solution and guide them to assay specific locations. Therefore this project aimed to produce magnetic nanoparticles functionalised to remove uranium ions from solution as well as to create a vehicle for assaying the presence of uranium in small quantities in installations to be decommissioned.

Magnetite (Fe_3O_4) nanoparticles were successfully produced, see Figure 8, and after functionalization with phosphate groups showed a high sorption capacity for U(VI): 1690 mg U per gram nanoparticles.

Kinetic experiments showed that the sorption is also very fast and the lack of Ca, Mg and Sr sorption demonstrates that the particles are highly selective for U, see Figure 9.
Further tests reproduced solution chemistries as found in selected SIXEP effluents at the Sellafield site and the high selectivity for U remained valid with no other ions removed. Moreover, effective sorption was maintained even when the U concentrations were very low, indicating the particles can also be used to assay for the presence of U.

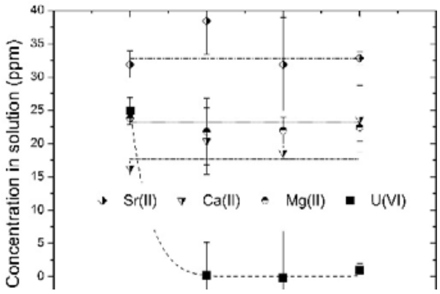

Figure 9. Competitive sorption tests

Shear Enhanced Micro and Ultrafiltration (Keith Schou, Richard Holdich)

By oscillating a filter during filtration it has been found that the pseudo steady state flux can be increased. For calcite an improvement of 2-3 times is common. Testing has demonstrated that this is linked to only the magnitude of the shear stress, and is independent on how that shear stress is applied (i.e. if the filter is oscillated one direction or another). For the mineral systems tested (calcium carbonate & magnesium hydroxide) the type of filter required was not important as the minerals filter on themselves. For the filtration of ferric floc, the filter choice is important. Preliminary results show that a marked increase in pseudo steady state flux rate can be gained. Magnesium hydroxide is used in SIXEP. Calcium carbonate is used in other (non-Sellafield) nuclear clean-up facilities (Fukushima), but was chosen as an initial study material due to the simple filtration characteristics and ease of handling. Ferric floc is used in EARP, and is the main interest for this project. The project has been looking at the principle effects of applying shear to the surface of a filter. We have now developed design equations based on first principles which are effective for cake-filtering mineral systems.

WP3 - Pond and Silo Sludges

Measurement and Modelling of Sludge Mobilisation and Transport (Derrick Njobuenwu, Mike Fairweather)

During decommissioning of UK legacy nuclear waste and those of any nuclear waste in general, in a temporal storage, the wastes will be retrieved and transported to a supplemental treatment facility for pre-treatment and immobilization before eventually ending up in a permanent storage. The aim of our project is to understand the influence of turbulence and gravity on particle agglomeration and breakup and how these phenomena affect the transport and deposition of radioactive particles suspended in the fluid phase.
We have developed a large eddy simulation and distinct particle simulation technique based on a robust and efficient deterministic collision model, energy-balanced agglomeration model and shear-induced agglomerate breakup. The CFD technique can handle correctly the interactions of particles with the carrier phase (in terms of two-way coupling and agglomerate breakup) and with other complex boundaries (in terms of other particles and geometry walls). We have successfully, simulated turbulent flows in full pipes at varying turbulence intensities. In addition, we have developed CFD technique to simulation turbulent flows in pipe with variable bed heights, mimicking flows with sludge deposit of various bed heights. The techniques developed will be useful in the formulation and validation of more pragmatic modelling approaches used within the industry in the design and operation of waste management processes.
We hope our research and findings will help in underpinning the understanding of the physics and technology for waste management. The techniques developed are of value to site licence companies and SMEs with the supply chain in improving our understanding of these flows, and allowing the better design of retrieval processes. The results are also of value to them in improving the accuracy of the engineering models used in process design, and safety and risk assessments.

In-line Rheometry and Flow Characterisation of Dense Slurries in Pipe Flow Using Acoustic Methods (Hugh Rice, Mike Fairweather, Tim Hunter, David Harbottle)

This project had a dual focus: (a) to measure the viscosity of flowing, liquid-solid nuclear waste suspensions using in-line rheometry and (b) to determine the critical deposition velocity (CDV) – that is, the flow rate at which the solid part of the mixture will be deposited on the bottom of the pipe – of the same suspensions. Such complex slurry suspensions are very common in the nuclear industry, and knowing how they flow is important for several reasons. In the case of (a), being able to measure the viscosity in-line (that is, as it flows) means potentially radioactive or chemically hazardous samples do not need to be taken for analysis off-line; in the case of (b), knowing that a slurry remains fully suspended, and therefore cannot build up on the pipe base and potentially cause local corrosion or chemical or radiative heating, means operators can select the most efficient flow rate. In both cases, the aim was to make the job of nuclear engineers engaged in the transport of hazardous waste safer, simpler and more cost-effective.

Tests were performed on magnesium hydroxide, calcite and barium sulphate slurries (all commonly utilized as nuclear waste test materials by the UK nuclear industry). The findings of the in-line rheometry part of the project were that the rheological behaviour of the slurries tested are well described by an extended version of the Herschel-Bulkley model that includes a Bingham-type limiting viscosity, but that the Bingham viscosity does not vary with solids volume fraction as expected. The key finding overall was that the inline rheometry technique (employing an ultrasonic velocity profiler) was able to match *ex situ* measurements, highlighting the potential application of the technique for online monitoring of waste slurry transport. The findings of the CDV component of the project, experiments for which were performed at intermediate solids volume fractions as a follow-up to a previous study at lower fractions [12], were that the CDV does not reach a maximum value at a critical volume fraction as would be expected from the scarce data available in the literature, and that settling velocity and rheology of suspensions play a central role in flowability.

Gas Retention and Release from Nuclear Legacy Waste (Michael Johnson, David Harbottle, Tim Hunter)

Through the use of clinical x-ray computed tomography, this research has improved our understanding of how gas is transported through consolidated sludges and slurries found at various nuclear decommissioning sites in the UK and USA. Understanding the mechanisms for continuous, or chronic, gas release enables the identification of conditions where waste packages might be susceptible to large acute releases of flammable gas which could provide an avenue for the release of radioisotopes [13, 14].

This research directly relates to work either currently underway or undergoing preparation at the Sellafield site and so research findings are communicated regularly to industrial workers at Sellafield Ltd. The work has specifically informed the safety case for waste transfer operations from the First Generation Magnox Storage Pond to the Sludge Packaging Plant, and from the Magnox Swarf Storage Silos to $3m^3$ waste packages.

Characterisation of Flocculated Waste Suspensions with Acoustic Backscatter (Alastair Tonge, Tim Hunter)

Over the course of this project, we have developed the use and calibration of ultrasound to measure suspended particle concentrations in solution, for engineering applications such as in thickeners in the mining and water treatment industry as well as for sludge characterisation in applications where direct sampling is hazardous, such as the nuclear industry. Specifically, we have developed the use of ultrasound to calibrate and measure intermediate particle concentrations up to 75 kg m^{-3} for non-cohesive, spherical glass particles [15] and have begun applying the method to flocculated, cohesive sediments.

Quartz Crystal Microbalance as a Tool to Measure Complex Suspension Rheology (Andre Botha, David Harbottle)

Quartz crystal microbalance (QCM) is a research technique which has been widely utilized to study thin films and adsorption kinetics. It has not previously been considered as a measurement tool for particle suspensions. The current research has begun to demonstrate the potential of QCM to measure the rheology of yield stress suspensions. By monitoring the frequency and resistance responses of the QCM sensor, it is now possible to correlate those resonance properties to the suspension yield stress. Studying $Mg(OH)_2$ suspensions (an analogue for nuclear legacy sludge), the research has demonstrated a direct correlation between the suspension yield stress and resonance resistance (ΔR air $\dashrightarrow$ sample shift), while the resonance frequency more informs on the loading mechanics from inertial to elastic loading with increased solids concentration. Further work is ongoing to determine the yield stress from the yield modulus which can be directly measured from the resonance properties of several overtones ($n = 3, 5, 7 \ldots$).

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In-Situ Monitoring of the Legacy Ponds and Silos at Sellafield (Olusola Ayoola, Barry Lennox)

The research looked into the measurement of particle size distribution (PSD) as an indicator of the physical properties of sludge; the semi-solid slurry formed over time at the bottom of wet storage facilities from corroded nuclear waste, environmental debris and organisms. Sludge characterization is an important step towards removing radioactive waste that is temporarily stored in wet radioactive waste storage ponds and silos at legacy nuclear sites. Due to the challenging environments on nuclear sites, there are significant limitations in the quantity and quality of samples that can be taken from the storage facilities and analysed in the laboratory. The aim of this research was to identify experimental factors that influenced the quality of results from sludge sampling and characterisation campaigns, to evaluate their contributions to data confidence and to investigate the feasibility of an in-situ particle size analysis technique to improve sampling and analysis protocols.

The research has showed that in making inferences of sludge PSD characteristics at non-sampled locations, the use of deterministic methods such as the Triangular Delaunay Algorithm were more accurate than geostatistical methods in the absence of spatial auto-correlation. In the simulated and experimental sludge beds that were used, it was also observed that with a penetration depth of only 60 % and by using stratified random sampling, PSD maps with accuracies of 70% were achieved when samples from only 150 locations out of 200,000 possible locations were analysed.

Identifying the number of sludge samples that are necessary to generate an accurate map of a sludge bed is a complex challenge. In this study a novel statistical tool was developed that identified the benefits that may be realised through the collection of further samples. In doing this, the tool also provided an indication of when there was little or no benefit in collecting more samples. This is important as the collection of samples from radioactive sludge beds can be very expensive and it is important that samples are only retrieved when necessary. Finally, the research investigated the use of ultrasonic spectroscopy as a method for in-situ sludge characterisation. The main challenge in the adoption of ultrasonic spectroscopy has been its dependence on knowledge of various thermo-mechanical properties of the sampled materials, which are typically unavailable in legacy facilities. This research has identified techniques that may allow ultrasonic techniques to be utilised when the thermo-mechanical properties are unknown.

Computational Simulations of Waste Storage Pond Sludge (Olivia Lynes, Andy Kerridge)

Over the past three years of this PhD project an accurate model has been developed for the behaviour of radionuclides in water, in particular the alkaline conditions of the Sellafield legacy storage ponds. Further studies have examined this behaviour with smaller ions such as magnesium and calcium, as well as more radioactive complex structures such as the uranyl ion and bookend lanthanides. More recently, a process of building a mineral surface which replicates some of the waste material in the bottom of the waste storage ponds at Sellafield has been completed and current studies focus on modelling the interactions of the smaller radioactive ions with the mineral surface.

Development of Raman Spectroscopy Techniques for the Remote Analysis of Nuclear Wastes in Storage (Kate Wyness, John Day)

Raman spectroscopy is a light based technique that has been investigated as a potential tool for characterisation of nuclear wastes in storage as the equipment can be readily miniaturised and transferred from lab bench use to robotic equipment. The first phase of the work was to put together a spectral library of nuclear wet storage pond proxy materials and assess whether these are suitable for Raman Analysis. The next stage is to build a bespoke device suitable for deployment on a robot to take chemical analysis measurements in situ. This will benefit sites like Sellafield and their continuous management of the pond conditions via a quick and easy analysis method for confirming some of their waste products, especially actinides.

Modelling Hydrogen Generation from Radioactive Sludges (Conrad Johnston, Fred Currell)

The goal of this project is to identify the chemical reaction mechanism by which hydrogen is evolved from Magnox sludge when irradiated. Using a computational approach, two types of damage to the electronic structure (which determines the resulting chemistry) were examined as an approximation to the ultimate effects of ionising radiation. The material of interest is the mineral brucite in its solid phase, which is the main component of the sludge. It was found that excess electrons (additional electrons that are introduced in to the material) localised between the layers of brucite. In quantum mechanical molecular dynamics simulations, there were no indications of damage happening at room temperature because of these excess electrons. This may be because the energy barriers that must be crossed for any chemical reaction to proceed are still too large for the short timescales accessible to these kinds of simulations. When an electronic hole was created in the material (by removing an electron), the hole tended to form on the oxygen atoms of hydroxide groups. Room temperature simulations showed that immediately after the hole was introduced, the O-H bond in the hydroxide where the hole was located would break, and that the H atom would transfer to a neighbouring hydroxide, forming a water molecule. Ongoing work is examining how this result might change for the surface of brucite, rather than the bulk-phase crystalline solid, with or without coverage by water. Additionally, it is planned to quantify the height of the barrier to this process. This finding may demonstrate the first step in the reaction pathway, and suggest what role radiation plays.

Irradiated Sludges, a Joint Theoretical/experimental Study (Mel O'Leary, Fred Currell)

Measurements of the amount of hydrogen produced and how quickly it can move (diffuse) through mimics of the sludges found in the waste ponds at Sellafield have been made. These appear to be the first measurements of these important parameters and they have a potential bearing on the formation of hydrogen in these ponds through radioactive decay. More importantly, they have a bearing on the transport of hydrogen produced in these ponds by any mechanism, including through corrosive processes. There is a clear indication that the transport of the hydrogen by diffusion through the sludges is significantly slower than would be expected by geometrical considerations alone. This implies that the hydrogen is 'sticking' to the grains in the sludge with possible implications for safety case formulation when the sludges are disturbed. Ongoing research is looking at the mechanism both theoretically and experimentally of this 'sticking'.

CONCLUSIONS

A wide range of studies have been done as part of the Legacy Ponds & Silos Theme of the UK DISTINCTIVE project with an aim to provide a fundamental understanding of the processes occurring in the sludges and novel solutions for the treatment of the sludge materials and effluent to effect decommissioning and produce good wasteforms. Highlights of these include:

- The development of new atomistic models of the solid interfaces in Glass/Crystal Composite wasteforms for the immobilisation of ILW.
- Assessment of the phases, microstructures and elemental leach rates of six ILW wasteforms fabricated at Sellafield using Joule heating techniques and plasma furnace methods.
- The development of low melting lead borosilicate and lead borate fluxes that are suitable for encapsulating spent ion exchange materials such as zeolites and IONSIV.
- The development of soda lime silica glass cullet as a glass forming additive to aid in vitrification of Pu containing waste.
- The first studies of the integrity of metallic ILW encapsulated by grout in UK packages.
- The development of computational models and a mechanistic understanding of the interaction of solvated Sr^{2+} species with a hydrated brucite surface.
- The development of new tin silicate and zirconium germanate ion exchangers that are effective in removing Cs and Sr from effluent that could potentially replace the clinoptilolite currently being used in the SIXEP plant at Sellafield.
- The development of new phosphate derivatised magnetite nanoparticles that can remove U from effluent and then be collected by magnet means.
- Studies of how to improve the micro- and ultrafiltration processes of various sludge simulants.
- The development of new simulation techniques of sludge mobilisation and transport that can predict sludge flow in pipes at varying turbulence intensities.
- The development of in-line rheometry measurements using an ultrasonic velocity profiler that has potential for use of online monitoring of waste slurry transport.
- Studies using x-ray computed tomography to further understanding of how gas is trapped and transported in consolidated sludges and slurries.
- The development of acoustic backscattering techniques using ultrasound for measuring suspended particle concentration in solution.
- The development of quartz crystal microbalance techniques to measure the rheology of yield stress suspensions.
- A study of the factors influencing the quality of results from sludge sampling campaigns and assessment of an in-situ particle size analysis technique based on ultrasonic spectroscopy.
- The development of models of radionuclides in alkaline water and how they interact with brucie surfaces.
- Assessment of Raman spectroscopy as a tool to be deployed robotically to monitor pond materials.
- Computational modelling of the effect of radiation on brucite.
- Measurement of the amount of hydrogen produced by radiolysis of brucite and its diffusion rates through sludge mimics.

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