The TRANSCEND University Consortium: Integrated Waste Management – 22109

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ABSTRACT

TRANSCEND (Transformative Science and Engineering for Nuclear Decommissioning) is a collaborative research consortium comprising 11 universities and 8 industry partners. The £9.4 million research program, funded primarily by the Engineering and Physical Sciences (EPSRC) Research Council of the UK, incorporates >40 projects in total, which will address some of the key challenges within the areas of nuclear decommissioning and waste management; including mobilization, processing, packaging, storage, transport and final disposal. This paper will outline a summary of the current progress and impact of *Theme 1 - Integrated Waste Management*. This theme focuses on underpinning science and engineering in areas of relevance to hazard reduction and decommissioning, where the three key work package objectives are: (1) New materials and methods for effluent decontamination; (2) Modelling and experiments for understanding pond and silo sludge/slurry behavior; (3) Innovative wasteform materials. In total, this theme has 15 different projects, delivered through both postdoctoral and PhD researchers, all with specific industry supervision from our partners, led by the NNL. The following provides a review of the project summaries to date, and their critical impact.

INTRODUCTION

The primary purpose of the Transformative Science and Engineering for Nuclear Decommissioning (TRANSCEND) consortium, is to secure the UK's nuclear future, by developing critical science and engineering solutions to safely treat, process and store nuclear wastes from the UK's legacy reactor programs, including site decommissioning and remediation. Additionally, this joint government and industry funded program is tasked with building, training and retaining the UK nuclear skills base, as well as cementing strong research links between the nuclear industry and academic community. The Overall consortium is divided into four main themes, where this paper presents an overview of *Theme 1 – Integrated Waste Management*. Work undertaken on this theme is concerned with developing new materials for effluent treatment, investigating sludge transfer operations from current pond containments, and also Developing new wasteforms for safe and efficient encapsulation of low level wastes (LLW), intermediate level wastes (ILW) and high level wastes (HLW).

Overall, the theme is broken down into 15 separate projects, undertaken by both PhD researchers and postdoctoral research assistants (PDRAs) where each project has both an academic and industrial partner. Across page in Table 1 is listed the entire program of projects and the lead researcher on each.

TABLE 1: Overview of projects associated with Theme 1 of TRANSCEND

TRANSCEND Theme 1: Integrated Waste Management				
Title	**Leading Institution**	**Researcher**	**Academic Supervisor**	**Type**
New Materials and Methods for Decontamination of Effluent	Birmingham	Antony Nearchou	Joe Hriljac, Phoebe Allan	PDRA
Nanotechnology for effluent treatment and radionuclide assay	Imperial	Gurpreet Singh	Luc Vandeperre	PDRA
Novel zeolite composites for remediation of aqueous nuclear decommissioning waste	Birmingham	James Reed	Joe Hriljac, Phoebe Allan	PhD
Particle-laden flow characterisation and prediction	Leeds	Lee Mortimer	Mike Fairweather	PDRA
Radiation Induced CHanges in Effluents/Sludges (RICHES)	Manchester	Mel O'Leary	Fred Currell	PDRA
Simulation of behavioural modification effects in suspension waste pipe flows.	Leeds	Bisrat Wolde	Mike Fairweather	PhD
Advanced characterisation of waste pipe flows with polymeric behavioural modifiers.	Leeds	Joseph Hartley	Timothy Hunter	PhD
Modelling nanoscale radiation physics/chemistry processes in sludges	Manchester	Ella Schaefer	Fred Currell	PhD
Durability of magnesium silicate cements	Imperial	Mercedes Baxter Chinery	Luc Vandeperre	PhD
Radiation effects on wasteforms	Manchester	Tamas Zagyva	Laura Leay	PhD
Charge compensation mechanisms in zirconolite ceramics for actinide disposition	Sheffield	Merve Kuman	Neil Hyatt	PhD
Development of sustainable substitutes for Pulversized Fly Ash in Cement and Concrete	Strathclyde	Andrea Kozlowski	Joanna Renshaw	PhD
Characterisation of thermal treatment products	Sheffield	Daniel Parkes	Claire Corkhill	PhD
Process monitoring of thermal treatment of nuclear wastes	Sheffield Hallam	Alex Stone	Paul Bingham	PhD
Understanding glass melt chemistry in thermal treatment of nuclear waste	Sheffield	Lucas-Jay Woodbridge	Russell Hand	PhD

The program is now around halfway through its five-year time frame. With impact now beginning to be realized, it is an exciting time to review progress. A brief summary of the three associated work packages is given below:

(i) *Removal of radionuclides from effluent:* Work at the University of Birmingham has optimized the synthesis of a metal-doped tin umbite showing exceptionally fast kinetic uptake of Cs. Birmingham has also developed a methodology to transform single natural zeolite ion exchangers by base treatment. The most promising material investigated to date is mordenite, which can be transformed to zeolite-P, where the hybrid mordernite/zeolite-P material shows excellent uptake of both Cs and Sr. Complimentary work at Imperial College has commenced on the improvement of nanomagnetite precipitation and thermal decomposition to produce well-dispersed functional magnetite particles with a narrow size distribution, to target actinide and lanthanide removal from effluents.

(ii) *Pond and silo sludge behavior:* The University of Leeds has focused on using advanced computational fluid dynamics (CFD) to simulate behavioral modification using polymer additives of waste slurries associated with the decontamination of legacy ponds and silos. In particular, a novel particle and polymer-laden flow technique based on the finitely extensible non-linear elastic dumbbell model has been developed, implemented and validated. Direct numerical simulations of particle laden flows are also being investigated. Further work at Leeds is establishing the use of ultrasonic backscatter systems as a remote in situ monitoring and characterization technique for the same systems, enabling complex validation data for the CFD models. The University of Manchester is also examining *in situ* techniques; in this case, acquiring *in situ* hydrogen bubble formation data in simulant Magnox sludge during irradiation. Manchester has also developed simulations of radiation deposition into nanoparticles of Au, Al_2O_3 and $Mg(OH)_2$ at a range of deposition energies. Current work is focused on building a scorer to detect ionizations and excitations caused by electrons in water.

(iii) *Wasteform Development:* A wide range of projects are ongoing for encapsulation of various high, intermediate and low-level wastes. Imperial college is currently investigating three different synthesis routes to form magnesium silicate cement, including one in which simulant Magnox sludge will be used, while Manchester University have completed the initial production of glass-ceramic materials and simulant high level waste glasses. Irradiation experiments on the base glass are currently underway, using the Dalton Cumbrian Facility particle accelerator. The University of Sheffield has acquired a full-scale simulant of thermally-treated (by plasma vitrification) plutonium contaminated material and is currently undertaking characterization and durability assessment of these materials. Other work at Sheffield University is focused on promotion of a suite of sodium titanosilicate glass compositions for the immobilization of Ionsiv E-11, based on the SiO_2-TiO_2-Na_2O phase diagram. Work at Sheffield Hallum University is also focused on glass development, specifically, glass compositions with high ion exchange material content, for disposal of resin wastes. Lastly, Strathclyde University is investigating different sustainable wasteform additives for acceptance to the Low Level Waste Repository (LLWR) in mixed cements. Work here includes assessment of advanced x-ray CT for analysis.

The following *Results & Discussion* provides an overview of current research highlights within the theme, grouped within each of the three key work packages.

RESULTS & DISCUSSION

<u>WORK PACKAGE 1: Removal of radionuclides from effluent</u>

PROJECT TITLE: New materials and methods for decontamination of effluent

Researchers: Antony Nearchou, Phoebe K. Allan and Joseph A. Hriljac
Affiliation(s): University of Birmingham, Diamond Light Source

Our team has been studying new materials for abatement of Cs-137 and Sr-90 radionuclides from nuclear waste streams. Focus is on selective uptake of these cations at low concentrations, in caustic solutions containing an excess of competing species. One material of interest is umbite, a zeolite-like silicate which can be doped with higher valency metals to enhance their ion exchange properties [1].

Assessment of the abatement properties of umbite have shown that high Cs^+ removal from solutions is achieved in the presence of excess competitors Na^+, K^+, Mg^{2+} and Ca^{2+}. In particular, the selectivity of Cs^+ over K^+ persists across the pH range, with a minor decline with increasing K^+ concentration (Fig. 1). Batch studies on the kinetics of the ion exchange process have shown that equilibrium Cs^+ uptake is achieved within the first 5 minutes of contact with the solutions. This is significantly faster compared to the zeolite clinoptilolite commonly used in industry. In addition, the rate of Cs^+ uptake by umbite is unimpeded by the presence of K^+ competitor. These highly advantageous properties cement umbites as strong candidates for use in industry.

To scope their industrial applicability, we have optimized the hydrothermal conditions needed to prepare these doped umbites. This has involved reducing the synthesis time and temperature for potential scale up, with successful synthesis achieved within one hour through microwave heating. Recently, we have integrated the umbite material into bound pellets (Fig. 2), which maintain their selective abatement properties. In addition, preliminary studies have shown that umbites partially exchanged with Cs^+ can be converted into dense solid phases where the radiocations will be immobilized, mitigating leaching into the environment [2].

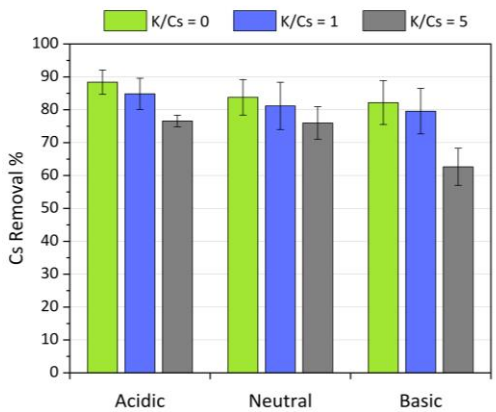

Fig. 1. Static batch ion exchange tests on doped umbite in acidic (pH 1.0-2.5), neutral (pH ~7), and basic (pH 9.5-11.0) solutions. Cs Removal % from Cs 10ppm solutions with different K/Cs ratios 0 (green), 1 (blue) and 5 (grey).

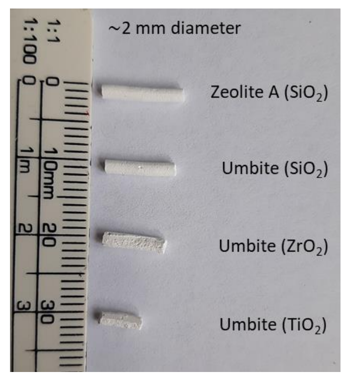

Fig. 2. A photograph of zeolite A and umbite pellets prepared using different binders (in parentheses).

PROJECT TITLE: Nanotechnology for effluent treatment, radionuclide assay and repair of ageing facilities

Researchers: Dr. Gurpreet Singh, Prof. Luc Vandeperre, Prof. Mary P. Ryan
Affiliation: Department of Materials, Faculty of Engineering, Imperial College London, UK.

Remediation of nuclear legacy pools is an area of high priority for the decommissioning objectives of the UK's nuclear roadmap. This is also in line with the government's 2030 and 2050 sustainable energy agendas to achieve Net Zero objectives. However, treatment of such enormous volumes of radioactive pool solution is still dependent on conventional filtration column processes. It is not just cumbersome to filter millions of liters of radioactive solution, but also highly energy and cost intensive. Furthermore, the used filter beds add enormous volumes to the secondary waste generated.

Regeneratable magnetic nanocomposites is a suitable alternative to filtration procedure, thereby creating a substantial impact on nuclear sector, especially by eliminating majority of energy costs, treatment times and reduction in secondary waste volumes. Previous work [3]. has demonstrated a high uptake capacity for selective removal of uranium from solutions using a phosphate-coated magnetic nanoparticle. However, the synthesis process to develop these novel nanoparticles is highly complex and lengthy. Furthermore, the particles can only be used in neutral and alkaline environments, which limits their use as acidic conditions are widespread within the nuclear sector.

The current work is focused on demonstrating a similar level of performance (even at acidic pH), by synthesizing these novel magnetic nanoparticles using a low-cost and simple work-up procedure, as shown in the schematic (Fig. 3). Latest progress on this project has demonstrated successful synthesis of spherical magnetite nanoparticles within a narrow range of 15 to 20 nm, with low polydispersity index. This step can be upscaled to large volumes using cheap raw materials and within a total run time of less than 60 minutes from start. Present efforts are focused on optimizing the procedure for coating these magnetite nanoparticles with a well-defined 3 to 5 nm layer of silica coating to withstand acidic conditions. Currently, there are some challenges to achieve this coating uniformly over individual magnetite particles, due to its high surface energy, which causes aggregation and thus form multi-cores. Solutions, such as introducing a surfactant, or altering the coating procedure is under evaluation to mitigate this problem.

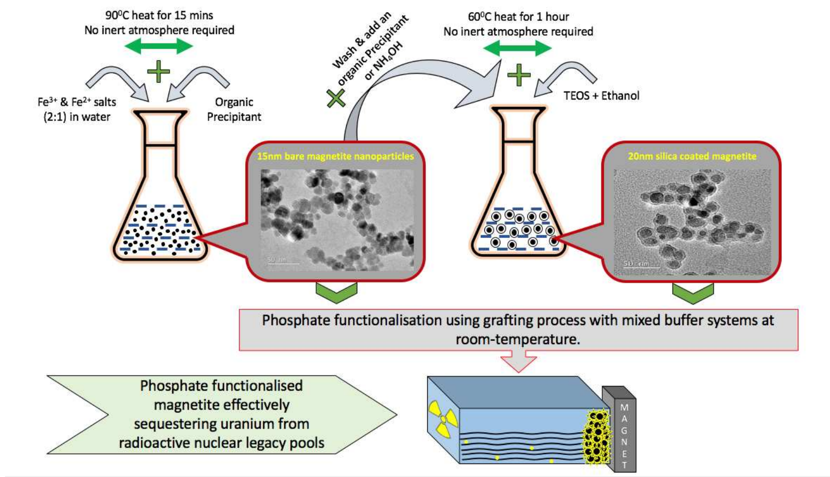

Fig. 3: Schematic summary of facile production of magnetic nanoparticles, for uranium removal.

PROJECT TITLE: Novel zeolite composites for remediation of aqueous nuclear decommissioning waste

Researchers: James Reed, Joseph Hriljac, Thomas Carey and Phoebe Allan.
Affiliation(s): University of Birmingham, Sellafield Ltd, National Nuclear Laboratory.

An industry requirement exists to develop innovative materials that have the capability to remove Cs-137 and Sr-90 from waste effluent streams. This is due to the varied composition of future feed-steams and the dwindling supply of industry-used Mud Hills clinoptilolite (HEU topology); a natural zeolite material which has been utilized at the UK's Sellafield site for >30 years due to its high affinity for both cesium and strontium [4]. In addition to being sourced naturally, zeolites can be obtained from other zeolite precursors via an inter-zeolite transformation, where the parent framework is broken down and recrystallized into a new phase (Fig. 4). This work primarily focuses on the chemical modification of Cs-

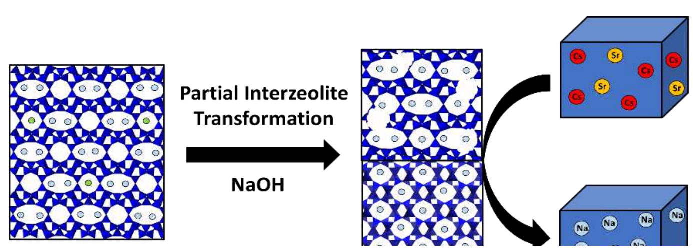

Fig. 4: Schematic of an inter-zeolite transformation and subsequent removal of Cs and Sr from wastewater.

favoring natural zeolites to generate composites with improved strontium affinity; hence providing a route to create Cs and Sr sorbents from a host of low-cost precursors.

A range of zeolite composites, with graduated phase ratios, have been generated from five natural zeolite precursors. Four different zeolites (three clinoptilolite phases and one mordenite) underwent transformation into an Na-P-type framework (GIS topology). An additional clinoptilolite zeolite, namely Mud Hills clinoptilolite, saw transformation into a chabazite-type structure (CHA topology). Transformations were monitored by PXRD and XRF, where an incremental conversion into the new phase was shown to occur as well as a steady decrease in the Si/Al ratio. Batch ion-exchange testing showed an increase in strontium uptake as the transformation proceeded from all five starting materials. This was likely due to both the development of a more aluminum-enriched phase and desilication of the parent zeolite, although the smaller cavities present in the newly crystalized structure could also have been significant. Cesium uptake remained high at early stages in the transformation but diminished at later stages, due to the dissolution of the parent structure. Composite materials of around a 50:50 ratio of phases generally showed a good removal of cesium and strontium. The lone mordenite material exhibited the greatest cesium uptake but lowest affinity for strontium. The effect of partial transformation on this structure was therefore the greatest: strontium removal increased markedly, and cesium uptake remained high (Fig. 5).

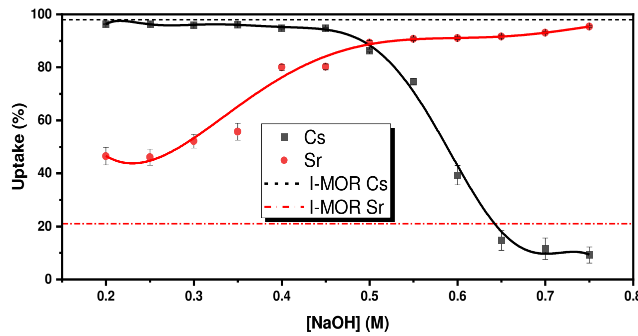

Fig. 5: Cs and Sr uptakes of MOR/GIS composites from batch ion exchange studies (10 ppm Cs/Sr; 50 ppm K/Ca). Dashed lines display uptakes achieved by the parent material.

In summary, this work shows the development of competent dual-uptake materials from low grade minerals. The high level of control also demonstrates the premise of ‘chemically-tuning’ a stock material to a given feed-stream, as opposed to a ‘one size fits all’ approach.

WORK PACKAGE 2: Pond and silo sludge behavior

PROJECT TITLE: Particle-laden flow characterization and prediction

Researchers: Lee Mortimer, Michael Fairweather
Affiliation(s): School of Chemical and Process Engineering, University of Leeds, UK.

The decontamination of legacy nuclear facilities, and waste clean-up and disposal, stand as matters of increasing urgency throughout the nuclear industry, with the UK government recognizing decommissioning and waste management as a national priority. In facilities around the UK, waste suspension flows transport solid-liquid mixtures of legacy material from historic ponds to other interim locations where they are safely stored. However, at present, these processes are performed poorly and with caution due to a lack of efficient design and understanding. High-fidelity particle-laden flow simulation techniques using first principles mathematical modelling have been developed at Leeds in order to explore the fundamentals of slurry flow dynamics and develop behavioral modification techniques.

Flows relevant to nuclear waste processing have been shown to be sensitive to various bulk flow chemical and physical properties, as well as the presence of additives such as nanoparticles or polymers. In order to gain insight into and develop such behavioral modification techniques, binary particle interactions have been studied using a high-fidelity immersed boundaries technique alongside direct numerical simulation (see Fig. 6). The effects of modifying Hamaker constant, ionic strength, coefficient of restitution, temperature and turbulence strength have now been studied, with the results published [5-7]. Critical results indicate that in turbulent wall-bounded flows, agglomeration can be encouraged by increasing the Hamaker constant of the flow, as well as reducing the coefficient of restitution through methods such as particle coating or tweaking other properties. Agglomeration was also identified to occur more frequently in low-Reynolds number flows, with the dynamic mechanisms studied in detail.

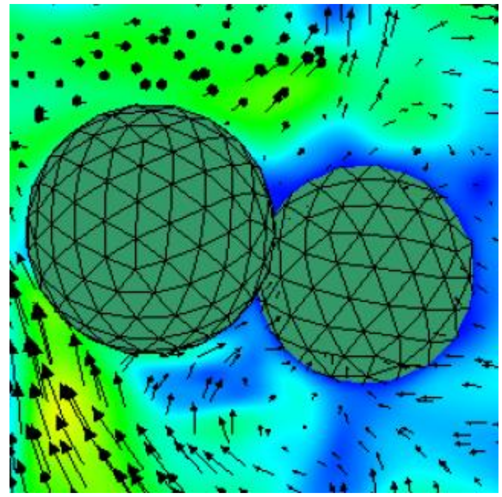

Fig. 6: Pseudo color and velocity vector representation of binary particle interaction at point of impact during collision event.

Furthermore, the use of polymer additives to modulate the turbulent properties of the flow as well as the aggregation behavior is fast becoming a promising method of modifying such flows with minimal additive concentration. High-fidelity modelling techniques have been employed to explore development of behavioral modification effects through polymer injection (Fig. 7). A novel particle and polymer-laden flow technique based on the finitely extensible non-linear elastic dumbbell model has been developed, implemented, and validated. After using the method to consider the effects of polymer-induced drag reduction on particle-laden flows, the technique has now also been extended to account for polymer-particle interaction. This is presently being used to provide insight into the potential and feasibility of using polymer additives to tune agglomeration and dispersion properties for nuclear waste transport flows. A novel polymer-particle interaction modelling technique based on electrostatic adhesion has now been developed and implemented and is being in the process of being tested and applied, with aims to augment and provide benchmarks for other relevant TRANSCEND experimental projects. The results provide insight into the potential and feasibility of using polymer additives to tune agglomeration and dispersion properties for nuclear waste transport flows and are currently being written up for publication in two papers, one examining the effects of polymer-fluid interaction, and another focusing on the mechanisms for floc formation under the effects of shear.

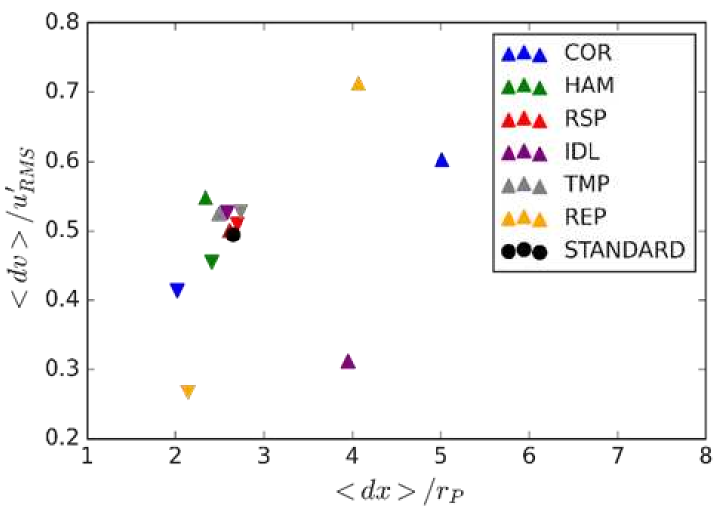

Fig. 7: Effect of behavioral modification parameters on the mean interparticle distance <dx> and the mean relative velocity <dv> during an interaction event. Up and down arrows indicate increase and decrease in parameter, respectively, whilst fixing all other parameters. COR: Coefficient of restitution; HAM: Hamaker constant; RSP: Reduced surface potential; IDL: Inverse Debye length; TMP: Temperature; REP: Reynolds number.

PROJECT TITLE: Simulation of behavioral modification effects in suspension waste pipe flows

Researchers: Bistrat Wolde, Michael Fairweather
Affiliation(s): School of Chemical and Process Engineering, University of Leeds, UK.

The overall aim of this study is to address fundamental technical difficulties that are encountered within the nuclear industry. Developing and facilitating approaches for safer, cost-efficient waste management and decommissioning is the focus of the research. Understanding and modelling pond and silo sludge behavior is essential to the management of radioactive wastes. In legacy ponds and silos, for example at Sellafield, characterizing how sludges and slurries containing dense particulates will behave is vital for post-operational clean-out (POCO) operations. As noted, in this project the aim is to establish a predictive tool to support POCO operations through improvements in the flow, mixing and separation of wastes during retrieval and POCO operations. In particular, the impact of behavioral modification on particle agglomeration, and hence the likely deposition of particles during processing, will be studied.

To investigate behavioral modification effects in suspension waste flows, wall-bounded pipe flows are being simulated. Modifications of fluid and solid particle properties present in the inventory can be implemented practically by changes in temperature, ionic strength and pH of the liquid-phase, and injecting additives such as polymers into the liquid phase that will attach to the particles, modifying their surface properties. The impact of particle coatings will also be investigated. These modifications will change the way particles interact by affecting van de Waals forces, the restitution coefficient and electric double layer repulsion forces.

A direct numerical simulation was carried out for a fully developed turbulent pipe flow at three different turbulent bulk Reynolds numbers, Re_b = 3975, 5330 and 11,700. Mean velocity, and normal and shear stress, profiles within the flow were gathered to validate the code deployed. The predictions have been validated through comparison with literature simulations and experimental datasets. The present work is in good agreement with literature results – both DNS and experimental. Similar validations against particle-laden flows have been performed. Validation of the predictive methods against experimental data on the critical particle deposition velocity is also underway. To establish the impact of behavioral modification effects, a range of suspension waste pipe flows will be simulated. The use of modifications to fluid and solid particle properties to promote desired outcomes such as reducing particle agglomeration will be considered. This has entailed the implementation of two-way and four-way coupling between the particles and the fluid flow, as well as the incorporation of models for particle collision and agglomeration**.**

PROJECT TITLE: Advanced characterization for suspension wastes with acoustic backscatter and behavior modification polymeric additives.

Researchers: Joseph Hartley, Jeffrey Peakall, Richard Bourne, Timothy Hunter
Affiliation(s): School of Chemical and Process Engineering, University of Leeds, UK.

The clean out and processing of the UK stores of legacy ILW sludge is underway, and due to the technical challenges of monitoring and characterizing these wastes, a new approach is under consideration; acoustic backscatter. Characterization by Acoustic Backscatter Systems (ABS) can allow for remote, online monitoring of waste slurries through the processing stages, where concentration and size data recorded. Current acoustic theory allows for understanding of mono-disperse sediment systems with respect to sediment particle size, but bi-disperse systems, and measurement of dynamic systems, are not well practiced. Consequently, this project will seek to fill these gaps in understanding, and to automate and improve much of the data analysis, where Machine Learning (ML) techniques will also be used. Thus, in short, the projects research aims are; (i) Size characterization of virgin vs. sieved size fractions and bimodal size fraction mixtures of spherical glass particles. (ii) Development of ML code to characterize size and concentration of spherical glass particles. (iii) Application of research aims one and two to more realistic flocculated waste sludges.

The use of acoustics to look at sediments has been used in estuarine and riverbed environments for some time, where the basic theory from this has been progressed by researchers looking to apply this to nuclear waste sludges. This acoustic theory states that when investigating sediment laden suspensions at a size range of microns to hundreds of microns, the particles attenuate the sound signal via two main mechanisms, namely viscous inertial and scattering. A natural logarithmic term has been identified, the *G* function, defined by Eq. (1), which allows the concentration independent sediment attenuation coefficient to be calculated [8].

$$G = \ln(\Psi r V) = \ln(k_t k_s) + \frac{1}{2} \ln M - 2r(\alpha_w + \alpha_s) \qquad (1)$$

Currently, work has been completed on calculating this sediment attenuation coefficient of different sizes of spherical glass beads at various frequencies, using a Met-flow Ultrasonic Velocity Profiler (UVP). Here, probes inserted directly into the suspension ('*in situ*') as well as connected to the outside of the calibration tank ('*ex situ'*) were compared to understand the potential to use remote configurations industrially to limit exposure hazards. Fig. 8 shows the experimental results of two different glass bead sizes (*H22*, ~40 µm and *H16,* ~90 µm) when using a 4 MHz probe with the UVP, compared to calculated values from a scattering attenuation model [9]. Both configurations gave consistent values, which were also very close to the analytical correlation for the smaller *H22* particles. The slight deviation from the expected theoretical value for the larger *H16* particles may be from instrumental limitations of the 4 MHz probes, and lower frequencies are currently being investigated. Work to facilitate a reliable method that calculates the particle size from acoustic data by modifying existing acoustic theory is currently underway. As such, the future work objectives are to develop this method such that it can be used to determine a particle size distribution for monodisperse and bidisperse particle size systems. Within this, study of how particle size distribution of the test material affects the acoustic signal will be completed, via sieving the spherical glass beads into tighter size fractions and examining how this differs from the as received. Development of a ML coding package will then be worked on, so that a comparison of this data analysis method compared to the acoustic theory based method can be completed. Flocculant material will be introduced to the system to more realistically mimic end application, with the hope that the advanced understanding from the aforementioned research will allow tracking of the floc sizes through processing.

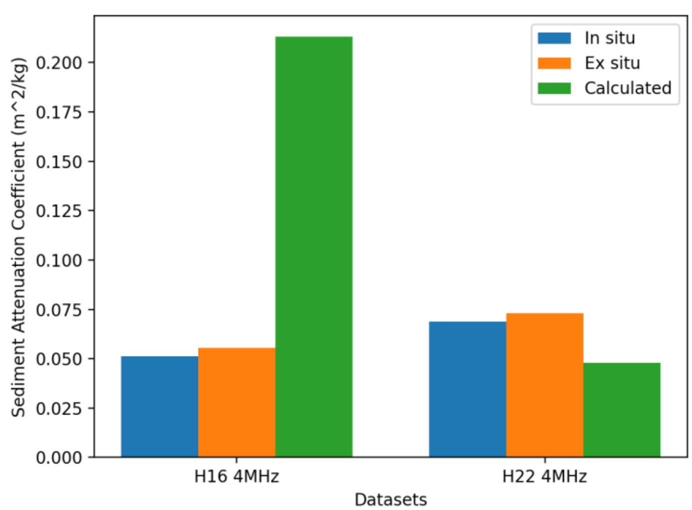

Fig. 8: Measured concentration independent sediment attenuation coefficients for two sized glass systems ('H16' & 'H22') with 4 MHz transducers, in comparison to estimates from the model by Betteridge et al. [9].

PROJECT TITLE: Simulations of processes at and across nanoparticle-water interfaces

Researchers: Ella Schaefer, Fred Currell
Affiliation(s): The University of Manchester, Manchester, UK.

Background: Irradiated nanoparticles (NPs) in aqueous environments have relevance to both the health and nuclear industries. This is due to the chemical changes the irradiated NP can cause in the surrounding media, such as the formation of •OH radicals, low energy electrons and H_2 [10-11]. Low energy electrons and •OH radicals cause DNA damage to cancer cells during radiotherapy [12], and as NP interfaces are present in nuclear waste, the formation of H_2 is highly relevant to nuclear safety cases [13]. The aim of this project is to cultivate an integrated account of all the processes that can occur at the NP-water interface.

Progress: A simulation method has been developed through the use of TOPAS software, that allows the user to deposit radiation into a NP within a hollow water sphere and calculate the resultant radial dose distribution. This simulation has been run with various NP species (Au, Al_2O_3, $Mg(OH)_2$ and water) of different sizes, densities and irradiated by a range of both high and low photon energies. Additionally, a process for detecting where an ionization or excitation occurs in a water sphere, following NP irradiation, has been created.

Future work: The next stage of this project is to run these simulations with a wider range of oxide/hydroxide species. From there the model should be expanded further to include the chemical stage of water radiolysis. So far excitons are not accounted for in this model; a supplementary model utilizing DFT theory to model the diffusion and subsequent energetic transfer of an exciton, should be built to address this.

PROJECT TITLE: Radiation Induced CHanges in Effluents/Sludges (RICHES)

Researchers: Mel O'Leary, Fred Currell
Affiliation(s): The University of Manchester, UK.

This project investigates the effect of irradiation on the properties of corroded Magnox cladding sludges. We have a paper currently being published in scientific reports on the radiolytic production of hydrogen in these sludges. Key findings here include:

- Determination of the radiolytic production yield of H_2 in Magnox sludges
- Determination of the diffusivity of H_2 in Magnox sludges
- Determination of the radiolytic consumption of H_2 in Magnox sludges
  A summary model from this data which established the equilibrium concentration of radiolytically produced H_2 in Magnox sludges
- First observation of the transition from dissolved to gas-phase radiolytically produced H_2 in Magnox sludges

We have also completed an experiment into the possibility of radiation induced electronic charge build up on particulate phase of the sludge. This build up was investigated in magnesium hydroxide and alumina, both of which are prominent components of the sludges. The deflection of settling nanoparticles of each material was measured while they were being irradiated. The magnesium hydroxide nanoparticles no deflection was observed from the magnesium hydroxide. A deflection was observed from the alumina nanoparticles, implying charge buildup 0.19 ± 0.02 aC per nanoparticle. These results imply that there is no net charge build up in magnesium hydroxide and significant charge up on alumina nanoparticles.

WORK PACKAGE 3: Wasteform Development

PROJECT TITLE: Synthesis and characterization of zirconolite with charge compensator cation for Pu immobilization

Researchers: Merve Kuman, Laura J. Gardner, Lewis R. Blackburn, Shikuan Sun, Martin C. Stennett, Claire L. Corkhill, Neil C. Hyatt.
Affiliation(s): Department of Materials Science and Engineering, University of Sheffield, UK.

Plutonium is formed in nuclear reactors by irradiating the uranium in nuclear fuel. Therefore, Pu is created by reprocessing the spent nuclear fuel. Plutonium is a potentially valuable energy source and there are two different ways for UK Pu management policy. For this purpose, it can be converted to mixed oxide fuel to reuse. However, the separated Pu that is not converted to mixed oxide fuel should be disposed by immobilization into ceramic or glass host matrix [14]. Zirconolite, which is natural mineral found in geological environments, is a single-phase ceramic host for Pu due to its high aqueous durability and radiation tolerance properties. Zirconolite provides 5 cation sites with Ca, Zr and Ti layers for Pu immobilization, the incorporation of charge compensators and neutron poisons [15].

The aim of the project is to research and development the zirconolite ceramic structure for treatment of contaminated Pu by investigating the effects of charge compensators and neutron poisons on the zirconolite phase assemblage and microstructure. Therefore, the effect of a cation charge compensator (Fe^{3+}) was researched on the zirconolite structure without Pu and its surrogates loading. So far, the charge compensator cation doped zirconolite structures with cold press and sintering method were produced to get dense ceramic matrix. The phase assemblages and microstructures were analyzed via XRD and SEM, respectively and zirconolite-2M was found as major phase with minor phases. In addition to these characterization methods, unit cell refinement was carried out to understand the incorporation of charge compensators into the zirconolite structure. The coordination environment and oxidation state of Fe ion was revealed via Mössbauer spectroscopy and X-ray absorption near edge spectroscopy (XANES) data to understand the Fe substitution in which Ti site. For future work, zirconolite matrix will be prepared with different charge compensators and neutron poisons, utilizing HIP method.

PROJECT TITLE: Characterization of thermal treatment products & understanding glass melt chemistry

Researchers: Daniel Parkes[1], Claire L. Corkhill[1] Mike Harrison[2], Sean P. Morgan[3], Clare Thorpe[1]
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This project is focused on the thermal treatment of intermediate level waste (ILW). ILW has a wide range of different compositions and different potential thermal treatment options. To look at them all is beyond the time scale of this project, therefore several industrial samples have been selected to investigate. Valingar have carried out several inactive trials for the thermal treatment of Plutonium Contaminated Material (PCM) using plasma processing [16]. Two of the five trials had remnant material available for analysis. Initial basic characterization has been carried out including XRD, XRF, acid-digestion with ICP analysis and SEM. The samples have also been crushed and washed ready for PCT dissolution experiments to analyze durability. Future work will involve trying to produce lab simulants of the Valingar melts with the addition of Ce as a simulant for Pu. These will be analyzed to assess the concentration and distribution of the Ce across the sample, focusing on the partitioning between the glass matrix and any crystalline phases. PCT tests will also assess the durability and potential leaching of Ce out of the waste form. Geomelt is another major thermal treatment technique that has been trialed in the UK, but it is not currently in the plans as a thermal treatment for ILW. In the USA, however, Veolia Nuclear Solutions Federation (VNSF) have carried out many inactive trials for both US and international waste including simulants from Fukushima in Japan [16-18]. Veolia have provided four glass samples, where initial basic characterization has included XRD, XRF, acid digest and ICP analysis and SEM. The samples include inactive Cs and Ce, and further analysis will investigate the distribution and partitioning of these inactive simulants. The samples have also been crushed and washed ready for PCT dissolution experiments to analyze durability and the potential leaching of the simulants.

PROJECT TITLE: Radiation effects on nuclear waste forms: How does the crystallinity of a glass-ceramic affect radiation tolerance?

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The High Activity Storage Tanks at Sellafield will go through a post operational clean out (POCO) phase [19]. The storage tanks feed the vitrification lines where the radioactive liquid waste is converted into a solid and durable form by incorporating it into a borosilicate base glass. The POCO waste is expected to have high concentrations of molybdenum. Molybdenum has low solubility; therefore, base glass made with Ca and Zn was developed to suppress the formation of undesirable water-soluble 'yellow phase' and to produce a glass-ceramic material where the molybdenum partitions into a durable crystal phase known as powellite ($CaMoO_4$). To be able to predict the durability of this waste over timescales of many thousands of years relevant to geological disposal, the effects of radiation on high molybdenum content glass-ceramic nuclear wastes must be understood. The amorphization of crystals accompanied by volume change could lead to cracking and higher radionuclide leaching rate to the environment. This information is essential in the process of determining long-term safe disposal conditions and will be invaluable to the community, industry, and broader stakeholders.

Non-active nuclear waste simulant glass-ceramic samples with various compositions and different crystallinity were produced by National Nuclear Laboratory. X-ray diffraction and energy-dispersive X-ray spectroscopy measurements revealed the presence of five common crystal phases (powellite, zircon, ceria-zirconia, zincochromite, and ruthenium dioxide). Electron microprobe analysis showed that rare earth elements (surrogates for radioactive actinides) mainly accumulated in powellite, zircon and ceria-zirconia. The size and morphology of powellite crystals varied based on their positions in the product container due to the different rates of natural cooling. Cracks formed in powellite and around zircon crystals, presumably due to a thermal expansion mismatch between the glass and these crystal phases.

Nickel and gold ion irradiation experiments were performed and subsequent analysis using scanning electron microscopy and electron backscatter diffraction measurements showed that ceria-zirconia, zincochromite, and ruthenium dioxide were highly radiation-tolerant phases while powellite and zircon seemed to become amorphous and swell considerably. The swelling of crystals was more substantial in the gold irradiated sample. Powellite has previously been reported as a highly radiation-tolerant material [20], therefore, further ex-situ and in-situ transmission electron microscope analyses will be performed to fully understand the irradiation-induced microstructural effects on powellite. While these experiments using heavy ions are representative of changes induced by the alpha recoil nucleus, ongoing Raman, and electron paramagnetic resonance spectroscopy measurements on He irradiated glass samples will examine alpha particle irradiation effects in the base glass. This research will provide new insights into the behavior of glass-ceramic nuclear wastes under conditions of relevance to long term temporary storage and disposal.

PROJECT TITLE: Investigation of pulverized fly ash substitutes in cement: Impact on physicochemical properties and waste encapsulation performance

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Clinker substitutes are frequently used in the cement and concrete industries to reduce CO_2 emissions associated with production, improve physicochemical properties and performance, and reduce costs. Pulversized Fly Ash (PFA), a fine waste residue produced in coal-fired power stations, is commonly used as a partial clinker substitute in Ordinary Portland cement (OPC), including for the immobilization of low-level nuclear waste [21]. Because of the global trend to shut-down coal-fired power stations, the production of PFA is decreasing and will eventually cease [22]. Alternative sustainable clinker substitutes are therefore needed. This replacement has to meet the performance standards within the application environment: physical, chemical, and mechanical properties, as well as performance and suitability for use.

In this study, we will investigate the compatibility of metakaolin, limestone, olivine, trass, and beneficiated pulverized fly ash as a substitute of PFA in OPC, comparing these substituted cements to the current standard (PFA+OPC). The focus of the study is on the cementing properties, such as setting time, hydration, strength, and rheology, and physicochemical properties of the cement and behaviour when used to encapsulate radioactive waste. In particular, I will examine the leaching behaviour and reactions with groundwater or the stored waste.

Currently, we are characterizing the standard PFA+OPC, using samples provided by the Low-Level Waste Repository Ltd. (LLWR) using. X-ray computed tomography (XCT) to characterize the internal microstructure. The current composition is: 1.35-1.70% air, 1.14-2.69% clasts, 80.22-87.29% grout, 14.72-15.38% other, giving a reference for comparison with the substitutes. In the coming months, the elemental composition of all alternative materials will be identified through inductively coupled plasma mass spectroscopy, and fluid and chemical analysis performed during leaching experiments in groundwater. These samples will be repeatedly scanned using XCT over the leaching period to link the spatial distribution of the structural changes to the chemical evolution. Future work will include studying the long-term leaching effects and the interaction of the Low-Level waste (using a mock waste formulation) with the concrete will be examined. These studies will allow us to identify changes to the cement microstructure and physicochemical properties arising from the PFA substitutes, and the chemical and physical interaction of the cements, especially with groundwater. Such understanding is critical for the adoption of clinker alternatives in nuclear waste encapsulation.

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