NUCL 1

Plenary: Spectroelectrochemical sensors for measurements on complex samples in harsh environments

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Sensors need good selectivity for accurate measurements on complex samples and ruggedness to survive in harsh environments. Spectroelectrochemistry offers a means of providing the selectivity to target a single analyte in a sample containing many potential interferences. In one type of spectroelectrochemical sensor additional selectivity is provided by subjecting the analyte to electrolysis that electrochemically modulates an optical signal. The modulated signal is distinguishable from the constant signal(s) from the potential interference(s). The analyte is quantified by the magnitude of the change in optical signal. This strategy can be implemented with an optically transparent electrode coated with a thin polymer film that preconcentrates the analyte for spectroelectrochemical detection by internal reflection spectroscopy. Spectroelectrochemical sensors using UV-vis absorption or fluorescence have been developed for detection of a variety of analytes: metal complexes; heavy metals such as lead, cadmium, copper and zinc; ferrous and ferric iron; polycyclic aromatic hydrocarbons; and nitrate. Sensors have been demonstrated on a complex sample of radioactive waste from the Hanford Site.

NUCL 2

Thin-film spectroelectrochemical sensor for technetium

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A spectroelectrochemical microelectrode sensor is being developed for the detection of technetium (Tc) in soil and subsurface water at the Hanford nuclear waste site near Richland, WA. The sensor comprises three modes of selectivity, which allow the analyte to (1) partition into a chemically selective polymer film coating an optically transparent electrode (OTE), (2) undergo electrolysis at a given potential, and (3) luminesce in either its oxidized or reduced form at a selected wavelength. The stability of the sensor is improved by modifying the reference electrode, which is composed of either vapor-deposited platinum or silver. The selective thin film allows the analyte to preconcentrate at the electrode surface, increasing the response signal. Luminescent modulation occurs in the visible region with the OTE indium tin oxide (ITO). Characterization of this

sensor is accomplished using rhenium and ruthenium analogues of Tc as model compounds.

NUCL 3

Formation and subsequent spectroelectrochemical sensing of Ru and Eu species in both solution and ion selective films

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Fast, robust, and cost-effective means of detecting various products of nuclear fission are necessary for process monitoring among other purposes. A sensor based on spectroelectrochemistry is an excellent candidate to meet these needs as it can specifically quantify lanthanides and transition metals by simultaneously monitoring at least two physiochemical properties. This applicability of spectroelectrochemistry is demonstrated with europium and ruthenium; these elements were chosen due to their spectroscopic and electrochemical characteristics as well as their relevance within the fuel cycle and industrial fields. Both Eu and Ru display II/III redox couples and have well documented luminescence characteristics that change with oxidation state, which will be utilized in the sensor methodology. Furthermore, upon complexation with the sensitizing ligand 2,2’-bipyridine, the spectroscopic characteristics, specifically quantum yield of emission, of both Eu and Ru are significantly improved. This significantly decreases detection limits of Eu and Ru. This work will explore the in-situ generation of $Eu(bpy)_n$ and $Ru(bpy)_n$ complexes and their subsequent spectroelectrochemical sensing using our sensor methodology.

NUCL 4

On-line process monitoring for plutonium oxide production

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Process monitoring in large nuclear reprocessing facilities is typically conducted in laboratory settings using labor-intensive destructive analysis techniques. Development and implementation of on-line process monitoring tools would be advantageous to these facilities by allowing for increased efficiency and throughput, reduced sample analysis cost, and decreased personnel exposure. Nuclear processing facilities, however, present a challenging environment for the implementation of on-line sensors for process

monitoring applications. Sensors placed in processing areas within these facilities are subjected to environments with harsh radiological conditions, high acid concentrations, and high temperatures. Researchers at the Savannah River National Laboratory (SRNL) have been utilizing H Canyon/HB Line, located at the Savannah River Site (SRS), as a test bed location to investigate the use of on-line monitoring systems in harsh radiological environments. H Canyon/HB Line is the nation’s only hardened nuclear separations processing facility. The facility is currently producing plutonium oxide for feedstock to the Mixed Oxide (MOX) Fuel Fabrication Facility under construction at SRS. In this work we explore the use and potential process improvement benefits of several detectors for process monitoring applications. Initial proof-of-concept testing with commercially available detection systems will be presented as well as process modeling results to predict throughput improvements.

NUCL 5

Batch, column, and timed-resolved U(VI) luminescence study on the effect of phosphate on U(VI) sorption and retardation in subsurface sediments

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Phosphate is an important chemical species for radioactive waste chemistry. Presence of high concentrations of phosphate not only precipitates uranium in both high-level waste tanks and low-level waste infiltration ponds, it also becomes a factor influencing the flow-and transport properties of tank waste due to possible precipitation of sodium phosphate, [$Na_3PO_4 \cdot 12H_2O$]. Recently, phosphate has been proposed as a potential remediation agent of uranium in contaminated soils and sediment, taking advantage of the low solubility and high long-term stabilities of most uranium (VI) phosphate species. However, our knowledge on uranium (VI)(commonly exists as the uranyl ion, UO_2^{2+})-phosphate nucleation, precipitation and surface complexation on soils and sediments are insufficient to predict U(VI) speciation and transport in subsurface environment. In this work, batch and column experiments are performed to identify the dominant U(VI) species and quantify the effect of phosphate on the sorption/desorption and transport of U(VI) in Hanford 300 Area sediments in synthetic groundwater emulating conditions at the site. Our results indicated that at micro-molar concentrations of uranium, the presence of mM-level phosphate already showed retardation to uranium release when the groundwater contains phosphate, and for some sediments, uranium immobilization persisted when phosphate was no longer in the influent. Sequential extractions of sediments confirmed that most uranium was retained in columns treated with phosphate. However, in none of the samples, no spectral features pf uranium-phosphate was observed. Likely, phosphate-bearing surface complexes are responsible for uranium immobilization under the present conditions.

NUCL 6

Development of a dual excitation fiber optic Raman microscope for the identification of mineralogical samples

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Raman microscopy is widely used in the identification of minerals. In most analysis, a near-IR laser is used to minimize fluorescence interference. However, even with near-IR excitation, background emissions such as F-center luminescence and blackbody emission can be a problem. For these minerals, a visible laser may work better and have less interfering background emissions. We have developed a dual excitation (532 nm and 785 nm) Raman fiber optic microscope probe with a common focus for both lasers and allows the simultaneous acquisition of the two Raman spectral regions. A video camera is integrated into the probe for live video capture of the magnified sample image, and all probe operations such as focusing, imaging and data acquisition are controlled through software. The development of the Raman microscope instrument and its applications to the analysis of nuclear waste materials and concrete corrosions in nuclear reactor structures will be presented.

NUCL 7

Methods for Pu valence determination in nuclear material processing solutions

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Monitoring and control of actinide oxidation states is critical to maintain safety and efficiency in nuclear materials processing. The absorption spectra of the actinides are sensitive to oxidation state, solution acidity (nitric acid), and temperature, making it difficult to establish an accurate universal regression model for all possible process conditions. Furthermore, for plutonium, oxidation and/or disproportionation will naturally occur at some conditions, meaning that stable standards cannot be made without introducing chemical stabilizers that can influence the calibration. Here, we describe the online measurement of chemically unstable forms of Pu. UV-visible absorption spectra are classified into one of several regimes. Localized calibrations are based on spectra taken as the solutions naturally evolve – the total Pu concentration remains constant but the relative amounts of different oxidation states vary. The relative concentrations of these species are determined by principal components analysis, and the results are used as the basis for subsequent predictive models. Because this approach is resource-intensive, we have incorporated calibration transfer schemes to allow a single calibration to be ported to multiple instruments. The calibration transfer is based on the measurement of fundamental properties of the spectrometers, which can be measured semi-continuously in the field and do not rely on the response to standard solutions.

This scheme leads to a robustly stable instrument. The implementation of these schemes into a Pu processing facility at Savannah River Site is described.

NUCL 8

Spectroscopic online monitoring for process control and safeguarding of radiochemical streams

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There is a renewed interest worldwide to promote the use of nuclear power and close the nuclear fuel cycle. The long term successful use of nuclear power is critically dependent upon adequate and safe processing and disposition of the spent nuclear fuel. Liquid-liquid extraction is a separation technique commonly employed for the processing of the dissolved spent nuclear fuel. The instrumentation used to monitor these processes must be robust, require little or no maintenance, and be able to withstand harsh environments such as high radiation fields and aggressive chemical matrices.

Our group has been investigating the use of optical spectroscopy for the on-line monitoring of actinides, lanthanides, and acid strength within fuel reprocessing streams. Acid strength/pH is of critical importance for process quality and control, as it affects speciation of the target analytes and thus their extraction efficiency and selectivity. In a full scale nuclear fuel reprocessing facility, classic potentiometric pH measurements are not suitable for obtaining real-time continuous data due to their requirements of frequent calibration and maintenance and poor long-term stability in aggressive chemical and radiation environments. Towards addressing this need, this work is aimed to develop a general method for determining pH by Raman spectroscopy, which provides real-time remote on-line monitoring capability. Our group's current research in this area will be presented and discussed.

NUCL 9

Single droplet analysis of metal-ligand solutions by electrospray ionization mass spectrometry using an induction-based fluidics source

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Electrospray ionization (ESI) revolutionized analytical chemistry research however; a drawback is that the large majority of the sample is not transferred into the mass

spectrometer aperture. This is a consequence of the fact that charged droplets produced by the electrospray capillary Coulombicly repel each other causing the majority of the solutes in the droplets to be deposited on the outside of the ESI source. A technique referred to as induction-based fluidics (IBF) has been used to form droplets as small as 17 nL and accurately aim the droplet directly into the aperture of an ESI mass spectrometer for detection, eliminating the deposition (or contamination) of sample on the outside of the source. With increased sensitivity and sample sizes being reduced to the nanoliter range, samples having modest levels of radioactivity can be analyzed in this fashion to support nuclear fuel separations research. Studies were completed to characterize the IBF source in comparison to nano-ESI sources focusing on the transfer efficiency of each source, the effect of droplet sizes in the IBF source and the agreement of ions generated with both techniques. Solutions containing lanthanide (Ln) nitrates and an organic ligand used in solvent-extraction processes for metal separations, particularly CMPO, TBP, EDTA and small organic acids, were analyzed in both the positive and negative ion modes to establish ion source (both IBF and nano-ESI) performance. This approach suggests utility for analysis of solutions where the sample quantity is limited, or where potential hazards associated with the sample solution (e.g. radiological) limit the applicability of a normal ESI source.

NUCL 10

Innovation in XRF: Determination of plutonium in spent fuel

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High resolution X-ray (hiRX) is a new analytical technology for the determination of plutonium in spent nuclear fuel. hiRX is based on monochromatic wavelength dispersive X-ray fluorescence (MWDXRF) and provides a direct, nondestructive assay for plutonium quantification with minimal sample preparation. The performance of a benchtop prototype hiRX instrument has been evaluated with spent fuel samples in a reprocessing environment. A disposable ultralow volume cell (5-7 µL), which is filled with sample using a pipette, was utilized in field testing. This low amount of solution enhances operator safety and reduces waste to be disposed. The hiRX prototype reports both plutonium and uranium content since uranium is the primary matrix element in spent fuel, so instrument calibration was performed with standards containing uranium in amounts up to 100:1 (U:Pu, g/L). Linear response and a limit of detection (100 s) of 1 mg/L were demonstrated for plutonium in a uranium matrix. Absorption matrix effects were observed for uranium content above 100 g/L. Repeatability was <5% RSD for multiple cells. Flow-based sample introduction has been studied in the laboratory using a synthetic spent fuel matrix and may enhance precision and accuracy for hiRX measurements. This highly selective and sensitive method offers a new capability for rapid plutonium quantification in spent nuclear fuel matrices and a range of

potential applications for actinide measurements in safeguards operations.
LA-UR-15-22138

NUCL 11

Where is the plutonium? Detection and location of plutonium-containing particles in Tank 18 waste at Savannah River site (SRS) using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), wavelength dispersive spectroscopy (WDS), and X-ray diffraction (XRD)

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The F-Area Tank Farm (FTF) Performance Assessment (PA) utilizes waste speciation in the waste release portion of the FTF fate and transport model for movement of chemical and radionuclide into the environment. The waste release modeling associated with the residual plutonium in Tank 18 has been identified as a primary contributor to the Tank 18 dose uncertainty. In order to reduce the uncertainty related to plutonium in Tank 18, a better understanding of the plutonium speciation in the Tank 18 waste (including the oxidation state and stoichiometry) is desired.
Savannah River National Laboratory (SRNL) utilized Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Wavelength Dispersive Spectroscopy (WDS), and X-ray Diffraction (XRD) to analyze Tank 18 samples to provide information on the speciation of plutonium in the waste material. The plutonium identified in the samples was in the form of discrete particles usually <1 µm, but ranging up to several micrometers in diameter. . Due to the small size and low concentration of the plutonium particles, the chemical form of the plutonium remains uncertain. Qualitatively, the particles of plutonium found in the SEM analysis do not appear to account for all of the plutonium in the sample based on analysis of the Tank18 samples as seen in Figure 1 and Table 1.

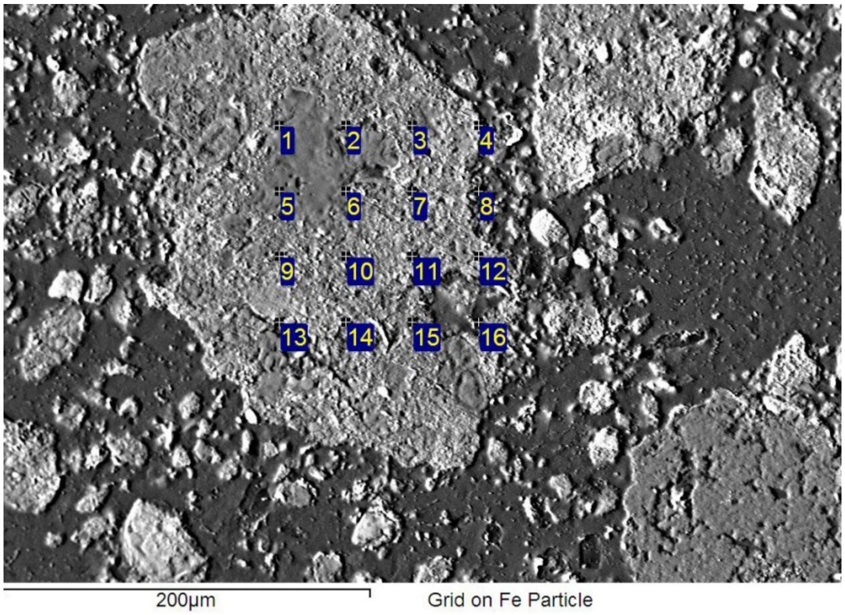
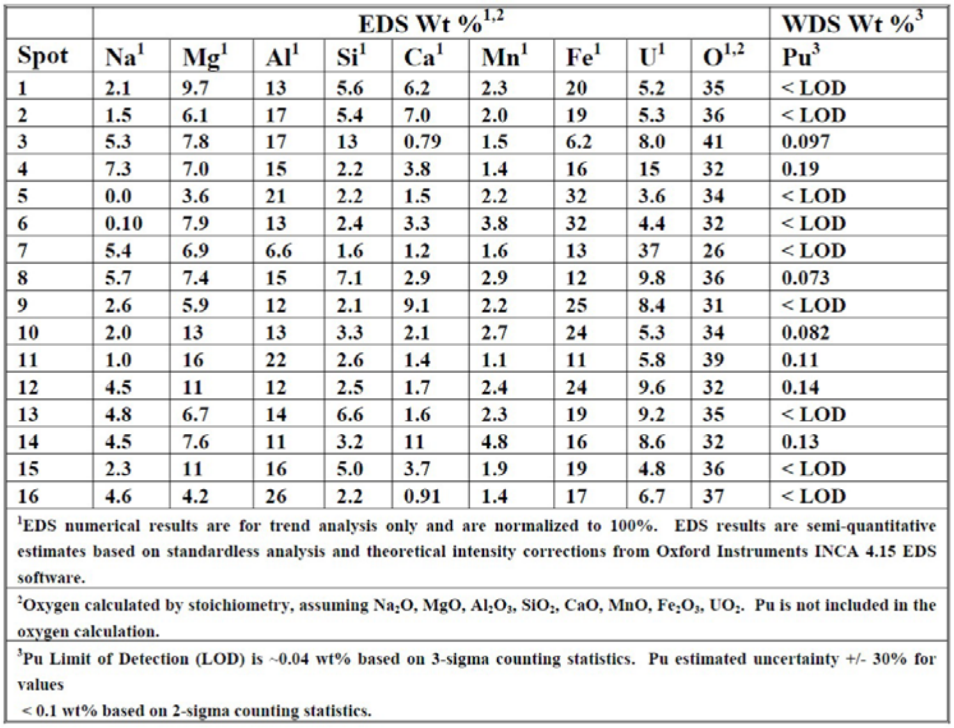


Figure 1. Grid of analysis locations on iron particle.



	EDS Wt %^{1,2}									WDS Wt %^{3}
Spot	**Na^{1}**	**Mg^{1}**	**Al^{1}**	**Si^{1}**	**Ca^{1}**	**Mn^{1}**	**Fe^{1}**	**U^{1}**	**O^{1,2}**	**Pu^{3}**
1	2.1	9.7	13	5.6	6.2	2.3	20	5.2	35	< LOD
2	1.5	6.1	17	5.4	7.0	2.0	19	5.3	36	< LOD
3	5.3	7.8	17	13	0.79	1.5	6.2	8.0	41	0.097
4	7.3	7.0	15	2.2	3.8	1.4	16	15	32	0.19
5	0.0	3.6	21	2.2	1.5	2.2	32	3.6	34	< LOD
6	0.10	7.9	13	2.4	3.3	3.8	32	4.4	32	< LOD
7	5.4	6.9	6.6	1.6	1.2	1.6	13	37	26	< LOD
8	5.7	7.4	15	7.1	2.9	2.9	12	9.8	36	0.073
9	2.6	5.9	12	2.1	9.1	2.2	25	8.4	31	< LOD
10	2.0	13	13	3.3	2.1	2.7	24	5.3	34	0.082
11	1.0	16	22	2.6	1.4	1.1	11	5.8	39	0.11
12	4.5	11	12	2.5	1.7	2.4	24	9.6	32	0.14
13	4.8	6.7	14	6.6	1.6	2.3	19	9.2	35	< LOD
14	4.5	7.6	11	3.2	11	4.8	16	8.6	32	0.13
15	2.3	11	16	5.0	3.7	1.9	19	4.8	36	< LOD
16	4.6	4.2	26	2.2	0.91	1.4	17	6.7	37	< LOD

[1] EDS numerical results are for trend analysis only and are normalized to 100%. EDS results are semi-quantitative estimates based on standardless analysis and theoretical intensity corrections from Oxford Instruments INCA 4.15 EDS software.

[2] Oxygen calculated by stoichiometry, assuming Na_2O, MgO, Al_2O_3, SiO_2, CaO, MnO, Fe_2O_3, UO_2. Pu is not included in the oxygen calculation.

[3] Pu Limit of Detection (LOD) is ~0.04 wt% based on 3-sigma counting statistics. Pu estimated uncertainty +/- 30% for values
< 0.1 wt% based on 2-sigma counting statistics.

Table 1. Elemental weight % for selected locations from Figure 1 based on energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS).

NUCL 12

Characterization of synthetic urban nuclear melt glass

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In order to create post-detonation solid urban debris surrogate, a standard urban matrix formation process that can be applied to specific urban scenarios has been created. Using public records and other open-source data, rough elemental formulas (to ± 2%) indicative of each city's composition were determined. Quantities of other elements were added in appropriate fractions in order to simulate weapon fuel and components. Of the eight candidate cities, two were chosen for debris production. This selection took place based upon activation and fission product inventory. Once candidate cities had been determined, samples were created by vitrifying the powdered matrix in a high temperature drop furnace heated between 1550 and 1700

Once the surrogates were created, a scanning electron microscope (SEM) analysis was conducted in order to determine surface features of the samples. These images were taken of the interior cross-sectional area of the previously made synthetic trinitite samples. The BSE provides a complimentary image of the same cross-sectional area. The same cross-sectional areas were also analyzed with energy dispersive x-ray spectroscopy (EDS), which provided elemental analysis at the surface
After the samples were analyzed with the SEM, the samples were then analyzed using a powder

NUCL 13

High resolution solid-state NMR on nuclear materials

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Thanks to a dedicated effort to adapt a magic angle spinning (MAS) NMR spectrometer for the measurement of highly radioactive materials, high resolution analysis (MAS>55 kHz) is now possible on a routine basis. We present recent results obtained at JRC-ITU devoted to the understanding of the atomic scale structure of complex 5f-paramagnetic materials. Here, we focus on the actinide dioxides, which are of fundamental interest due to their use as conventional fuels (U and Pu) and/or as targets for their transmutation (Np and Am).

Photo of the 9.4 T Bruker NMR spectrometer with the radioactive glovebox available at JRC-ITU.

NUCL 14

Computational studies of magnetic properties of f-element complexes

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In this talk, we will present results from recent computational studies of magnetic resonance parameters and the magnetic susceptibility of f-element complexes utilizing relativistic quantum chemical methods. Calculations and the analysis of magnetic resonance parameters of actinyl nitrate and carbonate complexes and of magnetic susceptibilities of selected U(IV) organo-metallic complexes will be discussed in detail. Ab-initio results will be compared with crystal field models. We will also discuss under which conditions contact and dipolar ligand NMR shifts in paramagnetic metal complexes may exhibit a different dependence on temperature.

NUCL 15

Spectroscopic investigation for the structure of actinides sorption on the solid/liquid inter-surface

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Knowledge of actinides sorption behaviors on solid/liquid inter-surface is of great importance to the study of radionuclide migration in the natural environment. Sorption of UO_2^{2+} on TiO_2 was focused on to introduce the use of various spectroscopic methods in this study. Spectroscopic methods such as laser induced fluorescence spectroscopy (LIFS), extended x-ray absorption fine structure (EXAFS), time-resolved laser fluorescence spectroscopy (TRLFS) were usually employed to the study the surface properties, to give the sorption structural information and to measure the species of actinides on on solid/liquid inter-surface. These measurements thus will have major implications, giving the information of the sorption mechanism of actinides sorption on the atomic/molecule scales. The use of these micro-investigations for actinides sorption on solid/liquid inter-surface is surely of great importance in understanding the species, migration of radionuclides and the performance and safety assessments of geological repository to long-life and high level radioactive waste.

NUCL 16

Analytical methods in support of waste processing operations at the Savannah River site

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Disposition of legacy wastes from fuel reprocessing at the Savannah River Site (SRS) requires separation of the radioactivity into a small volume for incorporation into a durable borosilicate glass wasteform for eventual emplacement in a federal repository. The decontaminated waste solution is incorporated into a grout wasteform for onsite disposal in near surface vaults. Pretreatment of the high-level nuclear wastes at the SRS includes an ion-exchange process for the removal of ^{90}Sr and alpha-emitting actinides (e.g., ^{239}Pu, ^{237}Np) and a solvent extraction process for separation of ^{137}Cs. Two pilot-scale pretreatment facilities, the Actinide Removal Process (ARP) and the Modular Caustic Side Solvent Extraction Unit (MCU), began using these separation processes in 2008. The same separation processes are also planned for the much larger Salt Waste Processing Facility, which is under construction. A variety of analytical methods are used to support the operation of the chemical separation processes and facilities. This paper will provide an overview of these analytical methods including their evolution after startup of the ARP and MCU facilities.

NUCL 17

^{226}Ra analyses on Savannah River site radioactive waste matrices

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Waste cleanup at the Savannah River Site, as well as other DOE nuclear sites, has created an ongoing need to characterize the radiological inventories of various waste tank heels prior to tank closure. Each tank heel has unique chemical and radiological distributions, rendering the use of routine analyses inadequate. Since each tank is a completely new matrix with often-unforeseen interferences, method development must be performed for each tank's residue material.

While currently representing only a small fraction of the activity in the various sites' radioactive waste inventories, Ra-226 and its progeny will eventually represent a more significant portion of the inventories due to its relatively long half-life. As a result, detection limit requirements for Ra-226 are often quite low. Ra-226 is an alpha emitter with weak gamma emissions. The required Ra-226 detection limit requirement can be 8 or more orders of magnitude lower than the activities of shorter-lived radioisotopes commonly present in various SRS sample matrices. Therefore, a very efficient separation of Ra-226 from high levels of interfering radionuclides is required. High sample radiological doses require initial radiochemistry to be conducted in SRNL's remote handled shielded cells facility. The separations are then completed in radiological hoods. A series of delayed gamma analyses are conducted for Ra-226 and for the Ra-224 tracer's progeny. Details of the Ra-226 analysis method development and implementation in these high activity matrices will be discussed.

NUCL 18

Development of the Field Alpha Spectrometry Tool (FaST)

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There is a continuing need to improve the field analysis of radioactive analytes. The Field Alpha Spectrometry Tool (FaST) is a system designed do just that. It enables the rapid field screening and analysis of samples containing alpha emitting radionuclides. The system consists of two major components; the first is a Polymer Ligand Film (PLF). The PLF enables rapid sample processing of an analyte in solid or liquid form into a planar form that is amenable to counting in an alpha spectrometer. PLFs have been shown to selectively extract actinide analytes from solution onto a substrate material. The substrate material can be directly measured with an alpha spectrometer with high resolution. The ability of PLFs to efficiently and selectively extracting certain actinides onto a substrate that facilitates measurement of high-quality spectroscopic data lends the technology as a field-based alpha measurement tool. The second part of the FaST system is an instrument designed for rapid, field-based measuring of alpha-decaying species. The instrument is designed to be operated by non-specialists and has a simple user interface. We will discuss system performance, time required to prepare a sample and collect data, and utility of the system for field-deployable applications. We will also discuss tests of the integrated system operability.

NUCL 19

High precision trace element determination for standard material production

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Trace elements or containments within bulk nuclear material provide information on a materials production, history, and/or origin. The standards available for this analysis often have only a few elements certified and/or have large uncertainty on the concentration values. The Department of Homeland Security's Domestic Nuclear Detection Office is funding the development of a trace element uranium reference material for use by nuclear forensics laboratories. The certificate values for trace impurities will be generated using a trident approach. This approach pairs traditional techniques such as matrix matched external calibration and standard addition with a high precision technique using isotope dilution mass spectrometry combined with separations using high pressure liquid chromatography (HPLC-IDMS). The Nuclear Analytical Chemistry and Isotopics Laboratories (NACIL) group at Oak Ridge National Laboratory leads the effort for the IDMS-HPLC measurement method. The method eliminates or significantly reduces interferences and matrix effects within the sample. Thus, the element precision can be improved up to an order of magnitude compared to tradition method of quantification alone. Here the approaches used to quantification multiple element standards with lower uncertainty will be presented.

NUCL 20

Investigation for source term for the incident in WIPP'S Panel 7 Room 7EHE

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On Friday, February 14, 2014, an incident in Panel 7 Room 7 (P7R7) of the Waste Isolation Pilot Plant (WIPP) underground repository resulted in the release of radioactive material into the environment. Early visual observations and analytical data pointed to a breach of a single drum containing remediated plutonium process waste from Los Alamos National Laboratory (LANL). However as investigations into the incident progressed, questions arose as to the possibility of other LANL waste drums, totaling 54 items and containing similar remediated waste, also being contributors to the event. To answer those questions and determine if indeed the radiological release could be contributed to a single source, the WIPP Technical Analysis Team (TAT) coordinated a study using visual evidence collected by the Accident Investigation Board (AIB), parent drum historical U, Pu, and Am data for all LANL material types stored in P7R7, Central Characterization Project (CCP) non-destructive gamma spectra for key LANL drums located in P7R7 using a High Efficiency passive Neutron Counter (HENC), and post-

event analytical data for U, Pu, and Am isotopics taken in the room, air monitors, and the ventilation system of the facility.

Presented will be key findings of this study and the WIPP TAT’s final conclusions for source term.

NUCL 21

Validation of Neptune Plus MCICPMS for high precision isotope ratio analysis of environmental U and Pu samples

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In the nuclear forensics arena, mass spectrometry is the tool of choice for isotope ratio measurements on long-lived radio-nuclides, specifically including most uranium and plutonium isotopes. In the laboratory setting, multi-collector inductively coupled plasma mass spectrometers (MC-ICPMS) are currently used to make very highly accurate and precise measurements on these types of samples.

The Chemical and Isotopic Mass Spectrometry (CIMS) laboratory at Oak Ridge National Laboratory (ORNL) recently installed a next generation Thermo Scientific Neptune Plus multi-collector inductively coupled plasma mass spectrometer for high precision isotope ratio measurements on trace (ng - <ng) actinide samples. The Neptune Plus design incorporates changes to the sample interface as well as the multi-collector detector block that increases sensitivity up to an order of magnitude over the previous Neptune instruments. The detector block of the Plus features the option of using up to five ion counting detectors simultaneously, providing the higher sensitivity necessary for measurements on very small samples.

However, the presence of the multiple ion counting detectors requires a new method to cross calibrate the yields of the various detectors, as is necessary for high accuracy isotope ratio measurements. There are currently very few widely available uranium Certified Reference Materials which can be used to simultaneously calibrate all five of the ion counters using paired isotope ratios. This necessitated the development of a new cross-calibration method for the five ion counting detectors.

This talk will outline the approach to detector calibration taken by ORNL, and provide results on a variety of isotopic control standards for both uranium and plutonium materials. Figures of merit such as ultimate sample sensitivity, abundance sensitivity on minor isotopes, and accuracy and precision on isotopic ratios measurements will also be addressed.

NUCL 22

Retardation and release of uranium on phlogopite mica at the absence and presence of humic acid: A batch and TRLFS study

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The batch experiments and cryogenic time-resolved laser-induced fluorescence spectroscopy (TRLFS) technique were applied to investigate uranium(VI) sorption/desorption on phlogopite at the absence and presence of humic acid (HA) in this work. The results showed that at the absence of HA, the uranium(VI) sorption on phlogopite was strongly dependent on pH while minimally affected by the ionic strength, multiple inner-sphere surface species (including $\equiv SOUO_2^+$, $\equiv SO(UO_2)_2(OH)_2CO_3^-$ and $\equiv SOUO_2(CO_3)_x^{1-2x}$) were formed with their abundance varying as a function of pH, and a portion of uranium precipitated as uranyl oxyhydroxides at high pH (> 9). The presence of HA made little difference below pH 4 while inhibited uranium(VI) sorption above pH 4, and such effects became much more pronounced by increasing HA concentration from 20 mg/L to 50 mg/L. Fluorescence spectra indicated the formation of ternary surface complex at low pH, uranium-humate complex preferred binding directly on surface rather than via HA. Multiple aqueous uranium-humate complexes were responsible for the suppression of uranium sorption at high pH. The presence of HA enhanced uranium mobility without altering dominant surface species before and after desorption treatment.

NUCL 23

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) applied to Waste Isolation Pilot Plant (WIPP) samples

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The Savannah River National Laboratory (SRNL) received a series of high priority samples from the Waste Isolation Pilot Plant (WIPP) in New Mexico beginning after the detection of a radiological release on February 14, 2014. Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) was used as a microanalytical technique to aid the many other, mostly bulk techniques. The data from many of these samples is presented as a way to show how the SEM/EDS technique, as a microanalytical technique, was used in complementary fashion to the other bulk techniques to determine the morphology and composition of many of the constituents of the samples. A unique completely glovebox contained SEM/EDS was used for radiological samples and a different clean SEM/EDS was used for non-radiological samples. The combination of the imaging capability of the SEM along with the elemental detection ability of the EDS allowed both morphological and elemental characterization of samples from various locations in WIPP and indicated which locations should be sampled further and which locations were of little to no interest. Samples varied from air

filters to powdered material. The backscatter imaging mode of the SEM, which shows increasing brightness with higher atomic number in the image, was extensively used in order to location regions of interest within the sample. EDS was used to identify the elements present in these regions and provide an interpretation of the images which allows the repeating motifs in the images to be identified based on the brightness or darkness of the feature from backscatter imaging, as well as use of secondary electron imaging to distinguish surface features and morphology of the samples.

NUCL 24

Results of an international interlaboratory comparison of NBL CRM 124-3 material

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The purpose of this study was an inter-laboratory comparison by two internationally known nuclear analytical laboratories focusing on the characterization of nuclear fuel in nuclear forensic investigations. The sample chosen for analysis using complete analytical and nuclear forensic protocols was certified reference material (CRM) 124-3 from New Brunswick Laboratory. Data clearly shows that both laboratories generate quality uranium assay and isotopic data regardless of what method is used. Agreement between quantitative and qualitative description of morphological attributes were observed by both the laboratories along with the lexicon used to describe those features. However, the minor differences that were observed could be traced back to sampling and mounting techniques used for scanning electron microscopy (SEM) at the two laboratories. This project identified several areas for improvement on identifying mounting techniques that enhance identification of material properties in a uniform way, ISO GUM calculations, and trace-element methodologies.

NUCL 25

Sharing the experience of changing gamma detector systems in a production laboratory

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The Savannah River National Laboratory's Environmental Bioassay Group recently completed changing it's gamma detection system from one based on Canberra's DSA-2000 MCAs and PROCOUNT running on a VMS mainframe to one based Canberra's Lynx MCAs and Apex-Gamma running on commodity PC-hardware. This talk will cover the production lab workflow, the legacy system, the replacement system, the challenges encountered during the change, solutions to those challenges, and tips for minimizing those challenges. This talk will provide information to others who expect to undertake a similar adventure and help minimize their time and costs.

NUCL 26

Radionuclide analyses supporting waste acceptance criteria for low level waste at the Savannah River site

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In order to immobilize and dispose of low-level radioactive and hazardous liquid waste (LLW salt solution) remaining from the processing of nuclear materials at the Savannah River Site, a quarterly Waste Acceptance Criteria (WAC) analysis is performed. These analyses are performed to verify compliance with the Saltstone Facility WAC to protect the Saltstone Documented Safety Analyses. The Saltstone Facility (Z Area) consists of two facility segments: the Saltstone Production Facility (SPF), which receives and treats the salt solution to produce saltstone grout, and the Saltstone Disposal Facility (SDF), which consists of Saltstone Disposal Units (SDUs) used for the final on site disposal of the saltstone grout. Class F fly ash. Metals, anions, certain organics and a suite of over fifty radionuclides are Saltstone is the cementitious wasteform for the LLW that is made from Type I/II cement, blast furnace slag and included in the salt solution WAC analysis. Twenty different radiochemical methods are performed to determine the radionuclides. Results from these methods are used to derive various acceptance criteria consisting of inhalation dose potential, hydrogen generation rates, nuclear criticality safety, radionuclide limits/targets and gamma shielding. This presentation will discuss the radiochemical methods used to detect the major species (99Tc, 129I, 137Cs and 135Cs), and the trace level detectable isotopes of U, Pu, Cm, Co, Sr, Sb, Te, Sn and tritium and carbon-14. Historical trends in the levels of detectable radionuclides as well as projections of future radionuclide distributions using decay calculation tools will be presented.

NUCL 27

Speciation of U(IV) in sediment microcosms and model biogeochemical systems under reducing conditions

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The chemical or enzymatic reduction of U(VI) to U(IV) has a significant effect on the mobility of uranium due to the lower solubility of uraninite (UO_2) relative to that of U(VI) species. This property of U has stimulated extensive efforts to understand the mechanisms of U(VI) (bio-)reduction and the susceptibility of uraninite to oxidation and dissolution. However, recent results from U L_{III}-edge x-ray absorption spectroscopy

suggests that the predominant fraction of U(IV) produced from U(VI) in reduced sediments is not in the form of uraninite. The precise identity and the stability of such non-uraninite U(IV) species remain unclear. We will present results from a study of the spatial distribution and speciation of U in biostimulated sediment microcosms from the former Oak Ridge Integrated Field Research Center, where the U(IV) associated with the sediments was found to be in a non-uraninite phase (i.e., one lacking the bidentate U=O=U bond between the U atoms, as determined by EXAFS). Several studies in laboratory systems are helping us identify the factors leading to non-uraninite U(IV) species, such as the mechanism of enzymatic U(VI) reduction, the presence of phosphate or carbonate in the groundwater, and the ratio of U to specific mineral surface sites. These results will be discussed in the context of the geochemical and microbiological characterizations of the groundwater and sediment in the microcosms to provide insight on the coupled biogeochemical processes that determine U speciation. The predominance of non-uraninite U(IV) species in reduced sediments presents new challenges for reactive transport modelling of U that will need to be addressed in the future.

NUCL 28

Predicting plutonium behavior in the environment: Linking mechanistic behavior to field processes

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Significant releases of plutonium (Pu) into the environment have resulted from nuclear weapons production and the nuclear fuel cycle. It is estimated that over 2200 metric tons of plutonium (Pu) has been deposited in the subsurface worldwide with an increase of approximately 200 metric tons each year from spent nuclear fuel. A major scientific challenge is to reliably predict and control the cycling and mobility of Pu that has been deposited into the environment. Some of this Pu has been transported in the subsurface on the scale of kilometers. However, the coupled biological, chemical, and physical processes that control this transport are not well understood.

In the last 15-20 years, it has been generally thought that due to its low solubility and high sorption affinity, Pu migration in the environment will be dominated by transport on particulate matter (i.e., colloidal particles). However, recent work performed by our group and others suggests that colloid-facilitated Pu transport may not be the only mechanism by which Pu is transported in the subsurface. In this presentation, I will discuss our recent work from both Hanford and the Nevada National Security Site (previously Nevada Test Site) that explores several possible different biogeochemical mechanisms that control Pu migration.

We posit that the biogeochemical processes that ultimately control plutonium subsurface mobility/immobility are driven by the local hydrogeologic and geochemical conditions, in concert with the chemical characteristics of the initial actinide source. This

has led to Pu transport as intrinsic colloids, pseudocolloids, and aqueous organic complexes. The temporal and spatial limits to Pu migration are controlled by the stability of each of these forms of Pu in groundwater.

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NUCL 29

Using flow-cell desorption experiments to understand colloid-facilitated Pu transport

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In part due to public health concerns over the risk of Pu contamination of drinking water, predicting the behavior of Pu in both surface and sub-surface water is a topic of continued interest. Recent work demonstrating the importance of colloid-facilitated Pu transport has led to renewed study into adsorption/desorption interactions of Pu with environmentally relevant minerals. This work examined the stability of Pu(IV) adsorbed on colloidal-sized particles of the clay mineral montmorillonite in a 5 mM NaCl, 0.7 mM $NaHCO_3$ solution. Plutonium, at an initial concentration of 1×10^{-10} M, was adsorbed onto the clay at pH values 4, 6, and 8 under oxic conditions. Desorption of Pu from montmorillonite by the appropriate Pu-free electrolyte displayed a pH dependency with the greatest amount of Pu desorbed at pH 8 and minimal desorption at pH 4. Experiments at pH 6 and pH 8 were repeated at an initial Pu(IV) concentration of 10^{-13} M. The desorption behavior was similar to that observed at 10^{-10} M, indicating that experiments at the higher concentration can be used to predict behavior at lower, environmentally relevant Pu concentrations ($\leq 10^{-12}$ M).
A simple model that accounted for Pu oxidation state changes was developed to simulate the Pu adsorption/desorption behavior in these experiments. By populating the model parameters as much as possible with existing literature values we were able to generate good fits to the data. The model values have allowed us to make predictions about the residence time of Pu associated with clay mineral colloids in subsurface environments. We generated half-lives for Pu adsorbed on montmorillonite at circumneutral pH on the order of years. This timescale is broadly consistent with estimated 20-40 year transport times for colloid-associated Pu at the Nevada National Security Site.

NUCL 30

Microbial iodine cycling: Effects on fate and transport in the Hanford subsurface

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Discharges from cribs and trenches, used for disposal of plutonium production waste, have resulted in ^{129}I contaminated groundwater at the Hanford Site. ^{129}I is of environmental concern due to its long half-life (1.6 × 10^7 years), toxicity, and mobility in the environment. Iodine plumes in the Central Plateau at Hanford cover 1,500 acres where ^{129}I concentrations average 3.5 pCi/L. Thermodynamic considerations dictate that iodide should be the dominant species in Hanford groundwater; however, speciation analysis shows that iodate comprises 70.6% of the iodine present, and organo-iodide and iodide comprise 25.8% and 3.6% respectively. Understanding cycling of iodine in the environment will provide insight into fate and transport processes controlling mobility in the vadose zone and groundwater.

Microbial diversity within the Hanford groundwater was determined from sediment traps that were incubated in monitoring wells within the iodine impacted groundwater plume and background wells. Clone libraries showed that the plume communities were dominated by bacterial taxa, such as *Pseudomonas* that have been shown to transform iodine. Bacterial diversity was greatest in wells from the high iodine portions of the plume (15-40 pCi/L).

A number of bacterial isolates from the sediment traps have been shown to oxidize iodide. *Pseudomonas*, *Agrobacterium*, *Arthrobacter*, and other isolates were shown to oxidize iodide at different efficiencies. While only a small amount of the total iodide was oxidized, levels of oxidation were comparable to the µM quantities found in the Hanford groundwater.

Sediment trap isolates also demonstrated the ability to reduce iodate. Bacteria from the Genera, *Pseudomonas*, *Arthrobacter*, and *Agrobacterium* were able to reduce iodate and nitrate. An iodate reducing organism, designated as *Agrobacterium tumefaciens* strain AD35 was isolated and characterized. Iodate (200 µM) was reduced by 36.3% in micro-aerobic cultures and 47.8% in anaerobic cultures in the presence of 10mM nitrate, which was reduced 81.4% and 80.9% respectively. Iodate was also shown to be reduced by 84.0% and 69.2% in microaerobic and anaerobic growth conditions respectively with nitrate spiking into the growth media. No iodate reduction was demonstrated without nitrate present.

These results indicate that microbes present in the Hanford subsurface are involved in iodine cycling, producing iodine species that react differently with sediments which will in turn affect migration.

NUCL 31

Determination of the spatial distribution and chemical state of Cs in model environmental samples

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The 2011 Fukushima Daiichi nuclear accident led to widespread dispersal of radionuclides into the environment [1], prominently including Cs-137 [2]. To develop effective remediation procedures for the resulting environmental and public health hazards, it is necessary to understand the distribution and speciation of radionuclides in the atmosphere, water, and soil near the site. In particular, the Cs present in Fukushima soils is typically aggregated in micron-scale particles [3]. Here, we report on the characterization of a set of reference clays (biotite and vermiculite or "weathered biotite") contaminated with non-radioactive Cs by use of a scanning transmission x-ray microscope (STXM). The spatial resolution, element-specificity, and sensitivity to low concentrations achievable with STXM are well-suited to the dilute and highly heterogeneous samples. Using the soft x-ray STXM installed at beamline 11.0.2 of the Advanced Light Source, we show that it is possible to identify Cs-rich particles and obtain chemical-state information from samples with average Cs weight fractions as low as 0.01%.

In addition, we present the near-edge x-ray absorption fine structure (NEXAFS) spectra at the Cs $M_{4,5}$ edges of a set of Cs compounds. As Cs materials have not been studied extensively at these edges, this standard dataset and the corresponding theoretical calculations will provide valuable context for STXM identification of the Cs species present in environmental samples.

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NUCL 32

Interactions of uranium and co-occurring elements in abandoned mine wastes

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The occurrence and mobility of uranium (U) and co-occurring elements in abandoned mine wastes from different sites in the Southwestern US was investigated using aqueous chemistry and spectroscopy experiments. Release of U and other metals from abandoned uranium mine wastes is a major concern for human exposure risks. Laboratory experiments suggest U can be released from abandoned mine wastes, even when reacted with de-ionized water. Spectroscopy and aqueous chemistry analyses suggest that U mobility is controlled by U-V phases and U-P phases present in different abandoned mine waste sites. Column experiments were also performed to investigate U mobility and transport under environmentally relevant conditions. Understanding chemical and transport mechanisms controlling U release is fundamental toward assessing the risks and potential remediation strategies that could be adopted in abandoned mine waste sites.

NUCL 33

Alkali technetium oxides as model compounds for Tc-99 incorporation in glass

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A priority goal of the United States Department of Energy is to dispose of nuclear wastes accumulated in underground tanks at the Hanford Nuclear Reservation in Richland, WA. Incorporation and stability of technetium (99Tc) into vitrified waste forms is a concern to the waste glass community and DOE due to its long half-life (2.1·105 y), and its high mobility in the subsurface environment under oxidizing conditions. We provide a progress report on our efforts to obtain first-of-a-kind chemical structure determination of poorly understood, environmentally relevant, alkali technetium oxide pure compounds. Knowledge of the structure and spectral signature of these compounds, will aid in refining the understanding of Tc-99 incorporation into and release from oxide nuclear waste glasses. Compounds currently under investigation, which are all, all non-pertechnetate Tc7+ and their rhenium analogs. This work provides much needed data for assessing reactions of water with Tc in glass, and thus improving understanding of Tc environmental release which impacts performance assessment models for waste repositories.

NUCL 34

Effect of uranium toxicity on the immobilization of uranium by subsurface microorganisms

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The bioreduction of U(VI) by metal-reducing microorganisms and the biomineralization of U(VI) phosphate minerals as a result of microbial phosphatase activity may both prevent the propagation of uranium in contaminated environments. Although U(VI) is toxic to most microorganisms, the effect of this toxicity on the mobility of uranium is not well characterized. In this study, the geochemical factors that control the toxicity of uranium to metal-reducing and phytate-hydrolyzing microorganisms were investigated using *Shewanella putrefaciens* strain 200, a well known metal-reducing bacterium, and *Variovorax* sp. recently isolated for its ability to hydrolyze phytate in the presence of uranium. Results from pure culture incubations reveal that the respiration of uranium by *S. putrefaciens* is controlled by the concentration of non-carbonate uranyl species which represent the most bioavailable species but are also toxic in high concentrations. In contrast, the exposure to increasing concentrations of uranium does not prevent the growth of *Variovorax* sp. but promotes the hydrolysis of phytate as a detoxification mechanism. Overall, these findings indicate that microorganisms in uranium-contaminated environments adapt different strategies to immobilize uranium and address its toxicity. Rate laws describing these effects in reactive transport models will be proposed.

NUCL 35

Structure and dynamics of mixtures of molten salts for the pyroprocessing of nuclear waste

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The European consortium SACSESS aims at studying the safety of nuclear waste reprocessing techniques dedicated to the separation of actinides. One of the methods considered is called *pyroprocessing*. In this method, the fuel bars are immersed in a bath of molten salts, directly on the way out from the reactor. By applying a series of voltage differences to the electrodes, one would like to deposit the target elements at the electrodes in a selective fashion. While the separability of the ions is governed by thermodynamics and in particular by the ratio of their activity coefficients, knowledge of transport phenomena is also necessary for the implementation of this technique.

In this work, we study by classical molecular dynamics, dynamic and structural properties of mixtures of molten chloride salts MCl_3-$(LiCl\text{-}KCl)_{eut}$ (M^{3+}=Y^{3+}, Tb^{3+}, La^{3+}, U^{3+}) or fluoride salts $NF_{3/4}$-$(LiF\text{-}AlF_3)_{eut}$ ($N^{3+/4+}$ = Y^{3+}, La^{3+},Th^{4+},U^{4+}) in which the relative composition of the basic melt is kept at the eutectic ratio, 58.2:41.8% for the chlorides and 85:15/65:35% for the fluorides. The simulations are performed using a polarizable force field extracted from DFT simulations and therefore of ab initio accuracy.

We calculate dynamic quantities such as the viscosity and the characteristic relaxation times of the systems and structural properties such as the radial distribution functions, the coordination numbers of the cations, the number of anions shared between two cations, etc., as a functions of the concentration of the $MCl_3/NF_{3/4}$ salt and of temperature. We also estimate the energy of the cation-anion bonds from the potential of mean force extracted from the radial distribution functions. We find that the average coordination number of the cations and the viscosity are anticorrelated with the energy of the cation-anion bonds. The most viscous systems are instead characterized by the presence of a high number of anions shared between two cations. This favors the the formation of an extend network able to resist shear stresses.

NUCL 36

Development of block copolymer materials for f-element separations

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The separation of actinides and lanthanides is essential for the reprocessing of nuclear fuel. Separations of these elements is challenging due to similarities in chemical properties, namely: most are in the 3+ oxidation state in acidic aqueous media, have similar ionic radii, and are considered hard acids. The CMPO ligand (carbamoyl phosphine oxide) has shown selectivity for actinides over lanthanides, but traditional systems which utilize this ligand require the use of organic solvents in liquid-liquid extractions for separations thus increasing the volume of waste during reprocessing.

Novel linear block copolymers prepared by ROMP, ring-opening metathesis polymerization, containing a polyoxanorbornene backbone and CMPO derivatized side chains, have been developed for the separation of f-elements. This system has shown enhanced extraction efficiencies over traditional CMPO materials. ROMP was chosen for its ease in synthesizing block copolymers. Block copolymers containing CMPO and triethylene glycol monomethyl ether moieties have also been synthesized. These block copolymer systems have shown comparable extraction efficiencies utilizing solid-liquid biphasic extractions, cutting out the waste of the organic phase required in other systems. The synthesis and characterization of the monomeric materials, the corresponding homopolymers, and the block copolymers that have been developed will be discussed. Also the extraction efficiencies of actinides exhibited by these materials for liquid-liquid and solid-liquid extractions will be discussed.

NUCL 37

Study of chemical behaviour of Tl and in as light homologues of element 113

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Investigation of the properties of transactinides provides important information for understanding the upper limit of Periodic Table along with influence of relativistic effects on chemical behavior of elements with $Z \geq 104$. Such a study is usually performed by means of comparison of chemical properties of heavy elements with its lighter homologues to both check the periodicity of a given group and to characterize a new element. One such element is element 113, which has never been chemically studied before by means of liquid phase methods.

Here we present our results on the investigation of its expected lighter homologs thallium and indium by ion exchange chromatography and liquid-liquid extraction techniques. It has been shown that both procedures are highly efficient for separation of the given elements in hydrochloric acid media.

The main advantage of the application of a cation exchange resin is the ability to change the elution order of In and Tl by varying the oxidation state of thallium. This gives us flexibility in terms of experiment design, and the data collected can be potentially used for element 113 oxidation state and complex formation study.

For liquid-liquid extraction of metallic ions, we obtained unexpectedly high distribution ratios of thallium(III) even by applying a pure ionic liquid as the receiving phase. Ionic liquids (ILs) are new type of compounds with a melting point below 100 °C which are considered to be environmentally friendly and “designers” solvents. The implementation of ILs for thallium and indium investigation provides an opportunity for simple and selective separation of these metals in solution.

The data obtained allow us to interpret the mechanism of thallium and indium extraction in ionic liquids media. The understanding of Tl and In chemical behavior in this new medium is imperative for the further improvement of the separation of these elements.

NUCL 38

Production of heavy and superheavy elements using projectiles with $Z \geq 20$

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In recent years, several superheavy elements have been discovered in irradiations of actinide targets with ^{48}Ca projectiles. These superheavy nuclei are expected to be shell-stabilized and spherical due to their proximity to predicted magic numbers. If additional new elements are to be discovered using complete fusion-evaporation reactions, then projectiles with $Z_p > 20$ will be required due to the lack of available targets with $Z_t > 98$. Experiments have been performed at Texas A&M University to study the reactions of ^{44,48}Ca, ^{45}Sc, ^{50}Ti, and ^{54}Cr with lanthanide targets to produce shell-stabilized, spherical nuclei near the $N = 126$ shell in order to study the influence of projectiles with $Z_p \geq 20$. Excitation functions for the xn and pxn exit channels of a large number of projectile/target combinations have been measured using the MARS spectrometer. The peak cross sections of the (^{48}Ca, 4n) reactions are substantially larger than for other 4n reactions, and the peak cross sections of the (^{44}Ca, 4n) reactions are also larger than for (^{45}Sc, 4n) reactions with the same target. In some cases, the (^{45}Sc, $p3n$) cross sections are larger than the corresponding (^{45}Sc, 4n) cross sections, and this indicates that ^{45}Sc is likely not viable as a projectile for superheavy element production. A simple model has been developed that incorporates an angular momentum-dependent fission barrier and collective effects. The experimental data have been compared to the results of the model calculations, which indicate that there is a significant reduction in fission survival due to collective effects. The production of nuclei near the N = 126 shell using fusion-evaporation reactions is heavily influenced by the projectile, but this is largely due to the change in the resulting compound nucleus and the change in its survival probability. The data suggest that cross sections for evaporation residues formed using projectiles with $Z_\mathrm{p} > 20$ may be substantially reduced relative to ^{48}Ca-induced reactions. This talk will summarize the most recent experimental results, discuss the theoretical model, and give some observations on the likelihood of future new element discoveries

NUCL 39

Deposit thickness effects on nuclear recoil attenuation and emission

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To accurately analyze the recoiled daughters emitted from a radioactive target, it is important to understand how the thickness of the target affects the emission of the recoiled daughters. Currently, it is standard to determine the maximum thickness of the sample where the recoil nucleus, at a specific energy, can still be ejected. With this, we make assumptions based on those calculated ideal thicknesses that will give the most recoil nuclides. To date, there have been little to no experimental analysis on the efficiency of the emission of the recoiled daughter nuclei. In this study we analyze the effects of various thicknesses. Targets were made by molecular depositing 10-200 ug/cm^2 HEU onto Al foils. Another Al foil was placed slightly above the target in a vacuum chamber for 12-24 hours. The recoiled Th-231 nuclei were caught by the upper Al foil. This Al foil was then counted on low axial gamma spectrometer to determine the efficiency of the recoil emissions and the amount of larger fragments by determining the half-lives.

NUCL 40

Update on the observation of gamma rays from the nuclear isomer of ^{229}Th

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The first excited state ^{229}Th is the lowest energy nuclear level known. The accurate determination of the gamma ray wavelength is necessary for applications of this unusual nuclear transition. These possible applications include a nuclear clock, a gamma ray laser, a variable intensity alpha source, etc. The ultraviolet light from ^{229m}Th has been observed at Los Alamos. The experiment that produced this result is

exceedingly difficult. These problems will be discussed in the context of failed experiments attempted by other groups. The preparation of the ^{233}U alpha recoil source is critical to success in observing the ultraviolet gamma ray. Choosing a reactive substrate, such as stainless steel, can compromise the recoil efficiency. The method of electro-deposition will affect the recoil efficiency. The collector crystal can phosphoresce when exposed to alpha rays. The intensity of the phosphorescence varies orders of magnitude from batch to batch of the ultraviolet transmitting crystal. The negligible effect of daughters from the ^{233}U decay chain will also be discussed.

NUCL 41

Interpreting radioactive microspheres released in Fukushima Daiichi Nuclear Plant accident in view of XANES and thermodynamic database

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On March 14th and March 15th of 2011, about 80-90 hours in the course of severe accident of Fukushima Daiichi Nuclear Power Plant, radioactive microspheres of 1-2 micrometer size were collected in Tsukuba, 170 km away from the site. The microspheres contained uranium, fission products and the other elements which correspond to the materials in the containment. Abe et al. [1] have reported the detailed analysis of the microspheres by micro XANES. We have measured Mo K-edge XANES of the series of Cs2O-MoO3 complex oxides. Those spectra were compared with the results by Abe et al. Mo K-edge XANES of Cs2Mo2O7 agreed surprisingly well with that of the microsphere. We also compared the U L3-edge XANES with the existing XANES database as well as the FEFF-9 simulation of various uranates and uranyl compounds. The XANES data will be further discussed in order to define the range of thermochemical conditions, where such radioactive microspheres can be formed.
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NUCL 42

Advanced tritium storage bed development at the Savannah River site

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The Savannah River Site (SRS) Tritium Facilities is home to the largest metal hydride-based tritium facility in the world. Metal hydride beds allow for safe and compact absorption, storage, and desorption of hydrogen isotopes at various points in the tritium processing cycle. This paper provides an overview of metal hydride bed development,

including design, fabrication, and testing, at SRS as it relates to both the immediate and future needs of the Tritium Facilities and its broader implications. The hydride beds discussed herein utilize a LAnthanum-Nickel-Aluminum (LANA) alloy in which the aluminum content is varied to achieve optimal absorption and desorption pressures upon thermal cycling. Full-scale hydride bed prototype testing allows for (1) design/risk reduction verification, (2) hydriding-induced wall stress analyses to ensure process vessels are within ASME allowable limits, (3) absorption/desorption testing to confirm that bed performance meets or exceeds that of current designs, and (4) In-Bed Accountability (IBA) testing to verify that tritium measurement uncertainty meets facility inventory requirements. The storage of hydrogen isotopes is a crucial aspect of every tritium fuel cycle, regardless of the application. The technology and expertise acquired through the development of next generation hydride beds for the SRS Tritium Facilities have also proven to be applicable to various tritium Fusion Programs around the world.

NUCL 43

Assessment of down-hole membrane-diffused hydrogen for stimulating uranium reduction and immobilization

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The focus of this study was to test the effectiveness of a In-Situ Bioremediation (ISB) process in restoring In-Situ Recovary (ISR) mining zones with the ultimate goal of making a more cost effective, sustainable process and advancing the viability of using fission as a larger part of the American power infrastructure. One major issue with this is the damage that current mining processes can have on the environment when trying to retrieve fissible materials and rare earths. The process of ISR mining has become a more cost effective and ecologically friendly mining practice than traditional shaft or strip mining. The most common technology currently used for restoring groundwater at ISR uranium mining sites is reverse osmosis (RO) and reinjection of the permeate. However, this practice does not restore the formation to its original reduced state, and in many cases groundwater uranium concentrations are not restored to pre-mining baseline levels. The effectiveness of introducing dissolved hydrogen into a post-mined formation at an ISR mining site to stimulate reduction and immobilization of residual soluble uranium was evaluated. The main objectives of this research were: 1) to develop and optimize a system for minimizing air entrainment during water injection when employing a membrane gas-transfer device for down-hole hydrogen infusion; 2) to assess whether injecting dissolved hydrogen using the membrane gas-transfer device can promote immobilization of dissolved uranium in groundwater to near or below pre-mining concentrations. In this test case, approximately 19,000 gallons of groundwater were pumped to the surface and then re-injected into the subsurface while being supplied with dissolved hydrogen using the down-hole membrane gas infusion device. The groundwater was pumped back to the surface after several months to evaluate the extent to which dissolved uranium had been removed. Initial results indicate an approximately 80% reduction in soluble uranium concentration was achieved. Microbial

analyses indicated a significant increase in iron-reducing bacteria, but less significant increases in sulfate-reducing bacteria. A bromide tracer study was performed concurrently with the hydrogen injection study so that the effective zone of influence of the push-pull test could be estimated, while pump tests were performed before and after the hydrogen injection study so the effect of the injected hydrogen on the formation permeability could also be assessed.

NUCL 44

Particle induced gamma-ray emission spectroscopy as a probe for perfluoroalkyl substances

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Various ion beam analysis techniques have been used with small accelerators for decades, especially Particle Induced X-ray Emission (PIXE) spectroscopy and Rutherford BackScattering (RBS) spectroscopy. These typically non-destructive analytical techniques allow the measurement of elemental composition and layer thickness on the surface of almost any solid target. We have been expanding the repertoire of samples studied by these techniques with Particle Induced Gamma-ray Emission (PIGE) spectroscopy, to include environmental samples such as lake sediment, forensic samples such as glass and automotive paint, and most recently environmental toxins in consumer products. This work includes the screening of polyurethane foams, textiles and plastics for halogenated flame retardant chemicals, and various consumer products for the presence of perfluoroalkyl substances (PFASs). A summary of these results will be presented together with future directions accessible to any ion beam analysis laboratory.

NUCL 45

Extraction comparison of light and heavy fission elements nuclear forensics analysis

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A growing focus of nuclear and radiochemistry is in the area of post-detonation material, both from a synthetic and chemical analysis standpoint. In previous work, there has been a keen interested in the development of synthetic melt glass, as well as an effort

to perform rapid analysis of these samples. It is the focus of this work to emphasize chemical analysis, particularly with regard to rapid separation of entrenched fission oxides. Prior to performing the thermochromatography separations, it is of interest to determine the extraction efficiency of various ligands, including 1,1,1,5,5,5-hexalfuoroacetylacetone (Hfac), 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (Hfod), and 2,2,6,6-tetramethyl-3,5-heptanedione (Hdpm). These ligands have been bound to lanthanoids (e.g. La, Gd, and Lu) in previous work. In addition to the rare earth species, these ligands have been combined with Y, Re (or Mn as a surrogate for Tc) and Ag, and the extraction efficiency and selectivity of these ligands to either extract or precipitate the fission products from the aqueous media. Once precipitated or extracted, the resulting compounds were analyzed via inductively coupled plasma time-of-flight mass spectrometry (ICP-TOF-MS) to determine the concentration of surrogate fission products in the resulting solution. This method will provide insight into the effectively of these methods with subsequent separations via thermochromatorgraphy.

NUCL 46

Destructive assay of nuclear melt glass for rapid forensic analysis

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In a post-nuclear weapon detonation, the ability to rapidly determine the elemental ratios of both stable and non-stable nuclei is very important. Previous work in this area has used either acid or base methods to obtain complete dissolution. In this work, a comparison of these methods will be performed on trinitite, synthetic trinitite, and urban melt glass. All dissolution samples will be analyzed via ICP-TOF-MS (Inductively Coupled Plasma Time of Flight Mass Spectrometry) and alpha spectroscopy as available. Further, this work will highlight the difficulties and possible sample matrix interfaces that exist in these samples. A comparison of the timeliness of these methods will also be discussed.

NUCL 47

Polynuclear technetium iodides cluster compounds

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A new solvothermal synthesis route for the preparation of technetium extended metals atoms chains (EMAC) and clusters have been developed. Technetium EMAC (Tc_2(μ-

$O_2CCH_3)_4I$) and Tc-iodide clusters ($K[Tc_8I_{13}]$ and Tc_5I_{13}) were prepared form the reaction of potassium pertechnetate with glacial acetic acid plus either hydroiodic acid or iodide salts under *in-situ* hydrogen production by sodium borohydride at various temperatures yields . These compounds were characterized by single crystal X-ray diffraction and their structures will be presented. In the solvothermal reaction the oxidation state of the Tc atoms in the reaction products is also dependent on temperature and pH of the starting solutions and will be explained in extensive detail. Magnetic susceptibility measurements have been conducted and will presented. These complexes might found in applications in the nuclear industry (waste forms) and in the radiopharmaceuticals industry as imaging agents.