

approach is not sensitive and will not effectively resolve microbial speciation. Another conventional method is cloning of the 16S rRNA gene, which requires transferring the amplified DNA fragments into a plasmid, and randomly sequencing a few hundred plasmids. In soil samples where one will expect to find at least 100,000 species then one would need to sequence 100,000 clones using this method, which is time consuming, expensive, and inefficient. Instead, a high-density photolithography microarray displaying 500,000 oligonucleotide probes complementary to diverse 16S rRNA sequences was used. This new technology, allowed us to identify species or groups of bacteria present in the soil sample more efficiently. The study showed the horizon B1 to have more microbial communities than horizon A. The observed microbial biomass also seems to increase at deeper horizons. Clostridia for example was found to be in higher microbial amounts in the 40-65 cm depth of the Hopland-B2 soil, where as Cellulomonas (Actinobacteria) and Phyllobacteriaceae (Alpha-proteobacteria) were predominately present at the top horizon (Hopland-A).

Chemistry

A Molten Salt Synthesis of Single Crystalline YBCO Nanorods.

DARYL WONG (University of California–Berkeley, Berkeley, CA 94720) **STANISLAUS S. WONG** (Brookhaven National Laboratory, Upton, NY 11973). $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) is a high T_c superconductor that has potential applications in both high field magnets and superconductive circuitry. Although its utility as a high field magnet has been realized, bulk YBCO loses its high temperature superconducting ability due to low critical current densities deriving from the bulk's polycrystalline nature which lacks directionality. One potential remedy, aligning monocrystalline subunits through material texturing techniques, can be achieved with the production of uniform, monocrystalline one-dimensional YBCO nanorod structures. The molten salt synthesis method has been shown to be a procedurally simple technique to create metal oxide nanorods. Using a molten salt method, attempts to make YBCO have been conducted with a number of yttrium, barium, and copper containing precursors which are combined with a salt, usually sodium chloride and/or potassium chloride, in varying precursor and salt ratios. These precursors were finely ground with a mortar and pestle and baked in a furnace to temperatures above the melting point of the salt. Powder x-ray diffraction (XRD) analysis was conducted to determine whether the molten salt samples contained the orthorhombic crystal structure indicative of high temperature superconducting YBCO, while scanning electron microscopy (SEM) and atomic force microscopy (AFM) images were taken to determine if a rod morphology had been formed. XRD analysis of the numerous molten salt products has shown that the desired orthorhombic YBCO nanorods cannot readily be formed, while SEM and AFM images show aggregates of nanorods and nanoparticles which vary in size. Other analytical techniques, including SQUID (Superconducting Quantum Interference Device) measurements, will be useful to further ascertain and characterize the properties of as-prepared YBCO nanorods. Because the mechanism of molten salt nanorod formation is not fully understood, creation of these desired nanorods involves a lot of experimentation with variable parameters. A more comprehensive analysis of precursors, precursor ratios, and baking temperatures should be performed before concluding the inefficacy of the use of the molten salt technique in the generation of nanoscale motifs of these superconducting materials.

A Search for Cerium Doped Lanthanum Oxide Scintillators.

LATORIA WIGGINS (North Carolina A&T State University, Greensboro, NC 27411) **DR. YETTA PORTER-CHAPMAN** (Lawrence Berkeley National Laboratory, Berkeley, CA 94720). The need for new and improved radiation detectors, scintillators, is at an all time high due a progression in detection knowledge. Commonly used scintillators such as BGO and LSO have undesirable properties such as low luminosity, and slow decay times. Discovering new scintillators required literature searches, synthesizing and the characterization of compounds. The research at hand concentrated on cerium (III) doped lanthanum oxides. Compounds were synthesized using solid-state chemistry techniques such as ceramic and hydrothermal methods. Characterization consisted of x-ray diffraction, fluorescence spectroscopy and pulsed x-ray measurements. Several new inorganic scintillators were founded, however, findings concerning lanthanum oxide synthesis warrant further investigation of the compound.

Analysis of the Water-Splitting Capabilities of Gallium Indium Phosphide Nitride (GaInPN).

JEFF HEAD (University of Arizona, Tucson, AZ 85705) **JOHN TURNER** (National Renewable Energy Laboratory, Golden, CO 89401). With increasing demand for oil, the fossil fuels used to power society's vehicles and homes are becoming harder to obtain, creating pollution problems, and are posing hazard's

to people's health. Hydrogen, a clean and efficient energy carrier, is one alternative to fossil fuels. Certain semiconductors are able to harness the energy of solar photons and direct it into water electrolysis in a process known as photoelectrochemical water splitting. P-type gallium indium phosphide ($\text{p-Ga}_x\text{In}_{1-x}\text{P}_2$) in tandem with GaAs is a semiconductor system that exhibits water-splitting capabilities with 12.4% solar-to-hydrogen efficiency. Although this material is efficient at producing hydrogen through photoelectrolysis it has been shown to be unstable in solution. By introducing nitrogen into this material, there is great potential for enhanced stability. In this study, gallium indium phosphide nitride $\text{Ga}_{1-y}\text{In}_y\text{P}_{1-x}\text{N}_x$ samples were grown using metal-organic chemical vapor deposition in an atmospheric-pressure vertical reactor. Photocurrent spectroscopy determined these materials to have a direct band gap around 2.0 eV. Mott-Schottky analysis indicated p-type behavior with variation in flatband potentials with varied frequencies and pH's of solutions. Photocurrent onset and illuminated open circuit potential measurements correlated to flatband potentials determined from previous studies. Durability analysis suggested improved stability over the GaInP2 system.

Calibration for Methane Hydrate Research Unit. XIAE SHI (State University of New York at Stony Brook, Stony Brook, NY 11790)

DEVINDER MAHAJAN (Brookhaven National Laboratory, Upton, NY 11973). Methane hydrate, one of the most common gas hydrates, forms at low temperature and high pressure; conditions typically found below the seafloor and permafrost. Although the amount of methane hydrate trapped under the seafloor on Earth has been estimated to be enough to meet human needs for the next several hundred years, due to their dispersed nature it is very difficult to extract the hydrates¹. A customized unit, named Flexible Integrated Study of Hydrates (FISH) that BNL is using for methane hydrate research, mimics seafloor conditions. In a typical process, methane gas is charged to the vessel, which initially contains a water/sediment mixture under high pressure, cooled down to 4 degrees Celsius. The hydrate formation can be visualized in the vessel through a 12-inch glass window. The kinetics of methane hydrate formation and decomposition could be studied through temperature, pressure and flow/mass meters for the duration of the experiment. The goal of my project is to test the operation and dynamics of the system, such as calibration of all flow/mass meters and BPR (Back Pressure Regulator), as well as testing the system's cooling rate. Preliminary results show that the system is well suited for hydrate formation. Volumetric balances at the inlet and outlet reveal a discrepancy of approximately 4 ml, which is well within tolerances for experimental error. Heat transfer analyses revealed a maximum cooling rate of 0.293°C/hr using a tube-like heat exchanger with forced convection in conjunction with a thermally controlled water-ethylene glycol bath.

Characterization of GaInPN:Si Tandem Cells for Hydrogen Production from Photoelectrochemical Water Splitting.

PAUL VALLETT (University of Vermont, Burlington, VT 05405) **DR. JOHN TURNER** (National Renewable Energy Laboratory, Golden, CO 89401). In order for hydrogen to be part of a renewable energy infrastructure, it must be produced from a renewable energy resource. The direct photoelectrolysis of water using certain types of semiconductors have been known to split water using absorption of solar energy, but difficulties concerning efficiencies and corrosion have limited this technology. This research focused on the ability of GaInPN grown on a silicon substrate to efficiently split water. Photocurrent spectroscopy determined the band gap of the material to be 1.96 eV, which is above the necessary 1.7 eV required for water splitting. Mott-Schottky analysis, photocurrent onset, and open circuit potential were used to determine potential of the Fermi level of the system in relation to the redox potentials of hydrogen and oxygen formation. These techniques showed that the Fermi level lied just below the oxygen redox potential. The electrodes were platinized and short circuit current density measurements under air mass (AM) 1.5 illumination determined extent of water photolysis. Unbiased water splitting was achieved, at a maximum of 0.65% solar to hydrogen conversion efficiency (SHCE). Corrosion of the semiconductor in solution was determined by applying a standard current to the electrode while in solution and using profilometry to estimate the volume of semiconductor removed. On average a 0.1 μm deep well was etched into the material after 24 hours. Incident photon current efficiency (IPCE) measurements of 30% revealed that the growing process for nitrogen addition to the sample decreased the electronic properties of the material. While this system is able to produce hydrogen from water using solar power as the only energy input, and the addition of nitrogen to the material appears to have increased its durability, the material suffers a heavy loss in

electronic efficiency, limiting its use in potential solar water splitting devices.

Clay Synthesis and Platinum Loading for Catalytic Applications.

LEAH PRANGER (Rhodes College, Memphis, TN 38112) KATHLEEN CARRADO (Argonne National Laboratory, Argonne, IL 60439). Contributions to the Catalyst Design Group were made concerning the development of synthetic clays for eventual catalytic and materials applications in three different areas. One project provides clay supports for metal species activity in catalysis. The variety of clays prepared includes silica-lithium-hectorite and tetraethoxysilane-hectorite in various dilutions. In the past, the group has used such supports in an array of projects, including loading cobalt-molybdenum-sulfide species for hydrodesulfurization and Pt(0) metal nanoparticles for oxidation catalysis. All of the samples prepared within this project were determined to be suitable for further testing. Loading of Pt(II) salts and reduction in H₂/N₂ atmospheres was performed. It was found that only very slight temperatures (50°C) were needed to effect reduction to Pt(0). Another task explored clay synthesis under extreme dilutions in order to foster a phenomenon called "exfoliation". Such samples lose all their layer-to-layer registry and instead the silicate layers are randomly distributed, similar to a "house of cards" structure. These materials are useful for atomic layer deposition experiments of catalytic species commonly used within the research group. Finally, work on another layered porous material was initiated. This involved reproduction of a literature synthesis of a layered zeolite dubbed "ITQ-2". Synthesis of these materials was performed in an autoclave under controlled temperature conditions. All materials were characterized by x-ray powder diffraction to establish crystallinity and thermal gravimetric analysis to determine water and organic contents. The Pt-loaded samples and dilute hectorites were determined to be of value for future research, while the ITQ-2 project had only partial success in synthesis.

Comparing the Physical Properties of Ionic Liquids Bearing Chiral and Achiral Hydroxyl Units. *JASMINE HATCHER (Queensborough Community College, Bayside, NY 11364) JAMES WISHART (Brookhaven National Laboratory, Upton, NY 11973).*

Ionic liquids have generated much interest due to their potential green chemistry applications. They are considered to be environmentally friendlier solvent alternatives to traditional volatile (and hazardous) organic solvents because of their lack of vapor pressure. We report here on the synthesis and preliminary characterization of achiral and chiral ionic liquids. The chiral species were synthesized by taking a chiral auxiliary, 3-chloro-1,2-propanediol, and adding it to a tertiary amine. The achiral ionic liquids were synthesized by adding our achiral auxiliary 3-chloro-1-propanol, to a tertiary amine. Some of the tertiary amines used were DMAP (4-dimethylaminopyridine) N,N,N',N' tetramethyl hexadiazine. The halide salts were converted into potential ionic liquids by anion exchange. Anions studied include phosphate and bis(triflyl)imide. A large problem with many ionic liquids is that they are very viscous. Theoretically, the induction of a chiral center would reduce viscosity, however this has not been the case with the materials synthesized using 3-chloro-1,2-propanediol. Preliminary results suggest that these chiral ionic liquids are more viscous than the achiral ILS. This may be due to the presence of an extra hydroxyl group, which increases hydrogen bonding. Future work will focus on finding a new chiral auxiliary and comparing the properties of racemic vs. enantiopure ionic liquids.

Controlled Synthesis, Characterization, and Properties of Tin Oxide Nanoparticles. *JENNIFER CODDING (McMurry University, Abilene, TX 79697) WEI WANG (Oak Ridge National Laboratory, Oak Ridge, TN 37831).*

Tin oxide nanoparticle based materials have various applications as sensors, catalysts, pigments, and electrode materials. Physical and structural properties, along with crystallinity and particle size and morphology of the tin oxide nanoparticles, depend on the method of synthesis. In this research, tin oxide nanoparticles were synthesized by forced hydrolysis of Tin(IV) chloride in a hydrochloric acid-alcohol aqueous solution. The use of alcohols in the synthesis of tin oxide nanoparticles provided the ability to correlate procedures of experimental synthesis with the properties of the desired compound. A systematic study was performed to examine nanoparticle formation at different conditions by varying the type of alcohol, alcohol/water ratio, reaction temperature, and time. Dynamic Light Scattering was used to verify the size and distribution of the particles and a UV-visible spectrometer was used to measure absorption to determine the temperature at particle appearance. Experiment shows that tin oxide nanoparticles form in alcohol-water media with alcohol volume fractions below thirty percent, and that particle size increases with a decrease in alcohol percentage. In an ethanol-water mixture, particle formation initiates at 84°C in thirty percent alcohol, while particles develop at 86°C

in twenty-five percent alcohol in a methanol- or butanol-water mixture and at 85°C in twenty percent alcohol in an iso-propanol or n-propanol-water mixture. Particle size and concentration also increase with an increase of reaction time above the formation temperature. Under uniform conditions, the size of the nanoparticle is directly proportional to the size of the alcohol molecule. Additional experiments are needed to determine more precisely the required time versus temperature ratio for the controlled synthesis of nanoparticles. Ultimately, forced hydrolysis is a good method to control the size and shape of discrete tin oxide colloidal nanoparticles.

***Designing Cyclic Polyammonium Salts for Potential Uses as Anionic Receptors.** *ALEJANDRA CASTANO (Queens College, Flushing, NY 11367) JAMES WISHART (Brookhaven National Laboratory, Upton, NY 11973).*

The goal of this project is to synthesize cyclic polyammonium compounds that will be able to accommodate an electron as a guest. There have been several reports of cyclic ammonium polycations used as receptors for anionic guests such as chloride. The newly synthesized anion receptors will be used to control the solvation environment for excess electrons generated by pulse radiolysis. Providing a well-defined environment for the electron will help us to understand (by comparison) how the electron is solvated in bulk liquids (ionic and molecular) where the environment is highly disordered. The cyclic cations were synthesized by reacting tertiary diamines such as diazabicyclo[2.2.2]octane (Dabco) and N,N,N',N'-tetramethylbutanediamine with dihaloalkanes to produce the polyammonium cyclic adducts. These polyammonium halide salts were then converted to bis(trifluoromethylsulfonyl)imide salts and were investigated as potential ionic liquids. Preliminary NMR and Mass Spectrometry results indicate that the target cyclic polyammonium compound was not isolated using current reaction conditions. There is evidence that the product isolated is an ionene polymer. Differential Scanning Calorimetry (DSC) and Mass Spectroscopy analysis of this polymer is reported. Future work will focus on synthesizing cyclic polyammonium salts using different reaction conditions and analyzing the products using NMR spectroscopy, elemental analysis, Mass Spectrometry and pulse radiolysis techniques.

Detection of Botulinum Toxin Using a Sandwich Assay with Quantum Dots as the Fluorophore. *ABBY TYLER (Utah State University, Logan, UT 84321) MARVIN WARNER (Pacific Northwest National Laboratory, Richland, WA 99352).*

Development of assays and technology for biological toxins is a priority in the world today. Botulinum toxin is a potential bioterrorism agent for which new detection technologies are being developed. Effective detection systems need to have high sensitivity, and be rapid, automated, and accurate. Automated fluidics systems using sandwich immunoassays for detection have been developed at PNNL to fulfill these requirements. In order to increase sensitivity of biotoxin detection, quantum dots are used as the fluorophore. Quantum dots, or semiconductor nanocrystals, are becoming widely used in bioimaging but their use in biodetection is relatively new. Some advantages of quantum dots are good photostability, and a broad excitation spectrum and narrow emission spectrum that is highly red-shifted compared to the excitation wavelength. A fragment of the botulinum neurotoxin was used in these studies as well as two antibodies that are specific for different epitopes on the toxin. One antibody was coupled to several types of beads and the other antibody was coupled to the quantum dot. Bench top sandwich assays were performed by mixing the antibody-labeled beads, a sample of the toxin fragment, and antibody-labeled quantum dots. After reacting and washing this mixture, the fluorescent response was recorded. Assays were also done by packing a column of antibody-labeled beads in a cell in the automated fluidics system, perfusing a sample of toxin over it, then perfusing the fluorophore over it. Detection of 10pM toxin in buffer was achieved using the bench top assay with Sepharose 4-B beads and 655nm quantum dots with a fifteen minute reaction time. Polyacrylimide beads were used for detection using the automated system. Detection limits were slightly higher and there was more variability in the on column assay. Quantum dots have been an effective reporting agent in the bead based sandwich immunoassay for botulinum toxin.

Determination of Binding Constants Between Thiourea Anion Receptors and Selected Monovalent Anions. *ALICIA POWERS (Georgia Institute of Technology, Atlanta, GA 30332) LAETITIA DELMAU (Oak Ridge National Laboratory, Oak Ridge, TN 37831).*

The selective extraction of anions, particularly those in nuclear waste, is desirable because some anions hinder waste processing. Anion receptors can increase anion extraction and can possibly exhibit selectivity when designed from ligand modeling calculations. In this project, three thioureas, chosen for their geometry and ability to develop hydrogen

bonds with anions, are compared as anion receptors for several monovalent anions—nitrate, chloride, bromide, iodide, bicarbonate, and perchlorate—by measuring the binding constants between each thiourea and anion. Radiotracer experiments are used to measure the distribution of cesium between the organic and aqueous phases at varying initial concentrations of cesium for systems with and without anion receptors. Data from these experiments is modeled using the Fortran modeling program SXLSQL. In this program the predicted species formed in the organic phase are entered and the binding constants are calculated. The stoichiometry of the predicted species is varied in order to determine which model best fits the obtained data. Electrospray mass spectrometry (ESMS) is used to provide further evidence that the species used in the model are the actual species formed. Results show that all of the thioureas increased cesium extraction for all anions except perchlorate, although the order of the amount by which the thioureas increased extraction varied by anion. Most of the systems were best modeled with one thiourea binding to each monovalent anion although some were best modeled by both one and two thioureas binding to each anion. ESMS results for the nitrate anion with one of the thioureas showed that nitrate did bind to one thiourea although some nitrate also bound to two thioureas. These results show that thioureas were successful both in increasing anion extraction and in selectively extracting certain anions.

Determination of Forcefield Parameters to Evaluate the Binding of Porphyrin Structures to c-type Cytochrome Architectures.

ADRIENNE EASTLAND (*Chicago State University, Chicago, IL 60628*) **DR. DAVID TIEDE** (*Argonne National Laboratory, Argonne, IL 60439*). The binding of porphyrin-like molecules to the surface of c-type cytochrome proteins allows the initiation of electron transport. In order to develop biomimetic photosynthetic devices, the initiation step must be tuned by the choice of substituents on the porphyrin molecules. Computational docking studies combined with experimental fluorescence studies allow the evaluation of the effects of substituent changes on electron transport rates. The aim of this work is to develop a scoring function that is fast enough to be successfully applied to the prediction of the binding energy of a c-type cytochrome to a porphyrin-like ligand. Docking studies depend heavily on the scoring function employed. By using ab initio calculations at the Hartree Fock//6-31G* level, bond, angle, and dihedral parameters for the CHARMM scoring function were developed for a series of small molecules, representative of functional groups found in organic and biochemical systems. Upon parameterization, the dihedral force constant, k_{ϕ} , for the CA-CC-OC-OC dihedral in carboxybenzene was determined to be 3.66 kcal/mol/degree with $n = 2$ (n is the multiplicity of the function). For naphthalene dicarboxylate $k_{\phi} = 1.16$ kcal/mol/degree with $n = 4$. The magnitudes of the k_{ϕ} values are in good agreement with existing CHARMM forcefield parameters. Furthermore, these values reproduce the quantum mechanical energy profiles as a function of angle with R2 values of 0.97 and 0.94 for the carboxybenzene and naphthalene dicarboxylate molecules, respectively. A successful method will bridge the gap between expensive free-energy simulations and empirical scoring functions that are currently used to predict binding energy.

Determination of the Efficiency of Mixed-Acid Digestions of Sediments. **ALEJANDRA HUERTA** (*Hartnell Community College, Salinas, CA 93901*) **GARY GILL** (*Pacific Northwest National Laboratory, Richland, WA 99352*). Mixed-acid digestion is a method often used for the determination of elemental analysis of sediment samples. It is crucial that efficiency details associated with the digestion method be well understood on an element by element basis. Battelle's Marine Sciences Laboratory Standard Operating Procedure for Sediment Mixed-Acid Digestions was modified to identify conditions which produce optimal recovery of elements. The parameters that were adjusted for testing were mass of sediment, mixed-acid volume, mixed-acid composition and digestion time. Digestion involves treatment of the sediment sample with mixed-acid mixtures at $135^{\circ}\text{C} \pm 10^{\circ}$ in a Teflon® digestion bomb. Typical analytical methods include Inductively Coupled Plasma—Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma—Mass Spectrometry (ICP-MS). Initial experiments involved determining the optimal ratio of acid volume to mass of sediment. Experiments were designed to identify the point at which insufficient acid was used to effectively digest a given mass of sediment. When the mass of sediment was varied between 0.2 and 1.0 gram using a 4 mL aqua regia acid mixture (3 mL hydrochloric acid and 1 mL nitric acid), there was no effect on the recovery of the elements Al, Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sr, Ti, V, and Zn. The next experiments focused on a time study to resolve the shortest digestive time for optimal elemental recovery. Two masses of sediment were investigated, 0.25 and 0.7 g, again utilizing aqua regia digestion (4 mL).

Maximum recovery was reached after 4 hours of digestion; additional digestion time released no or only minimal amounts of elements from the sediments. The final set of experiments was designed to identify optimal conditions for the total digestion of sediment using a mixture of hydrochloric acid, nitric acid, hydrofluoric acid, hydrogen peroxide, and boric acid. These experiments were designed to determine the optimal volume of hydrofluoric acid needed to achieve a total digestion. Utilizing two masses of sediment 0.25 and 0.5 g and varying the volume of hydrofluoric acid and boric acid. Total digestion was achieved with a minimum volume of 0.5 mL hydrofluoric acid and a .25 g of sediment. Future experiments incorporating the findings in these experiments will be executed using a heated carbon block as the source for thermal energy.

Determination of the Electrostatic Potential of Cytochrome c7.

BRIAN WRIGHT (*Chicago State University, Chicago, IL 60426*) **DAVID TIEDE** (*Argonne National Laboratory, Argonne, IL 60439*). Assemblies of c-type cytochromes may be capable of long-range electron transport and thus are being considered as components of electron transfer/energy storage devices. The electron transport mechanism requires the binding of a small porphyrin-like molecule to initiate the electron transfer. In order to determine the likely binding sites on the surface of c-type cytochromes, the electrostatic potential of cytochrome c7 taken from *Geobacter sulfurreducens* (Protein Data Bank entry 1OS6) and horse heart cytochrome c7 (Protein Data Bank entry 1HRC) were calculated by solving the Poisson-Boltzmann equation using Delphi, a program that is integrated into the Chimera molecular modeling program. These calculations allow the identification of electron-rich or electron-poor sites that should contribute to binding. Results with model 1HRC showed good agreement with literature values, validating the charge and radii parameters chosen for the calculation. The overall surface of cytochrome c7 in model 1OS6 is positively charged by the amino acid lysine (Lys) (electron poor). The amino acids aspartic acid and glutamic acid contribute to the negative charge (electron rich) of the 1OS6 model. One possible binding site is located near Lys-64, Lys-52, and Lys-9. Another possible binding site is near Lys-37, Lys-33, and Lys-29. These areas are being considered as binding sites because the surface may provide porphyrin-like molecules large enough areas to bind. The ability to determine which parts of the c-type cytochrome are involved in the binding will lead to an improved understanding and control of the electron transfer process.

Diffusion-controlled Apparatus' for Microgravity.

RAJENDRAN (*Stanford University, Stanford, CA 94305*) **DR. P. THIYAGARAJAN** (*Argonne National Laboratory, Argonne, IL 60439*). Large photoactive yellow protein (PYP) crystals are being grown using diffusion-controlled apparatus' for microgravity (DCAMs) for proposed neutron crystallography experiments. The basis for this experiment is that a short strong hydrogen bond (SSHB) appears to play an important role in the function of PYP in the photocycle. In order to fully understand the structure and dynamics of the SSHB, it is necessary to accurately locate the nuclear position of the proton (or deuteron) with respect to the heavy atoms involved in the hydrogen bond. Previous attempts to grow PYP crystals using the batch and hanging drop method have had limited success. The resolution of diffraction data collected from PYP crystals grown using these methods was determined to be between 0.95 Å to 1.40 Å. PYP crystallizes best between a concentration range of 2.3 M to 2.5 M. Two DCAM units have been set up. The units have a concentration of 1.6 M and 2.0 M $(\text{ND}_4)_2\text{SO}_4$ in the small chamber, respectively, and a concentration of 3.0 M $(\text{ND}_4)_2\text{SO}_4$ in the large chambers. As the higher concentration solution in the large chamber equilibrates with the lower concentration solution in the small chamber through the diffusion control plug, the concentration increases within the "button" containing the PYP sample, causing crystallization to begin. Large PYP crystals have been grown following these procedures using DCAMs.

Distribution Coefficients of Several Ion-exchange Resins for the Separation of Cobalt, Nickel, and Copper.

JILLIAN SMITH (*East Stroudsburg University, East Stroudsburg, PA 18301*) **MARGARET GOLDBERG** (*Argonne National Laboratory, Argonne, IL 60439*). A method for the separation and accurate quantification of cobalt, nickel and copper is needed for the age dating of certain irradiated substances. The separation will be completed by using ion-exchange chromatography. The objective of this project was to measure the distribution coefficients for cobalt, nickel, and copper as a function of acid concentration and resin (Chelex 100, AG 1-X8, AG MP-1 and AG 50W-X8) using batch ion-exchange. The equilibrium of the metal ions between the aqueous phase and the ion-exchange resin is represented by the distribution coefficient (KD). Initial and final concentrations of the cations were measured by using high resolution inductively

coupled plasma-mass spectrometry. The project, however, was halted when the results showed an apparent contamination of the analyzed final concentrations. With only one quarter of the samples run, further research is necessary to correct the calibration curve and to account for the interferences of the matrix before any more quantification is performed.

Effects of Microbial Activity on the Stability of Apatite. *DIANNA MANJARREZ (Pacific Lutheran University, Tacoma, WA 98447) DAWN M. WELLMAN (Pacific Northwest National Laboratory, Richland, WA 99352).* A proposed remediation technology is to immobilize uranium by injecting a soluble phosphate amendment into the contaminated soil. The addition of a soluble phosphate amendment would initially form autunite, the dominant uranyl-phosphate mineral, to directly immobilize uranium and prevent further migration through the subsurface. Secondary to this, apatite will precipitate within the subsurface serving as a long-term sink for uranium via sorption and/or precipitation of uranium phosphate minerals. The environmental stability of apatite has been the subject of numerous investigations. Although the results of these investigations have provided valuable information regarding the mechanisms and rates of apatite corrosion as a function of relevant environmental variables, the effect of microbial activity on the durability of apatite has been the subject of far fewer investigations. This investigation quantifies the effect of microbial activity on the degradation of apatite at $T = 23^{\circ}\text{C}$, pH 6-8. Preliminary results suggest pH does not affect the release of calcium or phosphorus from apatite. Also, the presence or absence of microorganisms did not have a significant effect on the reaction progress, as indexed by calcium or phosphorus, in the presence or absence of aqueous phosphorus. The formation of secondary phase formation is possible and is the subject of further investigation.

Effects of Reaction Time upon Mesoporous Carbon Self Assembly. *LAURA WANAMAKER (Middle Tennessee State University, Murfreesboro, TN 37132) SHENG DAI (Oak Ridge National Laboratory, Oak Ridge, TN 37831).* Mesoporous carbon materials, which have a wide range of applications, have previously been synthesized using silica scaffolds, which are fabricated from surfactant templates. This method, however, is very inefficient as it involves the waste of silica scaffolds and surfactant templates and the use of toxic chemicals for silica removal. Thus, a method has been developed using surfactants as direct templates for the synthesis of the carbon materials. As prescribed by this method, triblock copolymers were used as the surfactant templates and a phloroglucinol/formaldehyde copolymer was used as a carbon precursor. These triblock copolymers are ideal for use in this process as they provide for carbon through self-assembly under mild conditions. Also, they permit the production of carbon materials as monoliths, fibers, sheets, and films. In addition, this method allows for the management of pore size and structure of the carbon materials by regulation of concentration and the specific surfactant used, respectively. The purpose of the current research was to determine the optimal reaction time to produce carbon materials composed of polymers of predetermined sizes and of uniform pore size. Reaction times were varied between 20 minutes and 2 hours to determine the dependence of the self-assembly process. This process of polymerization of phloroglucinol/formaldehyde copolymers induced phase separation into an aqueous, inorganic layer, which was discarded, and an organic layer. The organic layer was separated out and dried at 80°C overnight and then at 140°C overnight prior to carbonization. Nitrogen absorption/adsorption measurements, although pending, will provide pore size, pore volume, and surface area of the produced carbon material.

Exploration of Using Starch as a Recovery Agent for Catalytic Iodine. *BEN SIKORA (Colorado School of Mines, Golden, CO 80401) JOHN VERKADE (Ames Laboratory, Ames, IA 50011).* Currently a method for conjugating soybean oil is being developed that uses Iodine as a catalyst. To help conjugated soybean oil be more economically comparable to other oils, on the industrial scale, Iodine must be able to be recycled. A survey of a variety of starches and mixtures of these starches with water at various concentrations has been conducted to obtain optimum conditions for the removal of Iodine from Hexanes, and subsequent recovery from the starch. When potato starch was used it was found that it worked best when only wetted. The wetted potato starch gave the fastest absorption time of Iodine out of Hexanes, but posed problems when trying to drive the Iodine back out of the starch by thermal decomposition of the starch-Iodine complex. "V" modified starch was found to work without an outside solvent, such as water. This helped make the removal process of Iodine much simpler by removing the need to separate another liquid from the process. The results obtained for driving Iodine out of the starch were different from

literature insight in the fact that literature suggests that Iodine will leave the starch under thermodynamic activation. Some complications are still perplexing and require future investigation, such as the best process to remove the Iodine from the starch back into the Hexanes for recycling.

Extraction of Actinide Elements. *SARA MONTGOMERY (Rochester Institute of Technology, Rochester, NY 14623) JEFF GIGLIO (Idaho National Laboratory, Idaho Falls, ID 83415).* Advanced fuel specimens of the Materials and Fuel Complex (MFC) containing Plutonium, Americium, Neptunium, and Zirconium are prepared and sent to the Advance Test Reactor (ATR) and exposed to neutron bombardment. Characterization is performed on fuel stock material products before fabrication of metallic rods, before irradiation, and post irradiation (PIE). Characterization of the fuel samples is complicated because of isobaric interferences using inductively coupled plasma mass spectrometry (ICP-MS). In addition, background complications and wavelength overlaps complicate analyses by inductively coupled plasma atomic emission spectroscopy (ICP-AES). To minimize interferences, and reduce the overall actinide content of the samples (ALARA considerations) a means of separating the actinides from each other and removal of the actinides from a sample (i.e., "Clean-up") is needed. The objective to the research was to simplify separation schemes using TRU™ resin and manual Gas Pressurized Extraction Chromatography. The removal of the actinides will allow for more accurate and safer analysis of fuel samples for trace element impurities (before irradiation) and fission products after irradiation. The TRU resin worked well for the retention of Pu and U. However, Np proved to be problematic. More work is needed to fix the oxidation state of the Np for better retention. The removal of Pu from the TRU resin was accomplished. However, the U was not removed from the resin material with the acid used. The TRU resin worked well in the "Clean-up" of the actinides.

Froth Flotation and Other Means of Separation of Plastics of Equal Density and/or Similar Characteristics. *MICHAEL MAJEWSKI (University of Pittsburgh, Pittsburgh, PA 15213) BASSAM JODY (Argonne National Laboratory, Argonne, IL 60439).* Froth flotation is a method of using the hydrophobic and hydrophilic properties of materials to selectively attach air bubbles to one type of polymer in a mix, allowing for separation. By manipulating surface tension, acidity/basicity and specific gravity of solutions, it is possible to isolate, purify, and clean polymers from various shredder residues into high value resin streams. Plastics that are of interest include polypropylene (PP), talc-filled polypropylene (PP w/Talc), polyethylene (PE), acrylonitrile-butadiene-styrene copolymer (ABS), and ABS-polycarbonate alloys (ABS-PC). After submersion in successive solutions in which some plastics float and others sink due to the previously mentioned parameters and froth flotation, individual fractions form, each with a high purity in one or more thermoplastics. After experimentation, FTIR spectroscopy, as well as some FT-Raman, is used to identify the polymers. Difficulty arises in the isolation of polymers from shredder residue, as numerous contaminants include oils, gasoline, other automotive and appliance fluids, foam, and metals. What is received as bulk shredder residue destined for a landfill can be processed, cleaned, pelletized, and re-molded. A PP/PE product has been isolated. Interior automotive plastic components, such as battery trays and knee bolsters, have been molded from the recycled material. I have spent time in the lab doing wet chemistry, including froth flotation and density separation, on various polymers, air classification using air columns, FTIR analysis to identify plastics, and measurements of the surface tension and specific gravity of solutions.

Functionalization of a Ceramic Membrane for Liquid-Liquid Extraction. *DERRICK WHITLOCK (Texas Southern University, Houston, TX 77095) SETH SNYDER (Argonne National Laboratory, Argonne, IL 60439).* Ethanol, a product available in large quantity from corn fermentation, has been proposed as a viable alternative for gasoline. However, major barriers to the successful implementation of ethanol as a major fuel source are high costs and energy consumption associated with routine distillation of aqueous mixtures. Hydrophobic membranes, which have been employed successfully in liquid-liquid extraction, should offer a viable alternative to distillation. Herein, we disclose a process using ethyltrimethoxysilane (ETMS) to functionalize ceramic membranes capable of separating ethanol from water with high flux and minimal energy costs. Overall hydrophobicity analyses conducted on functionalized ceramic test membranes indicated the development of successful and versatile hydrophobic functionalization protocol and the measurement of negligible H₂O flux.

Hydrothermal Synthesis and Characterization of Sodium Dawsonite. *DANIEL DWYER (State University of New York at Geneseo, Geneseo, NY 14454) DR. DAWN M. WELLMAN (Pacific Northwest National Laboratory, Richland, WA 99352).* Na-dawsonite

has recently been suggested as a long-term sink for storage of carbon dioxide. In order to evaluate the effectiveness of this technique the stability of Na-dawsonite must be quantified under relevant geochemical conditions. To this end, significant quantities of pure crystalline Na-dawsonite are required for testing. However, sufficient quantities are not naturally available. Hydrothermal synthesis of Na-dawsonite was conducted at a temperature of 215°C for 96 hours, with a NaHCO₃/Al molar ratio of 24:1. X-Ray diffraction (XRD) and scanning electron microscopy (SEM) results indicate this method produced highly crystalline Na-dawsonite.

***Imaging Brain Amyloid After Traumatic Brain Injury and Drug Use with [11C] 6-OH-BTA-1 (PIB).** CANDACE GIRARD (*Springfield Technical Community College, Springfield, MA 01056*) JOANNA FOWLER (*Brookhaven National Laboratory, Upton, NY 11973*). Cerebral deposition of B-amyloid present in amyloid plaque (AP) may present an early and necessary step in the pathogenesis of Alzheimer's disease (AD). Postmortem immunohistochemical analysis after traumatic brain injury (TBI) also indicates the presence of AP. Recently, [N-Methyl-11C] 2-(4-(Methylamino) phenyl-6-hydroxy-benzothiazole (6-OH-BTA-1), commonly known as PIB, was introduced as a high affinity ligand for imaging AP with Positron Emission Tomography (PET). In the present study, the synthesis and radiolabeling of PIB was accomplished according to modified published procedures. Using PIB for in vitro autoradiography studies, assessments of AP concentration from TBI specimens were evaluated. Frozen rat brain (5=injured, 4=normal) sections were exposed to B-sensitive PhosphorImager plates for 40+ min. The exposed plates were scanned in a PhosphorImager to produce digital images indicating high densities of ligand binding in the white matter regions of normal and injured rats. The presence or absence of group differences in grey matter areas awaits quantitative and statistical analysis. Additionally, PIB was used for the first in vivo evaluation of AP concentration secondary to Methamphetamine abuse using PET imaging. A male Sprague-Dawley rat (250g) was pretreated with Methamphetamine for 5 consecutive days. [11C] PIB was administered intravenously and a 90 minute dynamic PET scan recorded PIB uptake in specific brain regions. The highest levels of labeled PIB binding were in the corpus striata. These findings are preliminary and are part of an ongoing study to develop novel therapeutic strategies for drug abuse and treatment.

Improved Sample Preparation for Metabolites of Organophosphorus Insecticides in Biological Matrices. MELISSA PURPURA (*New Mexico State University, Las Cruces, NM 88003*) JAMES A. CAMPBELL (*Pacific Northwest National Laboratory, Richland, WA 99352*). Organophosphorus insecticides are broadly used in a variety of applications. Because of their widespread use, the potential exists for both occupational and environmental exposures that may cause a variety of health problems due to the inhibition of the enzyme acetylcholinesterase. The measurement of known metabolites in biological matrices through biomonitoring is a means for determining exposure to parent organophosphorus pesticide compounds. However, biological matrices present a unique challenge for analysis due to the potential interferences from compounds they contain. For this reason, methods for the purification and analysis of three metabolites of chlorpyrifos (diethylphosphate, trichloropyridinol, and diethylthiophosphate) were studied using whole rat blood. Techniques such as liquid-liquid extraction with solvents of varying polarity, centrifugation, and filtration were used in order to purify the samples and their extracted residues. All samples were derivatized and analyzed by gas chromatography/mass spectrometry. Preliminary data suggests that recoveries of diethylphosphate were better when the sample was extracted with ethyl acetate instead of methylene chloride. Although filtration prior to liquid-liquid extraction did not result in cleaner samples, it did improve the clarity of extracted residues. Centrifugation following derivatization produced cleaner samples without loss of the target metabolites. Future work will focus on the application of these methods for the analysis of samples collected from in vitro and in vivo studies of these compounds. Application of these methods to other matrices and other organophosphorus insecticides should also be examined.

***Investigating the Physical Properties of Liquid Ionic Phosphates (LIPs).** KATHERINE URENA (*Queensborough Community College, New York, NY 11368*) DR. JAMES WISHART (*Brookhaven National Laboratory, Upton, NY 11973*). Ionic liquids (ILs) are organic salts that exhibit melting points below 100°C. They are typically composed of ammonium cations and polyatomic inorganic anions. The attractive properties of ILs, including negligible vapor pressure, high conductivity, low flammability, low melting points, and recyclable nature make them ideal as environmentally friendlier solvent alternatives. We have synthesized a series of ILs based on functionalized 1-methylimidazole

and 1-methylpyrrolidine cations and phosphate anions. The resulting ILs are referred to as Liquid Ionic Phosphates (LIPs). The structures of LIPs have been confirmed using ¹H, ¹³C and ³¹P Nuclear Magnetic Resonance spectroscopy (NMR). The physical properties of LIPs including polarity, conductivity, viscosity, and decomposition temperature were determined. Polarity characteristics will be examined using the ET(30) polarity scale (an empirically derived reference scale based on the solvatochromic behavior of Reichardt's dye). Conductivity measurements will be done using a conductivity meter and viscosity measurements will be done using a viscometer. In addition the decomposition temperature (which indicates the liquid range of the IL) will be done using thermogravimetric analysis (TGA). Preliminary results indicate that we have successfully synthesized 1-Methylpyrrolidinium phosphates.

***Investigating the Use of a Diffusion Flame to Produce Black Carbon Standards for Thermal-Optical Analysis of Carbonaceous Aerosols.** DIANA ORTIZ MONTALVO (*University of Puerto Rico, San Juan, PR 00931*) THOMAS W. KIRCHSTETTER (*Lawrence Berkeley National Laboratory, Berkeley, CA 94720*). Combustion generated particles impact climate and public health due to their ability to scatter and absorb solar radiation and alter cloud properties, and because they are small enough to be inhaled and deposit in the lungs where they may cause respiratory and other health problems. Specific concern is focused on particles that originate from the combustion of diesel fuel. Diesels particles are composed mainly of carbonaceous material, especially in locations where diesel fuel sulfur is low. Diesel particles are black due to the strongly light absorbing nature of the refractory carbon components, appropriately called black carbon (BC). This research project focuses on the uncertainty in the measurement of BC mass concentration, which is typically determined by analysis of particles collected on a filter using a thermal-optical analysis (TOA) method. Many studies have been conducted to examine the accuracy of the commonly used variations of the TOA method, which differ in their sample heating protocol, carrier gas, and optical measurement. These studies show that BC measurements are inaccurate due to the presence of organic carbon (OC) in the aerosols. OC may co-evolve with BC or char to form BC during analysis, both of which make it difficult to distinguish between the OC and BC in the sample. The goal of this study is to develop the capability of producing standard samples of known amounts of BC, either alone or mixed with other aerosol constituents, and then evaluate which TOA methods accurately determine the BC amounts. An inverted diffusion flame of methane and air was used to produce particle samples containing only BC as well as samples of BC mixed with humic acid (HA). Our study found that HA particles are light absorbing and catalyze the combustion of BC during TOA. It is expected that both of these attributes will challenge the ability of TOA methods in distinguishing between OC and BC, such as the simple two step TOA method which relies solely on temperature to distinguish between OC and BC. The samples prepared in this study were analyzed using two TOA methods to compare the estimates of BC concentration. Future work will focus on the preparation of a variety of BC standards and comparing measurements of the prepared samples using a range of TOA methods.

***Isolation of a Single Parameter in Ultra High Purity Electroformed Copper.** CARMEN CAPETILLO (*Heritage University, Toppenish, WA 98948*) ERIC HOPPE (*Pacific Northwest National Laboratory, Richland, WA 99352*). Ultra high purity electroformed copper has the potential to be used as shields and cryostats for low background germanium spectrometry due to its distinct properties such as high electrical and thermal conductivity. However, there remain traceable radioactive contaminants of thorium 232 and uranium 238 found in most samples of high purity electroformed copper. There are many factors effecting the electroformation of ultra high purity copper some of which include: current, voltage, concentration of solution, mixing, and electrical waveform. There is significant difficulty isolating a single parameter when such a wide variety of variables exist. In these experiments, changing the anode to cathode distance without affecting the overall surface area of the electrodes was critical. The plating was performed using a small cylindrical container, solution of sulfuric acid and copper sulfate, and a reverse pulse plating power supply. The copper anode material was cut into vertical columns and placed into plastic tubing which was used for a cylindrical form. This allowed the distance between the anode and cathode to change without varying the surface area of either. Other parameters such as voltage and waveform, stirring, volume and components of solution were held constant. As expected, the closer the anode was to the cathode a greater amount of copper was deposited over a shorter time period due to the lesser impedance of the reduced path length. An unanticipated outcome was that a

smaller distance between the anode and cathode produced copper that had a smoother surface than that at the greater distance. Various purity assays must still be completed on the copper deposits produced. Further work must also be done to determine the optimum distance between the anode and cathode.

Linking Conductivity Measurements of Composite Heteropoly Acid Proton Exchange Membranes with Membrane Compositions and Fabrication Methods. DANA LIPFERT (Colorado School of Mines, Golden, CO 80401) JOHN TURNER (National Renewable Energy Laboratory, Golden, CO 89401). Fuel cells have been proven as an efficient energy conversion device and are employed in several applications (300°C) fuel cells require a cooling and humidification system to function properly. This increases weight, size, and cost of these applications, making fuel cells impractical for them. A proton exchange membrane that functions at high temperatures will alleviate these complications and allow for mass production of fuel cells for high temperature use. Composite heteropoly acid proton exchange membranes have shown promise for high temperature use, but a chemically and mechanically stable composite membrane with sufficient conductivity has yet to be obtained. The wide variety of heteropoly acids, membrane compositions and fabrication methods allows for a plethora of composite membranes, most of which do not satisfy all requirements. The objective of this work was to associate conductivity trends with fabrication methods, conditioning methods, and weight ratios of heteropoly acids and silanes (a fixing agent for heteropoly acids). For this work 12-silicotungstic acid (12STA) and tetraethyloxosilane (TEOS) at varied weight percents were used in composite membranes fabricated by either a sol-gel solution cast method or a doctor blade film forming method. Most membranes were cured, though uncured membranes were also tested. Conductivity tests were performed at a constant cell temp of 80°C with relative humidity (RH) ranging from 50-100%. Conductivities ranged from 0.36 mS/cm to 18.7 mS/cm, the highest conductivity produced at 100% RH by a membrane with 174 weight percent (wt%) 12-STA and 56 wt% TEOS fabricated by the solution casting method. Membranes fabricated by the doctor blade method were more flexible and produced higher conductivities than membranes of the same composition fabricated with the solution casting method, which tended to be brittle. Membranes conditioned in DI water produced lower conductivities than membranes of the same composition conditioned ambiently. UV-visible absorption analysis performed on water extracts for membranes after five day soaking showed that approximately 25 wt% 12-STA were leached out of the membranes. Uncured membranes were shown to have lower conductivities than cured membranes of the same composition.

Metabolic Profiling of Carboxylic Acids and Phosphorylated Species and Using Capillary Electrophoresis-Mass Spectrometry (CE-MS). MARIJA MENTINOVA (Lawrence University, Appleton, WI 54911) GARY J. VAN BERKEL (Oak Ridge National Laboratory, Oak Ridge, TN 37831). The analysis of metabolomes covers the identification and quantification of all intracellular and extracellular metabolites which exhibit molecular masses lower than 1000 Da, using a wide variety of analytical techniques. The goal of this work is to expand the analytical tool infrastructure at ORNL for analysis of plant and microbial metabolomes. A capillary electrophoresis system was coupled with an ion trap mass spectrometer. Capillary electrophoresis-mass spectrometry (CE-MS) is an ideal analytical tool for the analysis of charged species in solution. In the present work, CE-MS was applied to the separation of various candidate charged metabolites of plant metabolomes. This approach was used for the high resolution separation and sensitive detection of metabolites in the "negative ion" mass spectrometric mode. The "negative ion" mode on the mass spectrometer was used for detecting negatively charged components. Model compounds, such as small organic acids, phosphorylated carbohydrates, and adenosine phosphates, were separated and detected. For example, a three component mixture containing malic, citric and succinic acids was separated successfully using CE in its "reverse" polarity and detected by MS. In "reverse" polarity, the injection site on the CE was a high negative polarity (e.g., -20KV), and the electrospray emitter of the MS was positive relative to that (e.g., -3KV). The resulting electropherogram contained peaks with three different migration times, corresponding to each of the acids in the mixture. Similar results were obtained using the three adenosine phosphate species, as well as fructose mono- and diphosphate. These data, taken together, suggest that more complex metabolic mixtures could be separated, the individual components detected and quantified, and their metabolic profiles created. Further studies are needed to evaluate the separating power of CE-MS using more complex mixtures. This

fundamental project on metabolic profiling of phosphorylated species and carboxylic acids using CE-MS is a step forward to developing a new analytical infrastructure for ORNL in metabolic analysis.

Microwave Plasma CVD Diamond Stripper Foils for the Spallation Neutron Source. AMANDA MCDERMOTT (University of Virginia, Charlottesville, VA 22904) ROBERT W. SHAW, LESLIE L. WILSON, CHARLES S. FEIGERLE (Oak Ridge National Laboratory, Oak Ridge, TN 37831). Many accelerators use stripper foils to convert H⁻ to H⁺ as each pulse is injected into an accumulator ring. However, traditional carbon foils would have a short lifetime in the Spallation Neutron Source (SNS), and foil replacement requires significant beam downtime. Preliminary results suggest that diamond stripper foils could last ten times longer, or more, than carbon foils. The goal of this project is to grow foils under varying conditions for testing at the SNS to determine the best procedure to transfer to SNS technicians. Silicon substrates were patterned photolithographically, producing corrugations 5–7 μm deep around the outside edge to prevent curling of the free-standing films. The substrates were roughened in a stirred diamond-particle slurry in an ultrasonic bath to create nucleation sites. Diamond films were grown via microwave plasma assisted chemical vapor deposition (CVD) with a total flow rate of 100 standard cubic cm per minute (sccm). Nanocrystalline films were grown using 90% Ar and 1000 W microwave power at 130 torr; microcrystalline films were grown without Ar at 1300 W and 50 torr. In both cases the carbon source was 1 or 2% CH₄ with H₂ constituting the remaining flow. Growth temperatures varied from about 600–750°C. Scanning electron microscopy was used to determine grain size, presence of holes, and other characteristics. Finally, the Si backing was etched from acceptable foils using HF acid, leaving some Si for mounting. Films grown with CH₄ concentrations between 1 and 2% were investigated as a phenomenon consistently observed on the surface of 2% nanocrystalline films: small black spots of unknown composition. Nanocrystalline films were grown with 2% CH₄ at pressures from 100 to 140 torr resulting in varied temperatures. Larger particle sizes occur in 1% nanocrystalline films than in those grown with 2% CH₄, and micrographs of intermediate varieties showed that the transition in particle size is gradual. The density of black spots on 2% nanocrystalline films had a positive correlation with temperature, and a hydrogen-plasma etch procedure was developed to remove them. Foils with and without spots will be included in the next foil set for the SNS. When foil lifetimes are reported in several months, it will be possible to determine the ideal grain size and film thickness and whether removing black spots enhances performance. Examination of used foils will provide insight into failure mechanisms.

Neoteric Solvents for High Performance Liquid-Liquid Extraction. SHAYLA THOMAS (Texas Southern University, Houston, TX 77004) SETH SNYDER (Argonne National Laboratory, Argonne, IL 60439). Ionic liquids are neoteric solvents that may play an integral role in increasing the efficiency of ethanol extraction. Since many ionic liquids may be synthesized, selecting the best one for ethanol extraction is a difficult task. Herein, we qualitatively explore and discuss physicochemical properties of ionic liquids influencing the feasibility of ethanol extraction using a functionalized hydrophobic membrane. As modeling standards for extractants, two ionic liquids, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [bmpy][Tf2N] and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf2N], were selected. Consequently, reasonable exchange of anionic constituents and modification of cationic "R" groups of these standards resulted in the proposal of four designer ionic liquids (DILs), 1-butyl-1-methylpyrrolidinium perfluoroethyltrifluoroborate ([bmpy][CF3CF2BF3]), 1-methoxyethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([COe]mpy)[Tf2N], 1-hexyl-3-methylimidazolium perfluoroethyltrifluoroborate ([hmim][CF3CF2BF3]), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf2N]), optimal for the extraction of ethanol from aqueous mixtures using a functionalized membrane in a membrane contactor. Of these, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf2N]), was selected as the best overall DIL for complete application and processing.

New Liquid Precursors for the Deposition of Molybdenum. ROBERT PASQUARELLI (Rochester Institute of Technology, Rochester, NY 14623) CALVIN CURTIS (National Renewable Energy Laboratory, Golden, CO 89401). Copper indium diselenide (CIS) solar cells have demonstrated record high efficiencies, but the technology required and number of deposition systems necessary for processing CIS solar cells makes them expensive and difficult to scale up for manufacturing. A new means of depositing molybdenum (Mo), which serves as the back contact for these devices, from liquid precursors

can help lower costs and make CIS a more viable energy alternative. Deposition was studied using the organometallic precursors bis(ethylbenzene)molybdenum and tetraallyldimolybdenum dissolved in organic solvents. These solutions were deposited on glass microscope slides at temperatures between 100 and 340°C under nitrogen atmosphere. Commercial bis(ethylbenzene)molybdenum dissolved in both tetrahydrofuran and toluene was deposited on glass substrates at 200° and 340°C via spraying to produce films metallic in appearance. X-ray diffraction (XRD) showed broad peaks that could be assigned to Mo and carbonaceous contaminants (cubic Mo₂C and hexagonal β-Mo₂C), but most of the material present appeared to be amorphous. Elemental composition should be studied in future analysis to quantify the amount of carbide and metallic Mo present. The resistivity of a sprayed film was determined using a four-point probe to be $(3.23 \pm 0.76) \times 10^{-4} \Omega\text{-cm}$, a value about two orders of magnitude greater than that of pure Mo and one order of magnitude greater than the sputtered films currently used. Tetraallyldimolybdenum was synthesized under Schlenk line conditions and deposited from solution via drop coating to produce powdery films with poor adhesion. The composition of these films could not be determined using XRD given their amorphous nature. Future work will focus on removing carbide contaminants by depositing in the presence of hydrogen and producing more crystalline material.

NO_x and NO Adsorption on CeO₂: A Combined in situ FTIR and TPD Investigation. JOHN FAIN (*Sacramento City Community College, Sacramento, CA 95822*) JANUS SZANYI (*Pacific Northwest National Laboratory, Richland, WA 99352*). The NO_x adsorption/desorption properties of a high surface area CeO₂ (ceria) (an additive in practical lean NO_x traps) was investigated using in-situ Fourier Transform Infrared Spectroscopy (FTIR) in conjunction with mass spectroscopy (MS) and temperature programmed desorption (TPD). A high surface area ceria sample, treated under various conditions (oxidation or reduction), was exposed to either NO₂ or NO. NO₂ adsorption experiments revealed the formation of large amounts of nitrates on ceria. These nitrate species desorbed in two stages, similarly to that we have observed previously on BaO, suggesting that these two desorption states may arise from the decomposition of surface (NO₂ desorption) and bulk (NO+O₂ desorption) nitrates. The amount of nitrates formed upon exposure to NO₂ was higher on the oxidized samples than on the reduced ones, probably due to the consumption of some of the NO₂ to fill oxygen vacancies present in the reduced samples. Furthermore, over the reduced ceria samples the formation of both N₂O and N₂O₃ were observed in addition to the surface and bulk nitrates species. NO adsorption experiments showed limited N₂ production during thermal decomposition, due to the presence of small number of defect sites (oxygen vacancies where NO can decompose), associated with the low temperature during reduction with H₂ prior to NO adsorption. Keywords: NO_x reduction; lean NO_x traps; ceria; NO and NO₂ adsorption; FTIR; TPD.

***Optimization of an HPLC Method for Determination of Carbon-11 Specific Activity in [C-11] Methyl Iodide.** NATALIA SHAROVA (*Contra Costa College, San Pablo, CA 94806*) JAMES P. O'NEIL (*Lawrence Berkeley National Laboratory, Berkeley, CA 94720*). We have created a "standard mass concentration curve" for determination very small concentrations of the methyl iodide in the carbon-11 labeled methyl iodide for further calculation of a carbon-11 specific activity. The stock solution of methyl iodide was prepared by weighing and volumetric dilution with several precautions such as sealing the vials with Teflon faced septa. This solution was then diluted with water to prepare 5 standards with the methyl iodide concentration range 3.0–0.03 nmoles per injection. All standards were injected in the HPLC in triplicate and the responses were analyzed by the PeakSimple data system. Collected data allowed us to create a "standard mass concentration curve" and calibrate the PeakSimple for the specific methyl iodide components. Along the experiment we came to a conclusion that standard dilutions for this experiment could be done with water; however, water as diluent had its disadvantages that limited the minimal achievable concentrations of methyl iodide and increased uncertainty of the results. In order to increase the reliability of the standard curve, the experiment should be conducted within the time period that does not exceed 12 hours, and all standard samples has to be stored in small sealed glass vials at low temperatures (~ -5°C) while not being used.

Protonation of Molybdenum Cyclopentadienyl Phosphino Chloride Complexes with Triflic Acid. SHARON LEE (*University of California–Berkeley, Berkeley, CA 94720*) R. MORRIS BULLOCK (*Brookhaven National Laboratory, Upton, NY 11973*). The conversion of ketones to alcohols has a major impact on pharmaceutical chemistry due to its application in the synthesis of drugs. Current methods require expensive transition metal catalysts based on rhodium or ruthenium.

Harsh reagents such as LiAlH₄ and NaBH₄ require stoichiometric amounts and produce significant amounts of waste. Therefore, interest in catalytic molybdenum compounds that exhibit this reactivity has been growing. To be effective in an ionic hydrogenation mechanism, such molybdenum compounds must have the ability to protonate as well as transfer a hydride to a ketone to form an alcohol. This paper introduces molybdenum compounds made through the addition of triflic acid (HOTf = HOSO₂CF₃) in dichloromethane to synthesized Cp(CO)(Ph₂PRPPH₂)MoCl (R = CH₂, (CH₂)₃, or C₆H₄, Cp = C₅H₅) compounds. The resulting product, [Cp(CO)(Ph₂PRPPH₂)MoHCl]+OTf, of interest because of its potential to increase understanding of molybdenum interaction with its attached proton and the influence of different types of phosphino ligands on protonations. This knowledge can then lead to a more efficient molybdenum catalyst that can convert ketones to alcohols. The molybdenum compounds successfully synthesized are Cp(CO)Mo(dppb)Cl (dppb = 1,2-bis(diphenylphosphino)benzene), Cp(CO)Mo(dppp)Cl (dppp = 1,3-bis(diphenylphosphino)propane), and Cp(CO)Mo(dppm)Cl (dppm = bis(diphenylphosphino)methane). After protonation with triflic acid, the following compounds were made: [Cp(CO)(dppb)MoHCl]+OTf, [Cp(CO)(dppp)MoHCl]+OTf, and [Cp(CO)(dppm)MoHCl]+OTf. Using proton and phosphorus nuclear magnetic resonance and infrared spectroscopy, all synthetic products were characterized. In the future, structural characterization using x-ray diffraction on the crystals of the protonated compounds will be performed.

Radiochemical and Elemental Analysis of Zorita Pressure Vessel Materials. MICHAEL KING (*Baker University, Baldwin City, KS 66006*) JACQUELINE FONNESBECK (*Idaho National Laboratory, Idaho Falls, ID 83415*). Despite the fact that nuclear energy has the technological capability to take the place of fossil fuel as the world's primary energy source, there is still overwhelming opposition toward nuclear energy in many countries. One particular example of recent opposition to nuclear power occurred in Spain where President Jose Luis Zapatero shut down the Jose Cabrera (Zorita) Nuclear Power Plant in April of 2006 after thirty-eight years of operation. Closure of the plant not only reduces the energy production capabilities of Spain, but it also presents a convoluted and expensive clean up effort. Before demolition of the 160 MW pressurized water reactor used at Zorita can commence, various analyses must be performed to determine the level of radioactivity present in the reactor materials. The scope of work consists of the radiochemical and elemental analysis of the reactor pressure vessel plate materials that were abstracted from the Zorita reactor. The primary focus will be determining and classifying "Greater than Class C Waste" isotopes including: H-3, C-14, Ni-59, Ni-63, Co-60, Sr-90, Nb-94, Tc-99, I-129 and Cs-137. Class C Waste materials constitute the highest level of radioactivity which can be considered low level waste and is usually stored in a landfill. Storage protocol for greater than class C waste is more stringent and is typically stored in permanent repositories. In order to determine the composition and radiological hazards associated with the pressure vessel materials, various analyses and instrumentation is required. Neutron activation experiments will be performed at Washington State University to determine the majority of the elements present in the steel samples. Additional steel samples will be dissolved at the Materials and Fuels Complex and the dissolver solution will be analyzed using various spectrometers and counting instruments including: Inductively Coupled Plasma Mass Spectrometer, Inductively Coupled Plasma Atomic Emission Spectrometer, Gamma Spectrometer, Liquid Scintillation Counter, and X-Ray LEPS. Concurrently, solid pressure vessel samples will be combusted in a LECO Carbon Analyzer. The C-14 and H-3 will be collected from the combustion process and liquid scintillation counting used to determine the quantity of each. The results from all the analyses will be compiled and the quantity of each isotope will be reported to Westinghouse Electric in parts per million.

Ruthenium Isotopic Analysis: Comparison of Separation Techniques. VALERIE STUCKER (*University of New Hampshire, Durham, NH 03824*) CHRIS BROWN (*Pacific Northwest National Laboratory, Richland, WA 99352*). Technetium-99 (⁹⁹Tc), a beta emitter with a 213,000 year half life, is a contaminant of concern at several nuclear facilities. It is difficult, however, to use ⁹⁹Tc to distinguish between different contaminant sources and waste routes since it is a mono-isotopic fission product. On the contrary, the process of nuclear fission generates multiple ruthenium isotopes. These ruthenium (Ru) fission product isotopes offer a promising substitute for ⁹⁹Tc, testing due to the commonalities related to their subsurface mobility and the fact that their presence in nature is negligible. Comparing Ru isotopic ratios from different groundwater samples and water extracts from contaminated vadose zone sediments gives insight into the source

terms and pathways of the accompanying ^{99}Tc contamination. Methods of preconcentration and pretreatment for mass interference removal were developed to evaluate their effectiveness and establish new procedures for ruthenium isotopic separations. Anion exchange resin was assessed for total analyte recovery and preconcentration of Ru. Cation exchange resin was evaluated for its ability to remove cation analytical interferences and total analyte recovery. Solutions prepared from single element Ru standards were passed through columns containing either cation or anion exchange resin and the eluents were analyzed for total Ru and Ru isotopic ratios via inductively coupled plasma mass spectrometry. 50% of the ruthenium passed directly through the anion resin column, but 94.3% of it was recovered in three elution steps. The cation exchange resin had poor recovery (11–18%), but was efficient at removing cation interferences, reducing key interferent count rates (i.e., strontium) by 3 to 4 orders of magnitude. This cation resin was used in the reanalysis of previously tested contaminated sediment samples and similar results were obtained, confirming the usefulness of column pretreatment and preconcentration. The methods described herein present an efficient way to increase detection of ruthenium isotopes and quantify natural versus fission-produced ruthenium. This work is being performed in conjunction with other research being done by the Applied Geology and Geochemistry group to discover ways to identify, remove, and eliminate long term risks of technetium contamination from the Hanford Site, Washington.

Separation and Quantification of Cobalt, Nickel, and Copper by Anion-Exchange Column Chromatography Using the Dowex AG 1-X8 Resin. TERA SLONE (Texas Southern University, Houston, TX 77004) DR. TRACEY SIMMONS-WILLIS (Argonne National Laboratory, Argonne, IL 60439). Ion exchange column chromatography is a separation technique in which ions are exchanged, and separated by virtue of the differences in their distribution ratios between a mobile phase and a stationary phase that are in contact with each other. In this experiment an aqueous solution comes into contact with a resin packed in a chromatography column and causes the solution to exhibit the property of exchanging these ions and separating them. The ions are separated based on the solution's affinity and the resin's affinity for these ions. My overall goal in performing this technique is to separate three elements that are important to the forensic analysis of dirty bombs. Analysis of cobalt (Co), nickel (Ni), and copper (Cu) is necessary for age-dating the dirty bomb materials but they must be separated prior to forensic analysis. My research involves development of a preliminary separation method using a specific resin, the Dowex AG 1-X8 anion resin. This method is performed on the basis of an ion exchange column chromatography technique in which three different acids, hydrochloric acid, perchloric acid, and hydrobromic acid, are used to determine the optimum eluent for separating cobalt, nickel and copper while using the AG 1-X8 anion resin. Once this procedure is completed and several fractions have been collected, the separated elements will be detected and quantified by an instrument known as an inductively coupled plasma mass spectrometer (ICPMS) and the efficiency of the method will be determined.

Siloxanes: A Class of Silicon Based Polymers. SHARON LEONARD (Shasta Community College, Redding, CA 96006) PAVEL HRMA (Pacific Northwest National Laboratory, Richland, WA 99352). The very first technological developments occurred in what we now know as the Stone Age. Small discoveries, possible accidental, changed the way mankind operated, developed and even thought. As metals paved the way from the Bronze and Iron Ages and into present times, so has the use of silicon in computer chips and electrical transistors has ushered us out of the Industrial Revolution and into the Information Age. Currently we live in a world that has surpassed anything our grandparents dreamed of. And much of this is made possible by this one element. Silicon is the second most common element on our planet, 27.7% of the earth's crust, and the seventh most common in the universe. It is a gray, nonmetal, lightweight, semiconductor and is a component of a vast number of everyday items, present even in many biological systems. Several species require silicon as an essential element, it is present in human skin and connective tissue, and is even eaten by some marine tide pool organisms. When silicon is incorporated into a polymer, then the material properties may be superior to organic, carbon based materials in many situations.

Single Nucleotide Polymorphism Detection Using Nucleotide and Metal Phosphate Modified Apoferritin Nanoparticles. SHAWN RIECHERS (Washington State University, Pullman, WA 99164) GUODONG LIU (Pacific Northwest National Laboratory, Richland, WA 99352). Single nucleotide polymorphisms (SNPs) are common point mutations of DNA that are of interest to several areas of research, particularly as biomarkers for predispositions to diseases. Fast

detection and quantization of these mutations would be valuable to this research. The quantization of SNPs is addressed as a continuation of previous work. In this research the use of metal phosphate loaded apoferritin nanoparticles probe, as a detection method is explored. For this detection a section of biotin modified DNA probe is bound to streptavidin modified magnetic beads. DNA containing a single cytosine-cytosine mismatch is then hybridized to this probe, after which, perfectly complementary DNA is hybridized to any remaining free probe DNA. After this process nucleotides exposed due to the c-c mismatch should be the only exposed nucleotides. Apoferritin, a hollow spherical protein, is modified to contain cadmium phosphate in the inner cavity of the protein and guanine on the surface of the protein. This modified protein is then bound to the exposed nucleotides in the presence of polymerases (enzyme). An acidic buffer is added to release the metal component from the metal phosphate core into solution. This metal is then detected using highly sensitive electrochemical stripping analysis to give a signal, which is proportional to the amount of free mismatched nucleotides. An average RSD of 8.3% and an increase of 53% above the control was obtained for the SNP detection of 10 ppb mismatch DNA. It was shown that this is a viable method for the detection of SNPs, however, further research is required to increase the signal obtained from the mismatch and to minimize the signal due to nonspecific binding.

Solvent Purification and Fluor Selection for Gadolinium-loaded Liquid Scintillator. TIGISTI KESETE, AMANDA STORM (Central State University, Wilberforce, OH 43360) DR. RICHARD HAHN (Brookhaven National Laboratory, Upton, NY 11973). The last decade has seen huge progress in the study of neutrinos, which are elementary sub-atomic particles. Continued growth in the field of neutrino research depends strongly on the calculation of the neutrino mixing angle θ_{13} , a fundamental neutrino parameter that is needed as an indicative guideline for proposed next-generation neutrino experiments. Experiments involving reactor antineutrinos are favored for the calculation of θ_{13} because their derivation equation for θ_{13} is relatively simple and unambiguous. A Gd-loaded liquid scintillator (Gd-LS) is the centerpiece of the detector and it consists of ~99% aromatic solvent, ~0.1% Gd, and < 1% fluors. Key required characteristics of the Gd-LS are long-term chemical stability, high optical transparency, and high photon production by the scintillator. This summer's research focused on two important aspects of the detector: (1) purification of two selected scintillation solvents, 1, 2, 4-trimethylbenzene (PC) and linear alkyl benzene (LAB), to improve the optical transparency and long-term chemical stability of the Gd-LS, and (2) investigation of the added fluors to optimize the photon production. Vacuum distillation and column separation were used to purify PC and LAB, respectively. Purification was monitored using UV-visible absorption spectra and verified in terms of decreased solvent absorption at 430nm. Absorption in PC at 430nm decreased by a factor slightly >10 while the absorption in LAB was lowered by a factor of ~5. Photon production for every possible combination of two solvents, four primary shifters, and two secondary shifters was determined by measuring the Compton-Scattering excitation induced by an external Cs-137 gamma source (Eg ~ 662-keV). The ideal shifter concentration was identified by measuring the photon production as a function of shifter quantity in a series of samples. Results indicate that 6 g/L p-terphenyl with 150 mg/L 1,4-Bis(2-methylstyryl)-benzene (bis-MSB) produces the maximum light yield for PC and 6 g/L 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole with 50 mg/L bis-MSB optimizes the light yield for LAB. Future work should focus on obtaining the fluorescence spectra for each of the shifters and studying the optical transparency of the LS as a function of shifter quantity.

***Stereoscopic Projections of Organic Reactions.** PETER SHIN (Bergen Community College, Paramus, NJ 07652) ROBERT BENNETT (Brookhaven National Laboratory, Upton, NY 11973). In order to help students better visualize difficult organic reactions, both stereoscopic presentations of these reactions in motion and a user-friendly mechanism through which instructors can create their own reaction animations are being prepared. Stereoscopic projectors display two polarized images, seen by the viewer through passive stereo glasses, to create an image with depth. The project began by gathering information about any visualization tools freely available through the internet. The first search item was a method to translate a reaction into a portable data format. A website, Mol4D (cheminf.cmbi.ru.nl/wetche/organic/index.html, created by Centre for Molecular and Biomolecular Informatics), was found to allow the user input certain data and obtain the plots of atoms throughout the reaction. The input is done through a set of data known as the z-matrix, which consists of atoms, bond lengths, bond angles, and dihedral angles. After the website finishes

calculating the reaction, the user is able to extract an animated XYZ file which contains the Cartesian coordinates of the atoms during each frame or state of the reaction. The next step converts this set of coordinates into a format compatible with stereoscopic output. PyMol, a molecular modeling program created by DeLano Scientific, is capable of outputting a stereoscopic image of the molecules. However, the XYZ file format proved to be problematic when used with PyMol, due to its inherent lack of explicit bonding information. In a search for a more informative molecular format, Protein Database (PDB) proved to be an ideal candidate for conversion since it contains little more than the Cartesian coordinates of atoms and the explicit bonding information between each atom. In order to make the transition from Mol4D to PyMol as easy as possible, a C++ program was written which converts an animated XYZ file into separate PDB files of each state, checking for bond connections through an algorithm based on bond lengths. With this pathway in place, several stereographic animations of organic reactions were created for educational purposes. Although molecular modeling seems to be well-established, the path from reactions to stereoscopic viewing seemed to be a tedious process. By merging the ease of creating a reaction in Mol4D with the stereoscopic output in PyMol, this path has been made much quicker for instructors to create stereoscopic presentations of organic reactions.

Sugar Yields and Rheological Changes During Enzymatic Saccharification of High Solid Biomass Slurries. EVAN MITCHELL (*State University of New York College of Environmental Science and Forestry, Syracuse, NY 13210*) CHRIS SCARLATA (*National Renewable Energy Laboratory, Golden, CO 89401*). Cellulosic ethanol production involves several steps of biomass slurry processing that include extraction of sugars using chemical and/or enzymatic reactions, fermentation of sugars to ethanol, as well as transport of slurries between unit operations. It is desirable that the amount of water in these slurries be minimized to reduce equipment size and energy input required for processing. A lower water content, however, results in "high solid slurries" which are rheologically challenging. In this investigation, we have studied the effects of solid concentrations on enzymatic conversion and have quantified the rheological property changes in high solid slurries during enzymatic saccharification. Results from digestibility studies showed that cellulose conversion decreased from 72% to 39% when initial solid concentrations were increased from 15% to 40%. It was also interesting to note that final glucose concentrations increased from 83.6 g/L at 15% solids to 159.0 g/L at 30% solids, but stayed at nearly the same level at higher solids concentrations. Further, results from rheological measurements also showed that viscosity changes were more pronounced during digestions with the lower initial solid concentrations of 25 and 30%, when compared to digestions at higher initial concentrations of 35 and 40%. The preliminary rheological characterization also showed that the material stays pseudoplastic, or shear thinning, throughout digestion. However, a more complete rheological characterization of the material was not possible due to limited capabilities of available instrumentation, and warrants further investigation. These results indicate that lower conversions at high solid concentrations are likely due to sugar inhibition of enzymes. Overall, our studies indicate that the break point in sugar release at 30% initial solid concentration correlates with rheological property measurements. At higher solid concentrations, it is likely that enzymes are inhibited either due to lack of sufficient free water or due to build up of sugars in the liquid phase. Further kinetic and rheological studies are required to better elucidate this decrease in digestibility.

Surfactant-Templated Synthesis of Nanoporous Calcium Phosphates. JANESSA HARTMANN (*Georgia College & State University, Milledgeville, GA 31061*) DAWN WELLMAN (*Pacific Northwest National Laboratory, Richland, WA 99352*). This investigation presents the method development for surfactant-templated synthesis of nanoporous calcium phosphate materials. Calcium chloride and calcium fluoride were used as the metal sources, cetyltrimethylammonium chloride (CTAC), octadecyltrimethylammonium bromide (OTAB), octadecyltrimethylammonium chloride (OTAC), cetyltrimethylammonium bromide (OTAB) were used as surfactants, and phosphoric acid as the phosphorus source. The experimental matrix included 28 different syntheses which varied the surfactant, metal, phosphorus molar ratio. Three synthetic materials demonstrated potential promise for development of nanoporous materials and are subject to further analysis.

Synthesis and Characterization of a Kläui Complex Containing a Functionalized Cyclopentadienyl Group, Na[Cp'Co{PO(OC₂H₅)₂}₃]. MICHELLE MALONE, SURRIA JAMES (*The University of the Virgin Islands, St. Thomas, VI 00802*) GREGG LUMETTA (*Pacific Northwest National Laboratory, Richland, WA 99352*). The separation

of actinide ions from complex chemical matrices is of importance in terms of radioanalytical chemistry and the management of radioactive waste materials. The work described herein is part of an ongoing study involving the synthesis and characterization of materials that can selectively extract and concentrate radioactive nuclides from complex mixtures. The Kläui salt, Na[Cp'Co{PO(OC₂H₅)₂}₃] (Cp' = C₅H₄C(O)OCH₃), was synthesized. The route chosen to synthesize the ligand is similar to that used in the original reported synthesis. The functionalized NaCp' used in the synthesis was prepared by reacting NaC₅H₅ with dimethylcarbonate (CH₃OC(O)OCH₃). This product was then reacted in situ with anhydrous CoBr₂, forming Cp'Co. The Cp'Co was then refluxed with excess diethylphosphite forming [Cp'Co{PO(OC₂H₅)₂}₃]Co. Reaction of the latter compound with NaCN in air in methanol resulted in the formation of the sodium salt Na[Cp'Co{PO(OC₂H₅)₂}₃]Co. The new Kläui ligand and its precursors were characterized using IR spectroscopy and mass spectrometry. Attempts were made to grow crystals of all of the products and to characterize them using single crystal x-ray diffraction. The crystal structure of [(Cp')Co{PO(OC₂H₅)₂}₃]Co indicates that the ester functional group was reduced by excess diethylphosphite to a methyl group. Further studies will investigate oxidation of the cyclopentadienyl methyl groups to a carboxylic acid functionality, with the ultimate goal to covalently attach the functionalized Kläui ligand to a polymer support and to evaluate its potential to selectively bind actinide ions. The ability of these Kläui ligands to selectively bind actinide ions has been previously reported in both liquid-liquid and solid-liquid extractions. In those studies the ligand was weakly adsorbed onto the surface of an Amberlite XAD-7 extraction resin. With the functionalized ligand prepared in this study we can covalently attach the ligand to a functionalized polystyrene support, resulting in a more robust material.

Synthesis and Characterization of Ionic Liquids Based on DABCO (Diazabicyclo-2,2,2-octane). KIJANA KERR (*Queensborough Community College, Bayside, NY 11364*) DR. JAMES WISHART (*Brookhaven National Laboratory, Upton, NY 11973*). We report here on the synthesis of a series of ether and hydroxyl containing halide salts based on DABCO diazabicyclo[2.2.2]octane, for conversion into ionic liquids with varying anions. Some of these halide salts have been converted into liquid ionic phosphates (LIPs) and bis(trifluoromethylsulfonyl)imides. The halide salts were synthesized by reacting an alkyl halide with DABCO using microwave assisted synthetic techniques and conventional methods. The corresponding ionic liquids were synthesized by anion exchange. Microwave assisted synthetic reaction conditions such as temperature, the nature of the reaction solvent and length of reaction time have been varied. Results show that quaternization has been achieved. Structure determination of these ionic liquids was done using ¹H, ¹³C and ³¹P NMR. Preliminary characterization including differential scanning calorimetry (DSC) of a homologous series of compounds is reported. Dramatic differences in melting points were observed with anion variation of DABCO compounds. Future work will focus on continuing the synthesis and characterization of these compounds.

Synthesis and Characterization of Non-Platinum Cathode Catalysts for Polymer Electrolyte Fuel Cells. JASON GOODPASTER (*University of Illinois at Urbana Champaign, Urbana, IL 61801*) XIAOPING WANG (*Argonne National Laboratory, Argonne, IL 60439*). Noble metal and transition metal alloy catalysts were prepared and studied for their activity for the Oxygen Reduction Reaction (ORR). In this work, the B-G/C* bimetallic catalysts were prepared by co-impregnation at a variety of nominal molar ratios and subsequent heat treatment in regen gas. The ORR activity was evaluated by determining the current at 0.85V from the steady state cyclic voltammograms (CVs). It was found that there is an optimal heat treatment temperature for catalysts for their activity towards the ORR. X-ray diffraction was used after heat treatment to verify if an alloy of the noble metal and transition metal had formed. Acid treatment of these catalysts can increase their performance and the possible mechanism for increased activity is discussed. The B-G/C catalysts showed activity better than B/C, which approached that of Pt/C by producing current as early as 0.90 V. *Actual names of metals is proprietary, therefore this report will make no mention of what metals were used and will refer to metals as "A" through "H" skipping "C". C was skipped since it is used to refer to Carbon.

Synthesis of Magnetic Nanoparticles. DEANNA JONES (*Brigham Young University-Idaho, Rexburg, ID 83440*) SURYA MALLAPRAGADA (*Ames Laboratory, Ames, IA 50011*). In this work, a novel biomimetic synthesis was explored to form magnetic nanocrystalline iron and iron-cobalt oxides in-vitro. Magnetite and mixed iron-cobalt oxide nanocrystals were synthesized via a room-temperature co-precipitation

method in the presence of a recombinant, iron-binding protein Mms6. This protein is thought to be involved in the biomineralization and the formation of uniform magnetite nanoparticles in magnetotactic bacteria. Synthesis was performed in aqueous polymeric gels to slow down the diffusion rates of the reagents to better mimic biological conditions. These gels included: agarose gel, thermoresponsive Pluronic® F127 gel and thermo and pH-responsive pentablock copolymer. The resulting nanocrystalline magnetic particles were comprehensively studied using Transmission Electron Microscopy, Electron Diffraction Methods, X-ray Photoelectron Spectroscopy; and magnetization measurements. The oxide particles were found to be crystalline and superparamagnetic. They had a wide size distribution, depending on the media and whether or not Mms6 was present. This method provides a bioinspired route to nanomaterials synthesis and it is now being tested in synthesis of mixed iron-ruthenium oxides.

Synthesis of Novel Crown Ethers Bearing the exo-cis-2,3-Norbornyl Group As Potential Na⁺ and K⁺ Extractants for Nuclear Waste Remediation. RACHEL ROBESON (*Earlham College, Richmond, IN 47374*) PETER BONNESEN (*Oak Ridge National Laboratory, Oak Ridge, TN 37831*). The ability to extract sodium ions (Na⁺) from alkaline nuclear tank waste containing 1-2 molar (M) sodium hydroxide and 2-3.5 M sodium nitrate is of interest as a strategy for overall waste volume reduction. Lipophilic crown ethers with high sodium binding efficiency will be needed as extractants. According to molecular modeling, crown ethers that incorporate the exo-cis-2,3-norbornyl moiety may be effective sodium extractants due to the rigidity of the norbornane framework. The rigidity allows the oxygens, attached at the 2- and 3-positions, to be directed toward the center of the binding cavity. The proposed crown ethers may be superior to existing crown ethers (such as the octamethyl-16-crown-5) that are known as being effective sodium extractants. Thus, the goal of the project was to prepare a series of novel dinorbornyl-16-crown-5 and dinorbornyl-18-crown-6 ethers for sodium extraction studies. The key starting material for both families of crown ethers, exo-cis-2, 3-norbornanediol, was successfully prepared on a large scale in 88% yield. The syn and anti isomers of the dinorbornyl-16-crown-5 ether family were prepared using diethylene glycol and 2-substituted-1,3-propyl linkages; both isomers were separated using column chromatography. A single crystal of the syn isomer suitable for X-ray crystal structure analysis was obtained, thereby confirming the syn orientation. The syn and anti isomers of the dinorbornyl-18-crown-6 ether family were successfully prepared employing a different synthetic strategy, involving the connection of two, bis-hydroxyethoxy-substituted exo-cis-2,3-norbornyl groups. Intermediates and products were checked for purity using either thin layer chromatography or gas chromatography, and characterized by proton and C-13 NMR. Future research will evaluate the sodium extraction strength of these synthesized dinorbornyl-16-crown-5 and dinorbornyl-18-crown-6 ethers as compared to the extraction performance of known crown ethers, octamethyl-16-crown-5 and didecalino-16-crown-5.

Synthetic Clays for Chemical and Materials Applications. KENNY GUILLOTTE (*Central Missouri State University, Warrensburg, MO 64093*) KATHLEEN A. CARRADO (*Argonne National Laboratory, Argonne, IL 60439*). Contributions to the Catalyst Design Group were made concerning the development of synthetic clays for eventual catalytic and materials applications. One project provides clay supports for metal species active in catalysis. In the past the group has, for example, loaded onto such supports both cobalt-molibdenum-sulfide (CoMoS) species for hydrodesulfurization (HDS) and Pt(0) metal nanoparticles for oxidation catalysis. All of the samples prepared within this project were determined to be suitable for further testing. Another task explored clay synthesis from alternative starting materials, such as magnesium chloride salt rather than magnesium hydroxide. It was found that refluxing the precursor mixture was superior to mixing at room temperature, as had been previously published. Adding LiF mineralizing agent was also found to lead to more crystalline clay products. Finally, work towards optimizing organo-grafted materials for possible use in specialty polymer-clay nanocomposites was undertaken. The goal of this project is to combine alkoxysilanes and organoalkoxysilanes in various mixtures in order to create materials of various organo-group densities grafted to the silicate surface. Controlling the spacing between organic groups in this fashion can have effects on affinities for polymeric molecules in polymer-clay nanocomposite applications. All materials were characterized by x-ray powder diffraction (XRD) for crystallinity and thermal gravimetric analysis (TGA) to determine water and organic contents.

Task Specific Ionic Liquids. JENEE CYRAN (*Allegheny College, Meadville, PA 16335*) GARY A. BAKER (*Oak Ridge National Laboratory, Oak Ridge, TN 37831*). There are a number of advantages to performing enzymatic catalysis within ionic liquid-based solvent systems. Possible benefits include one or more of the following: reduction in water-catalyzed side reactions; reduced microbial contamination; higher activity; improved selectivity; better operational, thermal, and storage stability; elimination of solvent emissions; and clear opportunities for continuous recycling. In this work, exploration was completed on the design of task-specific ionic liquids (TSILs) deliberately engineered for use and compatibility with biocatalytic systems. Specifically, synthesis of several homologous series of TSILs with representative members from both the aprotic and Brønsted acid/base categories, including some examples containing halogen-free, pharmaceutically-acceptable anions as alternatives to the vastly popular, yet costly, bis(trifluoromethylsulfonyl)imide introduced by the battery industry. Ionic liquids were characterized using ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy and thermogravimetric analysis (TGA). In a major segment of the project, native and chemically-modified enzymes were investigated within a range of TSILs, both those miscible and completely immiscible with water. In this aspect of this research, the solubilities, partition coefficients, secondary structure, and activities of model enzyme systems within neat TSILs and TSIL/buffer mixtures were explored. The emphasis here is shifted to the use of optical spectroscopy to interrogate well-defined enzyme systems (cytochrome c, for example) within a diverse range of TSIL-based media. UV-vis of the cytochrome c and TSIL mixtures were more stable than mixtures with organic solvents. Thus, TSILs are more compatible solvents for biocatalysis. Further studies are planned to test more TSILs and various enzymes.

Testing the Solubility of Minerals and Metallic Compounds in Deep Eutectic Solvents. STEPHEN KANE (*Suffolk County Community College, Selden, NY 11794*) MARK FUHRMANN (*Brookhaven National Laboratory, Upton, NY 11973*). The purpose of this research is to compare the solubility of various compounds in Deep Eutectic Solvents (DES) versus water. These are ionic solvents that are formed from mixtures that have a lower melting point than any of its individual components. They are drawing the attention of industry and academia for a number of applications. We concentrated on their ability to dissolve metals and minerals. The DES of particular interest is a 2:1 molar mixture of Urea to Choline Chloride. These materials are used in large quantities in agriculture; Choline Chloride (vitamin B-4) is an additive to chicken feed, and Urea is used as a common fertilizer. They were combined at 60°C and formed a viscous Ionic Liquid (I.L.) at room temperature. Once mixed < 1g of metals were added to 5 ml of I.L. and allowed to sit in the solution overnight. The samples were then placed in a centrifuge for 25 minutes. 1ml of the sample was then diluted in a 100ml volumetric flask, then analyzed using the Liberty 100, Inductively Coupled Plasma Emission Spectrometer (ICP) for solubility of iron, copper, aluminum, silicon, and zinc compounds. They were then retested at elevated temperatures. The preparation was similar at elevated temperature, with the exceptions being that the centrifuge was not utilized and the samples were placed in an oven. The ionic liquid becomes considerably less viscous at elevated temperatures enabling the samples to be filtered using a 0.7-micron filter. Altogether thirty-eight samples were tested. Of those thirty-eight only eight proved to be more soluble in water cupric chloride, copper (II) nitrate, zinc chloride, zinc nitrate, ferric chloride, ferrous chloride, ferric ammonium sulfate, aluminum chloride. At temperatures above 25°C the solubility of the I.L. seems to increase and becomes considerably less viscous making it more workable and less prone to error. The effect of temperature on solubility was varied, and although additional testing is needed it seems that each compound may have a specific temperature range for maximum solubility, or possibly more important this could be an indication that a back reaction in which a new compound is being formed.

The Effects of Boron on Uranium(VI) Adsorption on Iron Oxide. LYNDASAY TROYER (*Whitman College, Walla Walla, WA 99362*) WOYONG UM (*Pacific Northwest National Laboratory, Richland, WA 99352*). The mobility of radionuclides such as uranium(VI) released from glassified low-activity radioactive waste in radioactive waste repositories is expected to impact both environmental and human health. Because boron (or borate) concentrations have been found in accelerated glass leachate, the effects of boron on U(VI) adsorption and mobility should be considered to assess the long-term performance of the proposed glassified radioactive wastes. Previous independent studies of boron and uranium(VI) adsorption onto sediment or minerals have found a similar bell-shaped curve when plotting adsorption (%)

against solution pH. These results indicate that the two could compete with each other for the same sorption sites causing boron to affect the mobility of uranium(VI). This study uses batch experiments to look at the adsorption of boron and uranium(VI) together for the first time. Three iron oxides, hematite, goethite, and two-line ferrihydrite, were synthesized, and ferrihydrite was selected as the sorbent because of its high adsorption capacity for both B and U(VI). Sample sets were prepared containing B alone, U(VI) alone, both B and U(VI), and both with U(VI) added 24 hours after B. Boron adsorption was lower in all open sets ($P_{CO_2}=10\text{-}3.5\text{ atm}$) than in the closed sets ($P_{CO_2}=0\text{ atm}$), because of carbonate competition in the open systems. The lowest adsorption occurred in the open set containing both U(VI) and B, indicating the preferential binding of U(VI) to the sorbent surface. Because of the high solid concentration used, the majority of U(VI) samples from pH 4-8 showed 100% adsorption making comparisons difficult. With our conditions U(VI) does not appear to be affected by boron's presence, however more studies should be conducted with lower solid concentration and with higher boron concentration. Spectroscopic studies should also be performed to examine surface complexation of B and U(VI) at a molecular level.

The Effects of Surface Chemistry on the Properties of Proteins Confined in Nano-porous Materials. LATASHA GARRETT (*University of Tennessee, Knoxville, TN 37996*) HUGH O'NEILL (*Oak Ridge National Laboratory, Oak Ridge, TN 37831*). Amorphous glasses formed by the sol-gel route provide non-native environments for the investigation of the physico-chemical and structural properties of biomolecules at the biotic/abiotic interface. These studies yield important information for the design of novel bioinspired functional materials. The sol-gel process can entrap biomolecules in their active form under conditions that mimic the naturally crowded cellular environment. The biomolecules are spatially separated and 'caged' in the gel structure but solutes can freely permeate the matrix. Thus, properties such as the folding of ensembles of individual molecules can be examined in the absence of aggregation effects that can occur in solution studies. In this investigation, wild-type green fluorescent protein (GFP) from *Aequorea coerulescens* was used as a model to examine the unfolding/re-folding properties of protein in silica gels. Recombinant GFP was isolated and purified from *Escherichia coli* extracts by cell lysis, three-phase partitioning, dialysis, and anion exchange chromatography. The purity of the protein was greater than 90% via SDS PAGE gel analysis. The yield was approximately 50mg per 1 liter of cells. Sol gels were formed using a combination of alkoxide precursors such as tetramethylorthosilicate (TMOS), methyltrimethoxy-orthosilane (MTMOS), ethyltrimethoxyorthosilane (ETMOS), 3-aminopropyltriethoxysilane (APTES), and 3-glycidioxypropyltrimethoxysilane (GPS). The protein containing sol solutions were cast in plastic 1mm thick cassettes, after gelation occurred the gels were overlaid with 10 mM sodium phosphate pH 7. The entrapped properties of GFP were analyzed by UV-visible, fluorescence, and circular dichroism (CD) spectroscopies. The entrapped GFP was denatured with hydrochloric acid (HCl) and the refolding of the protein was monitored at pH 7. No renaturation was observed in gels that were made with TMOS only, and in the presence of APTES (50%), MTMOS (50%), and ETMOS (50%). However, GFP in solution and in gels that were made with GPS, the CD and UV-visible spectra indicated that the protein had refolded. Gels were made with 10%, 15%, 20%, and 25% (v/v) GPS to TMOS, but gels made with 0.15 GPS indicated a 25% activity recovery. This study highlights the importance of the surface chemistry of the silica gels for the refolding properties of the entrapped GFP. Future studies will investigate the effect of surface chemistry on the thermal and solvent stability of the entrapped protein.

Thermoset Composites from Bio-based Oils and Spent Germ from Ethanol Production. JEFFREY BAKER (*Pennsylvania State University, State College, PA 16801*) DR. RICHARD C. LAROCK (*Ames Laboratory, Ames, IA 50011*). Thermoset composites have been prepared by the use of a bio-based resin and spent germ filler, which is a byproduct from a wet ethanol production plant. The bio-based resin is prepared by the free radical co-polymerization of tung oil (TNG), methacrylonitrile (MAN), divinylbenzene (DVB), and initiated with cumene hydroperoxide (CHP). This bio-based resin is pre-cured for a few hours before being mixed with the spent germ, the filler, upon which the mixture is cured under mechanical pressure, and then post cured in an oven. The resulting composite material consists of roughly a 1:1 ratio of resin to spent germ. The crosslinked thermosets are dark brown in color, hard and brittle, and have a slight burnt odor. Thermal and mechanical analysis of the composites has been performed via thermogravimetric analysis (TGA) and tensile testing. Results from the

TGA show that the composites have a multiple stage degradation with unstable intermediates ranging from 239–304°C and 465–478°C. The tensile tests show on average the modulus values range from 915–1375 MPa and the toughness values range from 0.02–0.05 MPa.

Computer Science

3D Animation of Pancreatic Molecules. BRITTANY PETERS (*Rochester Institute of Technology, Rochester, NY 14623*) DR. PAUL CRAIG (*Brookhaven National Laboratory, Upton, NY 11973*). The pancreas is the supplier of a variety of digestive enzymes and hormones, most notably insulin. In the past a virtual animation of the pancreas has been created, showing a tour of its internal structure. To continue this animation the goal is to introduce molecular detail into this virtual model of the pancreas. We are using Maya's 3D modeling and animation capabilities to address the challenging task of providing a greater understanding of the pancreas for students, teachers and doctors. Pancreatic proteins contain hundreds or thousands of atoms; the Protein Data Bank (www.rcsb.org) contains many pancreatic proteins structures with x,y,z coordinates of each of its atoms to form a molecule that can be visualized in 3D. The challenge for molecular artists who use Maya is to model these molecules accurately because their structure is too complex to create. One easy way to provide these molecules is to download the PDB files from the Protein Data Bank and visualize them in Maya, but Maya is unable to recognize them. However, the files can be manipulated and changed to achieve the objective. The PDB file first needs to be converted to a simple text document so that the 3D program can read its written information, then it can be drawn through a Maya tool called a mel script. This script is a code that allows Maya to read the PDB file, import it, and model it. From this point the molecular structure can be rendered and animated. This procedure will help to show an up close view of a pancreatic molecule in action. We are developing techniques to display these proteins in a surface format which highlights the overall shape of each molecule, as well as a ball-and-stick format, which emphasizes the individual atoms. One of the advantages of this approach is the molecular artist can import any protein structure that is available in the PDB file format, which will enable viewers to better visualize the physiology of the human pancreas at the molecular level.

***3D Stereoscopic Fantastic Voyage of the Heart.** NATHANIEL SKINNER (*Jamestown Community College, Jamestown, NY 14702*) LEN SLATEST (*Brookhaven National Laboratory, Upton, NY 11973*). For first year Anatomy/Physiology students, the visualization of various organs and body systems can be a bit daunting. This project was designed to combat that problem. Being the first in a long string of organs this model of the heart was designed to give students a working visual knowledge of the heart. The movie starts outside the heart and shows all of the major parts of the heart in their relative positions. The movie then takes the viewer inside the heart. The inside is the part that will be the most helpful for the students, because the best they will ever see if they are lucky are cadavers and drawings. By the end of the movie those viewing this movie will have seen not only the major parts of the movie, but they will also have had a first hand experience with watching the heart beat with the proper timing of the valves. This movie was also put into a stereo version, which will greatly enhance the viewing experience. The movie was created in the 3D design and rendering program, Maya. Each part of the heart was created as a separate object, which allowed easy manipulation of the parts to get them into the right proportions to each other. The overall movie is actually composed of several smaller movies that were combine with video editing software to give the impression of one voyage through the heart. As stated above the next step is to use some of the same techniques to create various other body parts and organs. The overall long-term goal is to have a flythrough video of every system in the human body.

***3D Visualization of Angle, Frequency, and Imaginary Impedance in AC Circuits.** ANTHONY SCALI (*Alfred State College, Alfred, NY 14802*) MIKE MCGUGIN (*Brookhaven National Laboratory, Upton, NY 11973*). For most up-coming electrical engineers the understanding of alternating current (AC) circuits isn't that easy when you consider it is based one factor of frequency that will change the imaginary power/resistance in the given circuit, and that there is a angle between the voltage and current is a bit hard to understand from just crunching numbers and accepting some things to just be true. To solve this problem I will create a virtual control panel in visual basic that will allow the input of arbitrary AC component values (inductor, capacitor, and resistor and input frequency, w) which are then mathematically computed to give the power factor the angle and the current in the