From the Laboratory Director

I am pleased to have the opportunity to introduce the 2009 Laboratory Directed Research and Development (LDRD) annual report. This important program displays both the breadth of SRNL’s research efforts and the depth of our commitment to grow the Laboratory.

Much of our LDRD funding was directed toward improving our nation’s Energy Security, centered around advanced energy storage and biomass processing. Ming Au’s work produced important advances toward a commercial rechargeable lithium ion battery. Max Gorensek and Steve Sherman developed a process for converting lignin from biomass into a higher value product. Chuck Turick, Kit Bagwell, and Chris Yeager all made significant progress in using microbes to produce, or enhance the production, of products important to our nation’s energy future.

In National and Homeland Security, Steve Chiswell developed a method to improve our ability to forecast winds that will enable us to better model airborne transport of contaminants. Lance O’Steen demonstrated how Unmanned Aerial Vehicles could also contribute to plume tracking. Eduardo Farfan – in conjunction with Russian scientists – looked at the penetration of radio-cesium and –strontium into concrete. This work has provided data that will be important for cleanup if our nation is ever attacked by a dirty bomb.

As DOE-Environmental Management’s “Corporate Lab,” we continue to expand the scientific basis for cleanup and immobilization of nuclear waste. Jim Marra’s work on the structure of plutonium-bearing glasses sets new benchmarks for what is possible with this material. Anna Knox’s work with additives to permeable concrete may pay big dividends in the future in terms of removing hazardous contaminants from waste water. Miles Denham’s demonstration of the ability of tin to immobilize technetium adds a new tool to our remediation arsenal.

And we continue to make important contributions in our “supporting sciences.” Andy Shadday and Greg Flach modeled an SRNL-developed approach for sequestration of carbon dioxide. Robin Brigmon demonstrated the ability of an interesting bacterium found at SRS to act as an anti-microbial agent. Liz Hoffman continued her excellent work aimed at determining the value of a ternary MAX phase carbide, Ti$_3$SiC$_2$, as a structural material in nuclear facilities. Mike Morgan demonstrated the importance of nickel content in steel to reduce susceptibility to hydrogen effects. Chuck Turick made considerable progress in understanding the mechanism of enhanced growth of certain microbes in radiation fields.

In reviewing the results of the program this year, it is clear that participation is much broader than in years past. It is gratifying to see organizations that have never before taken part in the
program use it to make new and exciting advances of potential value to our customers. The scientific and engineering progress described here will provide the foundation for future programs, helping SRNL maintain its position as DOE’s premier applied science and engineering laboratory. SRNL’s researchers have again shown that the LDRD program is a sound investment by the Laboratory that will pay off handsomely for the nation in the future.

Samit Bhattacharyya
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* Quick Hit project
Project Summaries
Microfabricated Quartz Tuning Fork Strain Gauge as a Rapid Switching, Selective Hydrogen Sensor
Blythe Ashcraft, S. McWhorter and H.T. Sessions

Quartz tuning forks (QTF) are piezoelectric materials that convert any force that excites a resonant vibration of prongs into an electric signal, providing a technique that does not require external optical detectors. Thus, if coated with a reactive species, they could be used as chemical sensors. The tuning forks are mass produced as timing devices for quartz watches, making them inexpensive and readily available. These devices typically demonstrate a high quality (Q) factor which often exceeds 10,000 in air. The large Q factor, coupled with the noise canceling aspect and their small size, results in extremely high sensitivity with minimal power dissipation.

In this project, microfabrication techniques were used to coat thin-films on a miniature quartz tuning fork and monitor the mechanical properties of the free standing thin-film after exposure to humidified air and H₂. The results show promise that a working prototype could be developed using this technology.

Novel Nanostructured Anode Materials for Li-Ion Rechargeable Batteries with High Capacity and Inherent Safety
Ming Au and Scott McWhorter

The goal of this work is ultimately to develop the next generation of rechargeable lithium ion batteries for energy storage and vehicular use. The focus is on replacing carbon anodes with metal oxide nanomaterials to achieve greater capacity. The practical capacity of carbon anodes is 200 mAh/g. Metal oxides can host large amounts of lithium ions as the anode. The theoretic capacity of metal oxides is much higher than carbon, on the order of 600-800 mAh/g. However, the Li conversion process in metal oxides is much slower than Li intercalation in the carbon. The initial high capacity of the metal oxides diminishes quickly in charge-discharge cycling.

We have shown that nanoporous hollow spheres of metal oxides can resolve the problems of low capacity and poor cyclability. With their unique structure, nanoporous hollow spheres of metal oxides (esp. SnO₂) in coin battery testing exhibit high electricity storage capacity (400 mAh/g), power density, and long cycling life. The metal nanorods anodes have great potential for sustainable high capacity if stronger adhesion with current collector and sufficient interred spacing can achieved.

SnO₂ nanoporous hollow spheres (X5000)  Mn₂O₃ nanoporous hollow spheres (X50,000)
Metabolic Engineering of Cyanobacteria for Liquid Fuel Production
Christopher E. Bagwell and Chris Yeager

There is a pressing need for clean burning, affordable transportation fuel. Biologically derived fuels are an option and can significantly reduce our dependence on geological petrol. The technology for biofuel production exists, though scientific advances are needed to improve the cost and energy balance in order to make biofuels economical on a production scale.

The overarching goal of this project was to utilize and develop photosynthetic microalgae for enhanced production of biological substrates for conversion to liquid fuels. A major accomplishment centered on the development of a 2 stage process in which algae were first grown under optimal conditions to maximize biomass and then in a second and separate stage, cells were incubated under conditions to promote oil production. We are currently pursuing the development of designer strains of bacteria that may be used for the continuous production of butanol and nonpolluting hydrocarbon fuels.

Investigation of Ce/Eu/Tb Activated Lanthanide Alumino-Borosilicate Scintillating Glasses for Nuclear Detection Technology
A.L. Billings, J. Ziska, J.C. Marra, D.P. Diprete and C.L. Crawford

Devices for radiation detection remain a crucial need for international and homeland security. Current single crystal detectors (e.g. Cadmium Zinc Telluride, CZT) are expensive to fabricate and are limited in their size and capabilities of detection. The goal of this LDRD Quick Hit was to screen high rare earth alumino-borosilicate glasses doped with Eu, Ce, or Tb for discriminate radiation source detection and high luminescence (signal strength) when exposed to a gamma radiation source (Co-60). Ideally, a successful glass detection material would have a high concentration of scintillating (fluorescing) ions (Eu, Ce, Tb) which would respond to different radiation sources as well as, if not better than, single crystal detectors. To achieve that, the glasses have to be optically transparent through visible wavelengths and into the UV region, have a high specific density to aid in neutron detection, and be fabricated using typical glass melting techniques.

Approximately 30 glasses were successfully melted, i.e. free of crystals and phase separation when quenched from the melt. These glass compositions contained between 25 and 30 mol% rare earth oxides, which is at the limit of rare earth incorporation in any silicate based glass system. While none of these glasses provided as intense a response as commercially available products containing Li, this is most likely due to their oxidized state. We believe that if melted under reducing conditions, these glasses may still fulfill their promise.
Electrochemical Separation of Americium with Ionic Liquids

Nicholas J. Bridges and Ann E. Visser

Both Am and Cm are present in the (III) oxidation state in most aqueous solutions making traditional extraction of Am from Cm very difficult. The driving force for solvent extraction is the charge to size ratio of the elements being extracted. Am can be oxidized to higher, stable oxidation states (i.e., (V) or (VI)), the altering of the oxidation state of Am will effect its interactions with a ligand and can be exploited in the separation from Cm. In this project, we attempted to separate Am/Cm through liquid/liquid separation in which one phase will be an ionic liquid (IL, a salt with a melting point less than 150 °C) and the other phase will be either an aqueous media or organic solvent (e.g., odorless kerosene, dodecane, etc.). In the IL, Am(III) will be electrochemically oxidized to Am(V), Am(VI), Am(V)O2+, and/or Am(VI)O22+ which will be extracted from the IL phase into the immiscible organic or aqueous phase. Cm(III) has a higher oxidation potential than Am(III) and would remain in the IL as the Cm(III) species.

These efforts were not very successful. Due to the formation of Am(VI), which is a powerfully oxidizing agent, it is now believed that upon reduction back to Am(III), insoluble Am oxide/hydroxides might have formed. The resulting Am complex apparently is not soluble in ILs or dodecane.

Development of New Antimicrobial Agents

Robin L. Brigmon and Mark Kingsley, SRNL, Jeremy Tzeng, Clemson University

In the event of a biological attack or emerging infectious disease outbreak, currently available antimicrobial agents may not be effective. Biological weapons (BW), by design, are typically antimicrobial resistant. A bacterium, Cupriavidus SRNL (CS), had been isolated at SRS that showed antimicrobial activity. Limited testing of Cupriavidus SRNL biocidal activity, on both bacteria and fungi, was the basis for further research and development on this agent.

Results of the current study re-confirmed CS antimicrobial activity and indicate the compound may be an antibiotic or possibly an antimicrobial peptide (AMP). AMPs tend to be highly hydrophobic molecules and would not be expected to diffuse far in an agar medium in a disk diffusion assays tested in this project with both a bacterium, (B. subtilis), and two fungi (Scytalidium & Pithomyces spp.). As well, the component was heat labile as all activity was lost with autoclaved CS-grown R2A supernatants. Optimization of antimicrobial activity was observed repeatedly after 48 h of growth in full strength R2A medium.

This work successfully demonstrates the antimicrobial agent produced by Cupriavidus SRNL is effective against both fungi and bacteria in limited testing. The agent could be an AMP as it passes through 0.2 μm filters and is heat inactivated. While a disclosure has been made on
Cupriavidus SRNL, this additional data will help in the patenting process. Further testing and optimization of the antimicrobial agent produced by Cupriavidus SRNL would be of great interest to other funding agencies and biomedical industries.

**Integrated System Strategies for Bio-Hydrogen Purification**
*K. S. Brinkman, C. Yeager, G. Morgan, S. McWhorter and B. Spencer*

Biohydrogen production via organisms such as cyanobacteria, currently the focus of SRNL’s biohydrogen program, is intriguing due to the simplicity for remote applications; they require only water, sunlight, and air during the production process. Current work exploring the tolerance for dehydration/rehydration cycles on some strains has lead to immobilization and the possibility to encapsulate these materials into thin film polymeric sheets. One can envision sheets of these materials being stored & transported to location, followed by exposure to water and sunlight for hydrogen generation. One of the challenges of using these materials for portable power is that the hydrogen stream is dilute with gaseous byproducts and requires a separation and purification step before the hydrogen can be fed to portable power generation systems such as PEM fuel cells. Additionally, the production without immediate use requires the capability to capture the purified hydrogen for later use.

This work focused on evaluating a low cost, portable, system based on commercially available gettering technology. Instead of using pressure driven membrane separations unit operations at ambient temperature or partial pressure driven membrane separations at elevated temperature, we have focused on partial pressure absorption of hydrogen in the presence of contaminant species in flow through reactors and static capture mode. The major conclusion of this initial scoping study is that the inert gases (Ar, He, N2) used during bio-hydrogen production are the major source of problems for hydrogen capture and purification using metal hydride storage and not the organic contaminants. It is suggested that membrane separation processes employing low cost metallic glass or palladium alloy materials be investigated for effective hydrogen separation before storage.

**Nanocrystalline Proton Conducting Ceramics for Hydrogen Separation Membrane Applications**
*K. S. Brinkman (SRNL), F. Chen (USC)*

Membrane separations are a key enabling technology for future energy conversion devices. Ionic transport membranes must have both proton and electronic conductivity to function as hydrogen separation membranes without an external power supply. In addition, the materials electronic conductivity or material crystal structure stability should not be greatly affected by the presence of contaminant gases (CO2, CO, CH4 and H2O from steam reforming/water gas shift reactions).

This work focused on the synthesis and characterization of dense nanocrystalline SrCe0.95Yb0.05O3 proton conducting ceramic membranes as a response to the demand for novel materials. Wet chemical techniques have been used to fabricate nanocrystalline ceramic membranes which enable lower temperature densification and result in dramatically smaller grain size membranes than that is obtainable with conventional solid-state reaction processing.
Thermogravimetric (TGA) analysis showed that chemically derived powders exhibited nearly four times greater loss of oxygen from the crystal lattice compared to traditional oxide routes resulting in enhanced electronic conductivity.

**Improved Wind Forecasts by Assimilation of Non-Standard Observations with Application to Airborne Contaminant Transport and Wind Energy Production**

*S. R. Chiswell and R. J. Kurzeja*

The goal of this project is to improve local and regional scale wind forecasts by assimilation of wind measurements of opportunity into high-resolution Weather Research and Forecasting and Regional Atmospheric Modeling System model simulations through the use of an ensemble Kalman filter approach in which observed data and previous forecast values are weighted to minimize the variance of the new forecast. Kalman’s procedure is a standard least-squares estimate, but computed in a unique, sequential way such that when new data arrive, only the most recent forecast is needed and the weighted observations and forecast fields are automatically optimized with all previous data as well. This approach provides a powerful way to assimilate data observations from a wide range of sources.

The Data Assimilation Research Testbed framework developed by the National Center for Atmospheric Research was employed to apply an Ensemble Kalman Filter to nudge model forecast parameters toward a state consistent with time varying sets of observations. Multiple model instances were used to generate an ensemble of model forecasts states based on the forecast estimates of the observations. Operational North American Mesoscale model output from NOAA/NCEP demonstrated difficulty in predicting sea-breeze onset, strength, and duration. Under these conditions, the assimilated observations significantly improved local mesoscale model performance when comparing 12 hour forecast output with assimilated forecast fields.

**Sustainable Remediation of Tc-99 Contamination in Groundwater Using Tin Compounds**

*Miles Denham and Maggie Millings*

Technetium-99 (Tc-99) in groundwater is a significant problem within the DOE complex for which there is no cost effective solution. It is a problem for Hanford, Paducah, Portsmouth, Oak Ridge, Ashtabula, SRS, and other DOE sites. Most proposed in situ remediation methods involve reduction of the highly mobile pertechnetate ion to less soluble Tc(IV) oxide. However, Tc(IV) oxide is easily re-oxidized, and then remobilized in groundwater. Removing Tc-99 from groundwater in a way that resists re-oxidation could be highly effective in preventing the spread of technetium. One way to achieve this is reduction and incorporation into tin oxide (SnO₂). Sn(IV) and Tc(IV) have similar cationic radii indicating that Tc-99 should co-precipitate readily with SnO₂. One way to do this would be to add stannous chloride, a strong reductant, to groundwater containing Tc-99. The ensuing oxidation of Sn(II) will reduce Tc(VII) to Tc(IV). Highly insoluble SnO₂ will precipitate and incorporate the Tc(IV). Tc-99 “locked up” in the SnO₂ will resist re-oxidation because SnO₂ is not subject to reoxidation or dissolution.

Experiments showed that Re(VII), a surrogate for Tc(VII), is reduced by stannous chloride and appears to be bound in solid solution with SnO₂. Re(VII) is not reduced by metallic tin powder or tin shot. Short term tests with stannous chloride showed more Re uptake when more stannous
chloride was used. Over the long term, higher Re uptake was observed with slow mineral precipitation. Thus, addition of stannous chloride appears to be a viable method for removing Tc-99 contamination from groundwater. This could lead to the only sustainable and cost effective remediation method available for Tc-99 contamination in groundwater.

Characterization of an Advanced Solid State Neutron Detection Material

Small, efficient neutron detectors are essential for Radiological Assistance Program teams conducting search operations, as well as for first responders to a nuclear incident. A Li-6 glass material for efficient thermal neutron detectors, developed by PNNL, was previously used as an optical fiber neutron detector, and was licensed to NucSafe, LLC. Several years ago, SRNL proposed using a thicker cylindrical section of this glass material coupled to a photomultiplier tube (PMT) to prepare a small, efficient neutron detector. The research successfully demonstrated that the material in a solid disk form offered more efficient neutron counting than was available in current hand-held instruments, could be coupled to miniature PMTs to generate light weight components, and could provide far better energy resolution than other glass scintillators. This last property was of special significance as it had the potential to reduce the number of false positive neutron alarms as well as enhance neutron detection limits in field units.

Although the glasses developed by SRNL appeared free of defects in essentially every case versus the NucSafe glass sample, which was so pock-marked with bubbles it was nearly opaque, the NucSafe glass outperformed the SRNL glasses in resolution tests in every case but one. However, some SRNL glasses had comparable or superior neutron counting efficiencies. SRNL made great strides in improving its Ce glass chemistry to ensure Ce remained in the lower scintillating +3 oxidation state compared to previous experiments. Using Te in place of Ce did not generate any usable scintillators. The incorporation of the enriched Li-6 as a component in the glasses compared to the natural lithium that was used in the earlier research had the desired effect of boosting the SRNL glass’s neutron counting efficiencies.

Impact of Metal Oxide Impurities on Radiolytic Gas Generation
J. M. Duffey, R. R. Livingston, R. A. Pierce, A. R. Jurgensen and D. M. Missimer

Safe transportation and storage of special nuclear and challenging materials rely on being able to package these materials in sealed containers. The limiting condition for packaging many radioactive materials is the flammable hydrogen atmosphere produced by radiolysis of the small quantity of moisture associated with the content. The safety analysis of challenging materials is complicated by an inability to effectively model hydrogen generation and total pressure. Understanding how metal oxide impurities impact radiolysis of moisture is essential to improving gas generation models. This research builds upon observed differences in radiolytic hydrogen generation associated with gamma irradiation of metal oxides with adsorbed moisture. Certain metal oxides (e.g., ZrO₂) were found to increase the radiolytic hydrogen yield from gamma radiolysis of adsorbed water by one to two orders of magnitude compared to gamma radiolysis of water only. Other metal oxides decreased (e.g., Fe₂O₃) or had little effect (e.g., CeO₂) on hydrogen yield. The impact of these metal oxide impurities on gas generation from special nuclear materials that are predominantly alpha emitters (e.g., U, Np, Pu, and Am) has not
been measured, but is postulated to follow the same trend. If so, this knowledge may be used to manipulate or model the hydrogen yield of challenging materials during transportation and storage.

The objective of this project was to determine the impact of various metal oxide impurities on the rate of hydrogen generation from alpha radiolysis of adsorbed moisture. Rates for mixtures containing CeO₂ and ZrO₂ are similar to those previously measured for pure PuO₂ containing adsorbed water. However, the H₂ yield for a mixture containing Fe₂O₃ is approximately five times lower. This result is in agreement with the reported gamma radiolysis experiments and suggests metal oxide impurities such as Fe₂O₃ may play an important role in suppressing H₂ generation in sealed containers of radioactive materials. Additional studies are recommended to elucidate the mechanism for decreased H₂ yield and to evaluate ways to exploit this behavior to improve safety in transportation and storage of challenging materials.

**Assessment of Sr-90 and Cs-137 Penetration into Reinforced Concrete Under Natural Atmospheric Conditions**

*E.B. Farfan, G.T. Jannik, J.C. Marra and S.P. Gaschak*

What if it happens? How to deal with it? These are some of the questions that must be properly answered if a Radiological Dispersion Device (e.g., dirty bomb) or Improvised Nuclear Device were to detonate in a major U.S. city. Experts say that the threat is imminent because of the large number of unaccounted radiation sources and nuclear materials (radiotherapy, irradiators, and Soviet-made electrical generator sources) that are readily available in the Third World and Eastern European nations.

A great deal of attention must be devoted to define the 1) levels and characteristics of radioactive contamination after a nuclear or radiological incident in a major city, 2) possibility of decontamination, and 3) future use of the city’s structures and buildings. However, presently little is known about the distribution, redistribution, and migration of radionuclides in an urban environment. Currently, there exists only one place on Earth where radioactive contamination in an urban environment can be studied: Pripyat, Ukraine.

The abandoned and highly contaminated city of Pripyat is 3 km away from the destroyed unit of the Chernobyl Nuclear Power Plant. Despite the decontamination efforts from 1986 to 1989
(mostly performed on only the lower stories of tall buildings), most buildings, structures, and roads are still highly contaminated.

Cores of contaminated concrete were taken from two structures. Over 90% of the total $^{137}$Cs inventory and 70% of the total $^{90}$Sr inventory are located within the first 5-mm layer of the reinforced concrete core. However, $^{137}$Cs and $^{90}$Sr were found throughout the entire 0-50 mm range of the cores. Water absorption by concrete plays a key role in radionuclide penetration. This raises the question of how best to decontaminate buildings made from reinforced concrete knowing that the contamination can penetrate 5 cm into concrete walls.

Data resulting from this project will be useful for the development of a strategy for handling concrete structures that have become (or may become) radioactively contaminated from terrorist acts, accidents or routine operations. The results of this study also suggest that the procedures implemented in the decontamination of tall buildings and structures be re-examined, since the data indicate that upper building floors might be more contaminated than lower floors.

**High Sensitivity Betavoltaic Radiation Sensors**  
*K.M. Fox, E.B. Fox and K.E. Kane*

Betavoltaic cells are semiconductor devices that operate similarly to photovoltaics. When a beta particle (or a photon in the case of a photovoltaic) strikes the p-n junction in the semiconductor, an electron-hole pair is created which results in the generation of a small current across the junction. Recent development work on betavoltaic cells for battery applications has identified silicon carbide (SiC) as an ideal substrate material for increasing the efficiency of the devices. The work completed under this LDRD program successfully adapted betavoltaic power generation technology to sensors, where the SiC-based cells are used as beta radiation detectors. Radiation sensors based on betavoltaic cells will be small, portable, require little power input and be maintenance-free. The use of SiC for a detector is advantageous over traditional, silicon-based, solid-state radiation detectors because of its very low leakage current, which can greatly improve the detection limits of the device.

**High-Temperature Direct Methanol Fuel Cells**  
*B. Garcia-Diaz, H. Colon-Mercado and E. Fox*

Direct Methanol Fuel Cells (DMFCs) are potential power sources for portable applications that have high energy density and the potential for rapid refueling using replacement methanol cartridges. A drawback to the technology has been the low efficiency of the electrode reactions. Theoretically, this efficiency could be greatly increased by operating the cell at high temperatures. This project used an advanced, high-temperature polybenzimidazole (PBI) polymer to construct a DMFC that can be operated at high temperatures. Also, research was conducted to identify electrocatalysts that will work well with the PBI chemistry.
The DMFC polarization results show that PBI membrane electrode assemblies (MEAs) outperform Nafion MEAs with electrodes that are not optimized for DMFC operation. The results from this project have shown that PBI DMFCs are promising power sources for portable power applications, but that optimization of the anode and cathode electrocatalysts is needed to improve the cell performance. Preliminary electrocatalyst screening identified Pt as the preferred catalyst for the methanol oxidation reaction and PtRu as the preferred catalyst for the oxygen reduction reaction in the presence of methanol. These results will be used to guide studies to develop electrodes for PBI MEAs with improved performance.

Suitability of Lignin from Switchgrass for the Manufacture of Carbon Fibers
Maximilian B. Gorensek and Steven R. Sherman

In place of corn or other food crops, switchgrass is being studied as a feed material for the production of ethanol. In the ethanol production process, cellulose and hemicellulose, which comprise about 60% of dry switchgrass by weight, are broken down into sugars using enzymes, and the sugars are fermented to produce ethanol. Lignin, which comprises about 25% of dry switchgrass, is a plastic-like material that surrounds and binds the cellulose and hemicellulose structures, and protects the materials against enzymatic digestion. Lignin must be at least partially removed during pre-processing and pre-treatment steps to free the cellulose and hemicellulose. A lignin waste stream is produced as a result.

The lignin waste stream may be burned as a source of heat in the plant, and its economic value would be equivalent to the cost of the natural gas that it replaces, which is in the range $0.06-0.12/lb. If instead the waste lignin is used as a source material for higher-value products, the economic benefits could be much greater. Earlier work by others has shown that lignin may be used to as a source material for high-strength carbon fibers. In this application, switchgrass lignin could be valued at $0.55/lb or greater, which is still much less costly than comparable source materials made from petroleum. At this price, the lignin waste stream would be worth more than the ethanol product stream, and the economics of the process would be greatly improved.

The goals of this work were to 1) develop an extraction and purification process for the removal and purification of lignin from switchgrass; and 2) study the melting, extrusion, and spinning characteristics of switchgrass lignin in order to assess its suitability for making carbon fibers.

The greatest accomplishment of this project was in the development of a lignin extraction process that is capable of removing between 70-80% of the lignin from a mass of switchgrass (which exceeds literature values of 50%) in a manner suitable for process scale-up. Over the course of the project, twenty-eight 50 g batches of switchgrass were treated, resulting in the recovery of more than 200 g of purified switchgrass lignin which can be used for future lignin studies.

Ionogels as Solid Electrolytes for Advanced Battery Applications

This research investigated the use of solid-state supported ionic liquids (ionogels) as possible electrolyte phases for lithium ion battery applications. An experimental setup and procedure
were developed to measure the conductivity using multiple methods for both liquid and solid phase systems. The results indicate that there is potential use for these ionogel phases in advanced battery electrolytes on the basis of the measured conductivity. Additional work should be conducted to optimize the ionogel phases and determine their practical performance and compatibility with other materials used in battery cell development.

**Fast Neutron Irradiation of Advanced Ceramics for Extreme Environments**

*E.N. Hoffman, R.L. Sindelar and D.W. Vinson*

As the nation’s nuclear power plants approach their original design lifetimes, construction of new nuclear power plants will be required to support increasing power needs. The new reactors will be constructed using new and more efficient plant designs, which will require materials capable of withstanding a more severe environment. To handle these extreme conditions, researchers have started research efforts in both advanced metallic and ceramic materials. The MAX phase carbides, such as Ti$_3$SiC$_2$, exhibit unique properties making them promising candidates for Next Generation Nuclear Power structural materials as they can withstand extreme environments of temperatures up to 1000 ºC. However, little is known about susceptibility to neutron damage of these complex carbides.

An Am-241/Be neutron source was established to irradiate samples of Ti$_3$SiC$_2$ and SiC (used as a reference material) at low temperature, low fluence conditions. Samples were periodically removed from the neutron source and evaluated for resistivity by measuring resistance of samples with known dimension. Resistivity was chosen as the primary characterization tool for evaluation of damage caused by neutron irradiation due to its high sensitivity to defect formation compared to other material properties or even microstructure changes. Initial irradiation results showed no significant changes in resistivity. The results of this work will not only provide insight into the neutron damage tolerance of Ti$_3$SiC$_2$, but it will also provide a basic understanding of how neutron damage initiates in layered materials with unique damage mechanisms of kinking and bridging grains.

**Proton Conductive Solid Polymer Electrolyte for Mg-Ni Rechargeable Batteries**

*Marie Kane and Ming Au*

Current rechargeable battery technologies offer portable power for hybrid electric vehicles, military applications, seasonal electric storage, and consumer applications. However, there are several inherent problems with various battery types, such as corrosion due to the aqueous electrolyte, safety issues with Li-ion batteries, and the cost of expensive raw materials. These issues can be resolved by designing a rechargeable battery with high theoretical capacity, economical starting materials, and a non-aqueous electrolyte. The objective of this work is to fabricate and test a non-aqueous polymer electrolyte material to promote ion conductivity from a high energy density amorphous Mg-based anode (previously developed). This proposed battery system has no inherent safety issues.

This research has accomplished several objectives. First, the capabilities to electrochemically test polymer electrolytes for conductivity, CV behavior and charge/discharge cycling have been established at SRNL. Several characterization techniques necessary to optimize the ionic conductivity of the electrolyte were identified and improved, including AFM, DSC, and
polarized microscopy. These techniques had not been utilized for this application before. More importantly, we demonstrated that a commercial polymer has some ionic conductivity and can be charged and discharged for 50 cycles for rechargeable battery applications with our specific electrode system (MgNi/Ni(OH)₂). We also have shown that by characterizing the degree of crystallinity within the polymer electrolyte sample, we can design and optimize an electrolyte for this particular system. A patent disclosure was submitted and accepted for this technology and the full patent application is being prepared due to the proof of concept shown in this work.

**Evaluation of the long-term effectiveness of enhanced soil remediation with mixed amendments using geochemical parameters and numerical modeling**

* A. S. Knox, K. L. Dixon and M. H. Paller

The key question to be addressed by this project was the long term performance of amendment mixtures and their overall benefits in remediation of contaminated soils/sediments. A numerical model was used to evaluate the long term effectiveness of various amendments and amendment mixtures. The model, which used the desorption Kₐ values, was used to develop breakthrough curves for numerous metals. These curves were then used to develop nomographs for estimating the required amendment thickness to delay contaminant breakthrough for a given period of time. These revealed that the amendment mixture containing apatite, organoclay, and chitosan (AOC) is more effective at retarding metals than apatite (A) alone.

The results provide a basis for the quantitative assessment of the long-term performance of in-situ remediation with amendments. Enhanced remediation with mixtures of amendments offers significant advantages over existing technologies because it can economically treat a broad range of contaminants in a variety of soil and sediment types and can control geochemical processes that contribute to contaminant mobility.

**Evaluation of mixtures of pervious concrete and sequestering amendments for erosion control and contaminant stabilization**

* A. S. Knox, M. H. Paller and K. Dixon

The objective of this project was to develop a permeable active amendment concrete (PAAC) consisting of apatite, limestone, vermiculite, sand, and concrete. PAAC has the potential to produce a barrier that combines high structural integrity with the ability to remove contaminants such as dissolved metals from water that passes through the concrete matrix.

This research developed a PAAC with active sequestering amendments including apatite, limestone, and vermiculite. The amendments replaced a portion of the crushed stone or sand in traditional concrete. Amendments that sequester and retain metals were successfully incorporated into permeable concrete (PC). PAAC with apatite, or limestone and apatite were more effective at removal of metals than conventional PC. The substitution of a small amount of crushed stone by amendments (e.g., 10% North Carolina apatite) was sufficient to effectively remove metals from the aqueous phase.
PAAC exhibited high retention (90% or more) of most tested metals indicating little potential for remobilization of contaminants. The PAAC created a structural barrier that contained contaminants while resisting physical disturbance and permitting the passage of water. Mixtures of permeable concrete and chemically active amendments may serve as alternative fill materials in reactor vessels and may produce structures such as retaining walls and seepage basins that treat dissolved pollutants economically, effectively, and with minimal expenditure of energy.


*P. Korinko, T. Adams, K. Brinkman and S. Garrison*

In the search for alternatives to fossil fuel for motive and energy sources, hydrogen offers many potential advantages as an energy carrier. Hydrogen is not without problems and challenges though. One issue is the ability to consistently produce a high purity hydrogen gas. This need has been recognized by the DOE, fuel cell developers, hydrogen gas producers, hydrogen delivery system designers, and national and international codes and standards organizations. While there certainly are well established methods that are used to purify hydrogen containing gas streams, new lower-cost, portable systems are of significant interest. For instance, palladium based metallic membrane reactor systems can adequately produce “pure” hydrogen from impure feed, such as reformate streams. However, the associated cost of these noble metal systems has sparked considerable technical interest in developing advanced non-noble metal based membrane reactor materials. Additionally, integration of the fuel purification technologies directly into lightweight portable storage systems has also gained much focus in recent discussion with both DOE and commercial hydrogen technology developers. Of the numerous materials potentially of interest, we chose to study bulk metallic glass (BMG) materials for hydrogen purification applications. These materials represent an exciting potential replacement for high cost Pd/Pd–alloy membranes for composite membranes while enhancing the efficiency of gas separations both in production processes and for fuel cell usage. Our goal was to study a model system and relate the energy of hydrogen clustering about Zr atoms with permeability. Our results indicated demonstrated that the potential exists to use BMGs in this manner. However, further work must focus on suppressing crystallization of these materials in use.

**Infrared Boundary Layer Profiler**

*Robert Kurzeja*

The purpose of the project was to determine whether a low-cost, compact instrument to monitor the vertical temperature structure in the atmospheric boundary layer (0-7000 ft) could be developed. The study was carried out in two phases. In the first phase the MODTRAN radiative transfer code was employed to investigate the sensitivity of radiance measured at variable zenith angle to height-dependent temperature changes. The second phase involved evaluation of field data with an infrared radiometer attached to a simple vertical scanning motor.

The MODTRAN results and Twomey-Tikhonov inversion calculations are proof of concept and show that only minor modifications are required to the proposed field instrument. The production cost of the instrument is estimated to be < $10k, which is much less than the $100k cost for alternative technology, e.g., Radio Acoustic Sounding Systems (RASS). In addition, the
instrument would be much smaller, unobtrusive, with greater vertical range than RASS systems. The MODTRAN calculations also showed that the technique could be applied to the vertical water vapor distribution, which is only measurable remotely with research quality instruments. The proposed instrument could also provide unexpected benefits. For example, the vertical scan sequence could encompass the entire sky to detect clouds and measure their temperature. The cloud temperatures could then be used with a vertical temperature profile to infer cloud heights.

**Humic Amendments to Sustain and Enhance Cometabolism in Groundwater**

*Brian Looney and Chris Yeager (SRNL), and Hope Lee (INL)*

Chlorinated industrial solvent contamination in groundwater is the most common environmental problem in the world. Traditionally, the contaminated groundwater is pumped to the surface for treatment, a process that can take decades, or the solvents are treated in the ground using reagents to use up the oxygen and stimulate anaerobic degradation. Unfortunately, the anaerobic conditions convert the groundwater into a putrid reactor and severely degrade the water quality. We proposed development of an in-place treatment that adds natural amendments to accelerate aerobic biodegradation so that the contaminants are destroyed without adversely impacting water quality.

The research confirmed that humate-enhanced cometabolism is promising in terms of hydrology, geochemistry, design, economics, and microbial stimulation. In performing the work, we: 1) developed, tested and implemented innovative-practical methods to separate DNA from oligotrophic groundwater, 2) verified and compared various qPCR primers for microbial DNA, 3) Measured sorption of humates to coastal plain sediments, 4) Separated bulk humate into humic and fulvic acid fractions for future experiments, 5) developed engineering model for humate deployment using Langmuir sorption coefficients, and 6) documented the stimulation of the microbial community by humate amendment.

This research provides an entirely new philosophy to remediate the most problematic chlorinated solvent contaminated groundwater – so called, “large-dilute plumes.” The SRNL research advocates enhancing the natural processes already occurring in those plumes to cause them to stabilize and shrink and the resulting technology eliminates the need to either pump and treat water for decades or to convert large treatment zones to anaerobic conditions. While some additional confirmation is needed, there has been significant national interest and excitement surrounding these developments and the potential for application of the resulting technology.

**Study of the Local Environment of Glasses Being Considered for Pu Disposition**

*J.C. Marra, C.L. Crawford and R.J. Lascola (SRNL) and S.V. Stefanovsk (SIA Radon Institute)*

The disposition of excess weapons-useable plutonium is an ongoing problem. Glass waste forms have been considered as suitable immobilization matrices for long-term Pu disposal. Understanding the local environment of Pu within these glasses is necessary for processing considerations and to gain insight into criticality concerns in the waste form in the intact mode and as a result of waste form degradation.
There is currently little (if any) data available on local structural environment of Pu in glasses when Pu is present in the glass in significant quantities. Furthermore, the validity of chemical surrogates for Pu that would facilitate testing and analyses in candidate glass systems is not well founded. This project aimed to determine the local structural environment of Pu and Hf as a surrogate for Pu in a lanthanide borosilicate (LaBS) glass and in an alkali borosilicate (ABS) glass.

This work provided insightful data to the structural role and environment of Pu in LaBS and ABS glasses. At high Pu concentrations Pu may segregate in the LaBS glass. Hf was determined to mimic Pu in the glasses quite well with the exception of solubility at high concentrations. The work has led to new FY10 funding from DOE-EM.

**Development of Hydrogen Compatible Ultra-Pure High-Strength Alloy Steels**

*M. J. Morgan*

Smaller, lighter, and more portable devices are needed for hydrogen storage. Higher strength alloys that are compatible with high hydrogen fugacity environments need to be developed. The 2008 LDRD project “Development of Hydrogen Compatible Ultra-High Strength Alloy Steels” demonstrated that remarkable resistance to hydrogen embrittlement of Navy pressure vessel steels (HY130) could be achieved by producing ultra-high purity alloys with alloy modifications that minimize impurity segregation. The objective of this project was to investigate similar alloy modification concepts for improving the stainless steels that are used for containment of hydrogen isotopes at Savannah River.

This project successfully demonstrated that the stainless steel alloys used for hydrogen containment at Savannah River and in the hydrogen economy can be made more resistant to hydrogen embrittlement through alloy modifications. The detrimental effects of hydrogen on fracture toughness can be offset by increasing nickel content or by modifying the alloy content so as to increase stacking fault energy. Fracture toughness was improved a factor of five by increasing nickel content from 6.4 to 7.3 wt%; these alloys became less tough after hydrogen exposure, but actually had higher fracture toughness than unexposed lower-nickel alloys.

**Plume Source Localization by Adaptive Sampling from an Airborne Platform**

*Lance O'Steen*

Locating the source of an atmospheric effluent plume from an unknown proliferant facility and/or estimating the effluent release rate from a known facility (and thereby inferring a production rate) has been a long-standing focus of non-proliferation programs involved in monitoring and sample analyses. Currently, effluent collections against suspect facilities almost exclusively utilize fixed, ground-based samplers that are primarily designed for monitoring known or suspected proliferant facilities. This collection method has two major shortcomings: (1) collections are only useful when the transporting wind direction carries the effluent plume to the sampler and (2) the method is dependent on simulated meteorology and atmospheric transport for actual source attribution, and therefore subject to the errors in these simulations. Even with no meteorological or transport simulation error, localization of an unknown source will still be uncertain due to the lack of knowledge with respect to the timing of the release.
Repeated measurements with different transport wind directions can narrow this source location uncertainty. However, this source attribution strategy is of limited utility for fixed samplers.

A more direct approach to plume source attribution would be to track the plume back to its source using a UAV with a sensor and an adaptive sampling and flight control strategy. While operationally more complex, this method would not be subject to the problems associated with fixed monitoring sites noted above. The use of UAVs will almost certainly be a component in future atmospheric effluent sampling systems and SRNL is heavily involved in monitoring programs and the development of innovative measurement technologies that support these collection programs.

Under this LDRD a computational algorithm was developed to track and continuously evaluate the location of an effluent source based on real-time, airborne measurements of ambient wind speed and direction and effluent concentration. These measurements were used to control the flight of the UAV and to drive time-inverted (adjoint) transport simulations to estimate source location and release rate. The results of this LDRD demonstrate that the proposed UAV control and sampling algorithm is viable for synthetic plume data and will serve to position SRNL for participation in future research in the area of adaptive sampling with UAVs.

**Evaluation of X-ray Photoelectron Spectroscopy (XPS) for Determination of Transition Metal REDOX in Representative Waste Glasses**

*Fabienne C. Raszewski and Henry Ajo*

X-ray photoelectron spectroscopy (XPS) is a quantitative analytical technique, which can be used to study the electronic state of elements that exist within a material with an atomic number of 3 (lithium) and above. Other applications in glass research include the determination of local chemical environment and bonding. In the past, XPS has been used to study the iron REDOX in simple iron-doped sodium silicate glasses. This technique has also been used to examine iron oxidation states in phosphate and borate glasses. Currently, a wet chemistry colorimetric approach is used at SRNL to measure the iron oxidation state ratios [Fe2+/Fe (total)] or REDOX in experimental waste glasses. More benefit would be gained if the oxidation states of not only iron, but of other transition metals, such as manganese could be measured. Since XPS is a nondestructive technique and requires little or no sample preparation, this method may offer more advantages than the traditional colorimetric approach. The ability to measure REDOX states of multiple transition metals in complex glass systems would be beneficial for i) altering acid addition strategies/equations used for REDOX control in the Defense Waste Processing Facility (DWPF), ii) developing alternative chemical processing cell flowsheets and iii) developing a new capability at SRNL, not only for determining REDOX, but for studying the structure of glasses.

The SRS Environmental Assessment glass was successfully “forced” into various REDOX values during re-melting by the use of coal. Environmental and Chemical Process Technology recently purchased a UV-Vis spectrometer, which proved itself to be a useful and efficient tool for the study of glasses.
Friction Stir Welding for Hydrogen Delivery Applications

George Rawls

Critical to the successful implementation of hydrogen delivery via pipelines is an understanding of the hydrogen compatibility of the materials of construction. Friction stir welding offers a new approach to reduce the installation cost of metallic pipelines and provides a more robust joining process for hydrogen service. Little effort has been focused on the development of a fundamental understanding of the behavior of friction stir welds with respect to materials performance in hydrogen service.

The friction stir welding process is rapidly becoming a preferred technology for the joining of metals. This process, which was originally developed for aluminum, is now being extended to include steels and polymers. Friction stir welding equipment has been developed for pipeline applications and data has shown that the friction stir process has the potential to reduce welding costs in field applications.

The results of this project provided first of a kind tensile test data for friction stir welds in 1500 psi hydrogen service. The test showed that the hydrogen embrittlement was reduced in the friction stir weld as compared to the E7018 fusion weld electrode material. The data showed that the friction stir welding process has the potential to provide welds that are no more susceptible to hydrogen embrittlement than the base metal.

Modeling to Support Developmental Design of In-Well Components to Support “In the Injection Well Saturation of CO2 for Geologic Storage”

Martin A. Shadday Jr. and Gregory P. Flach

There is considerable interest in the underground sequestration of CO2 produced in large quantities by industrial processes. SRNS personnel are investigating a process for injecting water saturated with CO2 into deep aquifers. Below a depth of 2000 ft., the CO2 saturation concentration in water, based on the hydrostatic pressure, is approximately 50 kg/m³. The increased density of the CO2 saturated water will cause it to stratify at the bottom of the aquifer. The plan is to inject flue gas into the downward flowing water in a well and dissolve the CO2. The goal of this investigation was to develop a model of the two-phase flow and the CO2 mass transfer between the bubbles and the liquid.

A two-phase flow numerical model of the flow within a module designed to dissolve CO2 in entrained bubbles has been developed. The mass transfer of CO2 between the bubbles and the water is calculated as functions of: pressure, the CO2 concentration in the water, the composition of the gas, and the bubble size. This model will be used to demonstrate the viability of this proposed sequestration process and to determine the performance of CO2 dissolution modules for a range of bubble sizes, water and gas flowrates, gas compositions, and pressures.
Flowsheet and Cost Analysis of Nuclear-Driven CO₂ Capture Process

Steven R. Sherman and Maximilian B. Gorensek

Atmospheric carbon dioxide levels have been steadily increasing since the Industrial Age. Consensus is building that anthropogenic CO₂ is responsible and that this increase is having an effect on climate. Natural CO₂ removal by photosynthesis and carbonate minerals formation does not have the capacity to reverse this trend within the current century even if combustion rates of biomass and fossil fuels were to be greatly reduced worldwide. Removing CO₂ from the atmosphere on a global scale has been proposed as a possible remedy. Nuclear energy has attributes that could make it attractive as the primary energy source for an atmospheric carbon capture process – it doesn’t make any additional CO₂ and it can operate on a large scale. This work explores the viability of a nuclear-driven CO₂ capture process using soda lime chemistry and high-temperature gas-cooled reactors (HTGRs).

Borrowing from earlier studies of atmospheric CO₂ capture using fossil fuel-fired lime kilns, and taking advantage of recent innovations in lime processing from the pulp and paper industry, four variants of a CO₂ capture process that use an indirectly heated (by nuclear energy) kiln were considered. Features incorporated in various combinations include: steam fluidization and/or calcination, steam drying, vacuum calcination, steam hydration, and steam recompression. In each case, air was blown through structured packing in an absorber fed with caustic soda to remove CO₂ and the used solvent regenerated in a pellet reactor causticizer. The most energy-efficient process operated at a kiln temperature of 850°C and ambient pressure, and used steam drying of lime mud, steam fluidization, and steam hydration with recuperation. The specific energy was 249 kJ/mol. CO₂ compression and air circulation could add another 100-150 kJ/mol, resulting in a net value of 350-400 kJ/mol, significantly better than any conventionally heated soda lime process proposed to date.

Organo-Boron based Chemistries for Self-Assembly and Growth

Lucile C. Teague (SRNL), W. R. Kwochka, T. D. Jones, S. L. Harper, K. Beeker, T. Wilson (Western Carolina University), and R. D. Pike (College of William and Mary)

The goal of this work was to utilize the unique chemistry of boron-containing compounds to create organic materials for subsequent surface deposition, toward directed self-assembly and “bottom-up” assembly of functional thin films. This project is motivated by the need to correlate and control materials on the molecular level, and the need to create and tailor the chemical, electrical, and mechanical properties of surfaces. The ability to control these surface properties will have a significant impact in many areas including molecular-based sensors, surface patterning, thin-film growth, gas sensing and storage, “bottom-up” assembly, photovoltaics, and organic-based electronics.

Our research has focused on the synthesis and analysis of conjugated organo-boron materials as molecular “building blocks” and their subsequent surface attachment. Over 20 organo-boron molecules have been synthesized for these studies, for both surface attachment, and solution-based exchange studies. These experiments have helped us understand how to manipulate trivalent boron compounds for future applications in selective or “tunable” surface-bound sensors.
Increasing Efficiency of Ethanol Production Processes by Coupling Waste Treatment to Electricity Production Using Microbial Fuel Cells
Charles E. Turick, Amy A. Ekechukwu and Charles E. Milliken

The recent discovery of direct electron transfer (ET) from microorganisms to microbial fuel cell (MFC) electrodes has created new possibilities for energy harvesting, with potential to generate 0.6-3kW/m² of electricity. Key components of ET to electrodes are electron shuttles (ES). This area of study was coined “electromicrobiology” and relates to specific mechanisms of ET to solid anodic materials. ES are redox cycling compounds that can receive electrons from microbes and transfer them to anodic materials. ES can be soluble or associated with microbial surfaces. Surface associated ES can increase E° of the cell surface while soluble ES minimize mass transfer limitations of ET, especially in anodic biofilms. Hence ES have significant potential to increase the power output of MFCs.

MFCs are bioreactors where specific microorganisms grow on an electrode. Electrons then travel to a cathode and electricity is generated. Limitations to optimal power generation inherent of anodic biofilms include electron transfer and insufficient surface area.

Limitations to electron transfer in biofilms have been addressed successfully during this LDRD. A 3-electrode cell of ES producing bacteria demonstrated doubled current production in non-optimized systems compared to ES deficient strains. Pyomelanin is the ES produced during periods of diminished oxygen tension and electrochemical analyses of the working electrodes from those cultures confirm pyomelanin was produced during growth on the electrode. We have successfully demonstrated that production of an ES by electrogenic bacteria can be used to substantially increase current production in MFCs without the need to increase anode dimensions.

Mechanisms of Enhanced Growth in Radiation Fields
Charles E. Turick, Amy A. Ekechukwu. Charles E. Milliken and David C. Beam

Recently, microbial isolates from nuclear reactor facilities in Chernobyl, Ukraine, were shown to have accelerated growth under gamma radiation. Since gamma radiation is most often lethal to all organisms, the discovery of microbes that not only survive but thrive in such an environment is very exciting! Electroactive polymers produced by these microbes are directly linked to increased growth under gamma radiation (These polymers are the common pigment melanin.). The mechanisms related to this enhanced growth are not known.

We have successfully demonstrated that gamma radiation has a profound effect on the electron transfer properties of melanin. The continuous oxidation of melanin in gamma radiation fields is the first step in demonstrating that this is how gamma-radiation stimulates microbial growth. In addition, this is the first demonstration of the electrochemical activity of melanin produced by fungi and confirms existing theories about the electrochemical properties of fungal melanin.

This work is significant on several levels.
• Elucidating this mechanism at the cellular level will enable DOE to understand and exploit accelerated microbial growth in extreme radioactive environments for in situ radionuclide immobilization.
• Identifying this mechanism will directly benefit DOE’s interest in determining the effects of radiation on biological systems (http://www.science.doe.gov/ober/LSD/lowdose.html).
• An understanding of how biological systems thrive in radiation fields will provide valuable insight into why other biological systems are damaged by radiation.
• This type of radiation-enhanced growth is a novel type of physiology and will be important in exobiology and future space missions dedicated to searching for extraterrestrial life forms.
• There is the potential to exploit radiation enhanced microbial growth for clean up after a dirty bomb attack.
• Furthermore, this work has potential from a material science perspective related to using a melanin/radiation-source composite electrode as a novel cathode material that could replace existing expensive materials.

**Magnetic Ionic Liquids for Metal Ion Separations**
*Ann E. Visser and Nicholas J. Bridges*

This program is focused on developing magnetic ionic liquid (IL) separations as a new technique to extract metal ions from aqueous solutions. For this project, the IL’s cation or the anion were synthesized to contain a paramagnetic metal ion that will make the IL responsive to an applied magnetic field facilitating phase separation. The magnetic ILs may also contain a traditional organic extractant molecule (e.g., tributylphosphate) to complex and extract metal ions of interest (e.g., actinides or fission products) from an aqueous solution. With the application of a magnetic field, a magnetic IL (containing the metal ion extractant and the extracted metal ions) could be moved/ transferred/held while independently manipulating the aqueous phase. Development of magnetic ILs could facilitate metal ion separation technologies beyond those that rely on gravity as the means for achieving the organic/aqueous separation.

Magnetic ILs have only recently been reported in the literature and have not yet been used in metal ion separations. We’ve prepared the first magnetic ILs to be used in liquid/liquid separation tests, but our results showed no metal ion extraction into the IL. Our incorporation of ligands into the ILs has potential, especially considering that a non-paramagnetic lanthanide compound has never been reported in the literature.

**Metal Hydride Based Thermoelectric Device**
*M. J. Williamson, K. S. Brinkman, and S. C. McWhorter*

This program is focused on evaluating the use of energy involved in metal hydriding reactions to supply heat (and thus a temperature difference DT), to operate a thermoelectric(TE) device. Preliminary work to investigate the reactions involved evaluating the heat produced when hydriding magnesium, palladium, and vanadium films. Subsequently, these metals were sputtered onto the hot sides of commercially available thermoelectric devices. The devices were placed in an apparatus which exposed the metal surface to a 96% hydrogen atmosphere and the current and voltage characteristics of the devices were measured.
The proposed metal hydride based power supply has been investigated. It has been shown that it is possible to generate heat on the hot side of the TE device through the hydriding of Pd. Limitations in the experimental program prevented quantification of this process by directly measuring current and voltage output from the half cell device described above. Further studies should focus on optimizing the growth of the metals and reduction of the thermal mass of the thermoelectric devices.

**Latex-Embedded Cyanobacteria as a Portable Source of Hydrogen**

*Chris M. Yeager, Christopher Bagwell, Michael Flickinger, Tanya Soule and Magdalena Piskorska*

Cyanobacteria are an attractive source of hydrogen in that they require only water, sunlight, and air during the production process and do not produce nor require hazardous substances. In addition, certain strains of cyanobacteria are extremely resistant to desiccation, able to survive years to decades in the absence of water, capable of immediate reactivation upon rewetting. Biocatalytic latex coatings are stable, nanoporous matrices useful for the immobilization of microbes. These solid supports are ideal for photosynthetic H₂ production because they provide an increased surface area for incident light, increased rates of gas diffusion compared to liquid-based systems, and can increase cell longevity by protecting the microorganisms from mechanical degradation and contamination. We intend to exploit these unique characteristics to develop a lightweight, pliable polymer, embedded with cyanobacterial cells, as a portable source of hydrogen.

The aim of this project is to embed cyanobacterial cells, which are naturally resistant to desiccation, into latex coatings supported by a pliable substratum. If successfully developed, the coatings would be “off-the-shelf”, lightweight bacterial catalysts for H₂ production.

Considerable progress was made toward achieving all of these objectives. Coatings of *R. palustris*, *Anabaena PCC 7120*, and *Synechocystis sp. PCC 6803* did not survive dry storage for periods greater than 24 hrs. *N. commune DRH-1* is a desiccation resistant strain. We are currently examining the ability of coatings of this organism to survive under dry storage conditions. *Anabaena PCC 7120* cells embedded in latex leach large amounts of phycocyanin. It may be possible to translate this observation into a cost-effective technology for extracting commercially valuable pigments (like phycocyanin) from cyanobacteria.
### Summary Statistics for the 2009 LDRD Program

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