SRNL LDRD Annual Report
2007

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We Put Science To Work

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We Put Science To Work™

From the Laboratory Director

I am pleased to present the fiscal year 2007 Laboratory Directed Research and Development (LDRD) annual report. This represents the first year that SRNL has been eligible for LDRD participation and our results to date demonstrate we are off to an excellent start. SRNL became a National Laboratory in 2004, and was designated the "Corporate Laboratory" for the DOE Office of Environmental Management (EM) in 2006. As you will see, we have made great progress since these designations.

The LDRD program is one of the tools SRNL is using to enable achievement of our strategic goals for the DOE. The LDRD program allows the laboratory to blend a strong basic science component into our applied technical portfolio. This blending of science with applied technology provides opportunities for our scientists to strengthen our capabilities and delivery. The LDRD program is vital to help SRNL attract and retain leading scientists and engineers who will help build SRNL's future and achieve DOE mission objectives. This program has stimulated our research staff creativity, while realizing benefits from their participation. This investment will yield long term dividends to the DOE in its Environmental Management, Energy, and National Security missions.

I am very pleased of the accomplishments of our staff and look forward to a steady growth in the impact and benefits for DOE in the future.

Dr. G. Todd Wright
Laboratory Director

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Project Summaries Full Projects

Advanced RNA and Protein-Based Tools for Microbial Systems

C. E. Bagwell, C. E. Milliken, B. W. Smith, C. M. Yeager, D. C. Beam

Objective: The goals of this project are two-fold. First, we aim to expand and integrate genomics based molecular technologies to provide comprehensive information about intact, whole bacterial systems, thereby enabling their use as *in situ* and real-time sensors of environmental conditions and expressed bio-processes in contaminated environmental settings. Secondly, we will hone these tools on the actinobacterium *Kineococcus radiotolerans,* to expand scientific knowledge and uncover potential environmental applications.

Laboratory dependent discovery of environmental applications for bacteria is inherently difficult because of our inability to accurately and reliably duplicate environmental conditions. Genomics enabled tools mark a significant advancement in that they provide an unbiased global view of microbial responses and activities to environmental conditions. However, genomics technologies have yet to result in major improvements for the applied sciences; thus, it remains unclear whether information gained would offer any predictive power over managing bacterial systems for application specific purposes. In this project we have fully integrated physiological experimentation, genome sequencing, global genome expression technology and spectrometry-enable proteomics to translate new technologies into practical solutions for intractable environmental problems.

Actinobacteria are ubiquitous, and quite often abundant in terrestrial environments, and several genera have been repeatedly recovered from heavily contaminated environments. As one example, *Kineococcus radiotolerans* and close relatives have been detected in SRS and Hanford high-level waste systems, as well as plutonium contaminated soils at Los Alamos, NM. In this project, global gene and protein-level responses in *Kineococcus* to lab-simulated contaminated environments was determined. The overarching goals of this proposal are to provide explanation for why actinobacteria, like *Kineococcus,* are routinely found in heavily contaminated environments - included HLW, and to better understand what they could be doing. Project objectives are designed to elucidate the expressed biological activities that could be harnessed in order to apply these highly resilient microbes to help achieve DOE EM's environmental objectives.

The DOE maintains interest in the extreme resistant bacteria for bioremediation because of their ability to withstand the toxicity of contaminated environments. A strong linkage between the utilization of non-redox active metals and the extreme resistance phenotype has been established in the literature, and here we have shown that the growth and metabolism of *Kineococcus radiotolerans* was significantly enhanced by copper during chronic irradiation. Copper is an essential cofactor for a variety of enzymatic processes; however, at elevated concentrations copper is toxic, thus intracellular levels are tightly regulated by the cell. *K. radiotolerans* was routine grown in medium containing 6 to 95 mg L^{-1} of copper (25 ug L^{-1} is widely considered toxic for environmental bacteria), resulting in intracellular copper accumulation up to 3.7 μg / mg protein without significant retardation in growth. Physiological assays and gene expression studies demonstrated that copper increased cellular growth rate and the expression of metabolic genes, and concomitant down regulation in the specific activity of cellular defense systems and expression of general stress markers and heavy metal exporters. These findings mark several important contributions to science. All bacterial model systems for copper resistance are Gram (-) bacteria, very little is known about resistance mechanisms in Gram (+) bacteria. Furthermore, it remains unclear why or how copper at such high concentrations stimulates energy metabolism in *Kineococcus*, particularly in a radioactive environment when the combination should be strongly inhibitory to cellular processes.

Suppression subtractive hybridization (SSH) was conducted in order to enrich and identify differentially expressed genes during growth and acute exposure to combinations of copper and γ-radiation. The SSH technique provides efficient means by which to compare global genome responses between an experimental culture and a control culture. Differentially expressed cDNA libraries have been constructed for *K. radiotolerans* during copper enhanced metabolism and growth during γ-irradiation and under ambient laboratory conditions. Both libraries are currently in the sequencing queue at the University of Georgia. These results will reveal biochemical and mechanistic roles for copper in *Kineococcus* facilitating energy metabolism in a radioactive environment.

A parallel proposal entitled "Proteome Enabled Discovery of Growth and Survival Strategies of the High Level Nuclear Waste Actinomycete, *Kineococcus radiotolerans*" was funded by the William R. Wiley EMSL at PNNL to provide parallel whole cell proteomics analysis. Proteomics technologies have proven useful for validation of bacterial genomes that present with assembly and annotation complications (e.g., *Kineococcus*), and will help provide functional role assignments for proteins expressed in response to copper and γ-radiation. These efforts should solidify copper's role in *Kineococcus* physiology; such as through discovery of metalloproteins involved in growth, defense, or biosynthesis that are unique or function differently in *Kineococcus* and are not conserved in other extreme resistant bacteria.

Through a combination of experimentation and insights gleaned from the genome sequence of *Kineococcus,* we aim to construct a more complete picture of the metabolic capabilities of this unique bacterium as well as a better understanding of the genetic and physiological adaptations affording survival in extreme and mixed waste environments.

Ionic Liquid Electrochemical Separations

T. M. Adams, A. E. Visser, J. I. Mickalonis

Objective: This program is focused on evaluating the use of Ionic Liquids (ILs) in advanced low temperature electrochemical separations process by focusing on the development of a fundamental understanding of the electrochemical redox potentials of ILs with a complementary effort to understand the radiation stability of the ILs and the consequences on the electrochemical processes of radicals/intermediate decomposition products resulting from irradiation.

As a result of renewed interest and funding, increased attention is being given to the development of advanced/alternative spent nuclear fuel recycling technologies. The final report from the recent BES workshop on Advanced Nuclear Energy Systems notes that. "*Closing the fuel cycle will create new needs for advanced separation techniques. One possibility is electrochemical separation in (inorganic) molten salts ("pyroprocessing"), a highly capable technique available for batch processing. A second possibility is the development of a variety of neoteric agents that have the potential to confer unprecedented capabilities for separation of spent fuels in continuous processes, which meet the competing demands of utilizing nuclides formerly considered waste, while providing a composition radioactive enough to deter theft and proliferation* and*…With the development of powerful new separation agents, complementary efforts are needed to understand, at a mechanistic level, the consequence on the separation processes of the substantial radiation fields from radioactive decay."* The use of Ionic Liquids (ILs) as an advanced electrolyte for an electrochemical separations process could potentially provide the path for combining the two aforementioned possibilities into a single point operation. The use of ILs in place of high temperature molten salt electrolytes for fuel reprocessing would facilitate operation at lower temperatures and can eliminate many of the technical, environmental, and safety concerns related to high temperature pyrochemical processing. Additionally, the use of ILs could lead to a greater understanding of actinide chemistry that would allow for creation of next-generation separation and purification processes. Further, the ability to tailor the properties of IL solvents holds the promise of room-temperature electrochemical techniques for purifying and recovering actinides. For use of ILs in an advanced low temperature electrochemical separations process, major emphais must be placed on development of a fundamental understanding of the electrochemical redox potentials, the radiation stability of the ILs and the consequences on the electrochemical processes from radicals and intermediate decomposition products formed as a result of radiation.

In FY07, SRNL conducted experimental work to evaluate ten commercially available ILs for potential application in an electrochemical separations process. Testing of these materials was focused on evaluation of the electrochemical stability through cyclic voltammetry (CV), which was used to define the potential range (electrochemical window) at which reduction or oxidation of the IL did not occur. CV testing also included assessing for a range of salts and oxides their solubilities in the ILs. Some chloride and nitrate salts had limited solubility while oxides were insoluble. .

In addition to the CV testing, radiation stability testing of the ILs was conducted using Co-60 gamma irradiation to a cumulative dose of approximately 120MRad. Samples of the ILs were characterized using UV-Vis and NMR prior to irradiation and then subsequently re-analyzed following irradiation. Additionally, electrochemical windows were determined for post-irradiated ILs. Results from these post-irradiation experiments indicated that while radiolytic darkening of the ILs occurred, NMR results showed less than 1 % change in structure or formation of decomposition products. CV analyses indicated significant reduction (~30%) in the stability of the ILs, with N-trimethyl-N-butylammonium bis(trifluoromethyl-sulfonyl)imide ([Quat][Tf_2N]) maintaining the largest electrochemical window.

Results form the both the cyclic voltametry and irradiation effects testing are as follows:

- Major challenge to replace high temperature molten salts with ILs for pyroprocessing is salt solubility
- Irradiation of ILs shows some changes in physical and electrochemical properties including color, viscosity, conductivity, and the electrochemical window.
- [Quat][Tf_2N] appears to be the most attractive candidate for further research since it maintained the largest electrochemical window following irradiation.

Low Temperature Waste Forms and Containment: Geopolymers

C. M. Jantzen, A. R. Jurgensen, P. R. Burket, D. M. Missimer, C. L. Crawford

Objective: This research applies nano-scale destabilization of common clay minerals (kaolin and montmorillonite) that are subsequently alkali activated to the stabilization of hazardous Resource Conservation and Recovery Act (RCRA) metal wastes and the stabilization of hazardous and radioactive thermal treatment residues. The destabilized clay and alkali forms an amorphous inorganic aluminosilicate polymer known commonly as a geopolymer.

Geopolymers are ceramic-like, inorganic polymers made from aluminosilicates cross-linked with alkali metal ions (M_2O), nominally $4SiO_2\bullet Al_2O_3\bullet M_2O$. Heat treatment of the clay destabilizes the clay and renders it amorphous at the nano-scale. The alkali species "alkali activates" the structure to reorganize into a cross linked polymer. Low temperature (40-45°C) curing and low water content prevents the components from crystallizing and the geopolymers remain amorphous. The Si:Al ratio of the geopolymers varies according to the desired application, e.g. bricks, ceramics, and fire protection applications have a 1:1 ratio, cements and concretes have a 2:1 ratio, and fiberglass composites have a 3:1 ratio.

The geopolymer cross-linked aluminosilicate structure has been used to stabilize heavy metal mining wastes in Europe. It's application to the stabilization of Environmental Protection Agency (EPA) RCRA metals has not been systematically examined and its application as a binder for hazardous/radioactive thermal treatment residues such as those produced during Fluidized Bed Steam Reforming (FBSR), calcinations, and/or incineration has not been studied. For radioactive applications, the low water content of the geopolymers should inhibit H_2 generation from radiolysis and, therefore, geopolymers should be superior waste forms compared to cement.

In FY 2007 Si:Al ratios of 1:1 and 2:1 were studied for stabilization of RCRA metals and thermal treatment residues. A simulant RCRA spike was made and analyzed. This spike contained the RCRA components at 60X the concentration of the RCRA treatment standards, e.g. the Universal Treatment Standards or UTS limits. The standard was acidic (pH<1). Thermal treatment residues from FBSR were available that had been created from a simulant of Hanford's AN-107 low activity waste that had been doped with Re^{+7} as a substitute for the radioactive Tc^{+7}.

Seven kaolin clays were studied, five of which were measured and determined to be high surface area (32-42 m^2/g). The high surface area clays contained significant quantities of montmorillonite clay as determined by x-ray diffraction analysis. Many clay properties were studied before and after the destabilization heat treatment. Clay particle size distribution had little effect on the RCRA and thermal residue stabilization. Zeta potential of the heat treated clays was less negative than in the un-heat treated clays at pH values > 7 but more negative at pH <3. The negative zeta potential at pH<3 helped the geopolymer matrix sorb the positively charged RCRA cations during geopolymer fabrication with the pH<1 RCRA spike solution.

Clays with surface areas in the 9-30 m^2/g were more successful at RCRA and thermal residue stabilization than the high surface area clays. These were also the clays with no montmorillonite. Clays with montmorillonite made the geopolymer waste forms crack during curing and this might be attributed to the known swelling nature of montmorillonite clays. During this study, it was also determined that the most successful clays were those with the least crystalline SiO_2 impurities (quartz and muscovite) as these silica sources are not reactive during geopolymer fabrication as is the aqueous alkali activator $Na_2Si_2O_5$ used in this study.

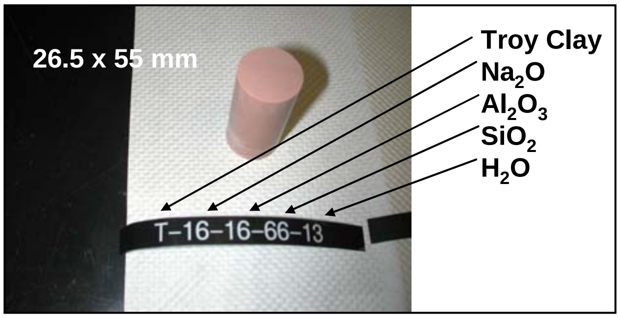


Figure 1 - A cured geopolymer with RCRA spike.

The RCRA stabilized geopolymers had measured densities of 1.66-1.75 g/cc and compressive strengths of 4400-6100 psi. The thermal treatment residue stabilized geopolymers had measured densities of 1.71-1.94 g/cc and the compressive strengths of 4400-7700 psi. The density and compressive strength increased with residue loading. The RCRA stabilized geopolymers met TCLP at less than the UTS limits even though the geopolymer contained 60X the UTS limits. ASTM C1285 durability testing is still in progress to determine the retention of the Re^{+7} non-radioactive simulant for Tc^{+7}.

Impact of Composition and Heat Treatment on Pore Size in Hollow Glass Microspheres

F. C. Raszewski, E. K. Hansen, S. D. Mann, R. F. Schumacher, D. K. Peeler

Objective: The primary objective of this research is to demonstrate the ability to influence pore size and/or pore size distribution through composition and/or heat treatment of porous walled hollow glass microspheres (PWHGMs).

Over the last fifty years, porous glasses have been prepared by various means and in many geometric forms, including solid beads, fibers, hollow fibers, and membranes. These porous materials have been used for several purposes including catalyst supports, gas filtration, and molecular filters. Recently, the Savannah River National Laboratory (SRNL) developed a new geometric form: hollow glass microspheres (HGMs), with unique porous walls, termed PWHGMs. The glass porosity of this material is in the range of hundreds to thousands of Angstroms and has permitted the introduction of materials for hydrogen storage and other materials into the interior of the HGMs.

The production of PWHGMs is based on the interconnected microstructure that is characteristic of phase separated glasses. In general, a glass composition prone to amorphous phase separation is used to produce a HGM. The HGM is heat treated to enhance or develop the interconnected microstructure. The heat-treated HGM is then subjected to a leaching process, which results in a sponge-like network structure or a PWHGM, consisting mainly of silica. These PWHGMs are characterized by channels and openings that can permit the transport of species of interest into and out of the HGMs.

During the first half of FY 2007, we developed a matrix of six glass compositions based on a composition from previous research that was successfully proven to form PWHGMs. Two critical parameters were varied; the silica concentration and the B_2O_3/alkali molar ratio. Glasses of these compositions were fabricated and feed material for HGM production was prepared. HGMs were produced by a flame process, using an experimental apparatus developed at SRNL.

The second half of FY 2007 was devoted to the production and analysis of PWHGMs (scanning electron microscopy and porosity measurements via mercury porosimetry). HGMs were heat treated under various conditions (temperature and time) and subjected to an acid leaching process to form PWHGMs. Samples of each composition were also *not* heat treated prior to acid leaching for comparison.

Heat treatment *temperature* was determined to be most effective in changing the porosity of PWHGMs. Pore diameter in a non heat treated sample is approximately 100 Å and with heat treatment at 600°C for 8 hours, the diameter is shifted to approximately 1000 Å; an increase of a factor of 10. A considerable increase in pore volume is also observed with heat treatment temperature. Composition may be a secondary effect as micrographs indicate variations in the degree of porosity, assuming that there are no confounding effects of HGM diameter and wall thickness. Heat treatment *time* (8 – 24 hours) has been found to have no effect on porosity. Micrographs suggest that the change in the degree of porosity is minimal as heat treatment time is increased. There results are confirmed by mercury porosimetry measurements; there is no shift in pore diameter and very little (if any) increase in pore volume.

We have successfully shown that we have the capability to control pore size of PWHGMs through heat treatment temperature and potentially composition in order to meet end – user needs. The ability to produce a PWHGM with a controlled pore size and/or pore size distribution would ultimately be a key characteristic to tailor the product for specific applications. Other key physical attributes for PWHGMs that could be play a significant role in defining specific applications include strength of the porous shell as well as wall thickness. Applications of these types of systems could range from hydrogen storage, molecular sieves, drug and bioactive delivery systems, to environmental, as well as chemical and biological indicators, relevant to Energy, Environmental Processing and Homeland Security fields.

Systematic Evaluation of Hydrogen Production by Diverse Cyanobacteria

C. M. Yeager, C. E. Bagwell, C. E. Milliken, P. A, Berseth, L. Staples, H. T. Sessions, Jr.

Objective: The aim of this project is to develop a robust, systematic method of comparing and evaluating the H_2-producing potential of diverse cyanobacteria and green algae.

Hydrogen energy development is one of DOE's top priorities, and developing an economically and environmentally sound H_2 production process is an important part of the Department's vision. Biological H_2 production by cyanobacteria or green algae is a highly attractive option in that it represents a renewable resource requiring only water, sunlight, air, and trace mineral salts. This process does not use or produce hazardous materials, is considered a carbon-neutral or –negative process, and could be coupled to the production of other commodities.

Most research efforts aimed at understanding and producing biohydrogen directly from sunlight have focused on developing operational, hydrogen producing bioreactors or conducting detailed molecular analysis of genes and proteins from several model organisms that were isolated decades ago. However, based on an extensive literature search and the recommendations of several recent DOE- and DOD-sponsored expert review panels it is obvious that an important element of the research continuum from genes to H_2-producing bioreactors has been largely overlooked - the physiology and diversity of naturally occurring, H_2-producing phototrophs**.** It is astonishing that our knowledge of photobiological H_2 production comes from just a handful of strains, when it is obvious that many thousands, or even millions, of species possessing this ability exist in nature. From a biotechnological perspective, it makes sense to explore (and potentially harness) the untapped diversity of H_2-producing capabilities that have been naturally evolving for billions of years. Such research will lead to a much improved understanding of the molecular biology, biochemistry, and physiology of biological H_2 production, and there is a strong expectation that it will reveal novel microorganisms with the capacity for continuous, highly efficient H_2 production.

The overall goal of our research was to develop and apply a systematic approach for evaluating the H_2-producing characteristics of diverse phototrophic microorganisms. Specifically we wished to: 1) develop a means to quickly screen H_2 producing potential among diverse phototrophic microorganisms, 2) compare physiological traits that control H_2 production among diverse heterocystous cyanobacteria, and 3) establish benchmark activities/phenotypes against which to routinely evaluate newly discovered H_2 producing microbes.

A systematic method of preparing cyanobacterial cells for H_2 evolution assays was established. Cyanobacteria were cultured in Roux flasks (2L) containing BG11$^-$ media bubbled rapidly with air under a light/dark photocycle (16:8). To assay biological hydrogen production we have developed an effective H_2 analysis platform consisting of: a dual GC system to simultaneously measure H_2, O_2, N_2, CO_2, and C_2H_4 (ppm), an O_2/H_2 electrode to provide instantaneous rates of H_2 or O_2 evolution/uptake, and a 80 channel Micro Oxymax respirometer capable of auto-analyzing H_2, O_2, and CO_2 concentrations during week- to month-long experiments.

Finally, in collaboration with Garriet Smith (USC-Aiken) and The Economic Development Partnership for Aiken & Edgefield Counties we are developing a colorimetric, high throughput method to quickly screen H_2 producing potential among other diverse microorganisms. The color indicator consists of Wilkinson's catalyst and a redox sensitive dye, such as methylene blue, crystal violet, neutral red, or methyl orange. Currently, we are adapting the method to screen bacterial H_2 production in 96-well plates.

Using this platform we have identified several key physiological parameters that control H_2 production in heterocystous cyanobacteria. N_2 severely inhibited H_2 production in all strains tested (at just 5% N_2 atm, the rate of H_2 production was inhibited 50%). The effect of N_2 on H_2 production was quite similar across a phylogenetically diverse collection of heterocystous cyanobacteria. From this data we have established a baseline from which to evaluate the "N_2 sensitivity" of H_2 producing, heterocystous cyanobacteria. Our results also highlight that it is critical to optimize reductant availability during the H_2 production assays. Addition of sugars may be useful for many strains. Finally, we find that although nitrogenase is sensitive to O_2, low levels of O_2 are required for metabolism of reduced hydrocarbons (sugars, organic acids, etc.) in order to generate sufficient electrons and/or ATP to drive H_2 production.

The physiological and culturing data obtained in this project will be helpful in advancing the development of H_2 photobiological production systems. Additionally, we believe that the experimental approach outlined in this proposal will provide us, or others, an excellent opportunity to identify photosynthetic microorganisms that exhibit superior H_2-producing characteristics.

Advanced Titanates and Applications for Their Use

D. T. Hobbs, K. B. Martin, L. N. Oji

Objective: This research seeks to explore new applications and novel deployment platforms for titanate-based adsorbents.

A number of titanium-based materials, such as monosodium titanate (MST) and crystalline silicotitanate (CST) have been found to be excellent sorbents for radioactive components found in the high level wastes produced from the production of nuclear materials for national defense. A new family of amorphous peroxotitanate (APT) materials has recently been reported that increased removal kinetics and enhanced selectivity. The use of these titanate-based materials in other applications has been scarcely studied. Thus, this project sought to explore new applications for the titanate-based materials with an emphasis on the MST and APT materials.

In general, the titanate-based materials feature very fine particle size (<20 μm). The very fine particulates produce very compact beds and very high pressure drops when used in a column configuration. Thus, we also sought to develop novel platforms for the deployment of these materials in continuous type processes.

Our research studies found that the MST and APT materials exhibit high affinity for the adsorption of a variety of metals under acidic and neutral pH conditions. For example, MST and APT samples removed more than 90% of the chromium, niobium, molybdenum, tin, vanadium, zirconium, aluminum, lanthanum, copper, lead and silicon from a pH 3 aqueous solution containing approximately 100 mg/L of each of 20 different metals. These results indicate that these materials exhibit high affinity for the adsorption of a remarkable range of metals including metals with high oxidation states. Single metal adsorption experiments revealed similar capacities for MST and APT materials for chromium, mercury, tin, copper and gadolinium. The measured capacities approached the theoretical ion exchange capacity for the titanates.

These findings, which we reported at the 234th National Meeting of the American Chemical Society, suggest that the titanates are attractive adsorbents for the removal and/or recovery of metals from a variety of industrial waste waters. For example, these materials could be used to remove hazardous metals such as chromium and lead from wastewaters or recover copper from spent plating baths.

The studies also showed that these materials have high affinity for a variety of metals in water at near neutral pH and in a phosphate buffer saline (PBS) solution that serves as a surrogate for physiological systems. Metals that were strongly adsorbed included gold, platinum, palladium, mercury and cadmium. These results suggest that these materials could serve to remove a variety of metals from biological systems to reduce the toxic effects of high concentrations of metals.

In addition to adsorption, we discovered that the metal-loaded titanates appear to release metals as well, which may lead to the use of these materials to deliver therapeutic metals or metals that are used in imaging techniques. Testing at the Medical College of Georgia established that MST and APT do not exhibit toxicity to monocyte and fibroblast cell lines. However, gold-loaded MST and APT materials inhibit monocyte and fibroblast cell activity establishing the possibility of using these materials to deliver therapeutic metals in biological systems. Several other metal-loaded titanates have been prepared and are currently being tested for biological activity. The synthesis and cytotoxicity of the unloaded and metal-loaded MST and APT materials has appeared recently in two papers published in the Journal of Biomaterials Research, with a third publication under review.

Deployment of the titanate-based materials in metal separation applications such as wastewater treatment would be particularly attractive if the materials could be incorporated into porous membranes. The waste solutions could then be easily passed through the membranes and contact the sorption media to remove the dissolved metals. During this project we demonstrated the incorporation of MST and CST materials into three different membrane frameworks, cellulose, polyethylene (PE) and polytetrafluoroethylene (PTFE).

The PE and PTFE membranes were prepared by our industrial collaborators, Porex and 3M using their respective proprietary technology. SRNL supplied samples of the CST and MST materials of the desired particle sizes to Porex and 3M. The membranes successfully removed more than 90% of the cesium and strontium present in aqueous solutions in a simple single pass filter mode.

Given these promising results, we then had the Porex and 3M membrane sheets incorporated into filter cartridges. Filter cartridges are commonly used in both small and large wastewater treatment and recovery applications. Currently we are pursuing additional funding to evaluate the performance of the filter cartridges to remove metal ions from acidic, neutral and alkaline waste solutions.

DNA-Based Artificial Nose Biological Agent Sensor

S. McWhorter, J. Geathers, R.J. Lascola, C.E. Milliken and R.L. Brigmon

Objective: Events surrounding the attacks of 9-11 have led to increased efforts to prepare the US against potential biological terrorism, including the use of agents that may be of unknown or recombinant microbiological threat. These agents also underscore the need for new technologies to selectively sense a broad array of trace levels of microbes and toxins. Researchers at the Savannah River National Laboratory, along with Cogniscent Inc., have been studying a novel DNA detection technology which consists of single-stranded oligonucleotides, with lengths of tens of nucleotide bases, which exhibit different cross-reactive affinities towards defined recognition targets (i.e., flexible but selective). These DNA sequences are created from random (non-specific) sequences of about 20 nucleotides, and then labeled with a fluorescent dye which acts as the transduction mechanism. The advantage of such an approach is the ability to exert rational control over design, development, and deployment of sensing materials that can be uniquely specified, mass produced, have large combinatorial potential, and can be screened using high-throughput methods. This project explores the application of this novel DNA sensor technology to detect and distinguish among several *Bacillus* species, which serve as surrogates for *Bacillus anthracis* (anthrax).

Traditional chemical sensor technology has followed a one-sensor-one-analyte approach, where a single, intentionally specific, sensor is created for each analyte or ligand to be detected. The mammalian olfactory system has evolved a biological sensing system that is dramatically different than the traditional chemical sensor concept, with the ability to selectively discriminate among a broad array of analytes or odors. Sensory neurons 'sense' an odor resulting in an activity pattern from multiple, different responses from many receptor cells to that one odor. The signal from the activated sensory neurons is transmitted to the olfactory bulb which sends the response patterns to higher-level brain regions for recognition and identification. This results in a large population of sensory neurons each responding discriminately to a given odor, creating an odor-specific output pattern. This concept of 'cross-reactivity' among receptors has been explored and described in detail. *We hypothesize that this same cross-reactive behavior could be applied to sense various classes of biological molecules, such as biological threat agents*. This project intends to advance the state of the science in biological sensing by utilizing the novel DNA detection method as a sensor (from CogniScent) coupled with highly sensitive laser induced fluorescence detection to detect biological agents, while being adaptable to agents of unknown or recombinant microbiological threat.

The DNA detection technology consists of single-stranded oligonucleotides with lengths of tens of nucleotide bases which exhibit different cross-reactive affinities towards defined recognition targets (i.e., flexible but selective). Random sequences are generated and labeled with a fluorescent dye which acts as the transduction mechanism. The inherent advantages of this approach are: 1) DNA acts like other dye labeled polymers giving varying degrees of enhanced response to different analyte interactions; 2) there are about 10^{12} different sequences in all possible 20mers – very large degrees of freedom; and 3) standard biotechnology exists to test millions of DNA strands in the same time it currently takes to test one non-DNA polymer (i.e., very fast throughput).

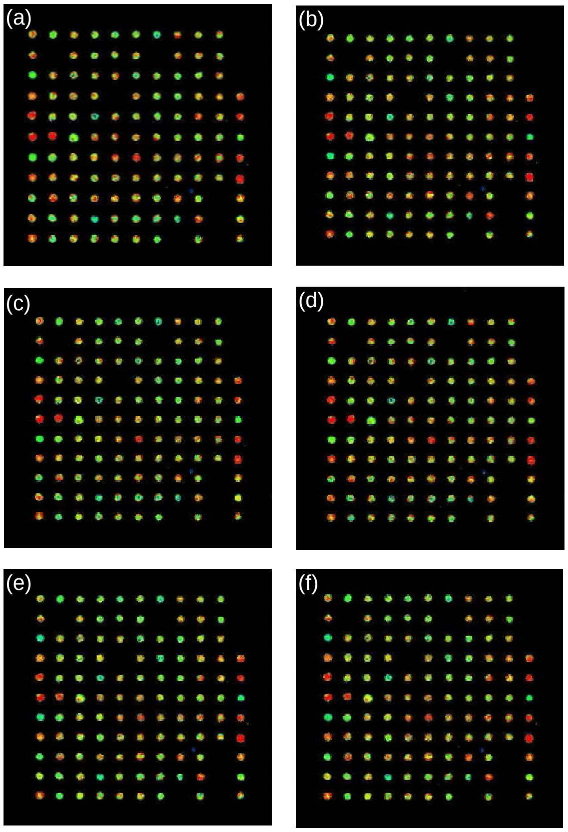
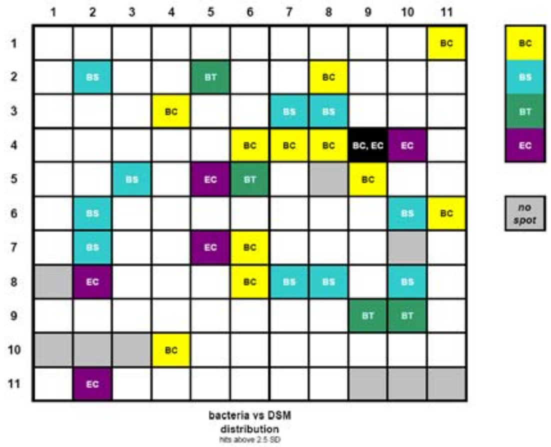


Figure 1 - Response pattern generated from high throughput confocal fluorescence screening of DNA gas sensors to (a) air, (b) phosphate-buffered saline, *(c) E. coli, (d) B. subtilis*, (e) *B. cereus* (f) *B. thuringiensis*.

We demonstrated "proof-of-concept" of this novel technology for bacterial detection by exposing the arrays of fluorescent labeled DNA sequences to volatile metabolites produced by *Bacillus* species and *Escherichia coli* while scanning under an automated confocal fluorescent microscope. Typical fluorescent images of one subarray from different bacteria are shown in Figure 1. Analysis of the data generated from these images confirmed that these collection of DNA sequences responded with some level of specificity which would allow predictions to be made using multivariate algorithms. A matrix summary of the array data is shown in Figure 2. A printed array typically consisted of fifteen repeats of 11 x 11 matrices that contained DNA of different sequences and reference points.

Additionally, in order to better understand the reactivity between the DNA and volatile metabolites, thermal desorption GC-MS studies were performed on the *Bacillus* species. The results (not shown) from those studies verified that each Bacillus species produced a collection of specific volatile metabolites which supports the premise of bacterial speciation based on gas detection.



	1	2	3	4	5	6	7	8	9	10	11
1											BC
2		BS			BT			BC			
3				BC			BS	BS			
4						BC	BC	BC	BC, EC	EC	
5			BS		EC	BT		▨	BC		
6		BS								BS	BC
7		BS			EC	BC				▨	
8	▨	EC				BC	BS	BS		BS	
9									BT	BT	
10	▨	▨	▨	BC							
11		EC							▨	▨	▨

Figure 2 - Analysis of confocal fluorescence screening identifying sequences which demonstrated specificity toward certain bacteria. Each result which showed a change 2.5 σ from the baseline was accepted.

This project demonstrated a unique methodology of using fluorescent-labeled DNA to create hundreds of reactive gas sensing elements. The sensors showed a multivariate response towards different species of bacteria which could lead to a useful tool in the identification and detection of weapons of mass destruction. Furthermore, this technology could potentially be applied to breath analysis for the diagnosis, prevention and cure of infectious diseases caused by pathogenic bacteria. While this technology shows promise, further development is needed before prototype development.

Detection of Viral-Size Particles and Nanomaterials in Aerosols as Surrogates for Biological and Chemical Weapons

R. L. Brigmon, C. E. Milliken, D. I. Kaplan, and B. B. Anderson

Objective: The purpose of this work was to develop technologies for improved collection, monitoring, and testing of aerosols for potential biological and chemical agents. In this project we tested the Air-to-Liquid Particle Extraction System (ALPES), an aerosol sampling device, for use as a biological weapon (BW) collector. The ALPES collects airborne particles into continually recirculating liquid medium. The ALPES was initially developed for rapid field analysis of aerosolized radionuclides by collecting and concentrating airborne particles through electrochemical separation. Here we extend this application for BW collection.

This first task of the project was to evaluate the effectiveness of commercially available nanomaterials, QDOTs (Molecular Probes) to serve as surrogate virus particles. Results proved that QDOTS in the >100nm range could be detected fluorometrically in phosphate buffered saline (PBS) when used for biocollection collection (Figure 1).

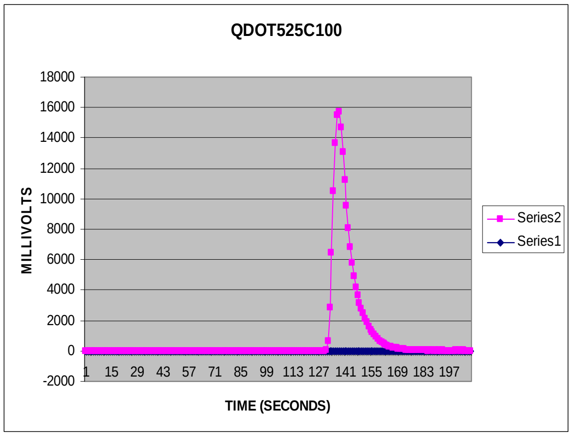


Figure 1 - Fluorometric detection of two types of QDOTS, 525 nm, diluted 100X in PBS.

The next task was to examine surrogate biological weapons (BW) WMD detection with the ALPES. Microbial viability and cell integrity is important for subsequent detection of biologicals after collection. Cell viability was tested using *Bacillus subtilis* (BS), a simulant for *B. anthracis*, the etiological agent of anthrax. Two ALPES units were tested and operated with the system charged "on", for electrostatic collection and off. Results demonstrated that viability decreased rapidly after *B. subtilis* cells were circulated in the ALPES for 20 min. The decrease in viability was greater with the systems charged or 'on" than "off. Spores were prepared from *B. subtilis, B. thuringiensis* (BT), and *B. cereus* (BC) and circulated in the ALPES 60 min. The charged system showed a decrease of 10% in spore viability in two hr for BS & BT.

After several engineering and system modifications to improve the safety and efficient operation of the ALPES, environmental testing began using outside air. Initial results from ALPES showed microbial collection (Figure 2) efficiency was not different for ALPES standpipe & wire powered vs power off (only fan and pump operating) with initially polarity of (+) charged standpipe & (-) charged wire.

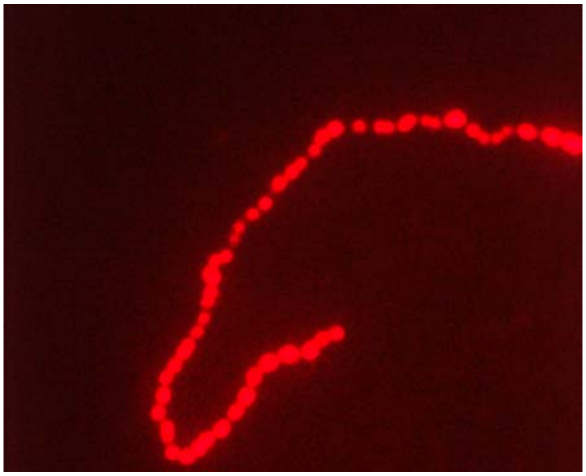


Figure 2 - Fungal filament observed in ALPES collection fluid from experiment (E35-Table 2).

Microbial collection efficiency improved with changing polarity to (-) charged standpipe & (+) charged wire. There was no change in viable cell collection efficiencies with altering charges. There was high spore viability and low cell viability after additions to the ALPES. Reversing polarity had no effect on microbial viability. Ozone is generated in the ALPES at biocidal levels (1-3 ppm) rendering cells nonviable. However, cells collected by the ALPES were still intact and quantifiable by microscopy (Figure2). ALPES collection efficiency was compared to an Andersen Sampler, an aerosol collection/detection system recommended by the US Center for Disease Control. The improved ALPES collected more total cells per unit time (10^5-10^5 cells per cubic foot of air sampled) compared to the Andersen Sampler (10^2-10^3 cells per cubic foot of air sampled) (Table 1). Improved (two-fold) ALPES collection efficiency was demonstrated at lower fan speeds.

Table 1 - Results w/ALPES 1 fully operational & ALPES 2 w/fan & pump only.

EXP	ALPES	Andersen Cells[*]	ALPES Cells**
e25	1	22	605
e25	2		298
e26	1	42	95
e26	2		92
e27	1	24	157
e27	2		126

e28	1	12	6
e28	2		18
e30	1	4	108
e30	2		63
e31	1	22	91
e31	2		190
Change Polarity			
E34	1	25	617
E34	2		261
E35	1	18	1067
E35	2		554
E36	1	43	554
E36	2		282
E37	1	10	586
E37	2		254

EXP=Experiment #
ALPES 1 Unit #
ALPES 2 Unit #
*AndersonCells=Mean Number of Viable Microorganisms per Cubic Foot of Air Sampled
**ALPES Cells =Total Number of Microorganisms per Cubic Foot of Air Sampled

A small (>1 m^3) test chamber was constructed for bioaerosol testing with the ALPES (Figure 3). This chamber was constructed with plexiglass lined with non-conductive material to reduce particle attachment to the surface. Special HEPA filters were built to assure no particles (>.2 µm) would escape from test aerosols generated within the chamber. Two types of particle generators were purchased for the project. One is a sonicator type system (Model 241PG SONAER, Inc) designed to convert low viscosity liquids into fine particles. A nebulizer was also obtained (TSI Model 3076) that can generate small particles suspended in a fine mist (< 1 µm diameter). In addition an aerosol dryer and particle counter (TSI) were also purchased for the bioaerosol testing.

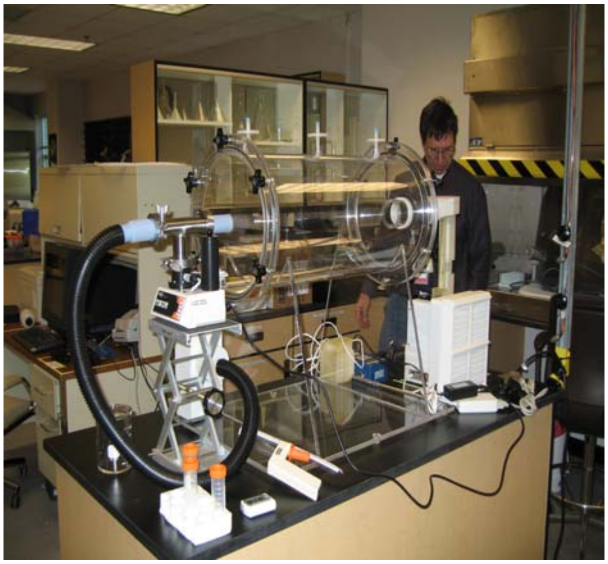


Figure 3 - Aerosol Testing Chamber with ALPES and nebulizer assembled for bioaerosol testing

Plans have been made for testing the improved ALPES in the SRNL wind tunnel. The results of this LDRD project improved the ALPES technology, made it easier and safer to operate, and demonstrated its wide-ranging capabilities. With further testing and operational modifications the improved ALPES could be useful to the DHS or DOD as a biocollection device.

Development of Nano-Scale, High-Efficiency Proportional Counters

S. Serkiz, J. Cordaro, and S. McWhorter - SRNL   L. Pruitt, T. DeVol, A. Rao - Clemson

Objective: A prototype gas proportional counter based on micro- and nano-scale electrodes was built and tested. Electrodes of controlled size were fabricated on the micro-scale from tungsten and carbon fibers and at the nano-scale of single and arrays of carbon nanotubes (CNTs).

At the micro-scale there is a systematic correlation between anode size and the voltage required to get into the proportional region. There appears to be an effect of anode material on the PC performance, with the 11 µm carbon fiber displaying proportional counting behavior at a lower voltage than the corresponding W wire.

On the nano-scale data from single CNT anodes are suggestive of a proportional counting response at about 2 and 35 volts followed by loss of the CNT from the anode. To overcome the problems of low effective volume and loss of the CNT from the anode, we have begun testing arrays of CNTs as an anode.

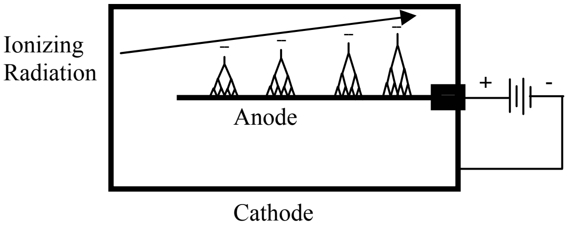
Research Objectives: This research (i.e., "proof-of-concept") was designed to utilize the unique properties of CNTs to develop a prototype low-voltage nano-scale gas proportional counter (*n*-PC) for application in gamma and neutron radiation.

Potential advantages of PC miniaturization include: increased counting sensitivity; lower operating voltages; reduced platform size; and directional radiation detection.

Background: Proportional counters have long been used in a sealed configuration to detect penetrating radiation (gamma rays or neutrons) and in a flow-through configuration to detect beta radiation (e.g., tritium). With conventional PC operations (i.e., anodes on the millimeter to tenths of millimeter scale), electrical potentials in the 1-2 kilovolt range are required to obtain electrical fields high enough to get into the proportional counting region. In contrast, a *n*-PC could theoretically operate at 3.5 volts and have the same electric field strength at the surface of the anode. In this region, gas multiplication to amplify the charge from the ion pair created by ionizing radiation in the gas phase created by the large electric field (see Figure 1).

Experimental: The general experimental approach in this work was to fabricate micro- and nano-scale anodes and evaluate these anodes in a prototype PC.

Figure 1 - Proportional Counter Schematic



Anodes of controlled sizes were fabricated from carbon graphene structures and tungsten metal to evaluate the influences of both anode size and material on PC performance. Carbon anodes were constructed from an 11 micron diameter carbon fiber (Figure 2A), a series of single carbon nanotubes (Figure 2B), and arrays of CNTs (Figure 3). The carbon fiber was commercially available and the CNTs, both single and arrays, were made by chemical vapor deposition techniques. The single CNT was attached to an electrochemically etched tungsten (W) wire. A series of controlled diameter (500 to 5 micron) W-wire anodes were also prepared by the electrochemical oxidation.

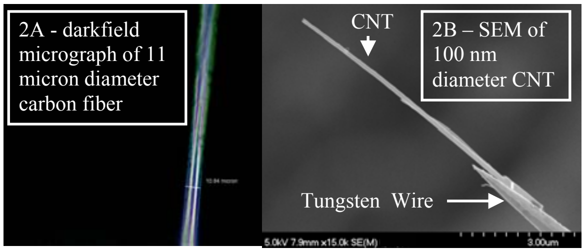


Figure 2 – Micrographs of (A) Carbon Fiber; and (B) Attached Single CNT Electrodes.

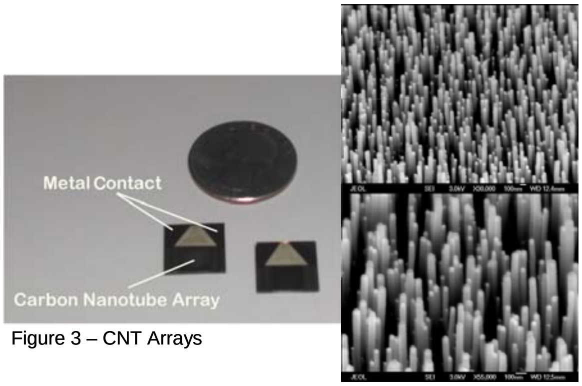


Figure 3 – CNT Arrays

A prototype PC was built from standard high-vacuum components (Figure 4). Fabricated anodes were attached to the electrical pass-through in the prototype PC (flange in center of Figure 4) using silver paint or conductive Epoxy™. During operation, the PC is filled with P-10 gas (Ar-90%, CH_4-10%) and exposed to a Cs-137 gamma-ray source (either 15µC_i or 5 mC_i). The current and peak height of signal was measured as the potential between the two electrodes was swept. For the micro-scale anodes, after the initial measurement the anode was removed, the PC refilled with P-10 gas, and the response of the PC measured again. For the nano-scale anodes, the integrity of the anode was evaluated by imaging the anode on the dark-field microscope.

Figure 4 – Disassembled Prototype PC

Results: The results for proportional counting on micro-scale anodes are summarized in Fig. 5. Within the W-wire anode tests there is a systematic correlation between anode size and the voltage required to get into the proportional region (i.e., sharp upturn in pulse height with increasing voltage). There appears to be an effect of anode material on the PC performance, with the 11 µm carbon fiber displaying proportional counting behavior at a lower voltage than the corresponding W wire. This behavior could be due to increased surface roughness of the W wires relative to the carbon fiber anode, but further experiments are necessary to elucidate mechanism behind the observed behavior. The detection efficiency is approximately 50 counts per second (data not shown) and is similar for all micro-scale anodes.

The nano-scale anode responses for single CNT anodes (see Figure 2B) are summarized in Figure 6. In contrast to the micro-scale anodes the detection efficiency is on the order of 0.2 counts per second (data not shown) for nano-scale single CNT anodes. This is not surprising given the small effect volume of this anode. For all the single CNT anodes there was no CNT when the anode was imaged in the dark-field microscope after testing. Given this result, the data in Figure 6 are suggestive of a proportional counting response at about 2 volts for CNT2 and 35 volts for CNT1 followed by loss of the CNT from the anode. To overcome the problems of low effective volume and loss of the CNT from the anode, we have begun testing arrays of CNTs as an anode.

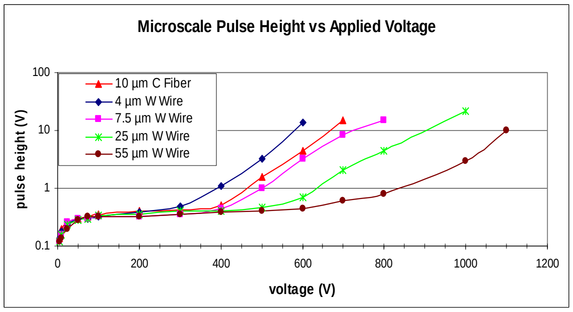


Figure 5 – Micro-Scale Anode PC Response.

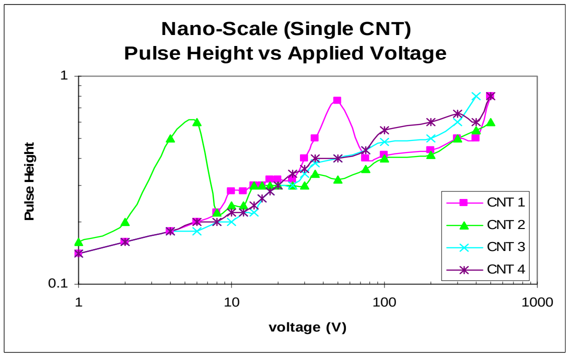


Figure 6 – Nano-Scale Single CNT Anode PC Response

Path Forward: Landon Pruitt, Master's student at Clemson University, will continue testing of nano-scale anodes as a part of his Thesis work. Anodes have been fabricated of CNTs with different separation distances to examine the separation required for the anode to exhibit nano-scale behavior. Mathematical modeling to optimize anode design is also part of his work.

A proposal has been submitted to the PDRD program for tritium detection in a flow-through configuration and is awaiting approval of the Federal Budget for funding to be released.

An invention disclose submitted on the subject concept will be updated with the most recent data.

Project Summaries Quick Hits

Radiotracer Method for Measuring Hydraulic Conductivity of Cementious Materials

C. A. Langton, D. H. Taylor, D. P. Diprete

Objective: This research aims to demonstrate the proof of principle for methodology to measure hydraulic conductivity using radioactive tracers. A method is needed to track the movement of water, gas, and contaminants through cementitious barriers used for the disposal of radioactive waste. The results will contribute to an understanding of transport phenomena through cementitious materials and in particular will provide data for cementitious engineered barriers (waste forms, vaults).

Quantification of water, gas, and radioactive contaminant transport through cementitious barriers is needed to support disposal low level radioactive waste. Hydraulic property data for water and radioactive contaminants is required for modeling Performance Assessments of low level waste engineered disposal systems.

A method was developed to measure hydraulic properties by spiking solutions with beta and gamma emitting radiotracers (tritium and sodium-22).

A mold was designed and fabricated with a series of sampling ports distributed horizontally and radially. This allowed sampling access in a monolithic cylinder without disruption of the as-cast microstructure. The method allows for measuring water, gas, and dissolved radio tracers under expected environmental pressures.

The method enables tracking both linear velocity and mass transport through the matrix. It also allows the comparison of the relative mobility and binding capacity of a range of both cationic and anionic radionuclides. A single sample can be used to obtain saturated and unsaturated permeability and to compare transport of several ions sequentially or in combination.

In FY2007 the sample holder was fabricated and initial testing was testing on a relatively porous cement-fly ash sample. Initial results confirm that Darcy flow (i.e. through the bulk matrix) is very slow at low pressures representative of environmental conditions. The unique spatial distribution of the sampling ports, confirmed that when measureable flow was achieved it was through cracks which appeared to open as a result of pressures less than 5 psi.

Current work is continuing to monitor the response of flow as a function of pressure and time. The method shows promise of being able to correlate crack formation and propagation as a function of pressure. It will also allow study of ionic transport in intact and cracked samples. Having demonstrated proof of principle, we are prepared to proceed with radiotracer work.

As a result of testing to date second generation molds were designed and fabricated for use with other cement formulations.

In Situ Generation of Oxygen Releasing Metal Peroxides

M. E. Denham, M. R. Millings

Objective: The goal of this research is to conduct laboratory experiments to test the hypothesis that in situ generation of solid metal peroxides during a subsurface injection of Fenton's Reagent caused an extended period of elevated dissolved oxygen in the groundwater.

In 1997 a field demonstration was conducted that injected Fenton's Reagent, a highly oxidized solution that produces hydroxyl radicals, into the subsurface to destroy non-aqueous phase solvents. The treatment zone was estimated to be approximately 20 meters in diameter. Reaction in the treatment zone was vigorous and a significant amount of solvent was destroyed.

In monitoring the site after injection, very high concentrations of dissolved oxygen were observed in the groundwater for an extended period of time. One year after the injection dissolved oxygen concentrations remained up to 4 times saturation with atmospheric oxygen. The concentrations decreased with time, but remained elevated relative to equilibrium with atmosphere for at least 3 years. Sulfate which was also initially elevated had long since returned to background concentrations because of the influx of untreated "fresh" water. Two possibilities could explain these observations – 1) the Fenton's injection left a large volume of gaseous oxygen in the pore space of the aquifer, or 2) the injection induced solid peroxides of natural metals to precipitate that slowly degraded releasing dissolved oxygen. Simple groundwater modeling suggested that much of the pore space in the aquifer would have to have been filled with gaseous oxygen for the elevated dissolved oxygen concentrations to remain high for 3 years. The second possibility, that solid natural metal peroxides were precipitated is thermodynamically favorable under the conditions of the Fenton's injection.

This is important because a method of producing a long-lasting source of oxygen in the subsurface would be valuable to groundwater remediation involving aerobic microbial processes or oxidation of metals. We received a U.S. patent (# 7,160,471 – "In situ generation of oxygen releasing metal peroxides") based on the field work.

For the current LDRD project, laboratory experiments were conducted as a first phase of testing the hypothesis that precipitation of solid metal peroxides was responsible for the prolonged elevated dissolved oxygen concentrations in the field. In the first set of experiments, hydroxyl radical generating solutions were reacted with a solution saturated with gypsum ($CaSO_4 \cdot 2H_2O$). The three solutions were Fenton's Reagent, sodium persulfate + ferrous sulfate, and hydrogen peroxide + ozone. Gypsum was added to provide calcium to promote precipitation of calcium peroxide. The second set of experiments reacted Fenton's Reagent with unamended soil and soil amended with gypsum. In both sets the reacted solutions were filtered to remove any potential solid peroxide and the filters were dried. Duplicates were done for the first set. One filter was re-hydrated and the solution measured for dissolved oxygen. Values that were greater than expected for equilibrium with atmosphere would indicate the presence of solid peroxides. The other filter was examined by scanning electron microscopy (SEM) with energy dispersive spectroscopy to look for calcium peroxide crystals. For the second set of experiments re-hydration of the filters was done, but no SEM analyses were performed.

None of the re-hydrated filters exhibited elevated dissolved oxygen concentrations. Likewise, no evidence of solid peroxides was observed during the SEM analysis of filters. Thus, we conclude that no solid peroxides precipitated during the tests or the amount that precipitated was insufficient to detect with the methods we were using.

In the third experiment calcium peroxide was dissolved in water to determine how much would have to precipitate in our experiments to be detectable by the filter re-hydration method. The results suggest that about 10% of the primary reactants would have had to produce hydroxyl radicals to observe a significant change in dissolved oxygen concentration due to calcium peroxide precipitation. Thus, it is possible that the mass of reactants used in the experiments was not enough to produce a sufficient mass of calcium peroxide to be detected by the re-hydration method.

These tests do not disprove the hypothesis that solid peroxides were precipitated during the field injection test. Several things could explain the lack of observed solid peroxides in the laboratory experiments. We may not have produced a mass sufficient to detect by filter re-hydration or SEM. Likewise, conditions other than the presence of the reagents may be important to solid peroxide precipitation. The field experiment produced significant heat, increasing temperature, which may be important. There was also an organic phase present during the field experiments that was not present in the lab experiments.

Feasibility of Perflourinated Liquids as a Collection Media for Biodetection

M. T. Kingsley, S. A. Chapman, P. C. McKinsey, Steven Walter, and M. A. Heitkamp

Objective: The goal of this investigation was to investigate alternative collection medium for microbial sampling, transport and preservation. Three perfluorinated liquids (PFCs) immiscible with water and 3 water-miscible PFCs, but having a low vapor pressure, were evaluated for use as culture preservatives for use in microbial samples. The PFCs did not affect microbial viability of the Gram negative test organism *E. coli* or the Gram positive test organism *Micrococcus luteus*. However, Bis(2-methoxyethyl)Ether (Diglyme), 2-(2-Ethoxyethoxy)-Ethanol (Carbitol), and 2-(2-methoxyethoxy)-Ethanol, 99% (Methyl Carbitol) were cytotoxic to the test organisms, although at a 10% vol/vol solution viable cells were still recovered. The further testing of FC40 as a collection medium for microbial cells when impregnated onto swabs and swipes is promising, but remains to be conducted. The immiscible PFCs encapsulate the microbial cells and protect them from desiccation.

A strong need exists for liquid-based biocollection technologies that preserve the viability of collected microorganisms and the integrity of their nucleic acid signatures. Current dry particle collectors do not maintain viability of collected vegetative microbes. SRNL particle collection device, such as the Aerosol-to-Liquid Particle Extraction System (ALPES) provide a liquid-based particle collection platform that may be optimized for vegetative cell biocollection. Although aqueous media preserve viability of microorganisms better than dry particle collectors, there is still a chance for secondary microbial growth or loss during long intervals of operation or at remote locations where refrigeration of collected samples is problematic. Therefore, it is desirable to investigate alternative, non-aqueous liquid collection media for bioaerosol collection. Additionally, aqueous collection media can affect the viability of environmentally stressed vegetative cells. Based on literature review, recent participation in a Biodetection Workshop (October 2006) and our knowledge of this field - we are unaware of any other laboratories or researchers that are pursuing this approach. In addition to their potential use in liquid bioaersol collection platforms these fluids may also have utility for incorporation into surface sampling swabs and swipes.

We tested three commercially available perfluorinated liquids (3M compounds FC40, FC70 & FC72) in microbial spiking and recovery experiments to determine their suitability as collection and preservation media for microbial sampling. We tested the PFCs with Gram negative and Gram positive (*Escherchia coli*, *Micrococcus luteus*, respectively) test organisms. The cultures were grown overnight, spun down and resuspended in sterile saline and the cotton and foam tipped swabs were impregnated with the saline cultures and incubated with the PFC solutions at 21C and 37C for variable periods of time. Samples were taken and plated relative to a control of cells spiked into sterile saline. FC40 is reported to carry oxygen and has been employed in perfusion as an artificial blood compound. However, to provide this function in rodents or other subjects these solutions needed to be emulsified, they are extremely hydrophobic. This property presents problems when working with aqueous cultures as the phases do not mix. This allowed swabs saturated with the test organisms to essentially be "sealed" into/onto the swab by the phase boundary between the saline suspended cells (trapped in the swab) and the PFC. To be evaluated at a future date would be swabs impregnated with the PFCs and used for surface sampling. We did not test a broad range of cell concentrations; we employed ca. 10^6 cfu/ml.

During the course of this short study the higher vapor pressures of the PFCs were deemed to make them potentially unsuitable for certain sampling and preservation situations such as in extreme environments (long transport times at elevated temperatures). Therefore a search of chemicals with low vapor pressures, that were non-toxic and miscible with water yielded three candidate solutions for evaluation: Bis(2-methoxyethyl)Ether (Diglyme), 2-(2-Ethoxyethoxy)-Ethanol (Carbitol), and 2-(2-methoxyethoxy)-Ethanol, 99% (Methyl Carbitol). The vapor pressures of these three solutions are low and would potentially allow there use in elevated temperatures without significant losses from evaporation. However, these solutions proved to be highly cytotoxic. Viable *E. coli* and *M. luteus* cells spiked directly into the solutions and incubated overnight at 37C could not be recovered 24 hours later. Only after the concentrations of diglyme, carbitol and methyl cartitol were reduced to 10% vol/vol with sterile saline did we begin to observe and recover viable cells after 24hrs. However, we only obtained about a 25% viable recovery of the bacterial inoculum. We deem these three aqueously miscible solutions would not make good candidates for use in either our bioaersol collectors or for impregnating swabs due to their cytotoxic nature. In summary, our wide-ranging proof-of-concept studies have demonstrated microbial preservation in non-aqueous medium and have identified FC40 as a promising choice for further exploitation for impregnating into swabs and swipes for microbial sampling and stabilization.

Neutron-Capture-Induced Radiation of Polymers

E. N. Hoffman, T. L. White, F. Fondeur, T. E. Skidmore, M. Lee, D. Robertson**

Objective: This research investigates altering the structure and properties of boron-containing polymers through neutron irradiation. The results will provide a treatment method for improving the mechanical properties, wear resistance, radiation resistance, chemical stability, thermal, electrical, optical and gas permeation resistance properties of selected polymers.

Improvements on the service life of polymers will reduce the costs, time, and risks associated with component replacement. This is particularly true for materials in critical applications such as nuclear service, energy production/delivery systems and communication systems. The end-use properties of polymers are strongly influenced by many factors including structure, molecular weight, molecular weight distribution, percent crystallinity and the degree of cross-linking. Studies have shown that controlled increases in the crosslink density in polymers can be achieved by several methods including chemical modifications, X-rays, and electron beam and gamma radiation. Although these methods can be effective, these processes often have undesirable side effects such as degradation or oxidation. Post-irradiation oxidation effects are likely to occur, particularly in materials exposed at very high dose rates. Subsequent diffusion of oxidation into the irradiated polymer allows the formation and reaction of free radical groups which lead to further degradation. Recent methods have found enhanced surface properties when polymers were cross-linked using light ion implantation methods, in which ions are injected from an external source into the surface of polymers. Light ions, which have energies on the order of 0.1-1 MeV, produce a sufficient linear energy transfer (LET) to induce cross-linking by breaking C-H bonds, as opposed to electrons or photons, which can lead to chain scission. Hydrogen recombines as hydrogen gas, and the free radicals of adjacent polymer chains combine to form C-C bonds. Bond breakage and reformation lead to highly cross-linked polymers.

The modification of only the surface properties of polymers is a limitation of the ion implantation approach. Though surface enhancement is desirable for many applications, once this layer is degraded or removed, the underlying bulk polymer does not have the same level of improved properties.

This project examined the transformation of polymer properties beyond the surface and into the bulk of the material using neutron capture approach over a 3 month time frame in FY 2007. The underlying principle involves the collision between a neutron and boron atom which yields an alpha particle and ^{7}Li. This prompt reaction results in 2.79 MeV energy release. The resulting ^{7}Li and alpha are ionized as they travel within the polymer and eventually are slowed to a stop by electronic and nuclear stopping within the material. Neutrons can easily penetrate the polymeric material, reacting with the boron atoms throughout the bulk. Therefore, with a large enough concentration of boron throughout the bulk polymer structure, electronic stopping will facilitate cross-linking.

In this study, boron was introduced into the polymers using the three boron-containing compounds: o-carborane, isoprenyl-o-carborane, and n-hexyl-o-carborane. The polymers were formed by mixing either polystyrene or poly(methyl methacrylate) with the boron agents, adding azobisisobutyronitrile (AIBN), and heating to 80°C for several hours. Polymerization process took place in either small glass vials or in 15 ml polyethylene tubes. The material formed was then removed by breaking the glass vials or slicing the mass synthesized in the polyethylene tubes. Eight different types of samples were produced with either 0 or 20% boron by weight.

Baseline (no boron) and boron-containing polymer samples were irradiated for seven, seventeen, or thirty seven seconds depending on composition in the University of Missouri Research Reactor (MURR) Row-2 pneumatic tube. The thermal flux in this position is approximately 8×10^{13} n /cm^2 s.

Irradiation of the polymer samples resulted in an obvious change in optical properties of the material, transitioning from colorless to yellow or amber in color. These color changes are consistent with self-heating and ionizing radiation exposure. Additionally, samples resulted in an increased opacity as a result of irradiation, typical for an increase in crosslink density and crystallinity.

Samples were characterized using several techniques including energy dispersive spectroscopy (EDS), Fourier transform infrared (FT-IR) spectroscopy using the attenuated total reflection (ATR) method, Raman, and nuclear magnetic resonance (NMR) spectroscopy. No measurable change in chemical surface termination and functional groups between the irradiated and non-irradiated materials was found, suggesting radiation did not induce a significant chemical change in the polymers. An increase in cross-linking confirms the theoretical model suggesting that structural modifications are due to collisions between neutrons and boron atoms.

This work is providing the foundation for development of a new class of modified polymers based on neutron radiation treatment. Additional research is needed to evaluate the effects of neutron irradiation, variable dose rates, post-irradiation oxidation, and long-term aging effects. Specific properties such as mechanical and electrical properties, and chemical stability also need to be determined. Initial results suggest neutron radiation treatment as a method to tailor polymeric structures for endurance in critical applications such as nuclear service and energy production.

Evaluation of Potential Side-Effects of Sequestering Agents Used for In-Situ Remediation of Contaminants

Michael Paller, Anna Knox

Objective: The objective of this project was to determine whether amendments used in active caps for the remediation of contaminated submerged sediments have potentially harmful effects on aquatic organisms. This information will be used to design active caps that prevent the movement of contaminants into aquatic ecosystems while avoiding deleterious effects on sediment dwelling organisms.

Uncontrolled hazardous wastes can result in chemical exposures that directly and indirectly damage aquatic ecosystems and affect human health. A pervasive source of such wastes are contaminated sediments that release recalcitrant chemicals into aquatic food chains contributing to thousands of fish consumption advisories nationwide. It is estimated that contaminated sediments affect nearly 10% of the nation's waterways with potential remediation costs in the billions of dollars. Current remediation technologies for contaminated sediments are largely limited to sediment removal and disposal, monitored natural recovery, and in situ methods such as isolation of the sediments by covering them with inert materials like sand or gravel. The latter approach, referred to as passive capping, can be effective and economical, but the inert materials used in passive caps are subject to leaching and mechanical disturbance that can release toxic contaminants.

In contrast to passive capping, active or reactive capping involves the use of capping materials that react with sediment contaminants to reduce their toxicity or bioavailability. Active capping is a less mature technology that holds great potential for a relatively permanent solution that avoids residual risks resulting from contaminant migration through the cap or breaching of the cap. Recent research shows that amendments such as phosphates, organoclays, and biopolymers have the potential to immobilize contaminants in submerged sediments and prevent contaminant migration into water supplies and human and ecological food chains. However, there are concerns about possible environmental side-effects of these amendments stemming from the presence of impurities that could leach into potable water or directly harm bottom-dwelling organisms. In addition, some amendments may possess physical properties (e.g., texture or particle size) that could indirectly harm aquatic life. The objective of the proposed research is to determine whether several amendments that hold promise for the treatment of contaminated sediments have potentially detrimental side-effects.

The amendments under consideration included apatite, organoclay, and biopolymers such as chitosan, guar gum, and xanthan. Sand, which is commonly used in the construction of more conventional passive caps, was also tested. Sediment toxicity tests were used to assess potentially deleterious effects associated with the application of amendments for the remediation of contaminated sediments. Both freshwater and saltwater sediment toxicity tests were conducted because the amendments under study may be used in both environments. These 10 day tests followed standard EPA protocols and involved the exposure of laboratory cultured *Hyallela* in freshwater and *Leptocheirus* in saltwater. Controls consisted of reference sediments from an uncontaminated natural environment. A standardized food supply was added to each chamber to prevent starvation, and the overlying water was renewed at consistent intervals to maintain water quality.

Sediment toxicity testing began with 100% exposures (i.e., sediments composed entirely of amendment). When 100% exposures resulted in significant mortality of test organisms, the amendment was diluted with different amounts of reference sediment to identify amendment to sediment ratios that were not lethal. The survival of *Hyallela* in the freshwater sediment was depressed in 100% organoclay. Biopolymer coated sand and apatite did not affect survival. Tests of mixtures of organoclay and uncontaminated reference sediment showed that considerable dilution of organoclay was needed to prevent significant mortality in freshwater sediments. Organoclay contains high concentrations of chloride that may raise salinity beyond the tolerance limits of some freshwater organisms. Additional tests are now underway with washed organoclay to evaluate this hypothesis.

Unlike the freshwater tests, salinity in the saltwater tests was unaffected by the addition of organoclay to the sediments. Organoclay was not toxic in the saltwater sediment tests suggesting that this material is unlikely to have deleterious effects in saltwater environments.

A different protocol was used to assess the potential toxicity of leachates from amendments. In these studies, elements were extracted from each amendment using the standardized, EPA approved TCLP leaching procedure, which employs a leaching solution consisting of 0.1*M* glacial acetic acid and 0.0643 *M* NaOH. Metals removed by the TCLP procedure have the potential to be mobilized from soils or sediments and harm aquatic life. Leachates from the TCLP procedure were analyzed for metals by ICP-AES, and the concentrations of the metals were compared with EPA TCLP limits. Metal concentrations in the amendment leachates were well below the TCLP limits.

The results of the laboratory bioassays conducted to date indicate that the potential impact of amendments on benthic organisms must be considered when developing active caps. Organoclay may need to be diluted by mixing with clean sediment, isolated from the sediment surface, or washed before application in freshwater environments. However, it is important to verify the results of laboratory tests with field studies because artificial conditions within the laboratory may fail to accurately represent the environment. Future work will include additional laboratory studies to better understand mechanisms of toxicity and ways to ameliorate it, as well as biological surveys of the organisms that colonize pilot-scale sediment caps composed of promising amendments.

Characterization of Volatile Components in Zircaloy Fuel Hulls

M. L. Crowder, J. E. Laurinat

Objective: This study demonstrates a method to measure tritium content in spent fuel hulls to provide information needed for future processing decisions and designs. *

Zircaloy fuel hulls make up about 25% by mass of the spent nuclear fuel in the United States. Leading treatment options for hulls – recycle and waste alloy processing – require heating, which causes release of tritium and other radioisotopes. Accurate information is needed on the volatile components of the large and growing amount of spent fuel and its zircaloy cladding. This study demonstrated a simple method to evaluate the tritium content of hulls via oxidation of the hull and capture of the volatilized tritium in liquids.

A study by the UK Atomic Energy Research Establishment showed that the linear power ratings of spent fuel elements did not correlate with the tritium content of hulls. A related study found that the total amounts of tritium present in the spent fuel and hull were not in agreement with calculated quantities. Yet, in both studies the zircaloy hulls tested contained from 13 to 24% of the total amount of tritium calculated to be present in the spent fuel. Since tritium content in hulls is significant yet difficult to predict, more characterization data would provide information needed for future processing decisions and project designs.

Past measurements at Hanford and Oak Ridge on the oxidation of zircaloy showed rates that were almost ten times faster than zirconium due to the presence of tin and other impurities in the zircaloy. Experimental data were used to develop an Arrhenius model of zircaloy oxidation, which included an initial, nonlinear rate and a faster, linear rate after "breakaway" of the oxide film. The model predicted an oxidation time of two hours at 1000°C for zircaloy hulls.

The zircaloy hulls used in this study had previously been separated from fuel via dissolution in nitric acid at elevated temperature and pressure. Hull portions were heated in air inside a thermogravimetric analyzer (TGA). The TGA was heated to 1000°C quickly to promote the oxidation and easy capture of tritium. To capture tritium, the TGA off-gas was bubbled through a series of liquid traps containing water, 5% nitric acid/10% hydrogen peroxide or ethylene glycol. The liquids were analyzed by standard counting methods.

The study demonstrated that complete oxidation of the zircaloy samples occurred within the two hours predicted. Also, tritium was captured at about 100 µCi per g hull. Mass spectroscopy of the bubbler solutions revealed trace components – at below ppb levels – that warrant further study. This work has opened up the possibility of future collaborations, and a proposal for work with a university is being developed.

Carbon Nanotube Electrodes for Ultracapacitors

R. Zidan, P. A. Berseth

Objective: This project aims to develop lightweight, high surface area carbon electrodes for use in ultracapacitor batteries.**

Carbon is one of the lightest elements, as well as being relatively inexpensive, so creating a high energy density electrical storage device that utilizes carbon as the main electrode component is very attractive. Today's state-of-the-art ultracapacitors (batteries) use carbon materials for both of their electrodes because of the high surface area. Materials with high surface area and good conductivity are key to the performance of these materials. Increasing the surface area substantially beyond that of the activated carbon material used in today's ultracapacitors is predicted to bring the energy storage capacity to the level of today's metal hydride batteries and possibly close to lithium ion batteries.

This quick hit LDRD project is intended to increase our overall knowledge and expertise in the ultracapacitor field and potentially lead to future partnering opportunities including a new BES solicitation due out next year in the area of Electrical Energy Storage Science. The SRNL research activities are well known in the energy community and Dr. Ragaiy Zidan was invited to speak at the ASME Energy Nanotechnology International Conference in September 2007. Our recognition by the energy community is expected to help to secure funding in this neighboring field of Electrical Energy Storage.

The goal of this proposed research was to synthesize carbon nanotube (CNT) samples for evaluation as potential ultracapacitor materials. Researchers at SRNL have experience with creating unsupported nanotubes, and nanotubes supported on insulating substrates. For this project conditions for creating carbon nanotube materials on conductive substrates were developed. Based on our previous experience the nanotubes were doped with Fe alone, or Fe combined with Ti to promote branching of the nanotubes to explore the affect of metal dopant on tube morphology and surface area.

The as-deposited films were examined by scanning electron microscopy (SEM), and material was removed from the substrate and placed on a sample grid for examination by transmission electron microscopy (TEM), where it was also examined by energy dispersive x-ray (EDX) analysis to identify the composition of the sample. The TEM provides images of the materials at the nanoscale, and allows tube diameters, monodispersity, metal particle position, and morphology to be observed. The most Ti rich sample shows evidence of an unusual structure. It appears to be an 80-90 nm CNT with spherical particles and smaller diameter tubes attached, shown below in Figure 1. Based on the EDX results, the bulk of the material is carbon (~58%) while Ti (~16%) and O (~22%) are the other major components. There is a small amount of Fe present (0.5 %) as well. The spheres potentially contain TiO_2 and other Ti containing species. This is an exciting example of the potential to increase surface area of the carbon samples by creating branched nanotube materials.

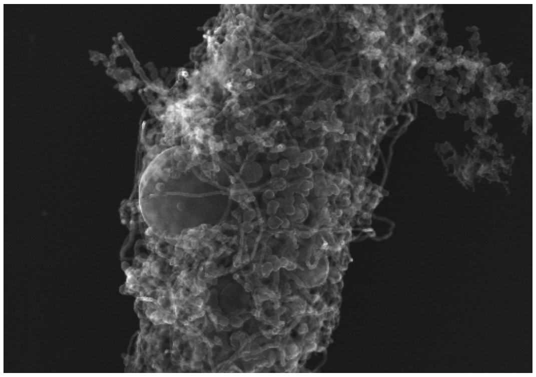


Figure 1 - Titanium doped carbon nanotube with many smaller carbon tubes growing from surface, which could be an excellent means of increasing surface area. EDX indicates Ti and O are present; it is likely that the spherical particle is composed of TiO_2.

The sample made with Fe and a small amount of Ti shows evidence of bends in the CNT where metal particles are present in the tube body. We are interested in pursing nanotubes with this morphology to maximize the surface area of the material.

Surface area measurements were done on three carbon samples using the BET method. Activated carbon had the highest surface area, with 2016 m^2/g, carbon nanotubes had a surface area of 152 m^2/g, while graphite had a surface area of 2.85 m^2/g. The large surface area of activated carbon is appealing, while the tunable electrical properties and unique morphology of CNT are potentially desirable for capacitor use. Future work would investigate combinations of CNT and activated carbon or carbon aerogels to create a composite material with increased surface area.

This work has provided an introductory foray into the field of ultracapacitor electrode materials. Carbon nanotubes were successfully grown on conductive substrates, and morphology differences as a function of metal catalyst were investigated.

Local Structural Environment Analysis of Plutonium and Neutron Absorbers in a Lanthanide Borosilicate Glass

J. C. Marra

Objective: This research involved performing detailed analyses on actual Pu containing glass samples to examine the glass microstructure and to determine valence state, coordination number, and bond lengths of species of interest in the glass. This fundamental glass structural information will be invaluable in understanding the atomic relationships within the glass and will facilitate glass composition optimization for actinide loading and product performance.

A lanthanide borosilicate (LaBS) glass containing oxides of lanthanum, neodymium and the neutron absorbers gadolinium and hafnium was developed as a matrix for long-term immobilization of plutonium. Experimental testing has shown that the LaBS composition can accommodate significant quantities of actinides into the glass structure and maintain excellent aqueous durability. However, there is little experimental data to facilitate the understanding of how the actinides (and lanthanides) are incorporated into the vitreous matrix and the role of these constituents in the glass structure. Thus, fundamental research was needed to understand the chemistry and local structure of actinide and neutron absorbers in the LaBS glass waste form.

The completed "quick hit" research project leveraged an existing collaborative research relationship between SRNL and the SIA Radon Institute in Moscow, Russia. SRNL performed scanning electron microscopy (SEM) analyses on Pu-containing samples. The SIA Radon researchers have ready access to X-ray Absorption Near Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) that was employed on actual Pu containing glass samples to determine valence state, coordination number, and bond lengths of species of interest in the glass.

Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) was completed at SRNL. The analyses showed evidence of undissolved Pu in the glass that was likely a result of insufficient mixing of the PuO_2 feed and the glass frit. Evidence of a distinct crystalline phase (with a star-like morphology) containing both hafnium and plutonium was also obtained from the SEM/EDS analyses. These crystals likely formed during cooling of the glass and nucleated on the glass surface or at the crucible wall. The relative durability of this PuO_2-HfO_2 solid solution phase may be of special interest since the phase contains both PuO_2 and a neutron absorber (HfO_2). The potential to intentionally precipitate this phase in the glass may offer the potential for a waste form with enhanced performance.

X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) were performed by SIA Radon. Experimental EXAFS spectra were fitted in R-space using an IFEFFIT package and reference crystal structures of various plutonium oxides and silicates were used for comparison of analytical results. In addition to the Pu-containing LaBS glass, powders of chemically pure Pu oxides Pu_2O_3 and PuO_2 were used as standards and measured under identical conditions. XANES spectra of Pu^{3+} and Pu^{4+} are markedly different and indicated that most of Pu present in the LaBS glass was present as Pu^{4+}. Computer simulation of experimental XANES spectrum of Pu L_{III} edge in the glass studied provided the best fit when ~90% of total Pu existed as Pu^{4+} and ~10% was present as Pu^{3+}. This result was in a good agreement with reference data for Pu in other silicate glass systems.

Fourier transforms (FT) of experimental EXAFS spectrum of Pu L_{III} edge in the LaBS glass containing 9.5 wt % PuO_2 and pure crystalline PuO_2 were obtained. Comparisons were made to a reference sodium trisilicate glass containing 1.7 wt % PuO_2. Comparing the LaBS glass data with data for reference glass containing 1.7 wt % PuO_2, it was observed that the peak positions were shifted to lower values due to reduction of interatomic distances and coordination number at the first coordination sphere. If the Pu-O_1 distance in pure PuO_2 was ~2.34 Å, then the same distance in the glass containing 1.7 wt % PuO_2 was ~2.23 Å and in the LaBS glass with 9.5 wt % PuO_2 the Pu-O distance was ~2.12 Å. The Pu coordination number in the first coordination sphere of PuO_2 is 8 whereas in the glass with 1.7 wt % PuO_2 is reduced to ~6.7. The coordination number of Pu in the vitreous phase of the LaBS glass was determined to be ~6.1.

This "quick hit" LDRD project provided valuable insight into the local atomic arrangement of Pu in the LaBS glass. Follow-on work is being proposed for further detailed study on a more pure LaBS glass (i.e. containing no undissolved PuO_2). Additionally, investigation into the formation of the PuO_2-HfO_2 crystalline phase observed in the glass will be proposed. This will include the study of phase relationships in the PuO_2-HfO_2 system.

Optical Modeling of a Hand-Held, Monolithic Cavity Ring-Down Spectrometer

B. Ashcraft and S. McWhorter

Objective: This project explores the feasibility of constructing a high finesse hemispherical lens cavity for use in a portable, hand-held, monolithic cavity ring-down spectrometer. The results from two optical design software packages show the cavity, under the right circumstances, will emit light and a working prototype should be developed from the model.

Cavity ring-down spectroscopy (CRDS) is a highly sensitive technique for detecting trace components (i.e., sub-ppb levels) in gas and liquid samples. Typical CRDS cavities consist of two mirrors of ≈ 97 - 99% reflectivity separated by 0.1m to 1m. A pulse of light is introduced into the cavity and makes hundreds of trips between the mirrors while a small percentage leaks out of the cavity; a measure of the loss of light over time is dependent on the mirror reflectivity, length of the cavity, and concentration of the absorbing species within the cavity.

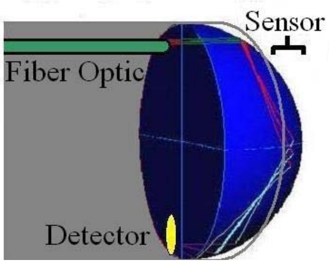


Figure 1 - Physical drawing of proposed hand-held CRDS probe including ray tracing.

Currently, CRDS is seen as a bench-type instrument that relies on very stable optical tables to maintain alignment. By introducing cavities that use total internal reflection, a more rugged and compact instrument is available. To date, evanescent wave cavity ring-down spectrometers use a variety of cavity shapes, but thus far none are hemispherical. This type of hand-held CRDS instrument would dramatically change the usage and design of CRDS by making it applicable to liquid and gas phases using a ½" diameter end-sensing probe. This probe could be used to support various DOE, DOD and HDS initiatives.

The completed research modified the CRDS setup by changing the cavity to a hemispherical lens (Fig. 1). Light from a fiber optic cable was introduced into the cavity from the flat, highly reflective side of the lens. The hemispherical portion had a thin film of reactive coating used for sensing. This novel cavity ring-down system would be beneficial for quick, cost-effective, real-time sensitive detection of any type of molecule in the liquid or gas phase that absorbs light.

After an extensive literature review and discussions with researchers from NIST's Optical Technology Division, we narrowed the optical analysis software choice to General Laser Analysis and Design (GLAD) code which was written by Applied Optics Research. The overarching plan was to purchase the software and then model the hemispherical cavity system.

Ray tracing software, Opticad, was used to design the optical cavity for the proposed sensor. Using a fiber optic cable as the light source a design of the probe was produced (Fig. 2). The light source was introduced into the fiber as five collimated rays in an oval configuration for simple viewing. The power of the light source was set to 0.5watts. A fiber optic cable with a diameter of 0.1mm was indexed to the flat side of the hemispherical cavity, which contained a 99% reflective coating, 4.33mm from the center of the hemispherical lens. The cable was assigned an index of refraction of 1.45. The reflectivity of the BK7 hemispherical lens was assumed to be 99%. The lens was constructed with a 5mm radius, 10mm diameter, and 5mm thickness. A detector was placed at the output to measure the position and intensity of the exiting beams (Fig. 3b and 3c). After 192 reflections the light decayed to 0.1% of the original value, which equates to an approximate ring down time of 3.4ns. Conventional photomultiplier detectors have a limit of detection around 4 x 10^{-7}watts and we are well within this limit.

Using the design elements from ray tracing an optical model was produced using GLAD. The information collected by studying effects on the hemispherical cavity resonator were used to determine the optimum design parameters of a super mirror and hemispherical lens combination to operate as a cavity ring-down probe. A full LDRD proposal will be submitted to develop a working prototype. Also, the skill-set derived from this project can be applied to many other sensor design projects to support DOE, DOD and DHS initiatives.

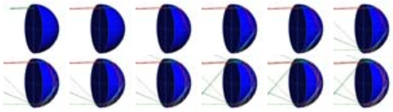


Figure 2 - Ray trace of five beam collimated oval light source. Stepwise progression of light as it hits a surface: first the reflective flat surface, then three reflections within the cavity, and finally the light either exits or continues within cavity.

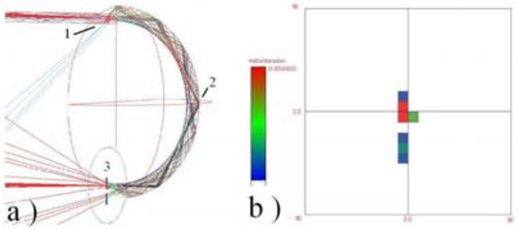


Figure 3 a) - An orthogonal view of the probe design including: (1) the fiber optic cable, (2) the point of sample interaction, and (3) the detector. **b)** The cumulative intensity profile after 48 ray reflections inside the cavity, the red corresponds to the most intense section of the output. After 0.86ns the light traveled a pathlength of 180mm and 0.11% of the original 0.5watts escapes the cavity in a concentrated area.

Project Metrics

LDRD Metrics

Project #	Lead PI	Other PIs	Project Title	Post Docs	Faculty	Students	Public-ations	Peer Rev. Public.	Invited Present.	Awards	Disclo-sures	Patents	New Prog. $	R & D 100
LD06-EM02-014	C. Bagwell	C. Yeager D. Beam	Advanced RNA and Protein-Based Tools (Full Project)		3	2	1	5	1					
LD06-EM04-076	T. Adams	J. Mickalonis A. Visser	Ionic Liquid Electrochemical Separations (Full Project)					[1]						
LD06-EM05-092	C. Jantzen	A. Jurgensen P. Burket D. Missimer C. Crawford	Low Temperature Waste Forms and Containment: Geopolymers (Full Project)				[2]	[1]	[1]					
LD06-ES01-008	D. Peeler	F. Raszewski E. Hansen S. Mann R. Schumaker	Impact of Composition and Heat Treatment on Pore Size in Porous Walled Hollow Glass Microspheres (Full Project)		2	4	[1]	[2]	1		[1]	[1]		
LD06-ES02-054	C. Yeager	C. Bagwell T. Sessions R. Zidan	Systematic Evaluation of Hydrogen Production by Diverse Cyanobacteria (Full Project)	1		1	[2]		1	1				
LD06-GEN-018	D. Hobbs	K. Martin L. Oji	Advanced Titanates and Applications for their use (Full Project)	1				2	1		2	[2]		
LD06-NS04-030	S. McWhorter	R. Brigmon	DNA-basedArtificial Nose Biological Agent Sensor (Full Project)			2			1		1			
LD06-NS04-052	R. Brigmon	C. Milliken D. Kaplan B. Anderson	Detection of Viral-Size Particles and Nanomaterials in Aerosols as surrogate (Full Project)		1									
LD06-NS04-080	S. Serkiz	J. Cordero S. Mcwhorter	Development of Nano-Scale, High-Efficiency Proportional Counters (Full Project)		2	3	1	[1]	1		1			
LDRD070079	C. Langton	D. Taylor D. Diprete	Radiotracer Method for Measuring Hydraulic Conductivity of Cementitious Materials (Quick Hit)								1			
LDRD070081	M. Denham	M. Millings	In-situ Generation of Oxygen Releasing Metal Peroxides (Quick Hit)											
LDRD070158	M. Kingsley	S. Chapman P. McKinsey S. Walter M. Heitkamp	Feasibility of Perfluorinated Liquids as a Collection Media for Biodetection (Quick Hit)											

[ ] = pending

LDRD Metrics

Project #	Lead PI	Other PIs	Project Title	Post Docs	Faculty	Students	Public-ations	Peer Rev. Public.	Invited Present.	Awards	Disclo-sures	Patents	New Prog. $	R & D 100
LDRD070161	E. Hoffman	T. Skidmore T. White F. Fondeur	Neutron-Capture-Induced Radiation of Polymers (Quick Hit)		2									
LDRD070177	M. Paller	A. Knox	Evaluation of Potential Side-Effects of Sequestering Agents Used for In-situ remediation of contaminants (Quick Hit)				2	[1]						
LDRD070181	M. Crowder	J. Laurinat	Characterization of Volatile Components in Zircaloy Fuel Hulls (Quick Hit)											
LDRD070183	R. Zidan	P. Berseth	Carbon Nanotube Electrodes for Ultracapacitors (Quick Hit)	1					1					
LDRD070211	J. Marra	S. Stefanosvsky	Local Structural Environment Analysis of Plutonium and Neutron Absorbers in a Lanthanide Borosilicate Glass (Quick Hit)											
LDRD070220	S. McWhorter	B. Ashcroft	Optical Modeling of a Hand-held, Monolithic Cavity Ring-down Spectrometer (Quick Hit)											

[ ] = pending