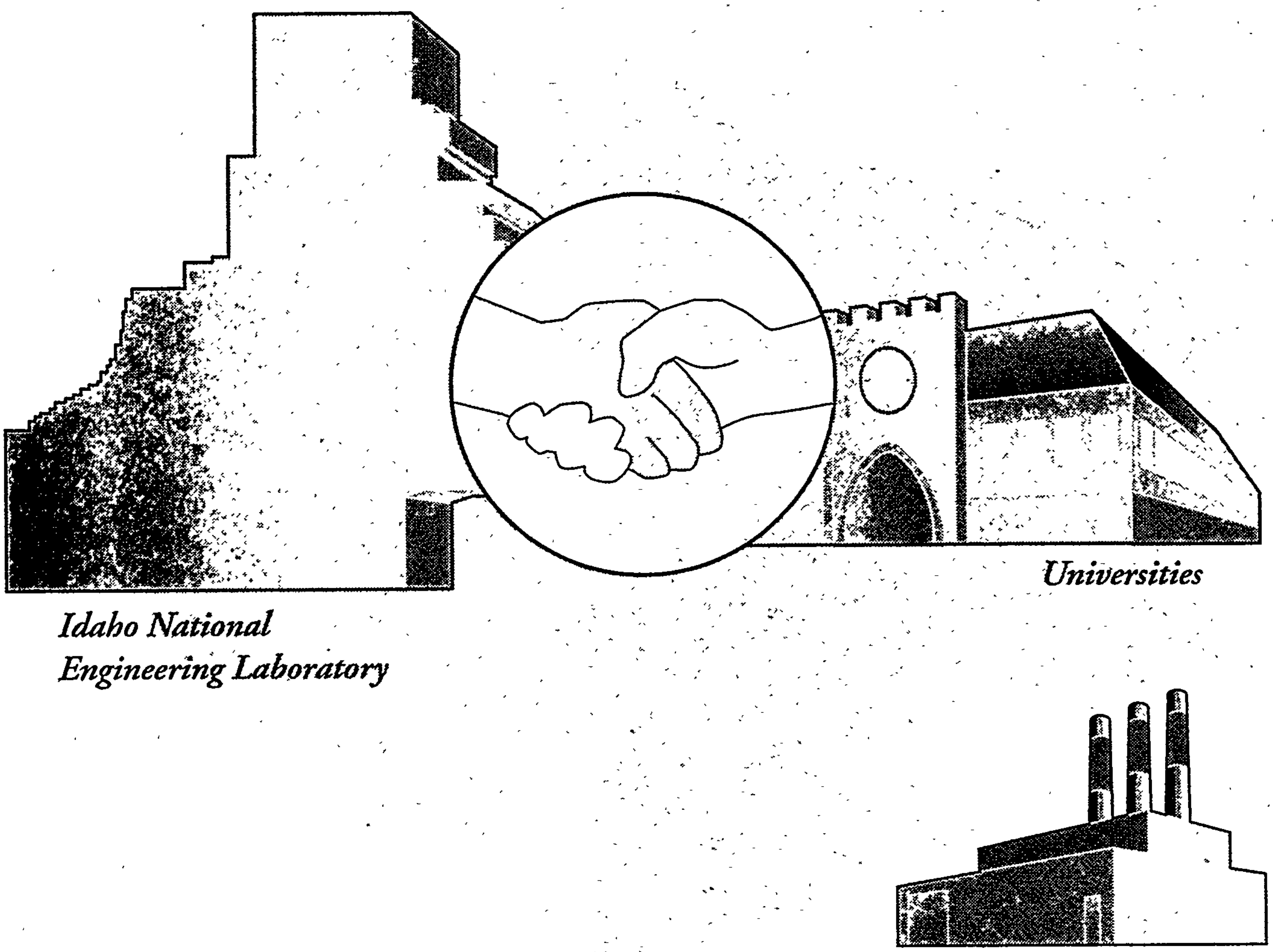
INEL-96/0253

LOCKHEED MARTIN

Idaho National Engineering Laboratory

University Research Consortium
Annual Review Meeting Program



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INEL-96/0253
July 1996

LOCKHEED MARTIN

University Research Consortium

Annual Program Review Meeting

July 29–31, 1996
Idaho Falls Center for Higher Education
Idaho Falls, Idaho

Idaho National Engineering Laboratory

Welcome to the First Annual Program Review meeting of the Idaho National Engineering Laboratory University Research Consortium (INEL/URC). Although our primary purpose is to review the progress of the research, we have structured the Annual Review to enable other important objectives. For those participants who have never visited the INEL, the meeting is an opportunity to become more familiar with the unique resources of the multiprogram National Laboratory, and to strengthen the research ties we have initiated through the URC Program. Conversely, it is an opportunity for INEL Scientists to become more familiar with the objectives and content of the URC Program.

A significant effort has been invested to make this meeting a productive one for participants. In addition to the Research Project Evaluation Committee and presenters already acknowledged in this Program, I would like to thank and acknowledge the following contributors:

INEL

A. B. Denison, Consulting Scientist

W. J. Toth, Advisory Scientist

R. C. Wilcox, Secretary

T. D. Dixon, Associate Administrator

D. R. Pack, Consulting Administrative Specialist

M. I. Valle, Administrative Specialist

B. L. Tracy, Secretary

Bus Operations, Technical Publications, and Printing

Idaho Falls Center for Higher Education

Dr. Fred Rose and staff

MIT

Professor Mujid S. Kazimi

Dr. Malcolm A. Weiss

Professor Jefferson W. Tester

Professor Kenneth A. Smith

Professor Michael Golay

Professor Thomas W. Eagar

Karen Luxton

—Debonny L. Shoaf, Ph.D., Manager
Academic and Professional Affairs Department

This project is funded by the Idaho National Engineering Laboratory University Research Consortium. The INEL is managed by Lockheed Martin Idaho Technologies Company for the United States Department of Energy, Idaho Operations Office under Contract DE-AC07-9411D13223."

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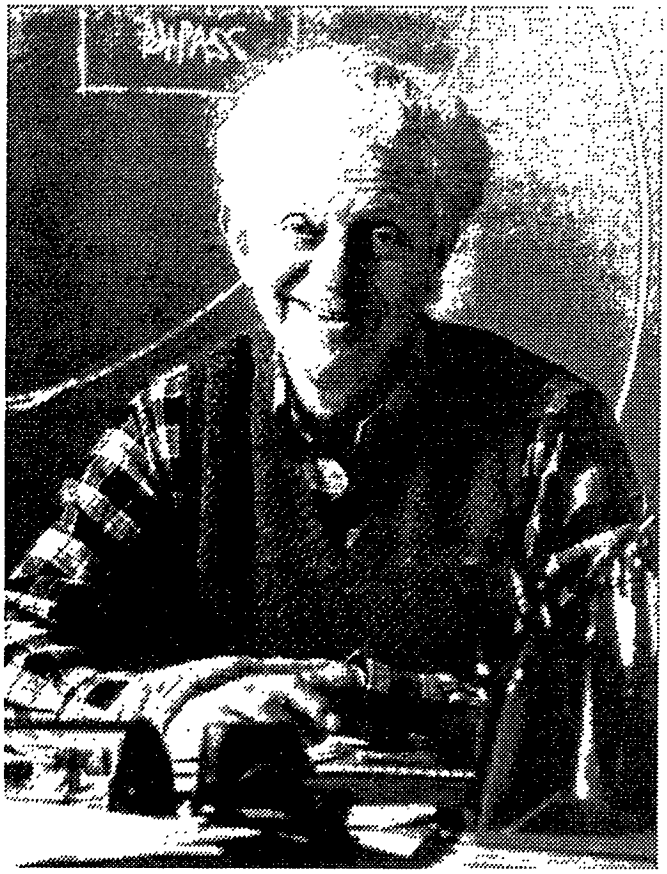
Contents



Keynote Speaker Leon M. Lederman has had a long and distinguished career in science and science education, receiving numerous awards and honors. He has been one of the primary explorers in both high-energy physics and the weak interaction. Lederman was awarded the Nobel Prize in Physics (1988) for showing the existence of two types of neutrinos, a key to understanding the weak interaction. He was Director of the Fermi National Accelerator Laboratory from 1979 until 1989. It was here that he and his fellow scientists discovered the fundamental bottom quark for which he was awarded the Wolf Prize in 1983. In 1993 he was presented the Enrico Fermi Prize by President Clinton. He is a supporter of the strength of the United States and its economy through technological innovation. During his term as Director, Lederman emphasized the importance of math and science education. He initiated the Saturday Morning Physics lectures and subsequently founded the Friends of Fermilab, the Illinois Mathematics and Science Academy, and the Teachers Academy for Mathematics and Science. Dr. Lederman is no stranger to Idaho and the Idaho National Engineering Laboratory. He actively participated in the Idaho Scholarship Olympics program and was one of the key members in the Prime Program, a workshop for junior high school teachers in the area.

John M. Wilcynski
Manager, U. S. Department of Energy Idaho Operations Office

John M. Wilcynski became Manager of the U. S. Department of Energy's Operations Office in October of 1994. In this position he directs the activities of the Idaho National Engineering Laboratory (INEL), an operation with approximately 8500 employees and an annual budget of $760M. The missions of the INEL include nuclear reactor research and development, environmental restoration (including waste management and remediation and technology development), and a broad suite of technological research and development programs. Mr Wilcynski has had a long line of key management and administrative experience in the Federal Government. Prior to his present position (October 1991 to October 1994) he was Deputy Manager of the Idaho Operations (1990-1991) and has served as Assistant Manager for Administration at the INEL. At the Richland Operations Office of the U. S. Department of Energy, he served as Director of the Human Resources and Planning Division (1986-1990) and for the period 1981-1985 he was Director of the Procurement Division and the Chief of the Contract Management Branch in the Richland Operations Office. Through 1988, Mr Wilcynski served on a developmental assignment in the Office of Assistant Secretary for Defense Programs in Washington, D.C. He is a graduate, with honors, from the Boston University Graduate School of Management and Business and has a Bachelors degree in mathematics from Gonzaga University in Spokane, Washington. He completed the Department of Energy Senior Executive Service Candidate Program, and in 1991 he completed the Program for Senior Managers in Government at Harvard University.

Warren E. Bergholz Jr.
Deputy Manager, U. S. Department of Energy Idaho Operations Office

Warren E. Bergholz, Jr. comes to the Department of Energy's Idaho Operations Office from the DOE's Savannah River Office where he was chief legal counsel. Bergholz sees his role at the INEL as assisting the Idaho Operations Manager, John Wilcynski, in ensuring that the INEL develops new missions while cost-effectively carrying out its existing environmental, national defense, and science and technology roles. As chief counsel at Savanna River, his responsibilities included management of the office's legal functions and providing legal advice and counsel to the manager and senior staff. Bergholz began his federal service in 1976 at the Energy Research and Development Administration headquarters in Washington, D.C. as an attorney in the Office of the General Counsel. He was named deputy assistant general counsel for international development and defense programs in 1982. Bergholz graduated from the University of Pittsburgh and served as an officer in the Navy. He attended the University of Wyoming, where he received his law degree, and he is a member of the Wyoming Bar Association.

W. JOHN DENSON

President, Lockheed Martin Idaho Technologies Company

As President of Lockheed Martin Idaho Technologies Company, W. John Denson brings to the INEL 34 years of experience in managing large complex technical programs. His responsibilities at Lockheed Martin Idaho include providing strategic direction, leadership, and management for all INEL programs, its activities, and employees. Prior to coming to the INEL, he was president of the Lockheed Environmental Systems & Technologies Company (1992-1994), where he was responsible for the company's DOE, EPA, and commercial environmental engineering, remediation, and analytical laboratory operations. Much of his career was dedicated to management of aerospace and space exploration technologies related to Lockheed's responsibility to NASA. From 1989 through 1992, Denson was program manager for the Shuttle Avionics Integration Laboratory at Johnson Space Laboratory, which provided the baseline for NASA to certify the space shuttle for initial flight. In 1981, he was program development director to lead the corporation's bid to win the Shuttle Processing Contract at Kennedy Space Center. Following that (1982), he became vice president of Lockheed Space Operations Company. Denson earned his bachelor's degree from Mississippi State University in 1960 and has taken a number of advanced engineering courses at Rice University, Lockheed, and Ford Aerospace.

Dr. Barton "Bart" Krawetz
Director, Idaho National Engineering Laboratory

Dr. Krawetz came to Lockheed Martin Idaho Technologies Company after Lockheed won the contract to manage the INEL in 1993. His responsibilities include planning, evaluating, and managing large complex research and applied engineering development programs for Lockheed Martin and the U.S. government. Prior to joining Lockheed Martin Idaho, Krawetz was vice president of engineering for Lockheed Corporation headquarters, where he developed science and engineering policies and processes, evaluated technical programs, and assisted with problem solving and improving cost effectiveness of engineering across the corporation. From 1987 to 1990, he served as executive vice president and general manager for research, technology, and engineering for the Lockheed Aeronautical Systems Company. Krawetz was vice president and assistant general manager of Lockheed's Skunk Works in 1986 and 1987, assisting with overall management of highly classified research and development of new technologies and prototypes for the U.S. government. For nearly 20 years prior to joining Lockheed, Krawetz held various positions and responsibilities for the U.S. Air Force, primarily with its laboratories. Krawetz has a doctorate in applied science from the University of California, Davis; a master's degree in space physics from the Air Force Institute of Technology at Wright-Patterson Air Force Base; and a bachelor's degree in electrical engineering from the Massachusetts Institute of Technology.

Dr. David P. Cauffman
Chief Scientist and Director of Research Products, Lockheed Martin Idaho Technologies

Dr. David P. Cauffman serves as Chief Scientist and Director of Research Products for Lockheed Martin Idaho Technologies Company. As Chief Scientist, he is directly responsible for the University Research Consortium, and directs the laboratory discretionary research programs. From 1979 to 1994, Dr. Cauffman was with Lockheed Missiles and Space Company, where for the last six of these years he was manager of the Solar and Astrophysics Laboratory in the company's Palo Alto Research Laboratories. He has directed a number of satellite projects involved in examining the electromagnetic radiation in our solar system. His specialty has been the study of electric fields and plasma convection in the earth's magnetosphere. As program scientist, Dr. Cauffman served for five years (1974-1979) in the Space Plasma Physics Section of the Space Science Division of NASA Headquarters in Washington, D.C., where he played an active role in formulating and gaining approval for a number of unmanned scientific research satellite missions. Dr. Cauffman earned a Ph.D. in space physics from the University of Iowa in 1971, and a BA degree in physics from Haverford College in 1966.

Schedule

Monday, July 29, 1996

9:00 – 11:00 a.m.	INEL Research Center tours (buses departing form AmeriTel Inn 8:15 a.m.)
11:00 a.m. – 1:30 p.m.	Registration and INEL and University exhibits (lobby, University Place)
1:30 p.m.	Plenary Session (University Place Auditotium)
	David P. Cauffman, Chief Scientist, Lockheed Martin Idaho Technologies Company W. John Denson, Lockheed Martin Idaho
	Barton Krawetz, Lockheed Martin Idaho
	Jefferson W. Tester, Massachusetts Institute of Technology
	Warren E. Bergholz, DOE-ID
3:00 p.m. – 4:30	Keynote Address: Leon M. Lederman, Fermi National Accelerator Laboratory
4:30 p.m.	Adjourn Plenary Assembly
5:30 p.m.	Research Collaboration Meeting, Holiday Inn Westbank

Tuesday, July 30, 1996

8:00 a.m.	Three concurrent review sessions
8:00 – 11:30 a.m.	Session 1: Biological Processes (Tester, Winston)
8:00 – 11:30 a.m.	Session 2: Materials Synthesis (Flemings, Seydel)
8:00 – 11:30 a.m.	Session 3: Reactor Performance, Degradation, and Regulation (Kazimi, Bennett)
11:30 a.m.	Lunch
1:00 p.m.	Three concurrent review sessions
1:00 – 4:30 p.m.	Session 4: Structures (Flemings, Seydel)
1:00 – 5:30 p.m.	Session 5: Nuclear Medicine Accelerators and Isotopes (Golay, Bennett)
1:00 – 5:15 p.m.	Session 6: Waste Processing at High Temperatures (Smith, Miller)
6:00 p.m.	Bus departs form AmeriTel Inn for Mountain River Ranch for dinner
6:30 p.m.	Chuckwagon dinner

Wednesday, July 31, 1996

8:00 a.m.	Three concurrent review sessions
8:00 – 11:30 a.m.	Session 7: Organic Waste Treatment and Reduction (Smith, Miller)
8:00 – 11:30 a.m.	Session 8: Advanced Reactor Technologies (Golay, Bennett)
8:00 – 11:30 a.m.	Session 9: Site Monitoring and Characterization (Tester, Winston)
11:30 a.m.	Lunch
1:00 p.m.	Three concurrent review sessions
1:00 – 5:15 p.m.	Session 10: Environmental Sensors and Monitors (Tester, Winston)
1:00 – 5:00 p.m.	Session 11: Materials Processing and Control (Hatton, Seydel)
1:00 – 4:30 p.m.	Session 12: Membrane and Adsorption Separation (Smith, Miller)

The Consortium Program

This brochure presents the program for the first annual review meeting of the University Research Consortium (URC) of the Idaho National Engineering Laboratory (INEL). INEL is a multiprogram laboratory with a distinctive role in applied engineering. It also conducts basic science research and development, and complex facility operations. INEL addresses national needs by applying expertise in environmental management research (for example, pollution prevention, waste remediation, and waste management); applied engineering, and systems integration; nuclear operations and materials disposition; and transfer of derived-use technologies (energy and environmental).

In 1994, the U.S. Department of Energy (DOE) selected Lockheed Martin Idaho Technologies Company to manage the Laboratory. Lockheed Martin Idaho established the URC when it assumed management responsibility. The purpose of the URC is to help INEL in its reorientation to new goals set by DOE for its national laboratories. Those goals include developing new technologies useful in our competitive economy or in meeting national needs such as environmental management.

The URC program consists of a portfolio of research projects funded by INEL and conducted at universities in the United States. In order to help reorient the Laboratory and to ensure commercial relevance, each project is intended to have at least one active collaborator on the INEL staff, and at least one active collaborator from the private sector; INEL collaboration has not yet been fully realized because of funding limitations.

Current URC projects are the outcome of a solicitation and review process that began in February 1995. In response to a published solicitation, 620 prospectuses (3-page informal proposals) were received from 80 universities in 41 states. Invitations to submit full formal proposals were extended to 133 prospectus writers. Of those proposals, 47 were awarded funds totaling $7.63 million in fiscal 1996, distributed among 23 universities in 17 states, listed on page 3. The solicitation and peer review process was managed for INEL by a team at the Massachusetts Institute of Technology (MIT). Ultimate funding decisions were made by Lockheed Martin Idaho management after considering the recommendations of an Oversight Board that included representatives of Lockheed Martin Idaho, MIT, and DOE. Those recommendations were based both on technical merit of the proposals and on their relevance to INEL objectives.

Of the 47 current projects, 25 began work on July 1, 1995, and the remaining 22 on December 1, 1995. Therefore, this review covers research on projects that have been under way for only about half a year, or a year at most.

In late 1995, universities in the Intermountain region were invited to join as official members of the URC. Our expectation is that Consortium members will advise INEL on fruitful research topics for future solicitation and funding, and will participate more actively in the proposal review and selection process. There is now a total of 15 members of the consortium, listed on page 3.

Although the first purpose of this annual review meeting is to report and evaluate progress on each of the projects, there is another important purpose. That is, the meeting provides an opportunity for faculty, industry, and INEL experts to meet each other in an informal setting that can encourage new and fruitful collaborations for additional work that furthers the missions and business objectives of INEL.

The general format of the meeting consists of a plenary assembly on Monday afternoon followed by twelve review sessions on Tuesday and Wednesday; three sessions will run concurrently throughout the two days. Each session covers three to five projects on a common topic. Each session has an MIT faculty chairman, an INEL co-chairman, and at least two other panelists to participate in evaluating the projects. One of those panelists is an INEL director or his designee, and the other is on the faculty of a Consortium member university.

In this program, summaries and participant lists for each project are presented as received from the principal investigators. They may be found in

Questions about the Consortium are welcome.

For information you may communicate with either MIT or INEL:

INEL URC Program Office
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Lockheed Martin Idaho Technologies Company
PO Box 1625
Idaho Falls, ID 83415-2214
Phone: (208) 526-0430
Fax: (208) 526-5327
e-mail: dls@inel.gov

the pages immediately following the schedule for the session in which that project is reported. Many pages facing the project summaries are deliberately blank, leaving space for your notes. An index at the end of this program lists the principal investigators and report presenters for each of the 47 projects.

Universities Conducting URC-Funded Research during FY 1996

Colorado
- Colorado School of Mines

Georgia
- Institute of Paper Science and Technology

Idaho
- Idaho State University
- University of Idaho

Illinois
- University of Illinois

Indiana
- Purdue University
- University of Notre Dame*

Massachusetts
- Harvard University*
- Massachusetts Institute of Technology

Minnesota
- University of Minnesota

Missouri
- University of Missouri*

Montana
- Montana State University

New York
- State University of New York-Stony Brook

North Carolina
- North Carolina State University

Rhode Island
- Brown University*

South Carolina
- Clemson University

Texas
- Texas A&M University*

Utah
- Brigham Young University
- University of Utah
- Utah State University

Vermont
- University of Vermont

Washington
- University of Washington
- Washington State University

* This university is collaborating with another listed university that holds the primary subcontract with the URC.

Consortium Member Universities as of July 1996

Colorado
- Colorado School of Mines
- Colorado State University
- University of Colorado

Idaho
- Boise State University
- Idaho State University
- University of Idaho

Massachusetts
- Massachusetts Institute of Technology

Montana
- Montana State University
- Montana Technology of the University of Montana
- University of Montana

Utah
- Brigham Young University
- University of Utah
- Utah State University

Washington
- Washington State University

Wyoming
- University of Wyoming

*This university is collaborating with another listed university that holds the primary subcontract with the URC.

Session 1. Biological Processes

Tuesday, 8:00 a.m. to 11:30 a.m.

Jefferson W. Tester (MIT), chair
Rebecca A. Winston (INEL), co-chair
Dale R. Ralston (U of I), panelist
Bob Snelling, Shirley Sandoz (INEL), panelists

8:00 a.m.	V220	James N. Petersen Washington State University	Development of Techniques for Bioremediation of Soil and Groundwater Contaminated with Toxic Heavy Metal Ions
8:45 a.m.	V258	Ernest L. Brannon University of Idaho	Fish Farm Effluent Treatment for Improving Wastewater Quality
9:30 a.m.	—	Break	
10:00 a.m.	V07	Ronald L. Crawford University of Idaho	In Situ Biological Destruction of Nitroaromatic Contaminants in Groundwater
10:50 a.m.	V177	Mary E. Watwood Idaho State University	Specific Labeling of Microorganisms Capable of Oxidative Biotransformation of Toxic Chlorinated Ethylenes with Enzyme-Activated Chemical Probes
11:30 a.m.	—	Adjourn	

Development of Techniques for Bioremediation of Soil and Groundwater Contaminated with Toxic Heavy Metal Ions (V220)

James N. Petersen, Washington State University

Co-PIs and University:

David R. Yonge and Donald L. Johnstone,

Washington State University

Postdoctoral Research Associates:

Yared Bereded-Samuel, Mahesh Rege

Research Associate: David Mills

Graduate Students: Chris Johnson, Donny Mendoza, Tim Ross, Eric Schmeiman, Dyane Sonier

Industrial Collaborators and Companies: Carl E. Camp, DuPont Central Research & Development; Brian Peters, Foster Wheeler Environmental Corp.; Charles L. Meyer, Shell Development Company; Paul T. Sun, Shell Development Company

INEL Collaborators: William A. Apel, Ms. Joni Barnes,

Charles Turick

Presenter: James N. Petersen

Contamination of subsurface groundwaters and process wastewaters by toxic and/or mutagenic mineral and metal ions is widespread. One technology which could be used to remediate contaminated soils and groundwaters, and to clean contaminated waste streams in a cost effective fashion, is bioremediation. The biological treatment of solutions that contain ions of two particularly toxic elements, chromium and selenium, are being addressed in this work.

Previous studies have shown that various species of bacteria can reduce these ions to less toxic, more stable states. However, most of these previous studies have not addressed system specific conditions that would be necessary for their application to site and/or waste streams. Hence, in this work, experiments are being performed that will allow the determination of kinetic expressions needed to facilitate the design of ex situ reactors and in situ remediation strategies. Experiments will then be performed to test the reactors and in situ remediation strategies that are devised using core samples from contaminated sites and process waste streams obtained from the industrial partners. Further, the technologies that are developed will be passed to the industrial partners for commercialization and implementation.

During this first phase of the research, analytical systems have been devised that allow the accurate determination of all compounds of interest, and experiments designed to determine the biological reaction kinetics have been started. Further, based on the advice from our industrial partners, we have begun other experimental programs to (a) characterize the sorption characteristics of a cell immobilization matrix that will be used in later portions of the work, and (b) develop methods which will allow the bacterial systems used to accomplish contaminant reduction to be characterized. In the latter, techniques that will allow the determination of the concentration of dead and live biomass, and the determination of the level of nitrite reductase activity in the cell broth are being developed. The activity of this enzyme is important because it has been implicated by others as the biological catalyst responsible for reducing the contaminants to less hazardous states.

During the next year, the following milestones will be met:

An Invention Disclosure describing a method devised to biologically reduce contaminants and then separate the reduced material from a process stream will be filed by 10/1/96.

All experiments needed to determine the kinetics of contaminant reduction with common bacteria will be completed by 1/9/97.

At its quarterly meeting on 1/10/97, the project team will determine the target waste site for Cr treatment. It is anticipated that this will be a DOE site.

A method for determining the ratio of active to inactive biomass in a culture will be developed by 1/15/97.

Appropriate parameters needed to describe the kinetics of the bacterial reduction of the contaminants using common subsurface bacteria will be determined by 5/1/97.

Appropriate parameters needed to describe the kinetics of the bacterial reduction of the contaminants using specialized bacterial systems will be completed by 9/15/97.

This page is for notes.

Fish Farm Effluent Treatment for Improving Wastewater Quality (V258)

Ernest L. Brannon, University of Idaho, Aquaculture Research Institute

Co-PI and University: Ron W. Hardy, University of Washington; Keya Collins, University of Idaho

Graduate Students: Steven Todd and Joel Green, University of Idaho

Industrial Collaborator and Company: Bill Jones, Owner of Bill Jones' Trout Farm of Hagerman, Idaho

INEL Collaborator: Bob Cherry

Presenters: Ernest L. Brannon, Keya Collins, Steven Todd and Joel Green

Following petroleum, fish products are the second largest valued natural resource imported into the United States. Over 65% of the fish consumed in the US are imported, accounting for nearly $10 billion of the US annual trade deficit. The potential for the US aquaculture industry to supply that market, therefore, is very good, but the greatest restraint is the impact of the fish farm effluent on water quality. High-density rearing environments generate a pound of waste for every two pounds of feed fed, and discharge of that waste-stream in public waters is perceived as the major limitation to industry expansion. If effective technology for the reduction of fish farm waste can be developed, the ability to expand the aquaculture industry without negative impacts on water quality will provide the greatest incentive for growth of the aquaculture industry. Research on waste management, therefore, is being pursued through development of diet formulations for salmonids with reduced waste nutrient loads, increased efficiency of diet utilization, increased stability of the fecal solids generated, and improved methods to capture fish waste before rearing water is discharged. Our approach from the nutritional standpoint is to formulate balanced, nutrient rich, high energy diets to conserve protein and lower waste phosphorus. Low dissolved oxygen in the rearing environment tends to reduce food conversion. Therefore, waste reduction is also approached by researching methods to elevate the level of dissolved oxygen in the rearing environment. Once the waste load is generated, however, we are attempting further reduction by increasing the stability of the fecal pellet to reduce disintegration prior to waste extraction in routine cleaning operations. Finally, waste load reduction is also being approached mechanically by examining methods to enhance waste interception. These improvements in waste management technology on fish farms are expected to markedly lower nutrients in the waste-stream and allow the expansion of fish farming in the US with no net increase in effluent waste load.

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This page is for notes.

In Situ Biological Destruction of Nitroaromatic Contaminants in Groundwater (V07)

Ronald L. Crawford, University of Idaho

Co-PI and University: None

Graduate Students: Terry Hammill, David Duncan

Industrial Collaborator and Company: Gerald Mead, Vice President for Research and Product Development, J. R. Simplot Company, Pocatello, Idaho

INEL Collaborator: Daphne Stoner, Advanced Sciences Biotechnology Group

Presenter: Ronald L. Crawford

Our project concerns the biodegradation of 2-sec-butyl-4,6-dinitrophenol (dinoseb) and 2,4,6-trinitrotoluene (TNT) by strains Clostridium bifermentans, and has as a primary goal the use of one or more of these anaerobic bacteria for the in situ remediation of nitroaromatic-contaminated groundwater. Strain KMR-1 was isolated from a chemostat that was fed 2,4,6-trinitrotoluene (TNT) as its sole carbon and nitrogen source. Strain TBH-1 was isolated from environmental samples collected from an aquifer contaminated with dinoseb. Strain TBH-2 was isolated from a soil consortium used to bioremediate surface soils contaminated with dinoseb. We have determined that these strains are capable of degrading dinoseb at environmental temperatures (110°C), convert both dinoseb and TNT into products that are degradable to carbon dioxide when conditions are changed from anoxic to aerobic, and can be introduced as spores into aquifers and transported into regions of nitroaromatic contamination. Transport experiments have been performed in an actual dinoseb-contaminated aquifer at the University of Idaho. Present work involves additions through injection wells of fermentable carbon sources and clostridia spores to this dinoseb plume with concomitant monitoring of contaminant concentrations to confirm the efficacy of in situ destruction of the nitroaromatic pollutants. We are negotiating with a variety of site owners to also test our technology at a TNT-contaminated site, probably next year. If successful, this technology will be commercialized through our collaboration with the J. R. Simplot Company.

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This page is for notes.

Specific Labeling of Microorganisms Capable of Oxidative Biotransformation of Toxic Chlorinated Ethylenes with Enzyme-Activated Chemical Probes (V177)

Mary E. Watwood, Idaho State University

Co-PI and University: William K. Keener, Idaho State University

Graduate Students: None

Industrial Collaborator and Company: David Phelps, Director of Technology, Molecular Probes, Inc.

INEL Collaborator: William A. Apel

Presenters: Mary E. Watwood and William K. Keener

The accurate detection of environmental microorganisms that degrade toxic chlorinated solvents, such as trichloroethylene (TCE), is critical for refining bioremediation efforts. Most probes available for bacterial detection are based on bacterial characteristics that are only indirectly associated with TCE oxidation (e.g., genetic or protein specific probes), are very expensive, and involve complex laboratory procedures. The primary objective of this project is to develop enzyme-activated fluorescent probes to detect TCE degrading bacteria. With this approach the activity of the TCE degrading enzymes actually triggers or enhances probe fluorescence, which is detected spectrophotometrically or with fluorescent microsocpy. Activity-dependent probes will allow direct and selective enumeration of TCE degrading bacteria without the use of enrichment cultures which alter relative numbers of indigenous bacterial populations. This approach should yield probes that are specific, sensitive, relatively inexpensive, and have broad applicability.

The second project objective is to develop probes or methods to facilitate isolation of bacteria from environmental samples and to screen these isolates for catabolic pathways involved in TCE degradation. There is particular interest in bacteria with cometabolic TCE oxidation capacity due to enzymes associated with toluene degradation pathways. Methods for isolating and rapidly screening bacteria for TCE oxidation activity, specific toluene degradative pathways, and pathway control mechanisms will facilitate bioremediation feasibility studies.

A method for fluorescent labeling P. putida F1 has been developed which involves exposure of cells trapped on 0.2 mm-pore size membrane filters to gaseous phenylacetylene (a structural analogue of toluene). Eight toluene-degrading bacteria using 5 different pathways (7 strains degrade TCE) have been collected; methods for selectively labeling these organizms are being pursued. Obstacles currently addressed include natural fluorescence of intact cells (autofluorescence), bleaching of stain under light, diffusion of stain from the vicinity of active cells, and degradative pathways unsuited to labeling with phenylacetylene (e.g., P. mendosina KR1).

Semi-solid media are being formulated for the isolation and differentiation of the 8 toluene degraders. For example, agar media containing indole cause bacterial colonies to form pigments that are reproducible for a given strain. Toluene analogues (including phenylacetylene) are transformed to yield colored products, providing a basis for colorimetric assays to screen chemical inducers of degradative pathways that are less toxic than toluene or phenol. Preliminary experiments indicate that bacteria with toluene monooxygenase pathways (e.g., B. cepacia G4) transform hydroxylated toluene analogues more readily than nonhydroxylated versions, whereas bacteria with toluene dioxygenase pathways (e.g., P. putida F1) prefer the latter substrates. These observations provide a means of rapidly identifying pathways in isolated bacteria.

Probe syntheses for the TCE degraders Nitrosomonas europaea (ammonia oxidizer) and Methylosinus trichosporium OB3b (methane oxidizer) are nearing completion. Probes and methods for all 8 toluene degraders will be tested and refined within the next year. Preliminary methods for labeling N. europaea and M. trichosporium are expected by December 1996. New syntheses will likely be required for improved labeling. All methods will be tested using bacterial isolates from the TCE contaminated Test Area North (TAN) site of the INEL. These studies will be completed by September 1997.

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This page is for notes.

Session 2. Materials Synthesis

Tuesday, 8:00 a.m. to 11:30 a.m.

Merton C. Flemings (MIT), chair
James A. Seydel (INEL), co-chair
Joel Dubow (Uof U), panelist
Barry Short, Dave Cauffman (INEL), panelists

8:00 a.m.	G05	Herbert Herman State University of New York, Stony Brook	Plasma Processing of Functionally Gradient Materials: Diagnostics, Characterization, and Modeling
8:55 a.m.	G01	F. H. (Sam) Froes University of Idaho	Direct Production of Low-Cost High-Quality Titanium Powder by Mechanical Alloying
9:35 a.m.	—	Break	
10:05 a.m.	G23	Patrick R. Taylor University of Idaho	Plasma Synthesis of Nano-Sized Metallic Powders
10:45 a.m.	G146	Anne M. Mayes MIT	Towards Viable Lithium Solid Polymer Electrolyte Batteries: An Integrated Materials Approach
11:30 a.m.	—	Adjourn	

Plasma Processing of Functionally Gradient Materials: Diagnostics, Characterization, and Modeling (G05)

Herbert Herman, State University of New York—Stony Brook (SUNY)

Co-PIs and Universities: Sanjay Sampath, SUNY; Chris Berndt, SUNY; Subra Suresh, MIT

Graduate Student: William Smith

Industrial Collaborator: M. B. Beardsley, Caterpillar, Inc.

INEL Collaborators: Richard Wright, James Fincke, Barry Rabin

Presenters: Herbert Herman, Sanjay Sampath

This interdisciplinary research program examines the fundamentals associated with processing, diagnostics and materials properties associated with plasma spraying (high velocity melt spraying) of functionally gradient materials (FGMs). Metal-ceramic FGMs are being processed using simultaneous injection of metal and ceramic particles into a plasma flame at given ratios to produce various gradient profiles. Complexities associated with mixing of two (or more) different materials within the plasma are being investigated using modeling and advanced diagnostic tools in collaboration with INEL researchers. The deposits will be characterized for compositional uniformity, and microstructural attributes, linking these to the processing conditions and FGM properties such as residual stress distributions, mechanical behavior and high temperature oxidation/ corrosion properties.

It is anticipated that the program will yield methodologies for hardware development for multiple injection of feedstock with dissimilar physical properties and lead to analytical and empirical models with which to synthesize the processing-microstructure-property relationships in plasma spray formed FGMs. A close industrial collaboration exists with Caterpillar, Inc., who is using plasma spray FGM technology for the manufacture of energy efficient diesel engine components and earth moving machinery. It is expected that this fundamental research program will provide the basis for improved design and manufacturing processes, thereby enhancing the applicability of FGMs at Caterpillar, Inc., as well as other energy based industries.

During this first year, working with collaborators at INEL, we have built and tested a computer controlled FGM delivery system for plasma spray torches. Diagnostic experiments have been conducted on a variety of injection protocols and the underlying issues have been identified. The particle size effects have been identified. Working with the mechanics group at MIT, experimental and modeling efforts have been formulated and initial results are extremely promising. The second year program will focus on optimizing the processing procedures and to develop methods for fabrication of FGMs with different layer geometries. Caterpillar, Inc., has provided materials and specification input to both INEL and Consortium researchers. The program is progressing as originally planned.

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This page is for notes.

Direct Production of Low-Cost High-Quality Titanium Powder by Mechanical Alloying (G01)

F. H. (Sam) Froes, University of Idaho

Co-PI and University: K. Prisbrey, University of Idaho

Visiting Scientist: E. G. Baburaj

Graduate Student: Carl Powell

Industrial Collaborators and Companies: D. Suciu, ERAD; V. Moxson, ADMA; C. F. Yolton, Crucible Steel

INEL Collaborator: B. Detering

Presenters: F. H. Froes, K. Prisbrey

Titanium and its alloys are extremely attractive materials for use in many aerospace and terrestrial systems. However, a major impediment to more wide-spread use of titanium based materials, for example in the cost-conscious automobile industry, is the inherent high cost. Historically, the amount of titanium used in the final design of many military and commercial systems is considerably lower than initially planned in large part because of this high cost. To enter the high-volume automobile marketplace (16 million vehicles per year in the USA alone) would require getting the cost of titanium down to $1-2 per pound. But even 1 lb per automobile would increase titanium use by 50%. Thus the program has the potential of revolutionizing the titanium industry. The objective of this work is to substantially reduce cost by optimizing a new titanium powder production process, based on the emerging mechanical alloying (MA) technique of displacement reaction—the replacement of one element in a compound by another during MA at ambient temperatures. In Phase 1, the solid state reaction shown below has been studied:

$$TiCl_4 + 2Mg \rightarrow 2MgCl_2 + Ti .$$

The procedure used is to agitate the reactants in a SPEX mill containing steel balls. Reaction times and products have been measured using temperature, EDAX, X-ray diffraction, and SEM. The system was also modeled with differential equations derived from population balances. The result was a fine titanium powder at a projected price well below current product levels (a realistic estimate of the cost is currently being determined).

The modeling is being conducted to aid in scale-up of the process to be a continuous (rather than batch) process. The model involves the design of a neural network based, model predictive, advanced, multiple input/multiple output control system which is also being applied to parallel work on the W system. This W work has already resulted in an order for 400,000 lbs of tungsten product using a continuous implementation. This early success with the W system omens well for the early commercialization of the titanium process.

The product titanium is currently under evaluation with key issues being (a) whether the titanium produced can be separated from the MgCl2 salt byproduct and (b) control of the interstitial content (oxygen and nitrogen) of the product. If the salt can be almost completely removed (<10 ppm) the market which opens up will be even larger than if a low cost salt containing (~100 ppm) product is produced. Work is continuing to optimize processing conditions so that the matrix is the salt, embedded with titanium. This will allow removal of the matrix by leaching or vacuum distillation to produce a high quality titanium product (work with the University of Western Australia [Paul McCormick] is already addressing this issue, at no cost to the program). Interstitial levels are being lowered to acceptable levels by improved sealing arrangements, and possible use of a glove box to contain the MA equipment.

In the next year of this program the quality of the powder will be evaluated in conjunction with our collaborator at INEL and industrial partners (the number of which have grown). Key issues are salt content and control of the interstitial elements. Three other approaches will also be evaluated: (a) use of hydrogen to enhance the process, (b) low temperature processing with solid TiCl4 (presently at ambient temperature the TiCl4 is liquid) and (c) production of alloy powder such as Ti-6Al-4V, directly; the latter an even more cost-effective product. Preliminary mechanical property testing will also be conducted on compacted materials, with emphasis on low cycle fatigue which is sensitive to the presence of the salt particles.

Thus the program is proceeding on track with commercialization as close as 18 months away.

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Plasma Synthesis of Nano-Sized Metallic Powders (G23)

Patrick R. Taylor, University of Idaho

Co-PI and University: F. H. (Sam) Froes, University of Idaho

Graduate Students: Weinxan Zhu, Xiaofu Chen

Industrial Collaborators and Companies: Shahid Pirzada, Nanomaterials Research Corporation; Jianxing Li, Johnson Matthey Electronics

INEL Collaborator: Peter C. Kong

Presenters: Patrick R. Taylor, P.E.; F. H. (Sam) Froes

The overall objective of the project is to develop a thermal plasma reactor system to generate nanocrystalline metallic and intermetallic powders. This overall objective may be divided into several subsidiary objectives: (a) the development of methods to assure complete vaporization of the feed materials; (b) the development of a fundamental understanding of the reactor heat, mass and momentum transfer and particle nucleation and growth kinetics; (c) the development of methods for product collection and handling in an inert atmosphere; (d) the detailed characterization of the product powders for size, shape, crystallinity and purity; (e) the performance of experiments to evaluate the consolidation of the product powders, including characterization and structural properties; and (f) the demonstration of technological advantages of this process over competing technologies (reduced costs, enhanced properties and identification of markets).

A novel plasma system has been designed, built and operated. Experiments have shown the ability to generate nanometer sized metal powders. Samples of the product powders have been subjected to characterization using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and wet chemical methods. Other product samples have been subjected to hot isostatic pressing and characterization and progress has been made in using lower temperatures to retain nanometered sized grains with near full censification. The value of the project, if the overall objective is achieved, is the development of innovative technology to provide a new process for the production of nanometer sized metal and intermetallic powders, at reduced cost and with greater flexibility compared to physical vapor deposition and other competing processes. Jonhson Matthey Electronics has shown an interest in the production of several nanometer sized metal powders as feed to their electronic solder industry market. Nanomaterials Research Corporation has shown an interest in the potential commercialization of the process for a variety of new materials processes.

The approach being used is to inject coarse metal powders into a plasma flame, inducing vaporization, followed by rapid quenching through a deLaval nozzle. The product powders are collected in a secondary quench and high temperature filter system and handled in a glove box. The product powders are characterized and subjected to consolidation tests. The major accomplishments, to date, are: the demonstration of the ability to generate nanometer sized powders of a variety of metals and the engineering of a system to handle the product powders in an inert atmosphere.

The major obstacles encountered to date are related to the incomplete vaporization of the feed materials and the product consolidation without grain growth. Research is being performed to overcome both of these obstacles. The milestones planned for next year are (a) exploratory experiments for Johnson Matthey Electronics to see if their required products can be obtained; (b) operation of the reactor to provide kilogram quantities of product for consolidation testing; (c) the development of methods to consolidate the product and retain nanometer sized grains and the measurement of structural properties; and (d) preliminary economic evaluation of capital and operating costs, comparison to competing technologies and initial market evaluation.

This page is for notes.

Towards Viable Lithium Solid Polymer Electrolyte Batteries: An Integrated Materials Approach (G146)

Anne M. Mayes, Massachusetts Institute of Technology

Co-PIs and University: Donald R. Sadoway, Gerbrand Ceder, and Yet-Ming Chiang, Massachusetts Institute of Technology

Graduate Students: Patrick Tepesch, Philip Soo, Erin Lavik

Postdoctoral Associates: Mehmet I. Aydinol, Mackenzie E. King, Gregory J. Kellogg

Industrial Collaborator and Company: Robert Higgins, Manager, New Product Development, Eagle-Picher Industries, Inc., Joplin, MO 64802

INEL Collaborator: Gary L. Hunt, Automotive Systems and Technology Department

Presenters: Anne M. Mayes and Donald R. Sadoway

The market potential for rechargeable lithium solid polymer electrolyte (SPE) batteries is conservatively estimated to be $1 billion per year by the turn of the century. Impediments to commercialization of this technology are almost entirely materials related. To address materials challenges in the cathode, we have formed a research team of materials scientists with expertise in the subdisciplines of polymer science, ceramics, electrochemistry and computational materials science. The objective of our program is to fabricate an advanced composite cathode (ACC) operable in the service temperature range of -10 to +70°C, and resistant to failure beyond 1000 cycles. This new robust cathode will have a microstructure consisting of fine intercalation particles pinned at the interface between ionically and electronically conductive interpenetrating polymer networks. First principles computational modelling techniques are being employed to identify superior-performance, low-cost intercalation compounds (ICs).

Major accomplishments to date include the successful synthesis of new candidate polymer electrolytes for the ionically conductive component of the ACC. The conductivity of this polymer has been measured by a.c. impedance methods and found to be significantly higher than that of poly(ethylene oxide) at room temperature, while maintaining dimensional stability. Sulfonated polyaniline (sPAN) has also been successfully synthesized as a candidate material for the electronically conductive component of the ACC. This material has a reported conductivity of 0.2 S/cm and can be processed readily into films by casting from common solvents. We have additionally prepared a first-generation bicontinuous polymer matrix material by casting mixtures of sPAN and a candidate ionically conductive polymer from solution. The microstructures have been characterized by optical microscopy, transmission electron microscopy and electron diffraction. Model oxide particles have been incorporated into the mixed polymer system, and appear to localize at the interface between the two polymer phases.

Using first principles computational methods (LMTO-ASA) on materials exhibiting the layered NaFeO2 structure, the chemistry and heat treatment of lithium-metal-oxides have been related to battery operating voltage and intercalation range. Specifically, the relationship between voltage and choice of transition metal has been established. Based on these calculations, several promising new IC materials have been identified. Chemical precipitation routes are being explored for the preparation of ultra-fine particles of these candidate IC materials.

Milestones for the next year include fabrication of a first generation ACC incorporating a dispersion of ultra-fine IC particles, followed by structural characterization and electrochemical testing. First battery prototypes are anticipated for 6/97, to be built in collaboration with Eagle-Picher.

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This page is for notes.

Session 3. Reactor Performance, Degradation, and Regulation

Tuesday, 8:00 a.m. to 11:30 a.m.

Mujid S. Kazimi (MIT), chair
Ralph G. Bennett (INEL), co-chair
David M. Woodall (Uof I), panelist
Jim Lake (INEL), panelist

8:00 a.m.	N06	Neil E. Todreas MIT	Improvement in Nuclear Power Plant Capacity Factors Through Longer Cycle Length Operation
8:50 a.m.	N121	K. L. Murty North Carolina State University	Stress-Strain Microprobe for Assessing Degradation of Nuclear Piping and Vessels
9:35 a.m.	—	Break	
10:05 a.m.	N07	George Apostolakis MIT	Software Dependability and Its Impact on Risk-Based Regulation
10:50 a.m.	N212	Michael W. Golay MIT	Integrated Models, Data Bases, and Practices Needed for Performance-Based Safety Regulation
11:30 a.m.	—	Adjourn	

Improvement in Nuclear Power Plant Capacity Factors Through Longer Cycle Length Operation (N06)

Neil E. Todreas, Massachusetts Institute of Technology

Co-PIs and University: Prof. Michael J. Driscoll and Prof. Michael W. Golay, MIT

Graduate Students: Feng Li, Robert McHenry, Michael McMahon, Thomas Moore, Hideki Masui

Industrial Collaborators and Companies: Kord Smith, Studsvik of America; William Kline, Boston Edison Co. (Pilgrim Nuclear Power Station); Joe Vargas, North Atlantic Energy Service Corp. (Seabrook Nuclear Station); Edward Pilat, Yankee Atomic Electric Company

INEL Collaborators: Jerry L. Judd, Nathan Siu

Presenter: Neil Todreas (Michael Driscoll will be present)

The objective of this project is to develop tools to enable nuclear power plants to adopt extended (four-year) operating cycles between refuelings. Tasks to be completed include: long-lived core designs for both PWRs and BWRs; strategies for attaining the plant levels of reliability and availability needed to make a 48-month refueling interval attractive, and strategies for rationalizing current surveillance requirements to a 48-month fuel cycle.

An extended cycle will result in an improvement in plant capacity factor. A net economic benefit can result if the cost penalty of the longer-lived core can be offset by improved plant operational availability.

In the core design effort, state-of-the-art nuclear and thermal design codes are used to establish the feasibility and costs of a 48-month fuel cycle in PWR and BWR units. Neutronic analyses are conducted using the CASMO-3/TABLES-3/SIMULATE-3 reactor analysis suite developed by Studsvik. Fuel thermal and mechanical performance is evaluated with ESCORE from EPRI and with FROSSTEY from the Yankee Atomic Electric Company.

To develop a strategy for attaining required plant levels of reliability and forced outage rates, detailed models of plant systems are being created to analyze the relationship between component failure and repair rates, system capacity factor, and overall plant capacity factor. Additionally, thorough analyses of industry-wide component failure databases (NPRDS, GADS, etc.) are performed to determine current component failure and repair rates.

To rationalize surveillances, researchers identify and analyze each regulatory and investment protection based surveillance which currently precludes a 48-month cycle. Classifications are:

Category A: Candidates for on-line performance;

Category B: Must be performed while shutdown but are candidates for administrative extension to 48 months or more;

Category C: Must be performed while shutdown and do not support a 48-month cycle.

Category A or B items will support an extended cycle. Category C items require additional engineering work to resolve.

Accomplishment in the core design area is the development of a 48-month core design for an existing PWR plant using UO_2 fuel enriched to 7 w/o U-235 and Gd_2O_3 and IFBA (Integral Fuel Burnable Absorbers--a thin ZrB_2 fuel pellet coating) as burnable poisons. Achievements in the area of reliability include the completion of comprehensive analyses of the PWR Condensate and Feed and Main Turbine Generator systems and the development of a framework for reducing forced outage rates through the analysis of key plant components. In the area of surveillance intervals, a systematic surveillance resolution procedure to prepare for extended cycle lengths was developed, and all surveillances which currently preclude a 48-month operating cycle have been analyzed and categorized at both a PWR and BWR power plant. To date, no obstacles to project completion exist.

Project milestones for July 1996 to June 1997 are PWR systems availability enhancement; BWR core design.

Work will continue on: developing a quantitative basis for establishing optimum surveillance intervals; BWR systems availability enhancement; finalizing PWR fuel/core performance assessment.

This page is for notes.

Stress-Strain Microprobe for Assessing Degradation of Nuclear Piping and Vessels (N121)

Prof. K. Linga (KL) Murty, North Carolina State University

Co-PI and University: None

Graduate Students: Peter Miraglia, Ed Preble

Industrial Collaborator and Company: Fahmy Haggag, Advanced Technology Corporation

INEL Collaborator: Vikram Shah

Presenter: Prof. K. Linga Murty

The major objective of the program is to utilize the recently developed stress-strain microprobe (SSM) to first demonstrate its capabilities in assessing the degree of degradation of the mechanical and fracture properties of various structural alloys used in nuclear power technology. The second major objective is to develop the system into an in-situ nondestructive microprobe for characterization of the aging degradation of the nuclear power plant components, in particular, the nuclear pipes, pressure vessels and reactor supports, turbine blades, etc. The proposed microprobe is based on the principle of automated ball indentation which is rapid, nondestructive, adaptable for in situ testing, and could be made operator-insensitive. In addition, the probe provides a localized direct stress-strain curve determination. The same system will also be used in obtaining these properties using the traditional destructive tests (such as tensile, etc.) on subsize specimens and for correlating them with those obtained from conventional size specimens.

The ABI machine was procured from the Advanced Technology Corporation in April 1996 and typical tests were performed to verify its operation. The chamber and control systems for testing at low and high temperatures have recently been ordered (Applied Test Systems Inc.) and will be delivered by the middle of July. A number of steels were procured from ORNL with the help of our technology partner (Fahmy Haggag of ATC) which included weld and HAZs also. The delays in getting the allocated funds to the full amount precluded us in ordering the equipment at the proposed start of the project (in Dec '95); however, the ATC was able to get the equipment as soon as we ordered the machine (in mid-Feb). The subsize tensile specimens are now being fabricated in the machine shop at NCSU from the various steels and as soon as they are ready, the tests will be made. Meanwhile, INEL collaborator (Vik Shah) is getting the cast stainless steel specimens procured from various vendors for long term (6 months and more) thermal aging which will be used for characterizing aging effects on mechanical properties of these steels.

Meeting the second research objective involves adaptation of our probe for remote testing, and initially the magnetic attachments were suggested and tested by our industrial collaborator (ATC). While these techniques are promising, they are not adaptable for in-reactor use of all the materials, many of which are non-magnetic. We are also in the process of investigating various Robotics specialization companies for adopting our Stress-Strain Probe for remote operation so that property changes of reactor vessels and others can be made in situ.

The proposed research is expected to lead to the development of appropriate methodologies for assessing the in-service damage and the remaining life of the components in nuclear power plants. The technology can be applied for verification and quantification of the effectiveness of thermal annealing of embrittled nuclear reactor pressure vessels. Once the technology is developed, the adaptation of the system for in-situ application will be made in collaboration with utility companies.

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Software Dependability and Its Impact on Risk-Based Regulation (N07)

George Apostolakis, Massachusetts Institute of Technology

Co-PI and University: None

Graduate Students: Christopher J. Garrett, Andrew P. Gnau, Xinhui Chen

Industrial Collaborator and Company: Stephan J. Hetrick; Supervisor, Computer Engineering; San Onofre Nuclear Generating Station

INEL Collaborator: Nathan Siu

Presenter: Prof. G. Apostolakis

The overall objective of this project is the development of a methodology, tools and case studies which support Risk Informed Performance Oriented Regulation (RIPOR) of digital I & C systems in nuclear power plants. This project is using case studies to develop a methodology for establishing performance-based objectives and criteria in light of the uncertainties that the increasing use of digital software and its interaction with operators introduce. The major products of this work will be the development of the right mix of deterministic and probabilistic criteria that can be verified by acceptable methods, as well as the identification of appropriate actions in case the criteria are not satisfied, so that the overall objectives will be met.

We are currently pursuing three parallel courses of research aimed at identifying the strengths and limitations of some current and proposed practices, from a RIPOR perspective, in order to develop a basis of issues to be addressed during methodology development. The first of these is a critical review of the NRC's current approach to digital I&C. Over the previous quarter we have been examining Lawrence Livermore National Laboratory's (LLNL) proposed update to Chapter 7 of the Standard Review Plan. The primary objectives of the criteria they've proposed are to verify that an applicant has an adequate software development plan, with a well defined life cycle, and to verify that sufficient documentation is produced to support review of the process as well as the product. The lack of evident quantitative goals or objectives raises the question of how such regulatory guidelines could be integrated into a RIPOR framework. Current activities are being directed at evaluating the proposed guidelines, as well as similar guidelines and standards currently being applied in other industries, to identify, in detail, the research needs that need to be addressed in order to develop a RIPOR framework for digital I&C.

The other two research activities are applications of two proposed V&V techniques, namely, formal methods and DFM, to our first case study. Formal methods use mathematical or logic-based ideas and techniques in the specification, design, analysis and assurance of computer software. Using formal methods to perform V&V involves the construction of rigorous, mathematical proofs that each stage of the software design and is logically consistent and complete with respect to the previous stage. DFM is a model-based technique in which a digraph model expressing logical and temporal characteristics of the system, included in both the software and the hardware with which it interacts, is used to construct fault trees identifying paths which can lead to critical system events.

These research issues are being investigated in the context of our first case study, the MIT-SNL Period-Generated Minimum Time Control Law experiment, which utilizes a closed-loop digital control system for the time-optimal adjustment of a reactor's neutronic power. Objectives for next year involve the completion of our work on the case study in early fall, identifying the strengths and weakness of the three different approaches, and using that knowledge to set the groundwork for methodology development.

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Integrated Models, Data Bases and Practices Needed for Performance-Based Safety Regulation (N212)

Michael W. Golay, Massachusetts Institute of Technology

Co-PI and University: None

Graduate Students: Sarah Abdelkadar, Jess Iversen

Industrial Collaborator and Company: Sunil Weerakkody, Northeast Utilities Services Corporation (NUSCO)

INEL Collaborator: Nathan Siu

Presenter: M. W. Golay

The purpose of the project on Integrated Models, Data Bases and Practices Needed for Performance-Based Safety Regulation is to investigate and demonstrate the potential benefits of performance-based safety regulation (PBR), or as it has become known more recently risk-informed, performance-based regulation. These goals are explained further in the abstract from the project proposal, as follows:

"It is proposed to develop tools, methods and practices to support both the USNRC and nuclear power industry in structuring a practical approach to performance-based safety regulation. Success in this work will improve the safety of operating nuclear power plants and permit much more efficient use of nuclear power plant resources. The project's results can improve the capabilities of the INEL and enable the NRC to build the foundations and framework for performance-based regulation. The tools and practices developed in this work will demonstrate that the framework is realistic, and that the goals are achievable. At all stages of the project emphasis will be given to insights gained from industry experience. This is likely to produce results having a high acceptance level with not only the NRC but also with the nuclear industry."

Since this project began its importance has increased for reasons which include the following: the NRC and nuclear industry have continued working together to formulate policies and procedures for implementation of the performance-based Maintenance Rule, which went into effect in July 1996.; and the new NRC Chairman, S. A. Jackson, has given a priority to moving the NRC to using what she terms "risk-informed performance-based regulation." In order to speed this transition she has directed the NRC staff to reformulate its Standard Review Plan and to issue corresponding Regulatory Guides for the use of licensees, to incorporate use of PBR.

In our work we are focusing upon use of an on-line PRA, a Risk Monitor, for use in planning plant maintenance and revising the operational, surveillance and maintenance requirements of the plant. We are focusing upon the example of the plant's emergency diesel generator (EDG) system. The reasons for this choice are that (a) The EDGs are very important for safety, having the highest value of the Fussel-Vesely risk importance measure for core damage frequency (CDF) at that plant—meaning that failure of the EDGs would contribute more to core damage risks than would failure of any other system in the plant.; (b) The EDGs require frequent surveillance testing and mandatory maintenance, as required by the technical specifications, with the objective basis of these requirements never having been established; and (c) Potential improvements in terms of both safety and economics can be achieved by basing future requirements in these areas upon risk-based arguments.

In this work one of the project's two Research Assistants has been assigned to play the role of the utility licensee, identifying practices and requirements which should be changed, devising arguments and substitute requirements and practices for the current ones and proposals to be submitted to the NRC to justify these changes. The other RA has been assigned the role of the NRC, formulating PBR regulatory bases and practices which can be used to evaluate proposals which may be submitted by licensees in the EDG area. To do this we have undertaken study of the NRC's standard review plan and criteria (SRP) and the history of the development of its criteria. We are also studying the inspection and enforcement practices of the NRC regional offices concerning EDGs.

In performing this work we are focused upon the tasks described in our original proposal, which are the following:

Task 1. Evaluation of the merits and potential uses of the Risk Monitor.

Task 2. Investigation of replacing the relevant prescriptive regulations by proposed PBR alternatives.

At this point our work proceeds well and on schedule. We have identified several potential improvements in EDG procedures and requirements, and are now developing the arguments to justify changes in their regulatory treatments.

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Session 4. Structures

Tuesday, 1:00 p.m. to 4:30 p.m.

Merton C. Flemings (MIT), chair
James A. Seydel (INEL), co-chair
Joel Dubow (Uof U), panelist
Bill Blume, Bob Chaney (INEL), panelists

1:00 p.m.	G212	Christopher Leung MIT	Optical Fiber Sensors for Concrete Structures
1:50 p.m.	G229	Timothy A. Reinhold Clemson University	Wind Loading and Capacities of Components, Connections, and Systems
2:50 p.m.	—	Break	
30:20 p.m.	G35	M. Nafi Toksoz MIT	Spatial Variability of Earthquake Ground Motions and Their Contributions to the Failure of Major Structures
4:30 p.m.	—	Adjourn	

Optical Fiber Sensors for Concrete Structures (G212)

Christopher K.Y. Leung, Massachusetts Institute of Technology

Co-PI and University: Theodore F. Morse, Brown University

Graduate Students: Niell Elvin, MIT; Noah Olson, MIT; Yi-Fei He, Brown University

Industrial Collaborator and Company: Barrie Sellers, Geokon Inc.

INEL Collaborators: Judy Partin, Mark Stone, Rick Farnswort

Presenter: Christopher Leung

The objective of this four year research program is to develop optical fiber systems for the automatic continuous monitoring of concrete structures. Specifically, we are developing (a) a novel sensor to monitor flexural cracking in concrete bridges and grouted barrier structures, (b) Bragg grating strain sensors at 800 nm which can be used with low cost lasers and electronics, (c) sensor for combined strain/temperature sensing. The successful achievement of the research goals can lead to substantial savings in manual inspection costs as well as improved safety of concrete structures.

In FY-96, the research focus is to develop a crack sensor for concrete structures which can detect and monitor a number of cracks with a single optical fiber, without requiring a-priori knowledge of crack locations. The sensitivity and range of the sensor, as well as the number of cracks it can monitor, depend on a large number of parameters including (a) the mechanical properties, optical properties and size of the glass fiber, (b) the stiffness and size of the surrounding plastic coating, (c) the properties of concrete, as well as (iv) the fiber layout in the structure. With so many parameters that can vary, the design of an effective sensor based on empirical testing is not practical. A theoretical model which relates the loss of optical signal with crack opening along the fiber is therefore developed based on a combination of mechanical and electromagnetic wave analysis. An experimental set-up is also designed to simulate crack opening in concrete members and to measure both crack opening and optical signal loss. Theoretical predictions are then compared with experimental results.

To couple the crack sensor to an existing concrete bridge or grouted concrete barrier, special installation techniques are required. To monitor flexural cracks at the bottom of bridge decks, optical fibers are first embedded into a thin polymeric sheet, which is then glued to the structure. For cracking in the grouted barrier, optical fibers are wound helically around a rod which can be embedded into the hole before grouting takes place. These sensing sheets and rods have been made and tested in our laboratories. Preliminary results appear to be promising.

Besides research work related to the crack sensor, preliminary durability studies of optical fibers in the cementitious environment have also been carried out.

Research tasks planned for FY-97 include (a) further work on the theoretical model for signal loss vs crack opening, (b) design and verification of crack sensors with optimal performance based on the theoretical model, (c) further development of sensor installation techniques, (d) fabrication of novel fibers for strain and temperature measurements, and (e) further durability tests for optical fibers in the concrete environment.

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Wind Loading and Capacities of Components, Connections and Systems (G229)

Timothy A. Reinhold, Clemson University

Co-PIs and Universities: Ben L. Sill, Clemson University; Ahsan Kareem, Notre Dame University; Dale C. Perry, Texas A&M University; Norris Stubbs, Texas A&M University

Graduate Students: Edward Sutt, Clemson University; Muralidhar Kallem, Clemson University; Jefferey Sciaudone, Clemson University; Sang Hwun Choi, Texas A&M University; Sooyung Park, Texas A&M University

Industrial Collaborator and Company: Edward Laatsch, State Farm Fire and Casualty Co.

INEL Collaborator: Cheryl O'Brien, ACETS

Presenter: Timothy A. Reinhold

A full-scale test facility is critically needed for assessing the performance of buildings subjected to extreme winds. The objective of this project is to determine the technical feasibility of constructing such a facility and to determine critical elements required to produce desired profiles of mean wind speed and the turbulence structure of the wind and/or the magnitude, spatial distribution, and correlation of wind loading. A secondary objective is to formally develop a cost benefit analysis methodology which will provide focus to the building performance studies in such a facility.

In the first year, the project has developed a 1:25 scale model of a proposed high wind test facility. This facility concept, named the Wall-of-Wind, would involve an array of fans (either turbo prop or electric) to create peak winds of about 200 miles per hour. Each fan would operate under a control system which would allow separate control of the wind velocities being produced by each fan. The objective is to produce a variety of wind field conditions and subsequent loadings on buildings. Results are being compared with field data on wind conditions and surface pressures obtained from a full-scale experimental building tested at Texas Tech University. Preliminary results indicate that the concept is technically feasible but that it will probably require additional lateral turbulence generation devices.

The project is also evaluating the feasibility of using multiple actuators in a feedback control system to produce simulated wind loads for testing of components and connections. The hardware and software has been assembled for this system and initial testing has been completed. The project presentation will describe the accomplishments to date including proof of concept through matching of target and monitored time histories.

Development of the cost benefit analysis methodology is well under way using fuzzy analysis methodologies. Results of risk analyses for individual properties and groups of properties have been completed and results of sensitivity studies will presented at the annual meeting.

The project is on schedule to provide the basic aerodynamic design requirements for the Wall-of-Wind by the end of the fiscal year. The other tasks are proceeding according to the modified schedule submitted to MIT as a result of the late project start date. The second year will focus on simulation of flow around buildings to insure that testing of roof coverings can be properly simulated. The performance of components for the full-scale facility will also be evaluated to assist INEL in the selection of the most effective alternatives. A concept for a smaller scale roofing test facility will be investigated. The multiple actuator system will be extended to simulation of nonlinear non-gaussian loads. The cost benefit and risk assessment methodology will be evaluated against field data on losses obtained from insurers for recent hurricane events.

Successful completion of the three year project will provide the foundations for creation of a state-of-the-art full scale wind test facility. The cost benefit studies will help to focus the initial testing to be conducted in the facility to insure that the facility provides rapid value to the government and potential user industries. Creation of this facility will help to improve the performance of houses and commercial structures in severe wind events. The reduction in losses from future storms is critical to the economic health of the United States.

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Spatial Variability of Earthquake Ground Motions and Their Contributions to the Failure of Major Structures (G35)

M. Nafi Toksoz, Massachusetts Institute of Technology

Co-PIs and University: Emmanuel Chaniotakis and Eduardo Kausel, MIT

Graduate Students: None

Industrial Collaborator and Company: Steve Fairfax, Failure Analysis Associates

INEL Collaborator: Thomas K. Larson

Presenters: Prof. M. Nafi Toksoz, Emmanuel Chaniotakis, Dr. Steve Fairfax

The overall objective of this project is the improved earthquake-resistant design of man-made structures to significantly mitigate the severe effects of destructive earthquakes in urban areas. The severe human and economic losses resulting from recent earthquake disasters near urban areas demonstrate the need for better seismic modeling to improve building design codes for both new construction and in retrofitting older structures. The Kobe earthquake alone caused over 5,500 deaths, thousands of injuries and widespread homelessness, destruction and damage to thousands of buildings, and disrupted major transportation systems. The direct economic cost of this earthquake was about $200 billion. Obtaining knowledge about the performance of new earthquake-resistant designs and retrofitting techniques before future catastrophic earthquakes occur is critical to greatly reducing the enormous human and economic losses caused by such events. One of the most effective approaches to meet this objective is to develop a full-scale, three-dimensional seismic motion simulator to test experimental earthquake-resistant designs in natural-scale structures. A full-scale seismic simulator has the potential to overcome the limitations of sub-scaled experiments, and would be a major national resource.

The purpose of this project is to perform the design work necessary for the construction of a full-size, electromagnetic seismic simulator (EMSS) capable of faithfully reproducing the large and complex ground motions generated by destructive earthquakes. To accomplish this, we have assembled a multi-disciplinary team of scientists expert in the fields of seismology, civil, electrical, and mechanical engineering, and electromagnetic energy systems. This team has identified ten key tasks to complete the design work including: (1) evaluation of ground motion from recent large destructive earthquakes to establish the criteria for the motions generated by the EMSS; (2) analysis of the simulator base/ground interaction; (3) computer modeling of earthquake motions using 3-D heterogeneous earth models (4) test building/simulator platform interaction; (5) soil box testing to study soil/building interaction; (6) EM driver feasibility; (7) EMSS conceptual design; (8) a performance and cost comparison between EM and hydraulic simulator systems; (9) analysis of the power system required for the EMSS; and (10) engineering design of the EMSS. Tasks 1, 2, 4, and 6-9 have either been accomplished or are near completion, and their results are being presented at the INEL Summer Review Meeting.

Key milestones achieved in 1995 and 1996 were the evaluation of the ground motion and structural response data to define the necessary performance characteristics and limitations of the simulator, the favorable feasibility analysis of the power system and the EM driver, the design of a scale-model (table-top) EMSS scheduled to be implemented by June 1996, and the development of a detailed, conceptual design for the test facility. Another important milestone has been the flexible design of the power system to accommodate the requirements of other ACETS test facilities such as the "Wall of Wind." The specific goals planned for 1997 are (a) to perform computer modeling to generate the 3-D ground motion simulations for the site geology at the INEL facility to estimate the seismic wave propagation generated by the EMSS; (b) to design the soil box for the seismic simulator; and (c) to complete the engineering design for the EMSS.

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This page is for notes.

Session 5. Nuclear Medicine Accelerators and Isotopes

Tuesday, 1:00 p.m. to 5:30 p.m.

Michael W. Golay (MIT), chair
Ralph G. Bennett (INEL), co-chair
David M. Woodall (Uof I), panelist
Jim Lake (INEL), panelist

1:00 p.m.	N215	Jay F. Kunze Idaho State University	Laser Separation of Isotopes for Nuclear Medicine Applications
1:35 p.m.	N200	George H. Miley University of Illinois	Compact Neutron Source Based on Accelerator-Plasma Target Technology
2:20 p.m.	N01	Lawrence M. Lidsky MIT	Application of High Power Electron Accelerators to Isotope Production
3:05 p.m.		Break	
3:35 p.m.	N21	Jacquelyn C. Yanch MIT	Boron Neutron Capture Synovectomy (BNCS): Treatment of Rheumatoid Arthritis with the 10B(n, a) Nuclear Reaction
4:35 PM	N24	Frank Harmon Idaho State University	Compact Accelerator Neutron Sources for BNCT Using Near Threshold Charged Particle Reactions
5:30 p.m.	—	Adjourn	

Project Title: Laserl Separation of Isotopes for Nuclear Medicine Applications (N215)

Project PI and University: Jay F. Kunze, Idaho State University

Co-PIs and Universities: Jeff W. Eerkens, University of Missouri; Thomas LaHann, Idaho State University

Graduate Students: Chris Hunt, Idaho State University; Greg Anderson, University of Missouri; Donald Puglisi, University of Missouri

Industrial Collaborator and Company: Malinckrodt Medical, Inc.

INEL Collaborators: Steve Laflin, John Braisier

Presenter: Jay F. Kunze

The laser enrichment process being developed involves selective molecular excitation of a hexafluoride molecule using lasers, and then allowing chemical reaction of the excited isotopic species to occur, resulting in the precipitation of the reacted isotope from the flowing gas stream. The process has been designated CRISLA (Chemical Reaction of Isotopes by Selective Laser Activation). The process is somewhat like the Los Alamos MOLIS process, except that MOLIS used several dozen molecular activation steps to obtain complete dissociation of the desired hexafluoride molecule. In the case of CRISLA, chemical reaction energy does most of the work, rather than laser energy, since the laser merely excites the molecule to a relatively low excited state.

The process has been privately funded, for the intended purpose of uranium enrichment, in the USA since 1978, and was most recently a cooperative effort between the inventor, the USA company (Isotope Technologies, Inc.) and the large Canadian uranium mining company, CAMECO. However, when the uranium enrichment market became unprofitable as a result of Russia putting large quantities of enriched uranium from decomissioned weapons and from stockpiles into world markets, CAMECO opted to no longer support the research. Isotope Technologies, Inc. then donated the equipment and their share of the patents to the University of Missouri.

With the potential of the ATR and of accelerators to make medical isotopes of various kinds, it became apparent that separation of small quantities of isotopes, primarily for targets, would be a major need. The Calutrons at Oak Ridge had been shut down, and USA supplies of many separated isotopes were in short supply. The use of the CRISLA process to produce gram to kg quantities of an isotope seemed more reasonable than the goal for enriching uranium, which would demand outputs of many tons per day.

The experimental work on separation of molybdenum isotopes has been under way at the University of Missouri for over a year. ISU will be looking at the potential and future need for other isotopes, and of the toxicity of radio parmaceuticals that are currently being made without the use of separated target isotopes. The experimental work has proceeded through the phase of accurate measurement of vibrational lines of the various isotopes, and chemical raction rates at several temperatures have been measured for the MoF6 molecule. The next major experimental step will involve developing a small supersonic flow path so that the CO_2 laser can more effectively separtate isotopes as a result of the narrower vibrational frequency spread at the cooled expansion temperatures.

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Compact Neutron Source Based on Accelerator-Plasma Target Technology (N200)

George H. Miley, Fusion Studies Laboratory, University of Illinois, Urbana-Champaign

Co-PI and University: None

Graduate Students: Yibin Gu, John M. DeMora, Blair P. Bromley

Industrial Collaborators and Companies: John Sved, Deutsche Aerospace/Daimler-Benz; Tumay Tumer, NOVA, Inc.; Larry Jacobson, Halliburton; Bart Czirr, Mission Support, Inc.

INEL Collaborators: J. Hartwell, R. A. Anderl

Presenter: G. H. Miley

The objective of this research project is the development of a unique accelerator-plasma target neutron source. Neutron-generating devices are enabling technologies for a variety of industrial and medical applications, including non-destructive testing of hazardous and mixed wastes and assay of fissile materials for nuclear safeguards and arms control. A variety of first-step applications, such as activation analysis of coal impurities, currently use radioisotope sources (e.g., Cf-252) or accelerator-solid target neutron sources with a strength of 107 n/s. However, use of radioisotopes involves costly licensing and shielding, and currently available accelerator-solid target neutron sources are expensive and unreliable, due to the rapid deterioration of the target. Recently, University of Illinois (UI) workers have developed a unique plasma target source that avoids these problems. It employs an inertial electrostatic confinement (IEC) device that produces fusion neutrons by an accelerator-plasma target method, thus avoiding target deterioration and offering competitive yields in the 107 n/s range. Strong interest has already developed in commercialization of this device, e.g. one company recently obtained marketing license rights to sell demonstration units for activation analysis of coal impurities.

However, to expand the range of potential applications, this technology must be extended along two distinct paths: the development of devices based on alternate geometries for specific applications and the optimization of the concept to higher-yield sources. For example, potential medical applications, with immense markets in fast neutron cancer therapy and boron neutron capture therapy (BNCT), require a source capable of significantly higher neutron rates for human treatment. Thus, UI workers recently invented a variation of the original IEC, a unique compact cylindrical (C-) device. It potentially offers higher yields while eliminating internal wire-grid electrodes and associated problems of grid erosion, thus extending the device lifetime. Neutron emission simulates a "line source," making it especially attractive for applications requiring broad neutron coverage. A prototype C-device has demonstrated D-D yields up to 107 n/s. The goal of the present work is to scale up the C-device, (in multiple steps of 102 increase in yield) to obtain the database needed to design a 1015 D-T n/s device ultimately desired for high-yield applications. Intermediate-yield units developed in the phased scale-up plan will provide near-term "pay-offs" in terms of providing commercially attractive units for expanded activation analysis applications and local isotope production use.

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Application of High Power Electron Accelerators to Isotope Production (N01)

Lawrence M. Lidsky, Massachusetts Institute of Technology

Co-PI and University: Richard Lanza, Massachusetts Institute of Technology

Graduate Students: David Chichester, Randy Tompot

Industrial Collaborator and Company: Richard Testa, Thermo Technology Ventures Inc.

INEL Collaborator: Ralph G. Bennett

Presenter: Lawrence M. Lidsky

This project is an investigation of the use of photonuclear reactions to produce radionuclides of medical and industrial interest. We use electron-beam generated bremsstrahlung to produce intense radiation fluxes with photon energy in the Giant Dipole Resonance range of various target isotopes. Radionuclides are generated by (g,n), (g,p), (g,np), and higher-order reactions, depending on target isotope and beam energy. This technique is usually complementary to the more commonly used schemes for radionuclide production (ion beams, neutron absorbtion, fission product) but there are some notable cases where several techniques are capable of producing a given radionuclide. In such cases, the choice of the most economical production method often depends on a complex interplay of physics, technological capabilities, and existing medical-industrial infrastructure. Our program is focused on one such isotope, Tc-99m, but we are also investigating a range of other radionuclides of potential commercial interest.

We have developed the capability to predict the Mo-99 production rate for targets of potential commercial interest. We have performed two benchmark irradiations using the electron linacs at NIST (at 28 MeV) and at RPI (at 40 MeV). The experimental results tracked the predicted values within a few percent over an order of magnitude in specific activity. This cross-section set is being used to design several versions of production targets, based on parametric studies of the design space. The first version stresses design simplicity and uses a passive aluminum structure to minimize electron heat loading of the Mo-100 target slugs. The second version uses magnetic fields to sweep the electron beam but allows low energy photons to reach the target. Both versions use a helium cooled sintered tungsten convertor plate. We are in the process of determining the optimum operating point as a function of linac operating map and target power handling capabilities.

In support of the assessment of commercial potential, we have developed a buildup/decay model for the relevant isotopes which is capable of modeling an arbitrary schedule and efficiency of technetium separation from the irradiated target slugs. We have also investigated potential vendors of isotopically enriched molybdenum to provide data for economic optimization. We have procured and verified the composition of a sample lot of very highly enriched Mo-100 that will be used for irradiation studies.

In support of the study of other isotopes suitable for photoneutronic production, we have developed an interactive database based on the National Nuclear Data Centers Table of Isotopes. We have added nuclear decay systematics to the database, including decays to and from excited states whenever feasible. For any chosen isotope in the database, it is possible to determine the precursor and descendant isotopes for an arbitrary number of generations, and to quickly determine the identity and natural abundance of those stable isotopes in the neighborhood of each precursor which could be used as a target. We have also compiled evaluated photonuclear reaction cross-section sets for several isotopes of potential interest.

Major milestones for next year include the choice of commercial target design and operating parameters, and subsequent thermal-hydraulic tests under full heat load.

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Boron Neutron Capture Synovectomy (BNCS): Treatment of Rheumatoid Arthritis with the 10B(n,a) Nuclear Reaction (N21)

Jacquelyn C. Yanch, Massachusetts Institute of Technology

Co-PI and University: None

Graduate Students: Emanuela Binello, An Lu

Industrial Collaborators and Company: R. E. Shefer and R. E. Klinkowstein, Newton Scientific, Inc.

INEL Collaborator: David Nigg

Presenter: J. C. Yanch

The potential for the boron neutron capture reaction to be effective in treating rheumatoid arthritis is under investigation. Dubbed "Boron Neutron Capture Synovectomy" this potential new therapy procedure will involve the injection of a boronated compound directly into the arthritic joint followed by joint irradiation by a beam of low-energy neutrons. This is called 'synovectomy' since the goal is to destroy the inflamed synovium, the cause of the pain and ultimate disability associated with rheumatoid arthritis. Working with researchers at the Harvard Medical School, studies using live human arthritic synovium obtained from the operating room have been carried out. Three boronated compounds have been evaluated in terms of their ability to be taken up by the arthritic tissue. Uptake measurements were carried out using prompt gamma neutron activation analysis. Results indicate that, using a compound 100% enriched in 10Boron, 10B concentrations of 1500-2500 ppm are easily obtained. Similar concentration ratios are expected to be achieved in vivo due to the phagocytic action of synovial lining cells, and as a result of the synovial physiology. Uptake studies are underway to assess uptake of boron by articular cartilage in the joint. The next phase of work will involve studies assessing in vivo uptake of the boronated compounds using a rabbit model of human arthritis. These will be followed by studies to assess the efficacy of BNCS (i.e. boron administration followed by neutron irradiation) in the rabbit model.

Additional work in the area of optimal neutron beams for BNCS has been carried out and the ideal neutron energy range (0.025 eV - 100 eV) has been identified. This information has been used as input to the neutron beam design study currently underway. This study, carried out by Monte Carlo simulation, focuses on optimal moderator and reflector materials to produce the most useful neutron beam. Current results suggest that a heavy water moderator surrounded by a graphite reflector will provide high therapeutic ratios and will allow therapy to be completed very quickly. All milestones have been met to date, with the exception of modifications to the INEL treatment planning software which could not be accomplished due to lack of funding for the INEL collaboration. Milestones originally scheduled for FY-98 (not funded) are planned for FY-97.

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Compact Accelerator Neutron Sources for BNCT Using Near Threshold Charged Particle Reactions (N24)

Frank Harmon, Idaho State University

Co-PI and University: Xiao-Lin Zhou, MIT

Graduate Student: Charles Lee (MIT)

Industrial Collaborator amd Company: Robert Hamm, AccSys Technology, Inc.

INEL Collaborators: Yale Harker, David Nigg

Presenters: Frank Harmon (ISU), Xiao-Lin Zhou (MIT)

The objective of the project is to develop a commercializable design of compact, transportable neutron source for BNCT suitable for the hospital environment. Past effort in accelerator neutron source for BNCT has not been successful because of the difficulty in target design to withstand high current and the need of high current which cannot be easily met by compact commercial accelerators that produce low average current. Our project proposes to use the key idea of near-threshold charged-particle reactions to solve the difficulty and remove the limitations. In a near-threshold reaction, epithermal neutrons are produced directly without the need for moderation. Although the total neutron yield is lower than that at high charged-particle energies, the overall useful neutrons at epithermal energies will be much higher at near threshold. As a result, the need of proton current can be significantly reduced such that a compact accelerator can be used and the lower current need will also make target design much easier. In addition, the beam contains no fast neutron contamination, which is an advantage over reactor beams. If the project is successful, it will lead to the first commercializable design of compact neutron source for BNCT based on current commercial accelerator technology.

In the past year of the project, we have completed three major tasks at MIT. (Work at ISU and INEL will be summarized by Harmon and Harker separately.) First, we have conducted an extensive survey and study of experimental reaction data on p-Li and p-Be reactions and identified the areas where measurements are needed to obtain key data for these reactions. The result is compiled into a report which will be the basis for neutronic studies for target design in the next year. Second, we have established a computation setup and software for neutron transport studies and charged particle reaction calculations. Using this setup, I have trained Charles Lee, a Ph.D. candidate, to conduct MCNP transport computation and nuclear reaction analysis in the past year for this project. Third, Lee and I have carried out a series of reaction and neutronic computations and reaction analyses and obtained preliminary results which showed important properties of near-threshold reactions. These results indicated that 100 mA of current seemed to be sufficient for producing 109 n/cm2s epithermal flux based on near-threshold reactions. This amounts to a factor of 100 reduction in the need on proton current compared to the traditional mode of neutron production at high proton energies. These results are important and will be the basis for next year's work. In the next year, we will (1) systematically compute the epithermal fluxes achievable by near threshold reactions for various target materials, (2) select target material based on thermo-mechanical considerations and design and test the target, and (3) experimentally demonstrate intense epithermal neutron production using the target design. Step (3) will be conducted at ISU and INEL. Obviously, the tasks for the next year will be key to the success of this project as a whole.

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Session 6. Waste Processing at High Temperatures

Tuesday, 1:00 a.m. to 5:15 a.m.

Kenneth A. Smith (MIT), chair
David L. Miller (INEL), co-chair
Edwin W. House (ISU), panelist
Barry Short, Bob Snelling, Arvid Jensen,
Jim VanVliet (INEL), panelist

1:00 p.m.	V16	Adel F. Sarofim MIT	Application of Solution Thermodynamics and Aerosol Dynamics to Enhance Residue Segregation in Molten Metal Waste Processing State
1:55 p.m.	V39	C. M. Wai University of Idaho	Supercritical Fluid Extraction System for Toxic Metal Contaminated Environmental Matrices
2:40 p.m.	—	Break	
3:10 p.m.	V246	H. Jeff Empie Institute of Paper Science and Technology	Incremental Kraft Recovery Capacity Using Mixtures of Black Liquor and Bleach Plant Effluents
3:55 p.m.	V22	Scott S. Hughes Idaho State University	Chemical and Petrographic Characterization of Vitrification Products
4:40 p.m.	V242	Gary Lowe University of Idaho	Correlation of SREX and TRUEX Equilibrium Data for Use with the ASPEN Model
5:15 p.m.	—	Adjourn	

Application of Solution Thermodynamics and Aerosol Dynamics to Enhance Residue Segregation in Molten Metal Waste Processing (V16)

Adel F. Sarofim, Jefferson W. Tester, Merton C. Flemings, Massachusetts Institute of Technology

Co-PI and University: None

Research Staff: Anthony Modestino

Post Doctoral Associate: Gokhan I. Senel

Graduate Student: Jose Benavides

Industrial Collaborator and Company: Christopher J. Nagel, Executive Vice President, Molten Metal Technology Inc.

INEL Collaborator: Paul A. Lessing

Presenter: Prof. Merton C. Flemings

The use of molten metal processing of mixed wastes has the advantages of destroying organic hazardous components and the partitioning of the inorganic residue between metal, ceramic, and aerosol phases. The variation of the temperature and composition of the metal and ceramic phases permits a wide range of latitude in the distribution of toxic metals such as lead and radionuclides. The objective is to maximize the volume reduction of the disposal waste, the recycling of elements of value, and the delisting of the ceramic phase. The methods for estimating thermodynamics of the ceramic phases will be refined and the characterization of the dynamics of the aerosol produced during processing will be investigated in sufficient detail to achieve the above objective.

The research is based on the studies of small size melts at MIT and on the pilot plant facilities at Molten Metal Technology, Inc. The construction of the 10-pound capacity induction furnace system at MIT has been completed. In this system, argon gas injection through a submerged lance is used to improve the reaction kinetics.

In order to select proper feedstocks, the evaporation rate of different impurities from iron and copper melts was theoretically studied and a model describing kinetics and mechanisms of removal was proposed. The contribution of the liquid, interface and gas mass transfer coefficients on the overall process was evaluated. In this model, several elements having various physical properties such as vapor pressure and activity coefficients were considered. Estimations were carried out in several ranges of parameters including argon gas injection rate, and number and size of the gas injection orifices.

Based on the model, several solutes were selected for experimental investigation. The evaporation rates of (1 wt %) cadmium, bismuth and zinc from copper melts at 1473°K, and lead and bismuth from iron melts at 1873°K were measured. In some cases, the top surface of the melt was covered with a slag layer to determine the fraction of the evaporation that takes place through the top surface as compared to that through bubbles. Samples taken from the melt at discrete time intervals were analyzed using inductively coupled plasma/mass spectrometry (ICP/MS). Once the theoretical model is validated, the simultaneous evaporation of several elements will be considered.

Since special emphasis is directed to the aerosol formation mechanism, the aerosol will be collected by using a sampling probe/cascade impactor system and this ten-stage impactor will be used to size segregate the particles ranging from 0.056 mm to 18 mm. The composition of the particles will be determined using a combination of methods including scanning and transmission electron microscopy and ICP/MS.

The ability of several available thermodynamic databases will be quantitatively investigated to predict measured phase composition for the similar conditions to what is anticipated for molten metal/slag processing. The development of improved predictive models will also be attempted.

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Supercritical Fluid Extraction System for Toxic Metal Contaminated Environmental Matrices (V39)

C. M. Wai, University of Idaho

Co-PI and University: T. E. Carleson, University of Idaho

Graduate Student: R. D. McMurtrey

Industrial Collaborator and Company: Neil G. Smart, British Nuclear Fuels plc (BNFL)

INEL Collaborators: D. M. Ginosar, R. V. Fox

Presenter: Ryan D. McMurtrey

Suprecritical fluid extraction (SFE) offers several advantages over conventional solvent extraction, including the minimization of organic liquid waste generation and exposure of personnel to organic vapors. The high diffusivity, low viscosity, and T-P dependence of solvent strength are some attractive properties which make superciriitcal fluids excellent candidates for extraction and recovery of organic compounds from solid materials. Carbon dioxide is a gas of choice for SFE because of its moderate critical constants (T_c = 31°C and P_c = 73 atm), inertness, and availability in purified form. After extraction, the fluid phase is depressurized to separate solutes from carbon dioxide and the gas can be recycled for repeated use. The SFE technology has been applied to industrial scale operations such as the preparation of decaffeinated coffee and hop extracts.

Direct extraction of metal ions by superciritcal carbon dioxide is highly inefficient because of the charge neutralization requirement and the weak solute-solvent interactions. One approach of extracting metal ions by supercritical carbon dioxide is to convert the charged metal species into neutral metal chelates using a complexant dissolved in the fluid phase. This in situ chelation-SFE technique has been shown, in analytical scale, to be quite effective for removing toxic metals including Cd, Pb, Hg, and U directly from solid materials. Our work in SFE at the University of Idaho has advanced to a stage where scale-up of this technology for treating industrial wastes becomes possible.

In the past year, we have evaluated a number of commercially available chelating agents for extraction of heavy metals (As, Cd, Cr, Pb, and Hg) and actinides (U and Th) from different matrices including soil, wood, and aqueous solutions. Our calculations indicate that alkyl substituted ligands with a chain length of approximately 8 carbon units, preferably branched, have the most favorable properties in terms of achieving high solubilities in supercritical carbon dioxide. A number of commercially available ligands with alkyl chain lengths of between 8 and 10 carbon units were chosen for SFE in investigation in this study. Several organophosphorus reagents under the trade names Cyanex 301, Cyanex 302, and D2EHTPA show high efficiencies for SFE of a range of heavy metals from a variety of matrices. Real-world samples include arsenic-contaminated soil samples from a copper smelter in Tacoma, Washington, and lead contaminated soils from the Coeur d'Alene Mining District in Kellogg, Idaho. The extraction profiles generally show a rapid initial removal of metals from the soil followed by a gradual low level metal extraction from the solid matrix. The extraction efficiencies increase with increasing pressure (100-300 atm) and have little effect by temperature in the range 40°C to 60°C. These organophosphorus reagents are also effective for SFE of heavy metals (As, Pb, Hg), precious metals (Au, Pd, Pt), and uranium from acidic solutions.

The industrial partner, BNFL, has sent a senior scientist (Neil Smart) to Idaho to work with us in the development of this SFE technology. Our research group is also working closely with the INEL collaborator Bob Fox as demonstrated in a joint paper to be presented at the "Spectrum 96" meeting this August. A US patent derived from our research has been filed in July, and two manuscripts have been submitted for publication. Continuation of this work for a technology demonstration at INEL is proposed for the next year.

This page is for notes.

Incremental Kraft Recovery Capacity Using Mixtures of Black Liquor and Bleach Plant Effluents (V246)

H. Jeff Empie, Institute of Paper Science & Technology

Co-PI and University: None

Graduate Students: None

Industrial Collaborator and Company: Karl Morency, Georgia Pacific Corp.

INEL Collaborator: Dean Harding

Presenter: Jeff Empie

Closed-cycle operation of kraft paper mills is expected to be legislated for environmental reasons. Combination of bleach plant effluents (BPEs) with black liquor has been proposed as an attractive solution to the effluent disposal problem posed by closed cycle operation. Unfortunately, this will increase the liquor solids flow to be handled by the present recovery process equipment. Since most kraft mills are already capacity limited by their kraft recovery boiler and because incremental recovery capacity is prohibitively expensive, combining bleach plant effluents with black liquor presents a serious technical and economic problem.

Research is under way that, if successful, will enable kraft pulp mills to move toward environmentally mandated closed-cycle operation by developing a chemical recovery process based upon gasification technology that will combine BPE's with black liquor and recover the chemical and energy values contained in them in an economical, safe, and environmentally acceptable manner. Fluidized bed gasification, combined with autocausticization using an amphoteric salt, will provide the incremental recovery capacity by converting the feed liquor to kraft white liquor and process steam to be used internally in the mill.

Autocausticization of the sodium carbonate produced by black liquor combustion has been demonstrated in sulfur-free systems using Fe_2O_3, but not for the kraft liquors that dominate world paper production. Sulfur combines with the bi-valent metal oxide to put it in a stable sulfide form, rendering it useless for autocausticizing. This research will show how to temporarily remove the sulfur from the sodium chemicals in the liquor prior to carrying out the autocausticizing reaction.

The equipment needed for commercial production would be available in sizes and costs that are consistent with the needs of incremental capacity. In recovering the chemicals, calcination in a lime kiln would be eliminated, hence removing the need for an external supply of fossil fuel. The fuel gas generated from the organic fraction of the feed liquor would be used to raise process steam as well as cogenerate power.

An estimate of the incremental energy recoverable from the BPEs has been calculated, assuming the ratio of bleach plant effluent solids (BPES) to black liquor solids (BLS) to be about 0.01, and the Higher Heating Value of BPES to be about 90% of that for BLS. For a 2,000 tons pulp/day kraft mill and assuming 65% energy recovery efficiency for the liquors, the total energy recovered from the BPES is 0.0001 Quads/yr. Valuing the process steam that is generated at $4/MM BTU, this amounts to over $300,000/yr. savings for the mill. The avoided cost of lime kiln fuel (based on typical operating parameters of 6 MM BTU/ton of CaO produced, 1 ton of CaO required for every 4 tons of pulp produced, and a $3/MM BTU fuel) amounts to about $3 MM/yr. This assumes that causticizing requirements for BPES and BLS are the same. This is not a bad assumption, since the BPES and BLS both have a ratio of organics to inorganics of about unity and both originated with the brown stock washers.

It is crucial to establish, at typical gasification temperatures, the desired chemistry; i.e., formation of solid sodium metallite and H2S gas, but negligible condensed phase sulfides. This is being shown in a relatively simple and inexpensive, electrically heated reactor patterned after one developed for coal hydrogenation and subsequently used for black liquor. The key feature of this configuration is a rapid initial liquor heating rate of about 500°C/sec, followed by an extended time at the final reaction temperature of 700°C, all in an atmosphere of flowing steam. The time-temperature history of the reactants should closely simulate what a liquor particle would experience in a commercial fluidized bed gasifier under typical process conditions.

The focus this quarter has been on detailed design, procurement, and fabrication of the laboratory scale gasification reactor. Concept feasibility depends upon obtaining reaction rate, selectivity, and conversion data, including the composition of gaseous and condensed phase products. Because of the corrosive nature of the chemicals involved, several pieces must be fabricated out of high purity alumina, which proved to have a long delivery time, as dictated by the ceramic vendor. The electrical heating element made of nichrome wire has the required heat-up characteristics and corrosion resistance.

Milestones for completion of the project are: Reaction conversion and rate data (Sept.); Hydrolysis rate data (Dec.); Final report (Mar.).

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This page is for notes.

Chemical and Petrographic Characterization of Vitrification Products (V22)

Scott S. Hughes, Idaho State University

Co-PI and University: None

Graduate Students: None

Industrial Collaborator and Company: None

INEL Collaborators: James D. Herzog, Thomas P. O'Holleran, Bruce Staples, Richard A. Callow

Presenter: Linda L. Davis, Post-Doctoral Research Associate, Idaho State University

Chemical and phase variations in vitrification products are being studied to understand properties that will affect long-term storage or disposal. Elemental mobility and incipient crystallization are evaluated in order to measure the degree of homogenization and elemental diffusion. Analyses by instrumental neutron activation and inductively-coupled plasma emission spectroscopy are used in conjunction with polarizing microscopy to construct three-dimensional maps of melter-treated materials. Samples that were analyzed during initial phases of the project consisted of (a) plasma hearth and arc melter furnace test glasses to develop analytical methodology, (b) black vitreous slag, actually Fe-enriched basalt, and (c) glass Zr-127, melted in a ceramic crucible, which is the focus of much of our experimental work. Zr-127 is made specifically for vitrification of calcined waste and consists of high concentrations of Zr, F, B, and Li that would normally be found as trace elements in rock or soil.

Petrography indicates that Zr-127 contains as much as 50 volume percent radiating crystals smaller than 0.1 mm and less than one percent skeletal crystals (0.8-mm diameter). Distribution of crystals is irregular suggesting potential for preferred directions of fractures. A crystalline reaction rim 1.5-mm thick extends into the glass from the crucible. Vitreous slag is vesicular, nearly opaque, and appears to be strongly devitrified or altered to clay minerals. At least one sample has a network of long, trellis-like, quenched crystals.

Chemical analyses indicate a large degree of heterogeneity in trace element abundances within the glasses while most major elements are uniform. Results also indicate large discrepancies between reported analyses of prepared mixtures and our actual analyses. Chemical co-variation between specific elements is as striking as the overall range in trace elements. Although there is crystallization, there is no removal of crystals from the melt in the crucible. These intriguing results have prompted us to begin designing tests to determine the source of the inhomogeneities. Such co-variations of elements in a crucible of Zr-127 melt cannot be related to melt extraction from a solid source or crystal segregation from liquid.

Chemical analysis of the synthetic glasses is challenging with respect to unusual spectral interferences and small sample sizes. Nevertheless, the most significant setback we encountered was with an HP workstation which affected milestone dates. The problems stemmed from the combination of late vendor delivery, incomplete operating system, and insufficient documentation. The company recently delivered a complete operating system so we see no reason at this time to suggest changes in overall objectives other than to reassess milestone dates. During the coming year, we plan to investigate further the diffusion rates of specified radionuclides and heavy elements. Using surrogate elements, such as Th and U for transuranics, various compounds will be added to crucible vitrification charges at specified locations to determine their reactivity during the melting process. We hope that information thus obtained will lead to better compositions or methods used for vitrifying hazardous waste.

This page is for notes.

Correlation of SREX and TRUEX Equilibrium Data for Use with the ASPEN Model (V242)

Thomas E. Carleson, University of Idaho

Co-PI and University: None

Graduate Student: Gary Allen Lowe

Industrial Collaborator and Company: None

INEL Collaborator: Arlin Olson, Lockheed Martin Idaho Technologies Company

Presenter: Gary A. Lowe

Liquid-liquid extraction techniques to remove heavy and radioactive metals have been developed in recent years to reduce the volume of radioactive waste. Methods to extract strontium (the SREX process) and transuranics (the TRUEX process) have been successfully tested and found useful. ASPEN, a simulation program widely used to simulate chemical processes, is equipped with the capability to handle compounds not in its data banks.

Objectives

Overall project objectives include writing a subroutine used with ASPEN to estimate distribution coefficients (Kd), using the ASPEN data regression package to predict UNIQUAC (Universal Quasi-Chemical) Functional Group Activity Coefficients (UNIFAC), and comparing results with ASPEN's unaided estimations of the same system.

Value of Project if Overall Objectives Are Achieved

Successful completion of this project will allow LITCO to use subroutines and data generated at ICPP to model the required mass and energy balances necessary for RCRA Part B permits. ASPEN's optimization and cost estimation programs could then be used in implementing large scale operations of contaminant extraction. Resulting subroutines could also be useful to governmental laboratories such as Pacific Northwest Laboratory, Oak Ridge, and Savannah River.

The Approach Taken

Project methods include writing a FORTRAN subroutine to predict distribution coefficients and using this as a subroutine for ASPEN; correlating experimental results (for both SREX and TRUEX processes) to allow estimation of UNIFAC coefficients for species not in ASPEN's data bank; and comparing these results with an existing EXCEL spreadsheet for SREX and the Generalized TRUEX Model (GTM). Some of this work has been accomplished (see below).

Major Accomplishments and Obstacles

ASPEN Plus Release 9.2 was obtained and installed on a computer in the Chemical Engineering Department. A liquid extraction example (a three stage water-acetone-ethyl acetate extraction) was performed in ASPEN and compared to literature (Henley and Seader's "Equilibrium Stage Separation Operations in Chemical Engineering" text) and earlier (1994) work with ASPEN. The results agreed with earlier work. Calculated distribution coefficients from the SREX subroutine were also successfully imported into ASPEN. Comparisons to experimental data are under way. There are some differences between the earlier version and the current one that are not yet resolved. Previous work indicates up to 60% error between ASPEN predictions and experimental data for organic phase compositions. Work is continuing in an attempt to obtain better agreement between the experimental results and ASPEN predictions.

Milestones for This Year

Progress is expected to continue with the SREX simulation and refinement of the subroutine, completion of data regression to obtain UNIFAC coefficients, and comparison with recent experimental data obtained from Law, Wood, and Herbst at Idaho Chemical Processing Plant (ICPP).

A TRUEX model subroutine is also expected to be developed to yield transuranic distribution coefficients. Extraction simulation using the TRUEX subroutine with ASPEN should be accomplished within the year. Comparisons will be made with the GTM to show accuracy of ASPEN's prediction of outlet stream compositions.

Milestones for the Future

Regression of TRUEX experimental data should be done to obtain UNIFAC coefficients. Data from regression results should be used in ASPEN to estimate exit concentrations in the ASPEN EXTRACT model. Comparison should be made with GTM to show a correlation with existing estimation methods. Future preparation of an ASPEN EXTRACT block for evaluation in the ICPP process would be a beneficial milestone. These tasks will be the subject of a future proposal to the INEL URC or a private company.

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This page is for notes.

Session 7. Organic Waste Treatment and Reduction

Wednesday, 8:00 a.m. to 11:30 a.m.

Kenneth A. Smith (MIT), chair
David L. Miller (INEL), co-chair
Edwin W. House (ISU), panelist
Lloyd McClure (INEL), panelist

8:00 a.m.	V29	Chikashi Sato Idaho State University	Photo-Sololysis of Toxic Organics Using Ultraviolet Irradiation-Ultrasonication (UV/US) Processes
8:50 a.m.	V228	Jeffrey J. Rosentreter Idaho State University	Photo-Catalytic Assisted Chemical Treatment of Aqueous Cyanide Wastes
9:30 a.m.	—	Break	
10:00 a.m.	V12	Jackie Y. Ying MIT	Photocatalytic Decomposition of Halogenated Organics Over Nanocrystalline Oxide Catalysts
10:45 a.m.	V04	T. Alan Hatton MIT	Polymeric Solvents for Minimizing Pollution in Chemical Synthesis, Separations, and Cleaning Operations
11:30 a.m.	—	Adjourn	

Photo-Sonolysis of Toxic Organics Using Ultraviolet Irradiation-Ultrasonication (UV/US) Processes (V29)

Chikashi Sato, Idaho State University

Co-PIs and University: Solomon Leung and B.K Lao, Idaho State Universit

Postdoctoral Research Associate: Jingshi Wu

Graduate Students: John S. Kirkpatrick, Mamunure Rashid

Industrial Collaborator and Company: Tom Dekker, Water Department, Pocatello, ID

INEL Collaborators: Bill Motes, Steven Hartenstein

Presenter: Chikashi Sato

The overall objective of the project is to explore photo-sonolysis technology for the destruction of organic compounds in an aqueous phase. The technology to be developed would be used by both industries and government agencies to treat industrial wastewater and leachate from landfill/waste sites, and to clean up surface and subsurface water contaminated with biorefractory toxic organics.

The batch photo-sonolysis reactor was constructed, which consists of (a) an 800-ml quartz reactor vessel, (b) a photo-reactor chamber, and (c) sonicator with a 12.7-mm horn. The system was so designed that the contaminated solution is UV-irradiated from the outside of the reactor vessel and exposed to acoustic waves from the inside (in solution). We observed photo-sonolysis of PCE as compared with photolysis and sonolysis in the reactor. With the solution containing PCE at 100 mg/L, more than 90% of the PCE was decomposed within 20 min.

The construction of a continuous flow reactor is in progress. The flow system consists of (a) a 1860 mL quartz reactor vessel to which contaminated solution is continuously introduced by a pump, (b) an immersion well and a UV lamp, and c) a sonicator with a 139.7-mm cup horn. The system was so designed that the contaminated solution is UV-irradiated from the inside (immersion well) and exposed to acoustic waves from the bottom. The contaminated solution is introduced into the bottom of the reactor, and the treated water is removed from the top of the reactor. Data will be collected soon.

Remaining tasks for FY-96 include the enhancement of the UV/US treatment efficiency using hydrogen peroxide (H_2O_2) and/or titanium dioxide (TiO_2). An attempt will be made to identify intermediate byproducts using a GC/MS.

The milestones planned for the next year are completion of the design and construction of the pilot-scale treatment unit, and market survey for the potential commercialization of the technology.

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Photo-Catalytic Assisted Chemical Treatment of Aqueous Cyanide Wastes (V228)

Jeffrey J. Rosentreter, Idaho State University

Co-PI and University: None

Graduate Students: Renee L. Bunde, H. Swantje Quarder

Industrial Collaborators and Companies: G. Ryan Pattie, Laboratory Manager of Intermountain Analytical; John Dunkle, Applications Chemist, Greenspan Technology Ltd.

INEL Collaborator: Kevin Gering

Presenter: Jeffrey J. Rosentreter

The treatment and handling of acutely toxic aquatic cyanides are of significant interest in industrial process control and environmental protection. Our research has focused on the development and evaluation of anionic cyanide treatment systems for aqueous waste streams. The treatment technology is based on the homogeneous and heterogeneous photochemical reactivity of solvated cyanide compounds. Many of these compounds possess high stability constants and as a result are not amenable to routine oxidative treatment methods such as chlorination and ozonation. Yet, these same chemical species have proved to be readily photo-reactive. The treatment system incorporates the use of semiconductor oxides as photocatalysts. Through the use of catalyzed photolysis, even highly stable anionic metal cyanide complexes have been successfully dissociated. These dissociated anions are then oxidized utilizing either photo-catalytic or traditional processes.

To date, the project has focused on the design and construction of a laboratory scale flow injection photochemical reactor, the identification of candidate photo-active cyanide species, characterization of reactivity variables, and the investigation of various semiconductor oxide catalysts. All reactions utilized alkaline solutions in following the prescribed safe handling and storage procedures of the potentially hazardous cyanide wastes. The investigation has implemented various light sources including far and near ultraviolet and a simulated solar source. Preliminary data has been evaluated to identify the waste treatment product as a non-hazardous, non-regulated oxidation product, cyanate.

An analytical device capable of sensitive real time analysis of cyanide ions has been designed, fabricated, and tested. This work became necessary as a means of monitoring the reaction products of our irradiation experiments. The detector is based on the use of quartz crystals. These crystals display the piezoelectric effect when a d.c. potential is applied. Using a recently developed flow cell and gold electrodes on the crystal, the system essentially produced a small and sensitive microbalance. Implementation of selective reaction kinetics has produced a cyanide specific detection device. The result is a detector capable of real time analysis of cyanide solution concentrations. An invention disclosure report has been initiated for this novel detection system.

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Photocatalytic Decomposition of Halogenated Organics Over Nanocrystalline Oxide Catalysts (V12)

Jackie Y. Ying, Massachusetts Institute of Technology

Co-PI and University: None

Graduate Students: Chen-chi Wang, Zhibo Zhang

Industrial Collaborator and Company: Dan Chen, 3M

INEL Collaborator: Stuart Janikowsk

Presenter: Prof. Jackie Y. Ying

Treatment of chemical wastes represents a significant challenge to both the defense and commercial sectors of the United States. Photocatalysis is an attractive low-temperature, non-energy-intensive approach for treating halogenated organics. This project seeks to develop superior photocatalytic materials with increased surface reactivity and reduced charge carrier recombination rate. Major emphasis is placed on the designing of a novel nanostructured TiO_2-based system with tailored size, phase, doping, stoichiometry, and Pt dispersion to substantially improve the quantum efficiency of the overal photoprocess.

Nanocrystalline TiO_2 with well controlled size (5-100 nm) has been successfully synthesized through wet-chemical methods such as chemical precipitation and hydrothermal treatment. Transition metal dopants of controlled concentrations were introduced to tailor the electronic structure of TiO_2. Non-stoichiometric TiO_2-x was also prepared by reducing nanocrystalline TiO_2 under flowing H_2 at high temperature and by inert gas condensation method. Pt metal dispersion on TiO_2 particles was achieved by reducing H_2PtCl_6 with hydrogen, and citrate reduction was also exploited. TiO_2 with different morphology such as sphere, spheroid, and rod were generated in hydrothermal synthesis with different mineral addition. Pure anatasc, rutile, or mixed phase materials were also derived. Photoreactivities of the various TiO_2 samples were quantitatively evaluated by photocatalytic decomposition of CHCl3 using an immersion-type batch reactor. Nanocrystalline TiO_2 showed superior photoreactivites, and 10 nm was found to be the optimum particles size for pure TiO_2 in decomposition of halogenated compounds. Fe^3+ dopants in quantum-sized (~5 nm) particles and Pt loading on intermediate-sized (10-30 nm) particles were found to substantially enhance the overall quantum efficiency.

A versatile projection type flow reactor has been constructed, which allows us to flexibly control photon intensity and select desired photon wavelength. Combined with a mass spectrometer, the detailed kinetic study in both liquid phase and gas phase reactions will be carried out and all by-products can be carefully measured. Photocatalytic decomposition of $CHCl_3$, $ClCH{=}CCl_2$ (TCE), and CCl_4 in gas phase are being examined using this new optical set-up. A novel hexagonally packed mesoporous TiO_1 material has been synthesized, and the processing variables are exploited to make this material more stable and more suitable for photocatalysis applications. It is believed that this material will have superior advantage in gas phase reactions due to its extremely high surface area and novel pore structure. The detailed study of effects of morphology, non-stoichiometry, Pt dispersion, and pore structure on both liquid phase and gas phase reactions are also in progress. These fundamental studies will have critical impact on the successful development of photocatalysis as a viable technology for solving pollution problems associated with mixed waste and industrial volatile organic chemical waste streams.

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Polymeric Solvents for Minimising Pollution in Chemical Synthesis, Separations, and Cleaning Operations (V04)

T. Alan Hatton, Massachusetts Institute of Technology

Co-PI and University: None

Postdoctoral Associate: Minghui Zhang (started December 1996)

Graduate Students: Linda Molnar (Graduated May 1996), Julie Sherman (Started January 1996)

Industrial Collaborator and Company: Michael P. Thien, Merck and Co.

INEL Collaborator: Robert Cowan

Presenter: T. Alan Hatton

Most processes used in the pharmaceutical industry are, by necessity, carried out in organic solvents. In many cases these solvents are volatile and sufficiently water-soluble to contaminate air emission and aqueous discharge streams, adding to the environmental burden and the cost of downstream processing and recovery operations. One example is the use of tetrahydrofuran (THF) as the solvent for Grignard reactions which must be carried out under anhydrous conditions. The desired product is often obtained by aqueous precipitation, which gives rise to other processing problems owing to the solubility of THF in the water phase, with which it forms an azeotrope. Thus, THF must be recovered by azeotropic distillation. Solvent switches are also frequently required during processing, adding to the complexity of the overall process.

It is suggested that solvent replacements combined with recovery and recycling will be important in the development of benign chemical processes. For this approach to be successful it is crucial that appropriate solvation properties be attained in the replacement solvent while ensuring that the potential for environmental contaminations be minimized. Furthermore, difficult separation problems must be avoided so that more efficient recovery of solvents is facilitated.

Facile synthetic methods have been developed for both low molecular weight and polymer bound derivatives of THF for use as replacement solvents for THF. We have identified one step in the synthesis of the orally active HIV-1 protease inhibitor L-735,524 as a suitable model reaction to use in the evaluation of these novel solvents. This reaction is known to be very sensitive to the solvent medium and therefore represents a critical test of our replacement solvents. Reaction kinetics, as well as possible separation schemes necessary for regeneration of the low molecular weight and polymer-bound solvents have been investigated. Both types of solvent replacement have been very successful in the replacement of THF. The low molecular weight derivatized solvents can be carried through several reaction steps thereby avoiding costly solvent switches because of their minimal water solubility and volatility. The polymer-bound solvents, which are dissolved in a relatively benign continuous phase, can be recovered from the process stream by ultrafiltration and regenerated for re-use. Thus, it is envisioned that our replacement solvents can be part of an intelligent reaction/separation sequence that improves upon currently used sequences in terms of both environmental impact and productivity.

Over the next year, we plan to (a) synthesize a broader range of solvents with different chemical moieties and/or polymer backbones, (b) characterize these solvents in terms of their solvation and transport properties, specifically heats and entropies of solvation, micro- and macroviscosities, micropolarities, and diffusion coefficients of different components, (c) demonstrate a range of model reactions in these solvents, (d) develop process system models to assist in the optimization of the reaction/separation sequence, and (e) conduct pilot-scale testing using these new solvents in collaboration with Merck (under discussion); this will provide the ultimate test as to their utility in pharmaceutical and fine chemical processing.

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Session 8. Advanced Reactor Technologies

Wednesday, 8:00 a.m. to 11:30 a.m.

Michael W. Golay (MIT), chair
Ralph G. Bennett (INEL), co-chair
David M. Woodall (Uof I), panelist
Jim Lake (INEL), panelist

8:00 a.m.	N14	Thomas Downar Purdue University	Advanced Spatial Kinetics Methods for RELAP5
8:45 a.m.	N20	John H. Lienhard V MIT	Cooling Modules for Extremely High Heat Fluxes
9:30 a.m.	—	Break	
10:0 a.m.	N19	Mamoru Ishii Purdue University	Development of Multi-phase Flow Sensors and Diagnostic Systems
11:30 a.m.	—	Adjourn	

Advanced Spatial Kinetics Methods for RELAP5 (N14)

Tom Downar, Purdue University

Co-PI and University: Paul Turinsky, North Carolina State University
Post-Doctoral Student: Hisham Sarsour, North Carolina State University
Graduate Students: Douglas Barber, Purdue University; Ugur Meryurek, North Carolina StateUniversity

Industrial Collaborators and Companies: Ashok Arora, SAIC, Reston, VA; K. C. Wagner, SAIC, Albuquerque, NM

INEL Collaborators: R. J. Beelman, Jerry Judd

Presenters: Tom Downar, Paul Turinsky

High fidelity nuclear power plant simulators with advanced nodal neutron spatial kinetics methods pose a formidable computational burden. INEL has recently developed RELAP5/Mod 3.2 R/T: a real-time best estimate neutronics/thermal-hydraulics simulator which utilizes the NESTLE nodal kinetics code which was developed at North Carolina State University. The overall objective of the work in this project has been to investigate advanced computational methods that can substantially reduce the execution time of the NESTLE neutronics module in RELAP/Mod 3.2 R/T. The specific goal of this work is to achieve better than real-time simulation capability on a multi-processor computer.

Successful completion of this work will result in considerably more accurate and efficient predictions of reactor core performance within the context of the overall system simulation. For operating plants this will remove conservatism used in past analyses that can be taken advantage of by increasing operating flexibility and thereby reducing operating costs. For plants under design such as the advanced LWR concepts, less conservatism can be translated into reduced capital costs via improved design features. However, the immediate benefit of this work will be through the deployment of the RELAP/Mod 3.2 R/T as a training simulator. This will improve operator training by providing a more accurate and realistic description of reactor behavior. Also, this will provide an engineering quality simulator on which proposed design and emergency procedures changes can be accurately and quickly assessed prior to implementation. For the first time the nuclear industry will be able to consolidate the computational basis for plant licensing and operator training.

The primary focus of the research here is on the NESTLE neutronics code. During the past year an advanced Krylov sub-space method with an incomplete domain decomposition preconditioner was developed and implemented in NESTLE. This method employs the Bi-Conjugate Gradient Stabilized (BiCGSTAB) method as the base algorithm and is accelerated by a preconditioner based on three-dimensional incomplete LU factorization. Parallelism is introduced via an innovative incomplete domain decomposition method.

On a single processor, a substantial performance improvement was achieved compared to the standard nested iterative (Chebyshev Outer-LSOR Inner) method. On the DEC Alpha 2100 (250 MHz) multiprocessor, parallel efficiencies of nearly 100% were achieved. Overall the computational burden was reduced by over an order of magnitude and for a typical three-dimensional PWR model and a practical reactor transient problem, much better than real time performance was obtained. In July, testing was begun on the integrated RELAP/NESTLE simulator at the Cooper BWR in Nebraska.

Continuing work on NESTLE includes the development of a multigrid acceleration method and an adaptive spatial mesh capability. The incorporation of the Multigrid (MG) acceleration method has been essentially completed and full solution capability at all spatial grid levels is now possible. Testing of the method is currently in progress.

Work on time adaptive spatial gridding capability has been initiated. The specific activity undertaken involves adding the capability to NESTLE to complete a NEM consistent collapse. It builds upon MG capabilities, such as data structure for different grids and determination of coarse mesh homogenized group cross-sections. The additional capability required involves determination of coarse node discontinuity factors (CNDFs). In addition, some early work on obtaining spatial discretization error bounds associated with the NEM approximation has been completed.

Completion of this continuing work on NESTLE should further reduce the computational burden of the spatial kinetics module in RELAP/Mod 3.2 R/T and release more execution time that can be used to further improve the fidelity of the thermal-hydraulics module.

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Cooling Modules for Extremely High Heat Fluxes (N20)

John H. Lienhard V, Massachusetts Institute of Technology

Co-PI and University: None

Graduate Students: R. Dahbura, H. Younis

Industrial Collaborator and Company: S. J. Kim, IBM, Tuscon, Arizona

INEL Collaborator: Chang H. Oh

Presenter: John H. Lienhard V

We are developing cooling modules that support heat fluxes in the range of 10 to 100 MW/m2. The modules will use an array of high pressure impinging liquid jets and will be self-contained, apart from a liquid pumping/low flux cooling system. The jets cool the rear side of a faceplate that absorbs the heat load of interest. The faceplate will be a thin, high conductivity surface, possibly a refractory metal or a metal matrix composite. This plate must be carefully designed to accommodate both thermal stresses and the mechanical load from the impinging jet array. Development of these modules involves experimental testing of the liquid cooling and manifolding performance and analysis of the thermal and mechanical stresses on the face plate. Potential applications include cooling semiconductor laser arrays, microwave or RF components, high-end microprocessors, x-ray optical components, and plasma diverters. Our objective is that these modules will be useful in a range of applications without the need for any significant redesign.

Our approach is to apply analytical and computational tools to design a prototype module. This module will then be tested experimentally, using electrical resistance heating to simulate the heat load. Analytical studies of the thermal stresses have been used to evaluate various mechanical boundary conditions on the faceplate and to evaluate a number of candidate materials for the faceplate. Among the most promising materials are certain refractory metals and copper-based metal-matrix composites. Finite element simulations of the thermal and mechanical stresses are being used to optimize the faceplate thickness and the mechanical constraints applied to the faceplate. Fluid flow simulations of the liquid jet array are being used to assess the nozzle configurations. A prototype of the cooling module is now nearing completion. The prototype module uses small diameter water jets running at maximum speeds of 50 m/s. (Past studies have used high speed water jets to remove fluxes of more than 100 MW/m^2 in the stagnation zone.) The faceplate is a dispersion-strengthed copper alloy 2.5 mm thick. The total cooled area is 10 cm^2 and the design heat flux is 40 MW/m^2. The module's lower liquid manifold and jet array are completed, and the upper manifold and faceplate should be finished by mid-summer 1996. In addition, we have built a flow loop to pump water through the cooling modules. The loop has been calibrated and fully instrumented. The high flux resistance heater has posed particular challenges. Among these are the need to eliminate any contact resistance between the heater and the faceplate while providing electrical isolation of the heat from the faceplate. We have applied a thin film approach to reach a design that appears to overcome these difficulties. In addition, coefficients of thermal expansion for the faceplate and the heater must be closely matched to avoid fracture or delamination of the resistance heater.

In the year ahead, we will test and optimize the prototype at increasingly high heat fluxes. Initial tests at fluxes up to 20 MW/m^2 will be used to prove-out the concept. Higher fluxes will then be attempted, probably using a second-generation module. Factors limiting the fluxes attainable with these modules will be identified and design rules for jet array cooling modules will be constructed. A few areas that we expect will receive significant attention are (a) instrumentation for power and temperature measurement; (b) local convection coefficients beneath the jet array, particularly for high wall temperatures; (c) the use of metal matrix materials for the faceplate; (e) control of the stresses within the faceplate, and issues related to the plate's service life, such as creep.

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Development of Multi-phase Flow Sensors and Diagnostic Systems (N19)

Mamoru Ishii, Purdue University

Co-PI and University: L. H. Tsoukalas, Purdue University

Graduate Students: Ye Mi, Mulan Li, Zheng Xiao,

Industrial Collaborators and Companies: Bill Mortimer, Honeywell; Alexander G. Lissow, Scientech·

INEL Collaborators: Jim Anderson, Keith Condie

Presenters: M. Ishii, L. Tsoukalas, Y. Mi

The objective of the proposed research is to develop non-intrusive multi-phase flow sensors and diagnostic systems applicable to advanced light water nuclear reactor systems. In new generation nuclear power reactors utilizing passive safety systems, the development of reliable non-intrusive multiphase flow diagnostic systems to monitor the functions of passive safety systems will be of crucial significance. The non-intrusive systems can measure two-phase flow void fraction, perform flow pattern identification and output liquid mass flow by exploiting the mapping and flexible modeling capabilities of fuzzy and neural systems. Such non-intrusive multiphase flow sensor diagnostic systems would be of interest to the petroleum, refining, food, and chemical industries as well, where not only the void fraction but also a measurement of the interfacial structure could be achieved through the proposed systems.

During the past year, our major efforts were focused on vertical two-phase flows according to the project schedule. Significant advancements have been made in the theoretical, computational and laboratory investigations of the project, based on hardware and equipment developed and procured. They are documented briefly as follows.

The hardware of the system, which is composed mainly of impedance void-sensor and magnetic flow-sensor, was successfully developed. The theoretical foundations of the impedance void-sensor and magnetic flow-sensor have been established. An experimental loop with a vertical 2-inch test section was built along with a PC-based data acquisition/ analysis system. The tests show that the hardware of the diagnostic system and the testing loop function very well and can be operated under a wide range of flow conditions to satisfy our research requirements.

For flow pattern classification, we have investigated and implemented several kinds of neural networks or neural-fuzzy approaches, such as a supervised neural network and a self-organizing neural network, as well as a hybrid neural-fuzzy system. The capability of these neural networks to classify flow patterns is tested and verified.

The application of the impedance void-sensor to measure some important two-phase flow characteristics is intensively investigated. The theoretical predictions and experimental results for the area-averaged void fraction show very good agreement, which is also cross-calibrated by other techniques for averaged void fraction measurements. We have also conducted research for the feasibility of using impedance void-sensor and neural networks to obtain the void distribution information. The preliminary results are promising. For the measurement of void wave velocity, the results are consistent with the theoretical prediction by the drift flux model.

The experimental and theoretical works have been carried out to measure characteristics of slug flow, such as averaged void fraction of both Taylor bubbles and liquid slugs, film thickness along Taylor bubbles, slug frequency, and slug and Taylor bubble lengths. It has been shown that the impedance void-sensor can be used to measure most geometric information.

The analytical solution of the response of electrical magnetic flow-sensor for some simple geometric vertical two-phase flow has been obtained and compared to the experimental results. It is proved that the application of the magnetic flow-sensor can be extended to slug flow.

In the next year, we will conduct our investigation in horizontal two-phase flows.

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Session 9. Site Monitoring and Characterization

Wednesday, 8:00 a.m. to 11:30 a.m.

Jefferson W. Tester (MIT), chair
Rebecca A. Winston (INEL), co-chair
Dale R. Ralston (Uof I), panelist
Dave Cauffman, Bob Snelling (INEL), panelist

8:00 a.m.	V219	Peter R. Griffiths University of Idaho	Inexpensive Open-Path Atmospheric Monitoring with a Low-Resolution FT-IR Spectrometer
8:45 a.m.	N10	William A. Hoff Colorado School of Mines	Evaluation of Interactive Techniques for the Creation and Updating of Site Models for Remote Operations and Inspection
9:30 a.m.	—	Break	
10:00 a.m.	G14	Roger Turpening MIT	Borehole Seismology in Support of INEL's Ultra-Long, Multi-Sensor Array Project
11:00 a.m.	—	Adjourn	

Inexpensive Open-Path Atmospheric Monitoring with a Low-Resolution FT-IR Spectrometer (V219)

Peter R. Griffiths, University of Idaho

Co-PI and University: None

Graduate Students: Robert L. Richardson (Mr. Richardson was awarded his Ph.D. on May 18 and will remain on the project as a postdoc.), Brian K. Hart

Industrial Collaborator and Company: J. D. Tate, Dow Chemical Company, Freeport, Texas

INEL Collaborator: John G. Jolley

Presenter: Peter R. Griffiths

There are two goals to this project. The primary goal is the development of an instrument for open-path atmospheric monitoring by Fourier transform infrared (FT-IR) spectrometry. This instrument has several features that differ radically from existing designs. All contemporary instruments incorporate a mercury cadmium telluride (MCT) photoconductive detector that operates at 77K. These detectors are either cooled with liquid nitrogen (LN_2) or by a Stirling cycle cooler. The former method of cooling requires the dewar to be refilled regularly, while the lifetime of Stirling cycle coolers is usually about 3000 hours; thus completely unattended operation is precluded with either approach. We have also demonstrated that MCT detectors usually respond in a very nonlinear fashion to incident radiation, resulting in severe photometric errors. By contrast, our system is based on an inexpensive deuterated L-alanine doped triglycine sulfate (DLATGS) pyroelectric bolometer which operates at ambient temperature or with thermoelectric cooling. The photometric response of this detector is not only is far more linear than that of MCT but, by avoiding the need for LN_2, the instrument should operate for several months unattended. The main drawback to the use of a DLATGS detector is its low sensitivity relative to that of MCT. To allow most atmospheric species to be determined at the low parts-per-billion level, the optical efficiency will be increased by about a factor of 20 through the use of a high-temperature infrared source fabricated from $MoSi_2$, highly efficient, short focal length transmitting and receiving telescopes, and a novel retroreflector that has been designed in our laboratory. Spectra will be measured at low (about 8 cm-1) resolution, which also results in a significant gain in sensitivity, especially for the determination of many volatile organic compounds with molecular weights between 100 and 200. The study of all design parameters has been completed. Custom-designed retroreflectors and telescope mirrors have been fabricated in our laboratory by spin-casting an epoxy resin as it sets. We expect to have a working prototype of this system by the end of the year (December, 1996).

In the second part of this project, a new type of instrument for measuring automobile emissions traveling at highway speeds is to be built. This instrument will incorporate some, but not all, of the optical components being developed for the open-path monitor. The key difference will be the interferometer which will operate at a rate of 1000 scans per second. Since a car traveling at 70 miles per hour will travel about 3 cm in the time of a single scan (1 ms), it will be possible to measure a spectrum of the emissions from each car's tail-pipe immediately after it passes through the IR beam. Using rapid digital signal processing technology, it should be possible to obtain the concentration of the major components of each car's exhaust by the time that the next car's exhaust gases are interrogated. (This is just one example of the type of application that can be attacked with an instrument of this type: many more can be cited.) The interferometer has been designed and an order placed for the key components; the first prototype should be fabricated by the end of the year.

This page is for notes.

Evaluation of Interactive Techniques for the Creation andUpdating of Site Models for Remote Operations and Inspection (N10)

William A. Hoff, Colorado School of Mines

Co-PI and University: Robert King, Colorado School of Mines

Graduate Students: Frederick W. Hood, Khoi N. Nguyen, Torsten M. Lyon, Lin A. Xia

Industrial Collaborator and Company: Robert Taussig, Bechtel Corp.

INEL Collaborator: Mark McKay

Presenter: William A. Hoff

Graphical models are a useful tool for operators in the safe and efficient planning and control of remote robots. With graphical programming systems, the operator can visualize and understand the result of complex commands before moving any machinery. For these systems, there is a need to dynamically create and update site models which accurately represent the 3D locations and other properties of objects at the site. Unfortunately, automatic techniques for creating and updating models from vision data traditionally have been limited in performance and reliability. It is possible to greatly improve the performance of modeling systems by having the operator provide constraints and guidance to the vision system. A key issue is to have the operator provide enough input to the sensing system to achieve good performance without requiring unnecessary effort by the operator. The objective of the proposed work is to develop and evaluate a number of interactive techniques for fitting models of geometric primitives (such as cylinders, parallelepipeds, and spheres) to objects in range images, in terms of performance (accuracy and reliability) and cost (time and effort by the operator). The goal is to show how sharing of intelligence between human and machine can improve the robustness and flexibility of computer vision tasks.

The value of this work is that it can lead to productivity aids to lower the cost and improve the speed of remote operations. For large scale remediation operations, the cost savings can be significant. The results of this work will transfer into INEL applications for remote characterization and buried waste remediation. The results will also potentially be commercialized by Bechtel Corporation for use in their environmental remediation and construction field operations.

Our approach is to use range images from a stereo vision sensor, although other range sensors can be used. Our system allows the human operator to provide high level constraints to the system, such as selecting the type of object model to be used, and an indication of the approximate location of the object. We then use automatic model fitting algorithms, based on simulated annealing, to complete the exact fitting of the model to the data. The user watches the graphics depicting the model fitting process and can intervene if necessary to correct the fit or provide further constraints. We use a stereo viewing system on a workstation, along with a 6 degree of freedom input device. We are conducting evaluations to quantify the benefits and tradeoffs associated with the interactive modeling techniques. For example, overly constraining many of the degrees of freedom of the model improves the fit, but it may overly burden the operator.

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This page is for notes.

Borehole Seismology in Support of INEL's Ultra-Long, Multi-Sensor Array Project (G14)

Roger Turpening, Massachusetts Institute of Technology

Co-PI and University: Prof. M. Nafi Toksoz, MIT

Research Scientist: Richard Gibson, Jr., MIT

Graduate Students: None

Industrial Collaborator and Company: Larry Walters, Bolt Technology, Inc.

INEL Collaborators: James R. Fincke; David M. Weinberg

Presenter: Roger Turpening

Background

The Idaho National Engineering Laboratory (INEL) is undertaking a three-year project to design, engineer, build, and test a new downhole array of seismic sensors. The novel feature of the project is that this array will contain a large number (approximately 100) of individual sensor pods (sondes). Each one of these sondes will carry a three-component geophone and will have the capability of clamping itself to the borehole wall. This is a monumental undertaking and INEL should be applauded for pursuing this goal.

The geophysical community needs such a tool. A very promising geophysical technique—single well imaging, much in demand by the industry—will not be commercially viable until a noise-free, long array exists.

The fluid-filled borehole is a complex seismic waveguide that affects not only seismic wave propagation and the behavior of noise signals, but also the response of seismic sources and receivers in the borehole. These problems are so distinct from those of layered earth models that they led to the development of a sub-discipline called borehole seismology. The Earth Resources Laboratory (ERL) of the Massachusetts Institute of Technology has made major contributions in this branch of seismology with theoretical and experimental studies in borehole acoustics, logging, vertical seismic profiling, cross-well tomography, and single-well imaging.

Objective

With this background ERL will provide seismological support to INEL's engineering effort of the downhole array of seismic sensors. This support impacts both the design and testing phases of the array. During the design phase, ERL will

1. Numerically model seismic wave propagation phenomena that impact the design of a sonde and its interconnecting cable/coiled tubing segments
2. Use numerical modeling to assist in the design of tube wave dampers
3. Demonstrate the fundamental geophone/hydrophone processing techniques for tube wave rejection.

During the testing phase ERL will

1. Make our test site available for field testing of the prototype tool; and
2. Compute reception patterns of receivers in various borehole environments.

Approach

There are various numerical modeling techniques that are suited for the computation of the seismic wave field in and around a fluid-filled borehole. All methods have their advantages and their limitations but the finite difference method (FD) emerges as the most general. This is particularly true when a variable grid size is used and attenuation is included in the algorithm. The FD technique is computationally intensive and thus is only practical when used on a massively parallel computer. Industry support has installed a 512 node nCUBE with 100 gigabytes of disc space at ERL and we in turn will apply this computational power for INEL's tasks.

Accomplishments

This is a new project just entering its second quarter. Therefore coordination activities have been the focus of this early phase. We have made some preliminary studies of tube wave damper design.

Milestones Planned for Next Year

We will focus on the tube wave problems in the next year, in particular the design of tube wave dampers. This is a difficult problem since one wants a damper that indeed functions as a damper and does not reflect the energy into a nearby sensor.

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This page is for notes.

Session 10. Environmental Sensors and Monitors

Wednesday, 1:00 p.m. to 5:15 p.m.

Jefferson W. Tester (MIT), chair
Rebecca A. Winston (INEL), co-chair
Dale R. Ralston (Uof I), panelist
Bill Blume, Dave Cauffman, Bob Snelling (INEL), panelists

1:00 p.m.	V18	Harold F. Hemond MIT	Remote Monitoring of In Situ Contamination Using Optical Spectroscopy
2:00 p.m.	V27	Kent R. Mann University of Minnesota	Synthesis and Characterization of Vapochromic Materials for Environmental Sensors. Detection and Identification of Volatile Organic Compounds
3:00 p.m.	—	Break	
3:30 p.m.	V03	Joel Dubow University of Utah	Chemical Sensing Subsystem Components
4:30 p.m.	G219	Robert W. Gunderson Utah State University	Intelligent Fully Autonomous Micro-Robotic Control Systems for Hazardous Waste Site Characterization
5:15 p.m.	—	Adjourn	

Remote Monitoring of In Situ Contamination Using Optical Spectroscopy (V18)

Harold F. Hemond, Massachusetts Institute of Technology

Co-PI and University: None

Graduate Student: Joe Sinfield

Industrial Collaborators and Companies: Terry Hawk, EG&G Environmental, Inc.; Joda Wormhoudt, Aerodyne, Inc.

INEL Collaborator: Judy K. Partin

Presenters: Nathan Newbury, MIT Lincoln Laboratory; Joe Sinfield

Millions of acres of soil and groundwater within the United States are potentially contaminated with wastes, including, for example, petroleum based hydrocarbons (e.g., BTEX compounds) and chlorinated solvents. All clean-up of these contaminated lands requires quantitative assessment of the degree of contamination both before and during remediation efforts. Conventional sensing techniques, which require sample extraction and subsequent on-site or laboratory analysis, are too slow and labor intensive for the vast amount of land targeted for evaluation. Thus, there is an acute need for a reliable, inexpensive, and real-time method to measure chemical concentrations in situ in the soil and water environment.

In recent years, remote optical spectroscopy has evolved to address this need. The techniques most often employed are laser induced fluorescence (LIF) and Raman spectroscopy. In LIF, chemicals such as the BTEX compounds are excited by an ultraviolet laser. The spectral and temporal properties of the subsequent fluorescence is used to identify specific chemicals. Chlorinated solvents, such as carbon tetrachloride and TCE, will not absorb ultraviolet light in an easily accessible wavelength region. These compounds are identified instead by detecting the Raman scattered photons, which are laser photons scattered from the molecule and shifted in energy by a characteristic amount. Both LIF and Raman spectroscopy are amenable to in situ screening of sites since remote fiber-optic probes can be delivered down existing wells or in cone penetrometer shafts. Unfortunately, the few existing efforts in remote fiber spectroscopy all suffer from the same drawbacks, namely the lasers are bulky, expensive instruments and system ranges are limited because UV radiation does not propagate well in optical fibers.

The objective of our research is to develop and deploy a remote sensor that overcomes the aforementioned limitations by exploiting a recently developed UV microlaser. The laser consists of a near-infrared 1-Watt diode pump coupled, via multi-mode silica fiber, to a series of small (millimeter-scale) crystals, which produce short pulses of ultraviolet and visible radiation. Because of the high transmissivity of optical fiber in the near infrared, the diode pump can be located above ground while the UV-lasing crystals are incorporated within the probe itself, thereby avoiding fiber optic attenuation of the UV radiation.

We have recently completed assembly of a prototype probe that includes the microchip laser and optics to collect any fluorescence or Raman scattered light for transmission via optical fiber to a distant data acquisition system. Initially, we have examined the optical signatures of dilute aqueous solutions of contaminants. However, the signal characteristics will depend on the surrounding soil matrix. Therefore, we have also constructed a laboratory apparatus to test the probe with different soil types at varying levels of contamination. In parallel with these laboratory tests, we will shortly perform preliminary field tests to determine the probe durability and background signal levels. After these tests, we plan to deploy the probe in a well-characterized contaminated site the summer of 1997 in order to characterize the probe performance under real operating conditions.

This page is for notes.

Synthesis and Characterization of Vapochromic Materials for Environmental Sensors: Detection and Identification of Volatile Organic Compounds (V27)

Kent R. Mann, University of Minnesota

Co PI and University: None

Graduate Students: Christopher Exstrom, Charles Daws, Marie Pomije, Daron Janzen, Carolyn Anderson, Jon Evju

Industrial Collaborators and Companies: John E. Trend, 3M; Alex Burns, Life Sciences, Inc.; Dennis Levens, 3M

INEL Collaborators: Steven Hartenstein, Frederick F. Stewart, Glenn Moore

Presenter: Kent R. Mann

Goals

A long-term goal is to develop and commercialize a hand-held fiber optic based device that could identify and quantify volatile organic compounds (VOCs) in air at regulatory levels. Such a device would aid in pollution detection and monitoring of waste sites.

Objectives

To synthesize, characterize and study new vapochromic compounds that undergo reversible color changes when exposed to VOCs. The vapochromes will be the chemically sensitive layer for the environmental sensor that will use absorption or emission spectroscopy for signal transduction. These compounds may also find application in air quality monitors, monitoring badges, alkane detectors, and ground water monitors.

Major Accomplishments

The synthesis, characterization and Vis-NIR-IR vapochromic/ spectroscopic studies were concluded for isonitrile compounds of the form [Pt(arylisonitrile)$_4$] [Pt(CN)$_4$] (where arylisonitrile = *p*-CN-C_6H_4-C_nH_{2n+1}; n = 6, 10, 12, 14). These compounds represent a significant improvement over the previous vapochromic compounds available; we are applying for patent protection.

The synthesis and characterization of mixed salts of the form [Pt(bipyridine/phenanthroline)(p-CN-C_6H_4-C_nH_{2n+1})$_2$][Pt(CN)$_4$] (n= 6, 8, 12 for bipyridine; n= 6, 10, 12, 14, 16 for phenanthroline). These eight compounds offer outstanding stability improvements over the previously studied vapochromic compounds. The n = 6 compound is exclusively a vapochromic alcohol detector; the n = 12 compound detects a broad range of organic functional groups. The n = 12 compound could form the basis of an alcohol/ chlorinated hydrocarbon sensor.

Mechanistic studies and an x-ray structure of [(n-C_4H_9)$_4$N]$_2$[Pt(CN)$_4$] were completed. [(n-C_4H_9)$_4$N]$_2$ [Pt(CN)$_4$] is vapochromic in the UV and IR regions of the spectrum. Mechanistic studies with this compound answered a major question: the CN groups of the anion are important interaction sites for polar or hydrogen bonding VOCs.

The synthesis and characterization of salts of 2,2'-bipyridine-tetracyanoruthenate, [Ru(bpy)(CN)$_4$]$^{2-}$. These compounds are prototypes of a new class of vapochromic compounds that are not based on the Pt Pt or Pt Pd stacking chromophore.

Milestones Achieved

- The synthesis and characterization of two types of vapochromic platinum compounds and a completely new class of vapochromic compounds.
- The production of samples for INEL testing.
- Mechanistic studies were reported in two manuscripts.
- A ccd based absorption/emission spectrometer is under construction for future studies.

Future Objectives

- Completion of additional mechanistic studies with the [Pt(phenanthroline)(*p*-CN-C_6H_4-C_nH_{2n+1})$_2$] [Pt(CN)$_4$] compounds. Substituted precursors will be synthesized. We expect all of these compounds to be vapochromic.
- Develop an improved synthesis of the [Ru(bpy)(CN)4]$^{2-}$ anion and related compounds. These synthetic developments are straight forward and will produce many new compounds.
- New mechanistic studies with the diode array/CCD NIR fast timescale emission/absorption instrument will allow sensitivity and selectivity issues to be investigated.
- Continued development of neutral Pt compounds as vapochromes.

Proposed Milestones

- Quarterly/Final reports of future studies.
- Delivery (as per proposal) of at least 100 mg of the three best VOC sensitive materials available. These three will either be Pt salts, neutral Pt or the pseudo-octahedral compounds.

3. Submit additional manuscript(s) for publication in a technical journal.

This page is for notes.

Chemical Sensing Subsystem Components (V03)

Professor Joel Dubow, University of Utah

Co-PIs and Universities: Ian Hunter, MIT; Lawrence Sadwick, University of Utah

Program Investigator: Douglas Chinn, University of Utah

Graduate Students: John Madden, MIT; Luis Ortiz, MIT; Wenjia Zhang, University of Utah; Jeremy Riley, University of Utah

Industrial Collaborators and Companies: Bruce Nelson, Geocenters Inc., West Newton, MA; Franco Consadori, Attwood-Technical Systems, Salt Lake City, Utah

INEL Collaborator: Steven Hartenstein, Chemical Systems Group

Presenter: Joel Dubow

The objective of this project is to develop modular, miniature chemical sensing system components for a wide range of applications. The components include an inlet sampling valve and gas flow modulator, chemical field effect transistors, and nonlinear parameter estimation software. The hardware components are fabricated using silicon and polymer micromachining technology for the inlets, 1 micron CMOS fabrication technology for the chemical field effect transistors, and full 32 bit digital signal processing hardware for the parameter estimation. The initial effort has focused on chemfets using coatings of the cyanoplatinate compounds developed by URC partners INEL and the University of Minnesota, this effort will evolve into cyanoplatinate solutions cofabricated into polymeric chemfets. The initial approach also uses silicon technology, but the focus beginning next year, will be on moving to all polymer inlet pumps and transistors because of their inherent advantages in compatibility with sensing chemical, performance and adaptability. Our laboratory has the nation's first polymer microfabrication facility, and our extended project goal is the co-fabrication of all the components of these modules on a polymer substrate. This will include a polymer battery and a conductive polymer antenna for telemetry.This will be ultimately more reliable since it will eliminate the need for coated sensors.

If successful, the project will yield a family of wrist mountable and field deployable chemical sensing systems that are presently unavailable and which will provide new capabilities for integrated chemical and biological monitoring systems. Application of these systems include front end components for military and law enforcement chemical and biological detection and command and control systems, workplace monitoring, worker protection for hazardous locations, medical and home monitoring for potentially hazardous substances. Since detector arrays will be fabricated using VLSI techniques, these systems will provide an ultimately low cost, flexible means of adapting to a range of sensing targets .

The program is tightly coupled to INEL, to our industrial collaborators and to the University of Minnesota INEL URC collaborator. We are working with INEL on developing programs for wrist mounted chemical sensing systems, with Geocenters on spin coatable solution stabilized vapochrome coatings, with Attwood Technologies on parameter estimation and with the University of Minnesota on the effectiveness on various vapochrome compounds.

The program has made significant progress in all areas. Prototype pump designs have been developed for polymer and silicon pumps including lorentz force actuators (silicon and metal), peristaltic and membrane pumps (polymer) and polymeric bilayer gas flow modulation valves. Chemical field effect transistor wafers fabricated at MIT and coated with four types of vapochrome and high qualitative sensitivities to VOC's measured. Quantitative sensitivities will be determined before the end of this contract period. A novel inkjet coating technique has been developed to allow coating the fet gates directly. A wafer for evaluating various polymer actuator concepts has been designed. Alternative polymeric detector compounds have been studied. Volterra series parameter estimation techniques have been reviewed to improve selectivity and a system designed to test these concepts.

By the end of the next contract period the system will be integrated into a prototype miniaturized field testable sensing system will be delivered to INEL for evaluation. Efforts will continue to develop a new line of business based on this technology in partnership with INEL.

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This page is for notes.

Intelligent Fully Autonomous Micro-Robotic Control Systems for Hazardous Waste Site Characterization (G219)

Robert W. Gunderson, Utah State University

Co-PI and University: Nick Flann, Utah State University

Graduate Students: Steven Clarke, Brett Hancey, Eric Poulsen, John Jacobs

Industrial Collaborator and Company: Mel Greenhalgh, Caterpillar Inc.

INEL Collaborator: Robert Polk

Presenter: Robert Gunderson

The principal research objective of the project is to develop a fully autonomous micro-robotic vehicle system for hazardous waste site characterization, employing a new hybrid path planning technique for optimal mission execution. This method is based on integrating off-line reinforcement learning for rough planning with a unique fuzzy logic approach for obstacle detection and avoidance. T he idea is to greatly reduce the need for detailed knowledge of site environment by relying on the fuzzy logic system for local path execution, with the off-line reinforcement planner responsible only for global path supervision. The approach lends itself remarkably well to integration of fully autonomous cooperative robotic vehicle mission operations.

Significant progress has been made during the first seven months of the project. All of the milestones set for this period have been met, including readying a scaled up (by a factor of 1.7) ARC III vehicle for assembly and system integration, on-schedule the first week of June 1996. The path planning software subsystem was also completed on-schedule June 1, 1996, with its algorithms shown to be fully functional in arbitrary, partially unknown, simulated environments. No difficulties are anticipated in integrating the vehicle hardware and path planning software systems on-schedule by the end of August 1996.

One of the major objectives of this project has been to collaborate with INEL in identifying additional uses for the results of the research leading to the definition of new roles and missions which satisfy national needs. It is becoming clear that the results obtained to-date, especially the autonomous cooperative robotics aspects, have interesting and potentially significant applications for automating the effective, but highly labor intensive, practices of prescription agriculture. A joint university-INEL field demonstration of the dual (agricultural and hazardous waste site) applications of this research is currently scheduled for the first week of September 1996.

Two major milestones have been set for the end of month 6 and the end of month 12 next year. Development of the sensor and software system for dynamic obstacle detection and avoidance is to be complete by the end of the 6th month. By the end of the 12th month, systems definition and specifications and preliminary hardware and software development of a 'black box' retrofit controller-path planner is to be complete. Specifics of the latter milestone will be jointly defined with INEL and the project commercialization partner, Caterpillar Inc.

With numerous waste hazardous waste sites occurring in the surrounding regions of Southeastern Idaho and Northern Utah, INEL has a regional as well as national interest in meeting the challenges of hazardous waste site characterization and remediation. The usefulness of this project will be measured by the extent to which it contributes to the success of INEL and the DOE in satisfying these demands, as well as by the extent to which it helps INEL to identify and develop new roles in satisfying this nation's needs.

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Session 11. Materials Processing and Control

Wednesday, 1:00 p.m. to 5:00 p.m.

T. Alan Hatton (MIT), chair
James A. Seydel (INEL), co-chair
F. H. (Sam) Froes (Uof I), panelist
Jim Key (INEL), panelist

1:00 a.m.	N135	Jung-Hoon Chun MIT	A Real-Time Solidification Front Monitor for the Continuous Casting of Metals
1:45 a.m.	G22	Kevin L. Moore Idaho State University	Advanced Welding Control Technology
2:45 a.m.	—	Break	
3:15 a.m.	G04	Merton C. Flemings MIT	Sensing in Advanced Solidification Processing Systems
4:05 a.m.	G12	Uday B. Pal MIT	Inclusion Free Refining of Molten Metals Using Short Circuited Solid Electrolyte Cells
5:00 a.m.	—	Adjourn	

A Real-Time Solidification Front Monitor for the Continuous Casting of Metals (N135)

Jung-Hoon Chun, Massachusetts Institute of Technology

Co-PIs and University: Richard C. Lanza and Nannaji Saka, MIT
Graduate Students: Mark M. Hytros, Imad Jureidini, Dongsik Kim

Industrial Collaborators and Companies: G. Hildeman and H. Yu, Alcoa; J. Gallenstein, US Steel; I. Saucedo and H. Pielet, Inland Steel; J. Dorricott, IPSCO Steel; E. Schonauer, AISI

INEL Collaborators: Dennis C. Kunerth, Timothy Roney

Presenters: Jung-Hoon Chun, Richard C. Lanza

We are developing an industrial-scale high-energy computed tomography (CT) sensor to monitor the solidification of metals during the continuous casting process in real-time. The shape and location of the solidification front play a significant role in affecting the productivity of casting operations. By monitoring the solidification front, one can optimize the quality of the casting by reducing such defects as inclusions, cracks, and macrosegregation, in addition to optimizing the process by increasing production rate and eliminating breakout accidents.

The technique behind the sensor is based on the principles of CT and the attenuation of high-energy x-rays through a solidifying strand. The densities of liquid and solid metals differ by as much as 4 to 12%. Thus, it is possible to measure the intensity of transmitted photons through a section of strand to determine the relative proportions of the solid and liquid phases. With the application of CT, two- or three-dimensional images of the density distribution within the strand, and thus the solidification front, can be generated.

At present, the project is in its first phase of development: laboratory-scale development and testing of a prototype system. This will be carried out at MIT's Bates Linear Accelerator Laboratory, where a shielded facility is being built. The x-ray source is a 6-MeV, 300 rad/min linear accelerator. A controlled solidification platform will create steady-state solidification profiles in a laboratory environment. The solidification platform consists of a furnace capable of melting aluminum and its alloys, an air-cooling system, and a thermocouple-based data acquisition unit to monitor the location of the liquid/solid interface. An array of cadmium-tungstate scintillation detectors will measure the transmitted x-rays.

The project milestones for the coming year are to have all the components of the laboratory system assembled and operating properly, to conduct CT scans on phantom objects to determine baseline operation, and to begin detailed testing and analysis of sensor performance on the solidification front profile of aluminum alloys.

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Advanced Welding Control Technology (G22)

Kevin L. Moore, Idaho State University

Co-PI and University: D. Subbaram Naidu, Idaho State University

Post-Doctoral Fellow: Lyndon Brown (six months FY-96 only)

Graduate Students: Robert Yender, Justin Tyler

Industrial Collaborator: H. Redding, V.P., Eagle Rock Manufacturing

INEL Collaborator: John A. Johnson

Presenter: Kevin L. Moore

The Advanced Welding Control Technology project is a University/INEL/Industry collaboration working to develop methods for controlling gas-metal arc welding (GMAW) processes, with an emphasis on the control of the mass and heat properties of the process. Project activities to date have included: building the personnel and equipment infrastructure needed to support project activities, including an automated welding laboratory at ISU; carrying out basic research, in collaboration with INEL, aimed at modelling the GMAW process for controller design; and development of a novel constant-power GMAW controller, which has been validated experimentally at INEL. Current activities are focused on characterizing, both theoretically and experimentally, the capabilities of the constant-power control scheme; completing the experimental facility at ISU; and studying alternate control strategies for the GMAW system, including artificial intelligence methodologies and advanced control of weld pool thermal properties. Planned activities for the final phase of the project include continued controller design and validation; prototype development in collaboration with an industrial partner; and planning for turn-key software/hardware implementation of the controllers that have been developed.

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Sensing in Advanced Solidification Processing Systems (G04)

Merton C. Flemings, Massachusetts Institute of Technology

Co-PI and University: Anacleto Figueredo, MIT

Graduate Student: Yusuf Sumartha

Industrial Collaborators and Companies: Paul Mikkola, GM Powertrain; Keith Thompson, Dynacast Inc.; William Eisen, Crucible Research;

Jere Brophy, Brush Wellman

INEL Collaborator: None

Presenter: Prof. Merton C. Flemings

The aim of this research is to develop advanced sensing methods for studying the flow and filling of die castings, using prototype laboratory equipment to simulate the die casting process. A second, longer term, aim is to study die deterioration under severe thermal conditions. Die casting, including semi-solid forming are processes of central importance to production of modern, reliable, economic, fuel efficient automobiles. This program seeks to contribute to process reliability and economics in a significant way.

Laboratory equipment has been developed for the study which comprises (a) a melting and holding furnace, (b) a channel with test mold material comprising the "ingate" portion and a transparent material comprising the "die cavity, and (c) apparatus to apply a controlled vacuum to draw the metal into the die cavity at controlled rates. Advanced instrumentation being tested or employed in our experiments are (a) a state-of-the-art video camera capable of a frame speed of 40,500 frames per second and a spatial resolution of 64 × 64 pixels, (b) high speed optical pyrometry, and (c) fast response thermocouple pyrometry.

To date, approximately 50 runs have been made using aluminum and aluminum alloys, and 6 runs using copper alloys. The video camera is seen to be an excellent method of measuring flow velocities through the gate, and of determining the character of the flow front as it emerges from the gate. Thermocouple response times of less than a second have been achieved thus far, and work will be undertaken in the coming months on optical pyrometry. Emphasis of current work is on commercial aluminum Alloy 413 (Al-Si of approximately eutectic composition). Copper alloy being studied is Cu 37.8% Zn. Tests show that for higher melt temperatures and long flow times, accelerated die erosion is readily obtained under highly controlled conditions of melt temperature and flow.

During the coming year we anticipate meeting the milestones originally laid out for the program, including die life testing and initiation of tests on metal matrix composite slurries and semi-solid slurries.

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Inclusion Free Refining of Molten Metals Using Short Circuited Solid Electrolyte Cells (G12)

Uday Pal, Massachusetts Institute of Technology

Co-PI and University: Harold R. Larson, MIT

Graduate Student: Prashant Soral

Industrial Collaborator and Company: Brad Schroeder, Reading Tube Corporation

INEL Collaborator: Ronald Mizia

Presenter: Harold R. Larson

The objective of this project is to scale up the concept of deoxidizing metals by means of solid electrolyte cells to a unit that can be demonstrated on copper deoxidation in a plant environment. Technical difficulties limiting the industrial application of the approach will be identified and resolved. Data will be acquired to permit a detailed analysis of the economic viability of the process. The project involves both laboratory (MIT) and plant testing (Reading Tube Corporation). Copper is traditionally deoxidized by reaction with copper-phosphorus additions. This results in phosphate slag inclusions in the final product, and undesirable amounts of phosphorus in solution in copper, both of which are detrimental to the properties of copper. Earlier laboratory tests have shown that electrolytic cells can deoxidize copper without introducing any foreign elements at rates that could be of industrial interest. A pilot test fixture has been designed and fabricated, and the plant test site is being prepared.

In the laboratory, we have found that at dissolved oxygen contents above about 300 ppm the deoxidation kinetics can be enhanced by a factor of two or three by applying external voltage. Below this concentration oxygen diffusion in the metal becomes important (rate limiting), and applied voltage doesn't help and can be destructive to the electrolyte. Thermal shock problems have been resolved, and we believe we have a cell design that will withstand the plant environment. Copper has been successfully deoxidized to levels below 10 ppm. The solid electrolyte tubes must be coated with cermet on the inside surface to provide current collection and minimize contact resistances. The cermet coating protocol and assembly procedure is being optimized based on laboratory tests. Progress has been significant. The plant test fixture will have 55 cells and a total exposed surface area of about 625 square inches. We are evaluating the applicability to other metal systems. In the next program year we will complete plant trials on copper, and design a second generation pilot test apparatus. Cell life in the industrial environment will be determined, and process economics will be quantified. Testing on a second, industrially important, application will be proposed.

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Session 12. Membrane and Adsorption Separation

Wednesday, 1:00 p.m. to 4:30 a.m.

Kenneth A. Smith (MIT), chair
David L. Miller (INEL), co-chair
Edwin W. House (ISU), panelist
Jim Delmore, Lloyd McClure (INEL), panelists

1:00 a.m.	V19	Mark M. Benjamin University of Washington	Waste Component Separation and Volume Reduction of an Acidic, Heavy-Metal Bearing, Low Level Liquid Radioactive Waste
1:55 a.m.	N163	John D. Lamb Brigham Young University	Novel Separation Systems for Waste Processing and Resource Recovery Based on Macrocyclic Ligand Complexation
2:35 a.m.	—	Break	
3:05 a.m.	V101	F. P. McCandless Montana State University	Membrane Processes for the Recovery of Radioactive Species from Acidic Solutions
3:45 a.m.	V250	Christopher W. Allen University of Vermont	Improved Phosphazine Polymers for Membrane Technology
4:30 a.m.	—	Adjourn	

Waste Component Separation and Volume Reduction of an Acidic, Heavy-Metal Bearing, Low Level Liquid Radioactive Waste (V19)

Mark M. Benjamin, University of Washington

Co-PI and University: None

Graduate Student: Lloyd E. Voges

Industrial Collaborator and Company: Andro Wipplinger, The Boeing Company, Environmental Affairs Department

INEL Collaborator: Tom P. O'Holleran

Presenter: Mark M. Benjamin

Low-level liquid radioactive wastes (LLLW) are currently stored or will be generated from future processes at ICPP. Treatment options for the LLLW include waste component separation, volume reduction, immobilization and disposal.

The objective of this project is to develop methods of separating the waste components while minimizing the volume of each component, and especially of the hazardous components. The components of the LLLW are metals (0.5 M), acid (1 to 2 M), sodium (1 M), nitrates (2 to 3 M) and other salts (<0.2 M). Separation of metals is conventionally performed using hydroxide precipitation. Precipitation requires that the acidity of the LLLW be neutralized or removed. Whereas conventional neutralization of the acid with a base would increase the salt concentration in the system considerably, separation of the acid from the aqueous phase would not. Furthermore, since acids are required in parts of the process, separation of the acid presents the potential to reuse it, rather than purchasing additional acid and generating even more salt-containing wastes.

The dominant and most volatile acid in the LLLW is nitric acid. Evaporation of the nitric acid and water from the LLLW would leave a metal/salt residue. The LLLW also contains non-acidic nitrates that cannot be evaporated from the unmodified waste. Although nitrates remaining after evaporation do not contribute acidity to the residue, they are undesirable because they interfere with the ultimate immobilization of the residue in a grout. To our knowledge, sulfate ions do not have this drawback. Therefore, one management option is to replace the residual nitrates with sulfates. In tests performed to date using simple mixtures of nitric acid and sodium nitrate to simulate the nitrate-containing components of the LLLW, we have succeeded in removing almost all the nitrate from solution and recovering it as nitric acid.

Treatment of the residual metals and salts might involve dissolution in water followed by precipitation of metals, solid/liquid separation, and adsorption as a polishing step. The most concentrated metals in the residual are aluminum and iron. With proper pH control, these two non-hazardous metals can be precipitated as hydroxides while leaving the hazardous metals in solution. The hazardous metals can then be precipitated to generate a small volume of solid hazardous waste, in conjunction with or followed by an adsorption step to remove the residual dissolved hazardous metals from the water and non-hazardous salts. Solid/liquid separation after the precipitation and adsorption steps could be accomplished by crossflow microfiltration.

The heavy metal precipitation/adsorption portion of the treatment process and the membrane microfiltration step have been investigated using two forms of iron oxide (amorphous ferrihydrite and crystalline goethite) as adsorbents and filtration aids. Both simulated and real waste streams from an electroplating facility were investigated. Using either iron oxide, the permeate concentrations from the microfiltration process were consistently below 50 mg/L for each metal. Ferrihydrite had a higher capacity for metals than an equivalent mass of goethite, but goethite caused less resistance to permeate flux. Each was capable of releasing concentrated metals to an acidic regeneration solution.

Additional testing is planned to study nitric acid evaporation from concentrated metal and salt solutions and treatment of the metal/salt residue. The latter component will include a study of the regeneration and reuse of the iron oxide adsorbents. Achievement of the research objective will allow volume reduction of the disposed hazardous wastes and segregated disposal of the nonhazardous components. S uccessful results of the iron oxide treatment stage studies can also be applied to improve waste treatment operations at electroplating facilities.

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Novel Separation Systems for Waste Processing and Resource Recovery Based on Macrocyclic Ligand Complexation (N163)

John D. Lamb, Brigham Young University

Co-PI and University: None

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Graduate Student: Tatiana Levitskaya

Industrial Collaborator and Company: IBC Advanced Technologies, Inc

INEL Collaborator: Robert Lash

Presenter: J. D. Lamb

A novel polymer material composed of cellulose triacetate as support, different octyl ethers as plasticizers (solvents) and crown ethers as carriers, was investigated as solid extractant for metal ion sorption and as a membrane material for ion transport. Selective sorption and transport of Sr(II), Pb(II), U(VI), Ga(III) and Fe(III) was investigated. A diffusion-limited transport model has been found to accurately describe metal ion transport by crown ethers in these systems. The influence of counter- ion on sorption and transport processes was investigated. The membranes are easy to prepare in the laboratory, highly stable, and they may be useful in different separation and concentration procedures.

A number of new solvent extraction systems were studied for potential use in coalescence extraction. Extraction experiments were performed to compare measured extraction constants values to those obtained using traditional solvent systems. Extraction constants values for dinitrile solvents were ten to twenty times higher than those for traditional solvents.

Commercial polyethylene oxides and crown ethers form a second phase when trichloroacetic acid is added to an aqueous solution. This liquid phase is stable at high concentrations of HNO_3 and $NaNO_3$, being convenient for selective metal ion extraction. Experiments show complete extraction of lead in this system.

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Membrane Processes for the Recovery of Radioactive Species from Acidic Solutions (V101)

F. P. McCandless, Montana StateUniversity

Co-PI and University: None

Graduate Students: None

Industrial Collaborator and Company: Randi Wright Wytcherley, Glitsch Technology Corporation

INEL Collaborator: R. Scott Herbst

Presenter: F. P. McCandless

This research addresses Cs and Sr removal from acidic solutions of dissolved Idaho Chemical Processing Plant high level waste calcines and liquid sodium bearing waste. Effective methods for the separation of Cs are not well established. Selective separation of radioactive constituents would significantly reduce the amount of HLW that must be sent to a repository for permanent disposal, and the resulting low level waste may be stored at greatly reduced cost.

Parallel experimental and theoretical (modelling) studies were carried out to meet the goals of the project. Experimental permeabilities for ordinary (passive) diffusion of dissociated salts in solution through several immobilized liquid membrane phases have been determined in a batch test cell for Cs, K, Na, Ca, and Sr (nitrates). The ratio of permeabilities are $P^{Cs}/P^{Ca} \sim P^{Cs}/P^{Sr} = 2.75$, $P^{Cs}/P^{Na} = 1.44$, $P^{Cs}/P^{K} = 1.05$. These ratios were essentially the same for all membrane phases tested which include n-octanol, 2-octanol, 2-octanane, and cyclohexylamine. Single permeation stages, simple cascades, and countercurrent cycle cascade configurations containing perect-mix stages have been modelled to determine what membrane process configuration would be required to reduce the tails product Cs concentration in a hypothetical binary solution containing $x_{Cs} = 0.001$ by a factor of 1000, while increasing the Cs concentrattion in the heads product aby factors of 10 and 100. The results of the modelling indicates that the countercurrent recycle cascade configurations are required to make the desired separations, and that systems with higher selectivities are probably required if the process is to be attractive for the intended use. A large number of stages and corresponding large total interstage solvent removal rates would be required for cascades designed for the experimental systems investigated to date. For example, for a binary system with $\alpha = P^{Cs}/P^{Ca} = 2.75$, an ideal cascade containing 22 ideal stages would be required to make the desired separation (yP - 0.01). Since only dissociated salts are transported through the membrane, and since the driving force for diffusion is a concentration difference, stagewise re-concentration of the permeated strip and unpermeated feed solutions is necessary. For the above cascade, about 145 liters of solvent (water) per liter of feed solution would have to be removed by evaporation (or possibly reverse osmosis) if the stage feed and strip solutions were maintained at 2 and 0.1 Molar respectively.

The experimental investigation was carried out at a level much lower than anticipated in the original proposal because a graduate student was not available for the project because of the timing of release of funds for the project.

If this project is continued, emphasis should be on the development of a membrane that has a greater selectivity than for those observed for the ordinary diffusion process investigated to date. This might be accomplished by facilitated transport and/or other means of selectively complexing specific ions in the feed or strip solutions.

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Improved Phosphazene Polymers for Membrane Technology (V250)

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Industrial Collaborator and Company: Debra Saez, Technically, Inc.

INEL Collaborator: Eric Peterson

Presenter: C. W. Allen

Work at INEL has led to the identification and utilization of a class of hybrid organic-inorganic polymers, poly(phosphazenes), as membranes for selective removal or separation of various harmful components form harsh chemical systems thus representing a promising technology for environmental improvement.

The project involves a systematic approach to the design and synthesis of improved poly(phosphazenes) for membrane applications. A three-fold strategy involving preparation of polymers without the chemical defects which may exist in the current systems, chemically modified polymers to improve water transport and consideration of the membrane potential of a related class of polymers is being explored.

The ultimate goal of the project, if successful, is two-fold. The first goal is the improvement of properties and preparation routes of the system currently under investigation, (polydiphenoxyphosphazene) $[NP(OPh)_2]n$. The value of this part of the study would be development of membranes better able to withstand the demands of severe environmental stress. The second goal is the development of new materials with new properties thus providing membranes for new applications or improved performance in current applications. The approaches employed involved chemical synthesis and physiochemical investigations of materials. In this early stage of the project effort has focused in two areas (beyond recruitment of personnel and outfitting a new laboratory and equipment for the project). The first study involves optimization of the preparation of $[NP(OPh)_2]_n$ from $(NPCl_2]_n$. The role of the metal cation (M^+OPh^-; M^+ = Li, Na, Tl) as well as that of a catalyst, $(C_4H_9)_4N^+Br^-$, has been explored. The $NaOPh/(C_4H_9)_4N^+Br^-$ mixture is the superior system. Work on $[NP(OPh)_2]n$ preparation is continuing with exploration of alternate routes to $(NPCl_2)_n$ and polymerization of monomers containing the phenoxy substituent. The synthesis of carbon-chain polymers of the methylmethacrylate class with cyclophosphazene substituents has been explored. Derivatization with the phenoxide ion gives a polymer with side groups, rather than the back-bone, containing the $NP(OPh)_2$ moiety. The introduction of the phenoxide results in a significant increase in the thermal stability of the polymer. After scale up procedures are developed, this material will be examined as a potential membrane.

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Index of Principal Investigators and Presenters

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