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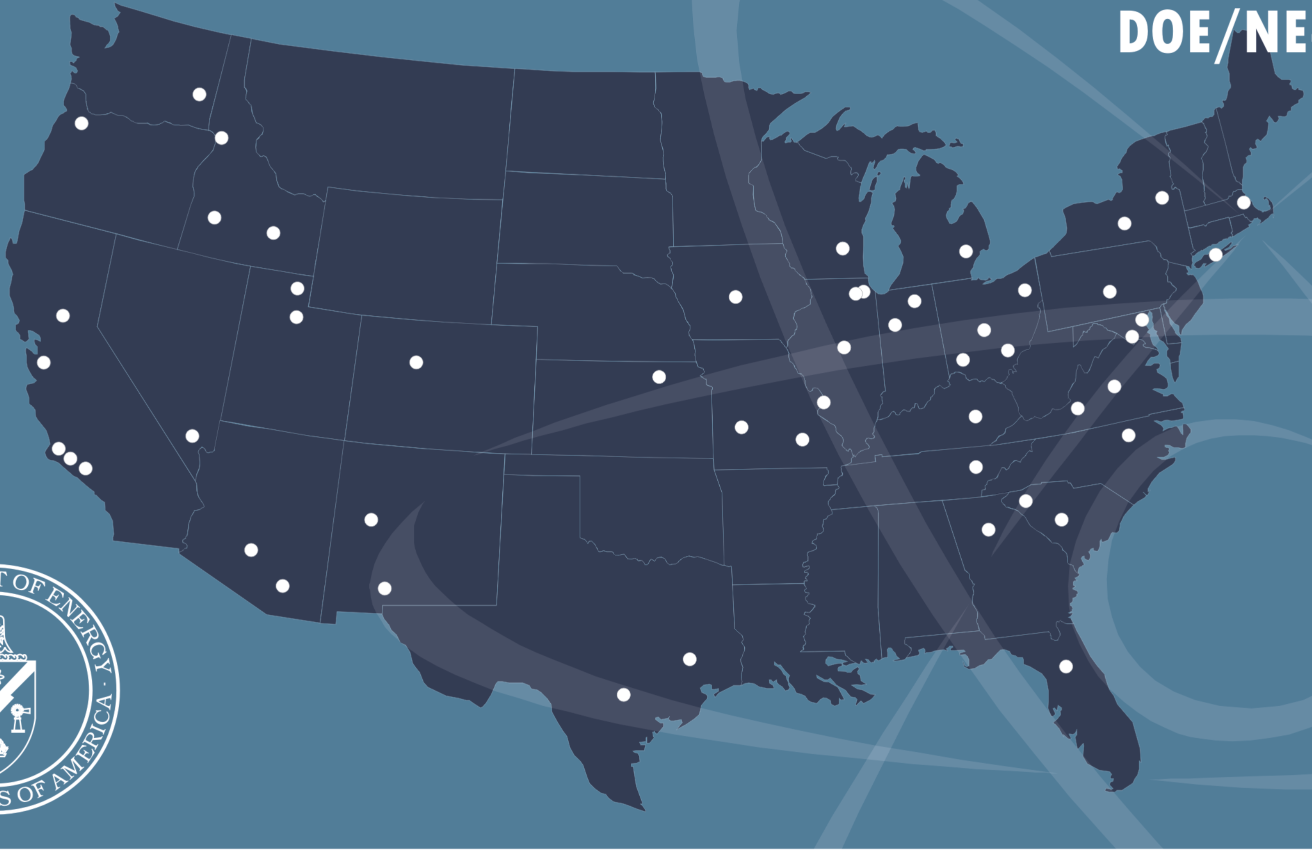


DEPARTMENT OF ENERGY
UNITED STATES OF AMERICA

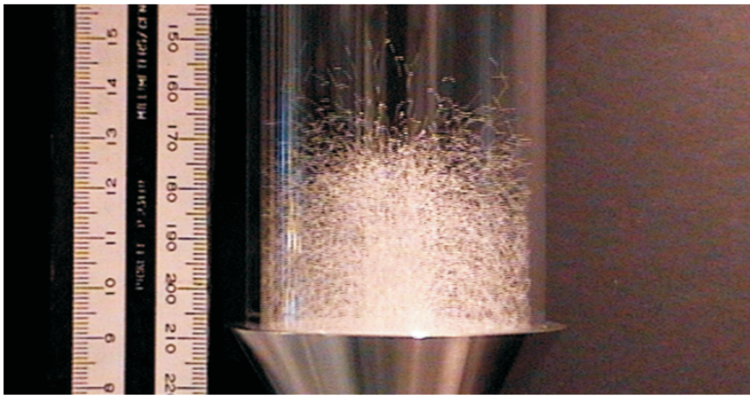
Nuclear Energy Research Initiative

2006 Annual Report

GEN IV Nuclear Energy Systems

Global Nuclear Energy Partnership

NHI
Nuclear Hydrogen Initiative



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Foreword

The Nuclear Energy Research Initiative (NERI) is at the core of a Federal effort to develop advanced nuclear energy concepts and technologies. This program supports the *National Energy Policy* by conducting research that addresses the long-term barriers to both maintaining and expanding nuclear generation of electricity in this country. Currently funded NERI projects are closely linked to the principal research programs sponsored by the Department of Energy's Office of Nuclear Energy (DOE-NE): the Generation IV Nuclear Energy Systems Initiative, the Advanced Fuel Cycle Research and Development program, and the Nuclear Hydrogen Initiative. With its focus on applied nuclear energy research, NERI has been realizing its goals of both developing advanced nuclear energy systems and providing state-of-the-art research concerning nuclear science and technology.

Since its inception in 1999, NERI has helped to maintain and improve the nuclear research infrastructure in this country by encouraging, preserving, and advancing nuclear science and technology research and development. To further this mission, NE decided to refocus NERI in 2004 to exclusively fund research led solely by the nation's universities, with national laboratories and industry partners providing valuable contributions as collaborators. Strong university involvement is particularly important to promote and maintain a robust nuclear science and engineering infrastructure to meet future technical challenges. This revised focus enables educational institutions across the country to remain at the forefront of nuclear science research. In addition, it renews student interest in pursuing degrees in nuclear engineering and related sciences and further integrates the nation's universities with the research efforts and initiatives at DOE.

The *Nuclear Energy Research Initiative 2006 Annual Report* summarizes the progress of the 35 research projects initiated in FY 2005, the 25 projects initiated in FY 2006, and the objectives and work scope of the 22 newly awarded FY 2007 research projects. The final summaries of projects initiated in FY 1999 through FY 2002 can be found in the previous NERI Annual Reports. This report disseminates the results of NERI-sponsored research to the wide R&D community to spur yet more innovation, assuring a bright future for nuclear energy in the United States and the world.

Dennis R. Spurgeon

Dennis R. Spurgeon, Assistant Secretary
for Nuclear Energy
U.S. Department of Energy

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1. Overview

The Nuclear Energy Research Initiative

The United States Department of Energy (DOE) created the Nuclear Energy Research Initiative (NERI) in fiscal year (FY) 1999 in response to recommendations provided by the President's Committee of Advisors on Science and Technology. The importance of nuclear power to the Nation's future energy supply requires that DOE apply its unique resources, specialized expertise, and national leadership to address all of the potential barriers to maintaining and expanding its use.

NERI is a national, research-oriented initiative managed and funded by DOE's Office of Nuclear Energy (NE). The purpose is to sponsor research and development (R&D) that addresses the principal barriers related to the growth of nuclear energy in the United States. The initiative has helped DOE foster innovative ideas in NE's primary research programs: advanced nuclear energy systems, hydrogen production from nuclear power, and advanced nuclear fuels and fuel cycles. In addition to responding to the Nation's need for current nuclear energy research to advance the development of nuclear energy technology, NERI is helping preserve the Nation's nuclear science and engineering infrastructure—enabling the United States to maintain a competitive position in the nuclear energy arena at home and abroad.

To achieve the Nation's long-range goal of establishing nuclear energy as a viable and expandable option, NERI has the following objectives:

- To address and help overcome the potential technical and scientific obstacles to the long-term, future growth of nuclear energy in the United States, including those involving non-proliferation, economics, and nuclear waste disposition.
- To advance the state of U.S. nuclear technology so that it can maintain a competitive position in overseas and domestic markets.
- To promote and maintain a nuclear science and engineering infrastructure to meet present and future technical challenges.

NERI 2006 Annual Report

This *Nuclear Energy Research Initiative 2006 Annual Report* serves to inform interested parties of progress made in NERI on a programmatic level as well as research progress made on individual NERI projects. Following is an overview of each section:

- Section 2 provides background on the creation and implementation of NERI, its corresponding international I-NERI component, and the evolving research focus.
- Section 3 presents the scope of the three NE R&D programs supported by NERI.
- Section 4 highlights program funding and participants in NERI research projects.
- Section 5 provides a discussion on the impact NERI has had on U.S. university nuclear programs.
- Section 6 presents progress reports for each of the 60 ongoing FY 2005-2006 projects and abstracts for the 22 projects newly awarded in FY 2007.

Projects are organized by their primary research area: Generation IV Nuclear Energy Systems Initiative (Generation IV), Advanced Fuel Cycle Research and Development (AFCR&D), and Nuclear Hydrogen Initiative (NHI). Numbering is designated by the fiscal year in which the award was made. At the end of this document, there is a complete index of NERI projects.

2. Program History

NERI Development

In January 1997, the President tasked his Committee of Advisors on Science and Technology (PCAST) to review the current national energy R&D portfolio and to provide a strategy to ensure that the United States has a program to address the nation's energy and environmental needs for the next century. In its report responding to this request the PCAST panel on Energy Research and Development determined that ensuring a viable nuclear energy option was essential to help meet U.S. future energy needs. Specifically, the panel recommended that DOE implement an R&D effort to address the principal obstacles to achieving a viable nuclear energy option, targeting such areas as nuclear waste, proliferation, safety, and economics. DOE was to fund research through this new initiative based on a competitive selection of proposals submitted by national laboratories, universities, and industry.

In response to these recommendations, DOE established NERI in 1999 and the program received Congressional appropriations to begin sponsoring innovative scientific and engineering R&D that address the key issues affecting the future use of nuclear energy and preserve the nation's nuclear science and technology leadership. Currently, NERI employs a unique process for selecting new projects. DOE-NE issues an annual solicitation requesting applications from eligible participants on a noted scope of work. Principal investigators (PIs) select research topics of interest and define the scope and extent of the R&D in their application responses. An independent peer review panel evaluates the scientific and technical merit of the R&D proposals. Subsequently, a relevance review is conducted by the program's National Technical Directors, Systems Integration Managers, and Technical Directors. DOE program managers then review those proposals judged to have the highest merit and relevance to ensure their conformance with policy and programmatic requirements and recommend project awards to DOE's Source Selection Official.

Additional information on the NERI program, including previous annual reports, is available at the NERI website: *http://nuclear.energy.gov/neri/neNERIresearch.html.*

International Cooperation (I-NERI)

Recognizing the need for an international component, PCAST issued a report in 1999 entitled *Powerful Partnerships: The Federal Role in International Cooperation on Energy Innovation* to promote "bilateral and multilateral research focused on advanced technologies for improving the cost, safety, waste management, and proliferation-resistance of nuclear fission energy systems." In response, DOE launched the new International Nuclear Energy Research Initiative (I-NERI) for bilateral and multilateral nuclear energy research. Since FY 2001, I-NERI funding has supported 66 bilateral, cost-shared research projects with the Republic of Korea, France, the European Union, Brazil, Canada, Japan, and the Organization for Economic Cooperation and Development (OECD). Similar international agreements are being considered with the Republic of South Africa with the intent of establishing additional collaborations in the future.

I-NERI allows DOE to leverage Federal investment and international resources through cost-sharing arrangements with each participating country on a wide range of nuclear technology topics. This initiative enhances the participation of the United States and DOE in international policy discussions on the future direction of nuclear energy. Further information can be found on the NE website at *http://www.nuclear.gov*, including separate annual reports for research conducted under the I-NERI program during the previous fiscal years.

NERI Focus

In order to determine the initial focus of the NERI research areas, DOE convened a workshop of nuclear community stakeholders in April 1998, representing national laboratories, universities, and industry. As a result, DOE established five specific scientific and engineering R&D areas:

1) Proliferation-resistant reactors and fuel technology
2) New reactor designs to achieve improved performance, higher efficiency, and reduced cost
3) Advanced nuclear fuels
4) New technologies for managing nuclear waste
5) Fundamental nuclear science

Since the initiation of NERI, several Federal directives have influenced NERI research activities. A synopsis of each of these directives is provided below.

The Long-Term Nuclear Technology Research and Development Plan. In 1998, DOE established the independent Nuclear Energy Research Advisory Committee (NERAC). This committee provides advice to the Secretary and to the Assistant Secretary for Nuclear Energy on DOE's civilian nuclear technology program. In June 2000, NERAC issued the *Long-Term Nuclear Technology Research and Development Plan*. This plan identifies the research and technology development that is necessary over the next 10–20 years to help ensure the long-term viability of nuclear energy as an electricity generation option in the United States. NERAC also established a task force to identify R&D needs related to non-proliferation issues associated with nuclear power production. Their recommendations for appropriate research in this area were provided to DOE in a January 2001 report titled, *Technical Opportunities to Increase the Proliferation Resistance of Global Civilian Nuclear Power Systems (TOPS)*.

The National Energy Policy. Issued in May 2001 by the Vice President's National Energy Policy Development Group, the *National Energy Policy* supports the expansion of nuclear energy as one of its major initiatives for meeting the growing energy requirements of the United States. The *National Energy Policy* provides the core element in the planning for DOE's nuclear energy research programs, addressing, among other areas, the research and development of advanced reactor and fuel cycle concepts, hydrogen production from nuclear energy, and the associated enabling sciences and technologies.

The Technology Roadmap for Generation IV Nuclear Energy Systems. In September 2002, NERAC issued the *Draft Technology Roadmap for Generation IV Nuclear Energy Systems*. In coordination with the eleven-country-member Generation IV International Forum, six reactor system concepts were selected for further development 1) the Very High-Temperature Reactor, 2) the Gas-Cooled Fast Reactor, 3) the Supercritical Water-Cooled Reactor, 4) the Lead-Cooled Fast Reactor, 5) the Sodium-Cooled Fast Reactor, and 6) the Molten Salt Reactor.

Energy Policy Act of 2005 (EPACT). On signing EPACT 2005 into law August 8, 2005, President George W. Bush reiterated the importance of nuclear energy as a clean, safe component of our nation's energy supply. "With the practical steps in this bill, America is moving closer to a vital national goal. We will start building nuclear power plants again by the end of this decade." The law directly addresses DOE-NE's core R&D programs, including NERI and its constituent parts: Generation IV, AFCR&D, and NHI. EPACT 2005 allows the Secretary of Energy to conduct a set of nuclear energy programs that increase the efficiency of nuclear energy-intensive sectors via improved technologies, promote diversity of the energy supply, decrease the Nation's dependence on foreign energy sources, improve energy security, and decrease the environmental impact of energy-related activities. It also authorizes $1.25 billion for fiscal years 2006 through 2015 to fund a prototype Next Generation Nuclear Plant (NGNP) to produce both electricity and hydrogen.

Advanced Energy Initiative. In February 2006, the President rolled out his Advanced Energy Initiative, which aims to improve the country's economic and national security by reducing dependence on foreign sources of energy. This initiative provides a 22-percent increase in funding for clean-energy technology research at DOE to change how Americans fuel their vehicles and power their homes and businesses. Generating electricity and hydrogen fuel from safe, advanced nuclear power is an important component. The initiative also calls for the development of a new Global Nuclear Energy Partnership (GNEP) to address spent nuclear fuel; eliminate proliferation risks; and expand the promise of clean, reliable, and affordable nuclear energy on an international scale. Under GNEP, nations with advanced civilian nuclear energy programs will develop technology to recycle nuclear fuel and supply small, secure reactors and fuel services to other countries in exchange for non-proliferation guarantees. *The National Security Strategy of the United States of America*, which the President issued in March 2006, further reinforces the importance of GNEP in meeting global energy demand while keeping nuclear weapons materials out of the hands of rogue states and terrorists.

With new federal directives, NERI's focus continues to evolve. Initially, projects provided a supportive role to government nuclear energy-related R&D programs. In 2004, the focus of NERI research changed to specifically fund applied R&D that supports NE's principal research initiatives: Generation IV, AFCR&D, and NHI. In addition, only U.S. universities are allowed to serve as the principal investigators for new projects. National laboratories and private companies can still participate as collaborating organizations. This new focus directly supports NERI's goal to preserve, improve, and advance the nation's nuclear science and engineering infrastructure and will further assist these nuclear energy initiatives in accomplishing their goals and objectives.

The scope of the FY 2006 NERI solicitation, for awards announced in early 2007, focused on current Federal R&D priorities as outlined in EPACT 2005 and the Advanced Energy Initiative. For example, the U.S. priority for reactor development work under the Generation IV initiative focuses on the Very High-Temperature Reactor (VHTR) for use as the NGNP and the Sodium Fast Reactor (SFR) as the GNEP advanced burner design.

3. NERI Research Areas

Projects undertaken since 2004 are aligned with NERI's new focus to conduct applied nuclear energy research related to the three primary NE R&D programs: Generation IV, AFCR&D, and NHI. These three initiatives are contributing to the revitalization of nuclear technology in our nation by developing efficient technologies for future electrical power production, hydrogen production, and other energy conversion systems. Following are descriptions of the three initiatives under which awards have been made.

Generation IV Nuclear Energy Systems Initiative

Generation IV nuclear energy systems are being developed to achieve high burnup using transmutation and recycled fuel, allowing for efficient use of domestic uranium resources and minimizing radioactive waste. Advances in safety and physical protection will guard against possible acts of terror or the diversion of nuclear materials, helping to ensure public confidence in nuclear technology. The program is focused on developing six new reactor systems to be deployed during the next 20 years:

1) Very High-Temperature Reactor (VHTR)
2) Sodium-Cooled Fast Reactors (SFR)
3) Supercritical-Water-Cooled Reactor (SCWR)
4) Lead-Cooled Fast Reactor (LFR)
5) Gas-Cooled Fast Reactor (GFR)
6) Molten Salt Reactor (MSR)

The U.S. is not actively pursuing all of these reactor designs at the present time. Current U.S. efforts are focused on developing the SFR and VHTR technologies, in conjunction with other foreign collaborators under the Generation IV International Forum (GIF).

In addition to the development of these six reactor systems, Generation IV includes three cross-cutting programmatic areas of research. These activities are germane to two or more reactor concepts:

1) Design and evaluation methods
2) Crosscutting materials for advanced reactors
3) Energy conversion

The ***Very High-Temperature Reactor (VHTR)*** concept is being pursued in the United States under the NGNP program. The major aim of NGNP projects is to build and demonstrate advanced high-temperature reactor technology to economically produce both hydrogen and electricity. The VHTR is believed to be the most suitable candidate. The first phase of project development may lead to the design, construction, and operation of a demonstration facility consisting of an advanced nuclear reactor coupled with a hydrogen production plant. New research projects focus on validating reactor physics and core design analysis tools, developing and validating reactor thermal-hydraulic and mechanical design analysis tools, performing materials research and power-conversion unit assessments, and conducting safety and risk analyses. The scope of these projects includes project design, system design and analysis methodology, and fuel development and qualification.

Sodium-Cooled Fast Reactor (SFR). The sodium-cooled fast reactor is the leading candidate design for the advanced burner reactor being developed under GNEP. The SFR system features a liquid metal fast-spectrum reactor that can operate on recycled spent fuel to help manage high-level radioactive wastes, particularly plutonium and other actinides. With innovations to reduce capital cost, the mission can extend to economic electricity production. The SFR can also lead to sustainable energy production, given the proven capability of sodium reactors to utilize almost all of the energy in natural uranium. Activities under this research area focus on comparative studies of various SFR designs, helping to reestablish the U.S. knowledge base, and transmutation of spent fuel from light water reactors. Other topics include selection and testing of materials and conceptual design studies of supercritical carbon dioxide secondary plant systems.

Supercritical Water-Cooled Reactor (SWCR). The objective of this research is to demonstrate the technical feasibility of a light water reactor design operating with supercritical water coolant, i.e., water above the thermodynamic critical pressure and temperature point. The focus of this research includes three main areas: 1) the evaluation of dynamic power/flow instabilities, 2) corrosion and stress-corrosion cracking testing of materials for the core and vessel internals, and 3) the investigation of basic thermal and heat transfer phenomena for the reactor. The U.S. is not currently pursuing this technology. In FY 2007, domestic SCWR activities will focus on monitoring international R&D efforts and participating in related international forums.

Lead-Cooled Fast Reactor (LFR). The objective of this research is to produce a small, proliferation-resistant nuclear energy system for deployment in remote locations and in developing countries. The LFR system has a closed fuel cycle and uses a fast-spectrum lead or lead-bismuth liquid metal coolant. This design allows for efficient conversion of uranium and management of actinides. R&D efforts will define and select the reference system, prepare a defensible safety case, and license a demonstration reactor system. However, the U.S. is not currently pursuing this technology. In FY 2007, U.S. LFR activities will focus on monitoring international R&D efforts and participating in related international forums.

Gas-Cooled Fast Reactor (GFR). The objective of this research is to develop a safe and sustainable helium-cooled fast reactor that has a closed fuel cycle, is highly efficient, and is capable of producing both electrical power and hydrogen. Preliminary design concepts use a direct-cycle Brayton Cycle secondary power conversion system. The fast spectrum and full recycle of actinides minimize the production of radioactive waste. Research for this reactor concept includes defining design features (fuel, coolant, and unit power), designing safety systems for decay heat removal, identifying/testing fuel and core materials capable of high-temperature operation including developing fuels with high fission product confinement and reasonable burnup and fluence, and developing fabrication techniques. NERI project researchers previously identified possible passive/semi-passive safety systems, conducted materials testing with carbon dioxide (CO_2) and identified candidate high-temperature fuels. The U.S. is not currently pursuing this technology. In FY 2007, GFR activities will focus on monitoring international R&D efforts and participating in related international forums.

Molten Salt Reactor. Molten salt reactors (MSR) can be used for the production of electricity, hydrogen, or fissile fuels, as well as actinide burning. In this design, the nuclear fuel is dissolved directly in a molten fluoride salt coolant which circulates throughout the primary system. Energy is transferred to a clean molten salt intermediate heat transport loop, then a high-temperature Brayton cycle power conversion system. As the NGNP uses similar liquid salt technology in the hydrogen production loop, many areas of research are shared, such as Brayton power cycles, compact heat exchangers, and carbon composite materials. Therefore, the U.S. is not pursuing this technology as a separate area of research.

Design and Evaluation Methods. Analytical methods, modeling techniques, computer codes, and databases must be developed for Generation IV plants. In addition, research needs to be performed to evaluate the economic feasibility of these new plants and to ensure the proliferation resistance and physical protection to the public. Major activities under this research area include 1) improving and validating NGNP analytical capabilities, 2) defining fast reactor modeling requirements for the GFR and LFR designs, and 3) improving Generation IV evaluation methodologies and selecting preferred options. Other activities include identifying phenomena and parameters to be included in thermal/hydraulic and safety analysis codes, and improving Monte Carlo and deterministic methods for neutronic, fuel depletion, and material damage analyses.

Materials. Projects in the materials area include the selection, development, and qualification of structural materials and other components necessary to design and construct the various types of advanced reactors. Material requirements for the NGNP, GFR, SCWR, and LFR reactor systems, as well as for their energy conversion systems, are addressed under this research area. Specific cross-cutting activities applicable to all designs will be performed including: 1) designing a test facility, then initiating low-flux and high-flux, high-temperature irradiations; 2) establishing a database of candidate materials for high temperature and radiation service, then performing studies to identify mechanical properties; 3) preparing documents for alloys 316FR and 617 to gain ASME code certification; 4) performing microstructural analysis and modeling for materials of interest; and 5) developing a high-temperature design methodology for materials/applications of interest.

Energy Conversion. Projects in this area will focus on research for both the supercritical carbon dioxide and the high-temperature helium Brayton cycles. Objectives associated with the supercritical carbon dioxide Brayton cycle include 1) completing system design and economic assessment, 2) performing experiments to validate key features, and 3) conducting research on engineering seals, materials, heat exchangers, and ducting. A planned demonstration experiment and simulation model will also help determine plant characteristics, performance, and the supercritical cycle dynamic response. For the high-temperature helium Brayton cycle, project goals include engineering analyses, designing heat exchangers and turbo-machinery, and constructing a small-scale demonstration experiment.

Advanced Fuel Cycle R&D (AFCR&D)

The AFCR&D program focuses on developing advanced fuels, spent fuel treatment techniques, and transmutation technologies to facilitate the transition towards a sustainable advanced nuclear fuel cycle. Beginning in FY 2007, AFCR&D will focus near-term activities to support the most promising technologies developed to date. The chief goals of AFCR&D are to reduce the amount of high-level radioactive waste requiring geologic disposal, to reduce accumulated plutonium from PUREX processing of commercial spent fuel, and to extract more useful energy from material that normally would be disposed of as waste. The program will develop fuel systems and create enabling fuel technologies such as fuel, cladding, waste forms, separations, and disposal technology to decrease spent fuel volume; separate long-lived, highly radiotoxic elements; and recover valuable energy from spent fuel. The technologies will support both existing and forthcoming nuclear energy systems.

Spent fuel treatment and recycling are critical to support the expansion of proliferation-resistant nuclear power. This multifaceted program involves recycling spent fuel, fabricating fuel assemblies containing the removed long-lived actinides and transuranics, burning the assemblies in a fast reactor, and developing more benign waste disposal technologies for the remaining radioisotopes and process wastes. Resulting technologies from this work will satisfy requirements for a controlled, proliferation-resistant nuclear materials management system. Planned NERI research efforts related to this program will focus on the following technologies:

- Separations
- Fuels
- Transmutation science and engineering
- Systems analysis
- Demonstration facilities

Separations. Research in this area includes the development of aqueous and pyrochemical separations technologies, advancement of spent fuel treatment processes, improvement of waste storage forms, treatment of spent fuel from the experimental breeder reactor (EBR-II) in preparation for disposal, and conceptual planning of future spent fuel treatment plants and advanced processing technologies. The current focus is on improving separations processes for LWR spent fuel reprocessing, fabricating waste/storage forms suitable for storage in a repository; demonstrating transuranic (TRU) extraction processes; accelerating the EBR-II blanket treatment with advanced processing technology; demonstrating advanced LWR spent fuel processing techniques; demonstrating americium/curium separations processes; and developing storage/disposal forms for uranium, plutonium-neptunium, americium-curium, and cesium-strontium.

Fuels. This research area is developing advanced fuels for LWRs, Generation IV reactors, and dedicated transmuter facilities. Researchers will model, fabricate, characterize, and test fuels of various compositions. Associated safety analyses, development of remote fuel fabrication techniques and advanced clad materials are included in the scope. Current NERI research projects focus on irradiation and post-irradiation examination (PIE) of fuels for the Advanced Burner Reactor (ABR).

Transmutation Science and Engineering. This research area is studying the use of the transmutation process to convert long-lived radioactive isotopes into short-lived isotopes via neutron capture or fission. Research supports accelerator-driven systems, transmuter materials and coolants, and transmutation physics. The primary purpose is to develop an engineering basis for the transmutation of plutonium and minor actinides. Current activities focus on 1) continued measurements and evaluations of higher actinides to reduce transmutation uncertainty, 2) new irradiations at the PHENIX reactor in France, 3) examination of irradiated materials from the Fast Flux Test Facility (FFTF) and the European PSI facility, 4) development of an intense fast neutron source for materials testing, and 5) development of alloys and surface treatment to increase the corrosion resistance of lead-bismuth eutectic (LBE).

Systems Analysis. This area includes broad-based systems studies and analyses, such as: 1) transmutation systems and integrated model development; 2) fuel cycle proliferation resistance; 3) economic analyses; and 4) material transportation, storage and disposal analyses. The objectives of research projects under this area are to analyze fuel cycle infrastructure needs, supply recommendations on fuel types and reactor systems from the perspective of the overall fuel cycle, and perform analyses to assist DOE in determining the need for a second spent fuel repository.

Demonstration Facilities. An Advanced Fuel Cycle Facility will be designed and constructed to provide enhanced separations and fuels research under the GNEP program. Powerful new simulation and modeling tools will predict reactor and fuel behavior in order to reduce the need for lengthy irradiation experiments. The initial focus of such tests is the treatment of spent nuclear fuel from existing light water reactors. Later, both aqueous and pyroprocessing of fast reactor spent fuel will be studied. Lastly, a sodium-cooled Advanced Burner Reactor will serve as the focal point for transmutation development. SFR technology will demonstrate the transmutation of both spent light water reactor fuel and fast reactor recycle fuel. Further R&D into advanced aqueous and pyroprocessing technologies, waste and storage forms, and metal and oxide transmutation fuels will continue.

Nuclear Hydrogen Initiative (NHI)

The mission of the NHI is to develop hydrogen production technologies that are fueled by nuclear energy. The goal is to demonstrate hydrogen production that is compatible with nuclear energy systems through scaled experiments, and then to couple an engineering-scale demonstration plant with a Generation IV demonstration facility by 2021. NERI research that is planned under this initiative includes projects that are associated with thermochemical cycles, high-temperature electrolysis, and reactor-hydrogen production process interface.

Thermochemical Cycles. The focus of this research area is to develop thermochemical cycles for hydrogen production that are suitable for nuclear application, such as sulfur-based cycles and alternative cycles. Researchers will provide flowsheet methodology for analyzing and comparing the thermochemical cycles, and high-temperature interface requirements for the heat exchangers and materials. These processes offer the potential for high-efficiency hydrogen production in commercial quantities, once technical issues are resolved. Cycles are selected for development based on a comparison of thermochemical cycles using a consistent analysis methodology. Research planned for the upcoming years will consist of laboratory-scale demonstrations of candidate processes for alternative thermochemical process assessment; and enhancement of membranes to increase process efficiency. Projects will include materials testing, control system design, and cost evaluations.

High-Temperature Electrolysis (HTE). High-temperature electrolysis uses electricity to produce hydrogen from steam. This technology has the potential for higher efficiencies than commercial processes currently available. This research area seeks to reduce the cost of manufacturing electrolytic cells and components and increase the useful lifetime of these components, thereby producing hydrogen at the lowest possible cost. Research activities include cell and stack experiments, modeling of plant and cell dynamics, and design of plants beginning with a laboratory unit and later scaling up to include a pilot-scale experiment followed by demonstration and construction of commercial units. Materials analysis for cells, heat exchangers, and separations will also be performed under this research area. Projects under this research area will be aimed at completing HTE cell and stack/module testing, completing the design and then assembling components for the integrated laboratory test unit in 2007, completing the design and fabrication of a pilot-scale experiment by 2013, and conducting tests for high-temperature heat exchangers and separations.

Reactor-Hydrogen Production Process Interface. The purpose of this research is to develop and optimize high-temperature heat exchanger (HX) designs (optimizing HX type, operating conditions, efficiency, and material qualification), implications of the intermediate heat transfer loop on reactor operation (e.g., corrosion, isolation, connection), and design of support systems. Program efforts over the next three years will explore laboratory-scale HX development for a variety of high-temperature hydrogen production processes, including design; short and long-term materials testing; fabrication; and system support, which includes assessment of the process, infrastructure, and facilities requirements for the pilot plant and the balance-of-plant (BOP) design.

All three initiatives clearly support R&D efforts necessary to position nuclear energy as a viable fuel source that will help the United States sustain its growing energy needs. The selection of new NERI research projects is based on their relevance to these specific initiatives, and their achievements will play an integral role in the success of the overall NE mission.

The graphic summarizes key features of NERI. The following chapter explains the work scope associated with these NERI research areas in more detail and presents progress reports for the FY 2005 and 2006 projects, along with brief abstracts of the FY 2007 projects that were recently awarded.

Vision

To maintain a viable nuclear energy option to help meet the Nation's future energy needs

Goals/Objectives

- Address potential technical and scientific obstacles
- Advance the state of U.S. nuclear technology
- Promote and maintain a nuclear infrastructure

Scope of Program

- Advanced Nuclear Energy Systems
- Advanced Nuclear Fuels/Fuel Cycles
- Hydrogen Production from Nuclear Power

R&D Priorities

- Advanced reactors, systems, and components
- Alternative energy conversion cycles
- Design and evaluation methods
- Advanced structural materials
- Spent nuclear fuel separations technologies
- Advanced fuels
- Transmutation science and engineering
- Fuel cycle systems analysis
- Thermochemical cycles
- High-temperature electrolysis
- Reactor-hydrogen production process interface

Implementation Strategy

- Competitive peer-reviewed R&D selection process
- Collaborative research efforts
- Individually managed projects
- Continuous DOE oversight

Results

- U.S. nuclear leadership
- Nuclear infrastructure development
- Nuclear public awareness
- Innovative technologies
- Advances in nuclear engineering
- Worldwide partnerships

4. NERI Accomplishments

This section discusses the program's progress in attracting research proposals, awarding annual R&D funding, and successfully completing NERI-funded research projects.

Project Awards

In FY 1999, DOE's NERI received 308 R&D proposals from U.S. universities, national laboratories, and industry in response to its first solicitation. The initial FY 1999 procurement was completed with the award and issue of grants and laboratory work authorizations for 46 R&D projects. The research represented participants from 45 organizations, including 11 foreign R&D organizations. The total cost of these 46 research projects for the three-year period was approximately $52 million.

Similar progress was made in FY 2000–2002, with an additional 47 NERI projects awarded. The total cost of these 47 research projects for the three-year period was approximately $58 million, shared among 20 U.S. universities, 10 national laboratories, 18 private businesses, and 7 foreign R&D organizations. No new NERI projects were awarded in FY 2003 or 2004.

In FY 2005, 35 projects were initiated under the newly revised program focus, and an additional 25 projects in FY 2006. The total investment in these projects over their three-year term is $32.1 million, distributed among 37 U.S. universities, 7 national laboratories, and 4 corporations. In addition, one university, one laboratory, and three corporations are participating, but do not receive federal funding. Two international educational institutions participate, but are funded by their own countries.

DOE awarded 22 projects in FY 2007, involving 22 U.S. universities, five national laboratories, two U.S. businesses, and one international laboratory collaborator. This represents a $11.4 million Federal government commitment to nuclear R&D during the three-year lifetime of these projects. With each university contributing an additional 20 percent cost-share, the total funds directed towards nuclear R&D increases to $14.4 million.

Funding History

Congress appropriated annual funding for NERI in FY 1999 through 2004 as a separate budget line item in the Energy and Water Development Appropriations Act. The U.S. government invested over $118 million to fund NERI research projects during the first six years of the NERI program. Figure 1 illustrates the cumulative number of research projects awarded through FY 2004 in each the four original R&D areas, while Figure 2 shows the distribution of this funding among the national laboratories, U.S. universities, and industry.

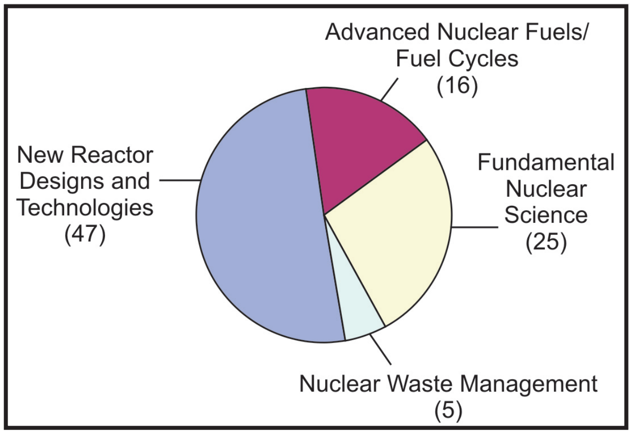


Figure 1. Distribution of FY 1999–2004 NERI projects by R&D area.

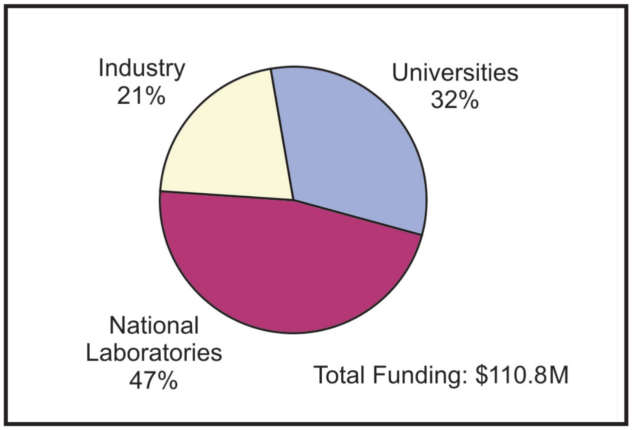


Figure 2. Recipients of NERI research funds in FY 1999–2004.

DOE does not fund international participants as part of the NERI program. Their participation has been supported by the international organizations interested in the research being conducted. Although the PIs are responsible for soliciting such support, foreign participation in NERI projects is contingent upon DOE approval.

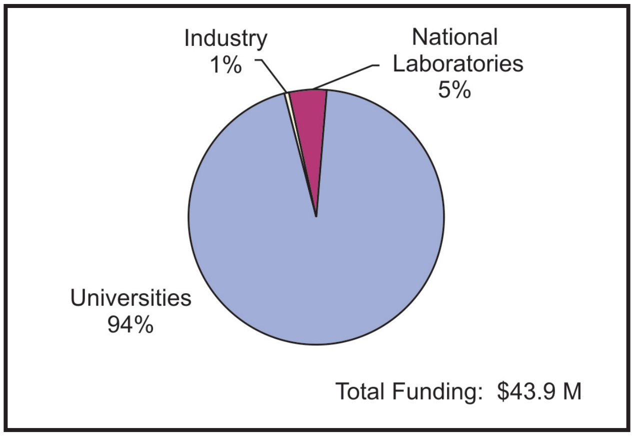


Figure 3. Distribution of NERI research funds by recipient in FY 2005–2007.

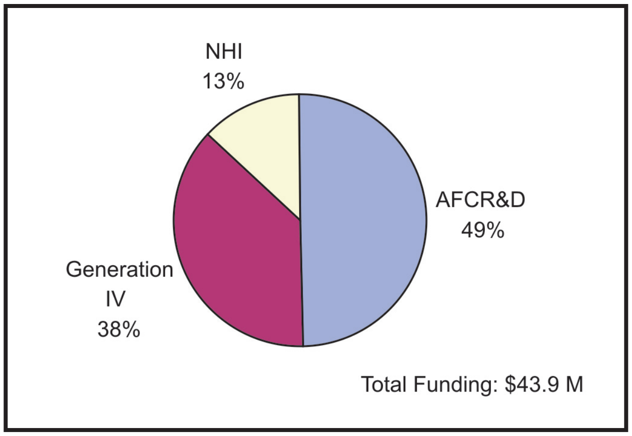


Figure 4. Distribution of NERI research funds by R&D program area in FY 2005–2007.

NERI was refocused in 2004 to directly support the goals and objectives of the Generation IV, AFCR&D, and NHI programs and to emphasize the leadership of university research programs. Figure 3 illustrates the effect of this new program emphasis, showing a significant redistribution in NERI research funds benefiting universities. Figure 4 shows the distribution of NERI research funds in FY 2005–2007 by R&D program area. Figure 5 notes the division of projects awarded in FY 2005 through 2007 by program area.

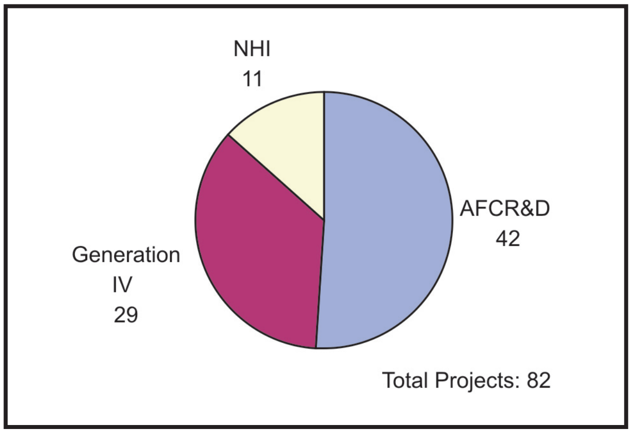


Figure 5. Distribution of FY 2005–2007 NERI projects by R&D program area.

NERI Participants

NERI research participants in 2006 included 36 U.S. universities, 8 national laboratories, 7 private businesses, and 2 foreign organizations. The participating organizations are provided in the following tables.

U.S. Universities

Arizona State University
Boise State University
California State University-Northridge
Clemson University
Colorado School of Mines
Georgia Institute of Technology
Illinois Institute of Technology
Iowa State University
Johns Hopkins University
Massachusetts Institute of Technology
North Carolina State University
Oregon State University
Pennsylvania State University
Purdue University
Rensselaer Polytechnic Institute
State University of New York-Stony Brook
Texas A&M University
The Ohio State University
University of California-Berkeley
University of California-Los Angeles
University of California-Santa Barbara
University of Cincinnati
University of Florida
University of Idaho
University of Illinois
University of Michigan
University of Missouri-Rolla
University of Nevada-Las Vegas
University of New Mexico
University of South Carolina
University of Tennessee
University of Virginia
University of Wisconsin-Madison
Utah State University
Virginia Polytechnic Institute and State University
Washington State University

U.S. DOE National Laboratories

Argonne National Laboratory
Brookhaven National Laboratory
Idaho National Laboratory
Los Alamos National Laboratory
Oak Ridge National Laboratory
Pacific Northwest National Laboratory
Sandia National Laboratories
Savannah River National Laboratory

Industrial Organizations

Aspen Technology, Inc.
Fluent, Inc.
General Atomics
Special Metals, Inc.
Studsvik of America
TransWare Enterprises, Inc.
Westinghouse Electric Company LLC

International Collaborators

Imperial College of Science, Technology, and Medicine (United Kingdom)
The Royal Institute of Technology (Sweden)

5. NERI and U.S. Universities: Advancing the Goals of Nuclear R&D Programs

Focus on Universities

One of NERI's long-term goals is to maintain the country's leading position in nuclear energy research by improving the nuclear science and engineering infrastructure. In order to achieve this long-range goal, NERI is focused on cultivating research partnerships with universities across the United States. This helps educational institutions remain at the forefront of science education and research, advances the important work of existing nuclear R&D programs, and serves as training for the next generation of nuclear scientists who will carry on the groundbreaking work being performed at national laboratories, universities, and private corporations. Funding creative research ideas at the nation's universities and colleges serves another purpose as well—it helps solve important issues that the private sector is unable to fund alone due to the high-risk nature of the research and/or the extended period before a return on investment is realized.

Participants in the initial planning workshop in 1998 recommended that NERI be viewed as a "seed program" where new nuclear-related technological and scientific concepts could be investigated. Based on this philosophy, NERI has provided universities and colleges with a competitive, peer-reviewed research program that allows faculty and students an opportunity to conduct innovative research in nuclear engineering and related areas. Of the 162 projects awarded through FY 2007, 86 percent involved U.S. colleges and universities as lead investigators or collaborators. To date, a total of 52 national universities and colleges have participated in NERI projects.

NERI has provided U.S. universities and colleges an opportunity to work closely with industry and DOE national laboratories and has introduced these researchers to other nuclear energy-related government programs. In addition to research related to the AFCR&D, Generation IV, and NHI programs, NERI's activities are coordinated with other relevant energy research in the DOE Office of Science, the DOE Office of Energy Efficiency and Renewable Energy, and the Nuclear Regulatory Commission. Furthermore, the Department leverages NERI program resources by encouraging no-cost collaboration with international research organizations and nuclear technology agencies. In this way, universities are given the opportunity to gain experience with international research interests and capabilities as well.

Student Participation

One great success of NERI and other DOE programs is that nuclear-related educational opportunities at the universities have significantly increased. Universities have benefited from increased research dollars which have served as incentives for new student recruitment. As a result of this involvement, student interest in nuclear engineering has been revitalized. In 1998, only 500 students were enrolled in U.S. universities seeking degrees in nuclear engineering. According to a survey performed for DOE in March 2006 by the Oak Ridge Institute for Science and Education (ORISE), approximately 2,000 students—1,000 undergraduates and another 1,000 graduate/doctoral students—are currently enrolled in nuclear engineering programs.

Approximately 600 undergraduate, graduate, and doctorate students have participated in NERI projects since the program's inception. Figure 6 shows how student participation has changed with time. In addition, numerous post-doctoral fellows at universities have been involved in NERI research projects. In FY 2006 alone, 78 undergraduate, 91 graduate, and 85 doctoral students participated in NERI R&D.

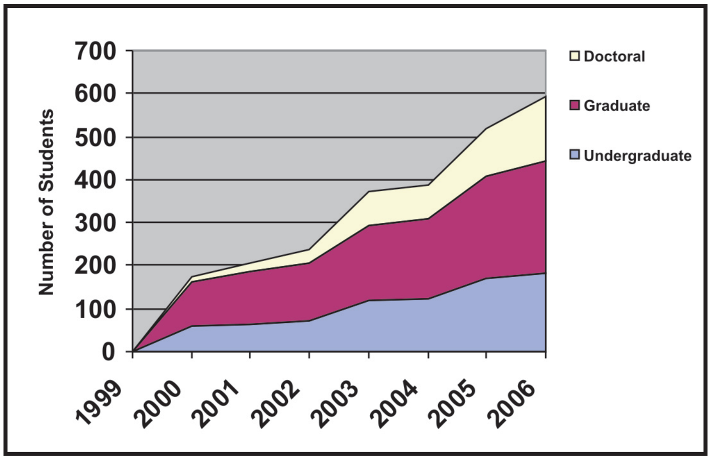
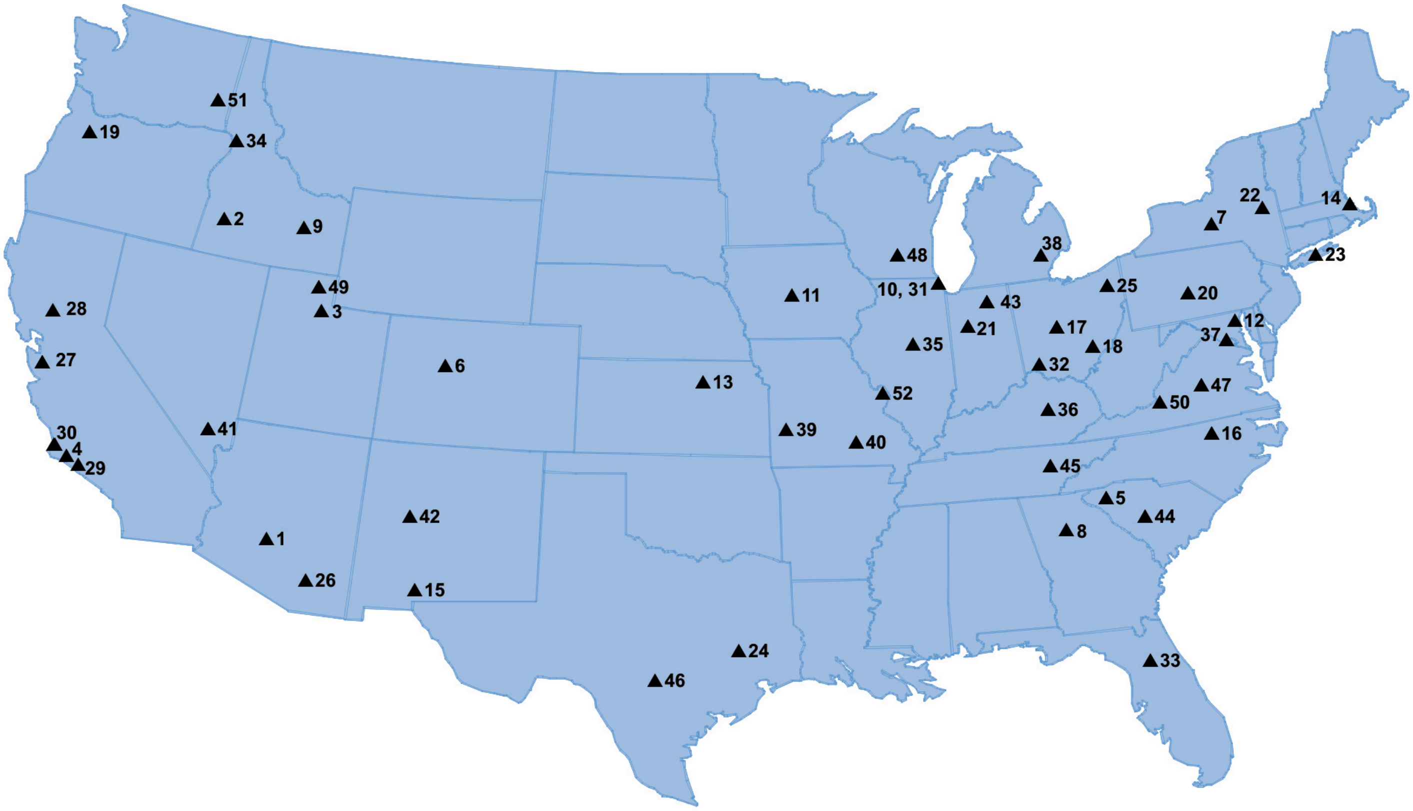


Figure 6. Annual NERI student participation profile - FY 1999 through FY 2006 NERI projects.

Over the past few years, graduates of these programs have had consistently high grade point averages, showing that these programs are training highly qualified individuals that will sustain the future growth of the nuclear power industry. Figure 7 provides a map and complete listing of the 52 universities and colleges that have participated in NERI since the program's inception.



UNIVERSITY KEY

1	Arizona State University
2	Boise State University
3	Brigham Young University
4	California State University Northridge
5	Clemson University
6	Colorado School of Mines
7	Cornell University
8	Georgia Institute of Technology
9	Idaho State University
10	Illinois Institute of Technology
11	Iowa State University
12	Johns Hopkins University
13	Kansas State University
14	Massachusetts Institute of Technology
15	New Mexico State University
16	North Carolina State University
17	Ohio State University
18	Ohio University
19	Oregon State University
20	Pennsylvania State University
21	Purdue University
22	Rensselaer Polytechnic Institute
23	State University of New York, Stony Brook
24	Texas A&M University
25	University of Akron
26	University of Arizona
27	University of California, Berkeley
28	University of California, Davis
29	University of California, Los Angeles
30	University of California, Santa Barbara
31	University of Chicago
32	University of Cincinnati
33	University of Florida
34	University of Idaho
35	University of Illinois
36	University of Kentucky
37	University of Maryland, College Park
38	University of Michigan
39	University of Missouri, Columbia
40	University of Missouri, Rolla
41	University of Nevada, Las Vegas
42	University of New Mexico
43	University of Notre Dame
44	University of South Carolina
45	University of Tennessee
46	University of Texas, Austin
47	University of Virginia
48	University of Wisconsin
49	Utah State University
50	Virginia Polytechnic Institute and State University
51	Washington State University
52	Washington University

Figure 7. Locations of NERI universities and colleges.

6.0 PROJECT SUMMARIES AND ABSTRACTS – FY 2005-2007

6.1 Generation IV Nuclear Energy Systems Initiative

There are 29 NERI research projects currently being performed under the Generation IV Nuclear Energy Systems Initiative. Fifteen of these projects were awarded in FY 2005, six in FY 2006, and eight in FY 2007.

Work under ***Generation IV*** focuses on developing new reactor systems to be deployed during the next 20 years. As discussed in Chapter 3, these systems will achieve high burnup using transmutation and recycled fuel, allowing for efficient use of domestic uranium resources and minimizing radioactive waste. Advances in safety and physical protection will guard against possible acts of terror and the ability to divert nuclear materials, helping to ensure public confidence in nuclear technology.

During FY 2006, researchers worked on projects spanning most of the Generation IV program elements. In the area of Advanced Gas Reactor fuel development, they are optimizing a supercritical CO_2 cycle, developing on-line failure monitoring, and improving analytical techniques. Design and evaluation projects focus on improving modeling capabilities, neutronic analysis, thermal-hydraulic/heat transfer analysis, model uncertainty evaluations, and risk assessment techniques. Energy conversion projects target nuclear heat transport and supercritical CO_2 systems. Materials evaluations continue to occupy a large percentage of the Generation IV program, with studies of radiation behavior, improving corrosion resistance, development of advanced ceramics and metal alloys, and improving modeling capabilities. Research is being conducted specific to four reactor technologies: the LFR, SCWR, VHTR, and SFR. These projects involve lead and lead-bismuth corrosion for the LFR thermal-hydraulic modeling and materials evaluation for the SCWR and design analysis methods and materials development for the VHTR. Projects related to the SFR can be found in Section 6.2, as they are currently funded under AFCR&D.

Planned NERI research efforts related to this initiative will focus primarily on NGNP and GNEP-related activities. No crosscutting research in design/evaluation or energy conversion is funded for FY 2007. Future projects will involve:

- Very High-Temperature Gas Reactor
- Sodium-Cooled Fast Reactor
- Materials

A summary of each project being performed under this initiative follows.

Nuclear Energy Research Initiative

Project Summaries and Abstracts

FY 2005 Project Summaries

FY 2006 Project Summaries

FY 2007 Project Abstracts

In-Situ X-ray Spectroscopic Studies of the Fundamental Chemistry of Pb and Pb-Bi Corrosion Processes at High Temperatures: Development and Assessment of Composite Corrosion-Resistant Materials

PI: Carlo U. Segre, Illinois Institute of Technology

Collaborators: None

Project Number: 05-028

Project Start Date: January 2005

Project End Date: December 2007

Research Objectives

The objective of this project is to characterize the corrosion tolerance of various materials for use in advanced liquid metal reactors. Researchers will probe surface interactions of lead (Pb) and lead-bismuth eutectic (LBE) liquid metal coolants at temperatures up to 1,000°C. A thin film of coolant, i.e., a few atomic layers, deposited on the surface before heating will enable researchers to study the solid-liquid interface between the candidate composite materials and the liquid metal coolants.

They will probe the coolant with X-ray absorption spectroscopy (XAS) to determine how it reacts with the solid underneath, and will utilize the undulator beamline, a unique resource available at the Materials Research Collaborative Access Team. These real-time, *in-situ* corrosion characterization methods will allow researchers to directly observe the fundamental chemical mechanisms that lead to corrosion. In addition, the team will study candidate materials and materials with surfaces modified by a new process—ionized plasma deposition (IPD). IPD revolutionizes the development of composite coatings by creating surface treatments not possible with simple deposition techniques. The process can impregnate a substrate material with a precisely designed coating having a specific composition, thickness, penetration, and nanostructure.

Researchers will conduct the following tasks as part of this research effort:

- Develop techniques to deposit thin coolant layers onto a substrate, heat treatment procedures, and XAS measurement methodology
- Study coolant interactions with steel substrates and candidate materials such as molybdenum (Mo), tantalum (Ta), zirconium (Zr), and silicon-carbide (SiC) and correlate data with conventional dip tests
- Apply IPD to prepare surface-modified steel samples and perform further *in-situ* and long-term static tests using the best candidate materials

Research Progress

During this period, researchers began analyzing the data from initial *ex-situ* experiments, including the visual observation of corrosion on 316L stainless steel, molybdenum, and spinel samples exposed to Pb vapor at 1,000°C for 50 hours, as shown in Figures 1–3.

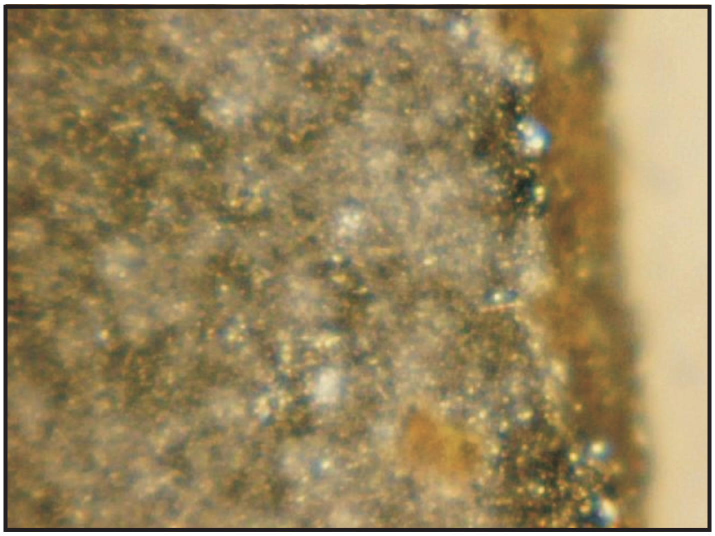


Figure 1. 316L Stainless Steel exposed to Pb at 1,000°C (50x magnification).

These images show that 316L steel is most affected by the Pb vapor, as it shows severe flaking from the surface and a distinct layer of lead. In contrast, molybdenum shows no flaking but exhibits a change in surface color. Spinel shows virtually no effect at all. This visual inspection was borne out by measurements of Pb fluorescence intensity as a function of material.

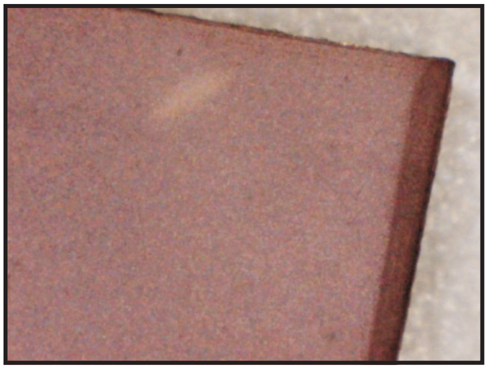


Figure 2. Molybdenum metal exposed to Pb vapor at 1,000°C.

Figure 3. Surface of spinel, exposed to Pb vapor at 1,000°C.

For their first *in-situ* high-temperature experiments (Figure 4), researchers used four days of beamtime at the Advanced Photon Source facility at Argonne National Laboratory. These experiments were conducted to:

1) Test the capabilities of the high-temperature furnace insert with Kapton windows
2) Perform preliminary experiments of Pb reaction with a metal surface in a helium atmosphere
3) Take extended X-ray absorption fine structure (EXAFS) spectra of the same sample processed at a series of high temperatures in inert atmosphere
4) Measure reactivity of Mo metal with Pb and residual oxygen by EXAFS

The experiments showed that *in-situ* processing temperatures up to 900°C can be attained without melting the Kapton windows. Researchers conducted examinations at room temperature after heating to the desired maximum temperature and have begun to analyze the data. They submitted abstracts to two conferences and presented a poster on this research.

Researchers measured the fluorescence spectra of the Pb-coated Mo sample *in-situ* at various temperatures. By integrating the counts under the Pb Kα fluorescence line, they determined that the quantity of Pb remains relatively constant as a function of temperature. This indicates that the Pb has reacted with the Mo surface and is not volatile, even at high temperatures.

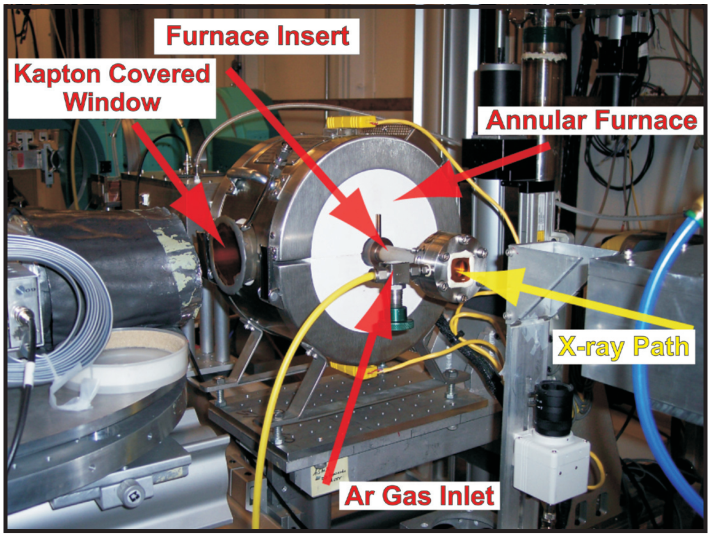


Figure 4. Experimental setup for *in-situ* experiments on the MRCAT beamline. The system was successfully raised to 900°C.

The radial distribution functions obtained from the Mo edge XAFS data after each heating step showed that the surface remains largely metallic, but an additional short-range order forms with high-temperature processing. Each data set was fit using a pure Mo metal model in the range 1.6Å <R<5.6Å. Subtracting this fit yielded a qualitative measure of the change in low-R intensity as a function of processing temperature. The low-R peaks exhibit a systematic growth in intensity, reaching a maximum at 750°C. However, the peaks disappear at higher temperatures, which may indicate the presence of a self-limiting mechanism.

Planned Activities

In the coming year, researchers will construct a new furnace to enable a more rapid change in temperature and finer control of the incident beam angle for further *in-situ* studies. They will apply the coatings to the steel samples using an in-house sputtering system with high-temperature substrate heating.

NUCLEAR ENERGY RESEARCH INITIATIVE

Detailed Reaction Kinetics for CFD Modeling of Nuclear Fuel Pellet Coating for High-Temperature Gas-Cooled Reactors

PI: Francine Battaglia, Rodney O. Fox, and Mark S. Gordon, Iowa State University

Collaborators: None

Project Number: 05-030

Project Start Date: April 2005

Project End Date: April 2007

Research Objectives

The objective of this research is to validate and improve computational models for coating uranium fuel pellets with carbon and silicon carbide (SiC) using the chemical vapor deposition (CVD) process in a spouting bed. Researchers will conduct a state-of-the-art computational study of the CVD process in order to further develop models of the reaction kinetics. This project will take a complementary approach using computational fluid dynamics (CFD) to model the CVD process and apply it as a tool for reactor design, scale-up, and optimization. The work will validate the computations with experimental data for the multiphase fluid mechanics and species chemistry predictions required to describe the CVD process. The specific tasks to achieve the objectives are to:

1) Develop detailed reaction kinetics models of the gas-phase and surface molecule interaction using computational chemistry to predict surface coating rates
2) Implement the reaction kinetics using in-situ adaptive tabulation for complex chemistry and couple to the Multiphase Flow with Interphase eXchanges (MFIX) computer code
3) Implement a polydispersity model in MFIX to account for effects of particle size distribution

Research Progress

The homogeneous chemistry mechanism for the chemical vapor deposition of silicon carbide includes 113 gas phase reactions and 50 species. Researchers studied the decomposition reactions of methyltrichlorosilane (MTS) – CH_3SiCl_3 – and consecutive gas phase reactions with the GAMESS package. They calculated single-point energies for the local minima and transition states (TS) by applying state-of the-art methods, which were then used to compute the reaction rate constants using the transition state theory. They compared values for heat capacity (C_p) and entropy (S) between theoretical calculations and experiments for various gas phase species. The calculated C_p and S values match well with the experimental values within a wide range of temperatures—from 298 to 2,000 K. Calculated reaction enthalpies agree with available experimental data within 1–2 kcal/mol.

Researchers performed constrained optimization calculations to investigate detailed paths of the association/dissociation reactions without a well-defined transition state, such as $CH_3SiCl_3 \rightarrow CH_3 + SiCl_3$. Hessian calculations have been done to obtain the partition functions for the structures along the reaction paths. A recently developed method, the left eigenstate completely renormalized coupled cluster method (CR-CCL), has been used to obtain single-point energies for every studied structure on the reaction path to locate the generalized transition state (i.e., the structure with the maximum free energy along the reaction path). Because this new coupled cluster method has only been implemented for singlet species, researchers could not use this method to examine doublet-constrained reaction paths.

Due to a discrepancy between the potential energy surfaces (PES) of ethylene (C_2H_4) predicted in the present work compared with previous studies, the researchers have applied a more accurate method to obtain the optimized structures of local minima and transition states. Hessian calculations were performed to obtain the zero-point energies at the CCSD(T)/aug-cc-pVDZ level of theory. The PES presented in Figure 1 shows that the C_1 symmetry ethylidene (CH_3CH) is a local minimum and there is no intermediate between vinylidene (CH_2C) and acetylene (C_2H_2). The CCSD(T) results agrees with Jensen et al. calculations at the MP2/6-31G(d,p) level of theory, but not with MP2/aug-cc-pVDZ calculations. This study completed the transition state search for all the gas-phase reactions in this work.

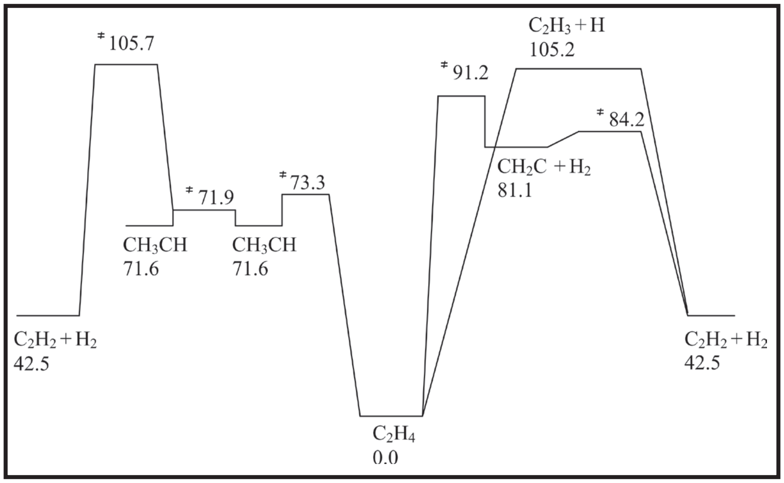


Figure 1. Potential energy surface of C_2H_4. Numbers are relative enthalpies in kcal/mol at 0 K. Classical energies and zero-point energies are obtained at the CCSD(T)/aug-cc-pVDZ level of theory. The symbol ≠ stands for a transition state.

In order to analyze the chemical species compositions involved in the decomposition of MTS, researchers compiled a thermodynamic database for each species. For the coupling of the MFIX code with ISAT, they created an input file containing the required chemistry information in a format compatible with the CHEMKIN software package. This format requires specific heat, enthalpy, and entropy to be stored as polynomials, while reaction rates are stored in the form of parameters characterizing the Arrhenius temperature dependence. Based on data for forward rate constants for each of the MTS decomposition reactions obtained from *ab initio* calculations, the researchers determined Arrhenius rate parameters for the pre-exponential factor, the temperature exponent, and activation energy, using a least-squares procedure.

Using the chemistry input, researchers obtained the evolution of the species concentrations by solving the corresponding ordinary differential equations. For a test case of 1 mole of MTS and 4 moles of hydrogen (H_2) at 1,000 K under constant pressure and adiabatic conditions, the dominant species at equilibrium include H_2, methane (CH_4), trichlorosilane ($SiHCl_3$), tetrachlorosilane ($SiCl_4$) and methyltrichlorosilane (CH_3SiCl_3), with mole fractions ranging from 0.1 to 0.7. They found several species had very low concentration values with mole fractions less than 10^{-6}. A reduced chemistry set was obtained by eliminating low concentration species (and the reactions containing them) that were not directly involved in the decomposition of MTS or were unimportant for surface reactions.

By analyzing the differential equations corresponding to the reduced chemistry set, researchers found that the evolution of the dominant species (and their equilibrium concentrations) in the reduced chemistry set were nearly the same as those in the full chemistry set. They used an alternative method to verify the equilibrium species concentrations, based on chemical element potentials, along with minimizing Gibb's free energy. Based on the results, the two approaches (i.e., differential equation integration and chemical element potential) gave the same species concentrations at equilibrium.

Researchers used the simple "pair-wise mixing stirred reactor model" to test the performance of ISAT (coupled with CHEMKIN) with the reduced-set MTS decomposition chemistry. They found that the ISAT tree reached a mature state in which almost every query point resulted in a retrieve. They have completed this phase of code development and are working to test implementation for a bubbling fluidized bed with the MTS reduced chemistry.

Planned Activities

Modeling will continue with SIMOMM calculations to study the thermodynamics and kinetics of the heterogeneous reactions between the gas phase species and the pyrolytic C and SiC solid surfaces. Researchers will perform comprehensive kinetic simulations using the VTST rate constants at various CVD temperatures to obtain an improved reduced set of gas phase reactions. They will also initiate kinetic modeling using the activation energies obtained from electronic structure calculations.

For the complex chemistry modeling efforts, researchers will continue to implement ISAT with MFIX using a reaction kinetics scheme based on the reduced reaction set determined from the computational chemistry. Simulations will be conducted to validate the multiphase fluid mechanics and chemistry predictions of major species and temperature for the spouted-bed CVD reactor.

In the final phase, researchers will initiate calculations of surface effects on the predicted rate constants. They will use the MFIX code will be used to address scale-up issues for the process-size coater and to study the hydrodynamics and particle mixing patterns.

NUCLEAR ENERGY RESEARCH INITIATIVE

Optimized, Competitive Supercritical-CO_2 Cycle GFR for Generation IV Service

PI: Michael J. Driscoll, Massachusetts Institute of Technology (MIT)

Collaborators: None

Project Number: 05-044

Project Start Date: April 2005

Project End Date: April 2008

Research Objectives

This project is developing an integrated overall plant design for a gas-cooled fast reactor (GFR) based on the compact and highly efficient, direct supercritical carbon dioxide (S-CO_2) Brayton cycle under development at MIT for Generation IV service. This plant will be capable of economical electric power generation, high uranium utilization, burning of transuranics (TRU) and/or minor actinides, and hydrogen production through the high-temperature electrolysis of steam. Researchers are evaluating prospective plant designs using existing Nuclear Regulatory Commission (NRC) deterministic regulations and proposed risk-informed licensing requirements. They are applying probabilistic techniques to optimize the tradeoffs between economics and safety assurance.

Most worldwide research on this type of gas reactor is presently based on a helium cycle that operates at temperatures approaching 900°C, which poses severe challenges to the core and component materials. Because the S-CO_2 cycle can achieve high thermodynamic efficiency (approximately 44 to 51 percent) at modest temperatures of 550 to 650°C, researchers can utilize already-proven technologies in their design.

Major tasks of this project focus on designing the reactor core and the decay heat removal systems. In designing the core, researchers have optimized features of the vented fuel concept using tube-in-duct (TID) assemblies. In addition they are developing a pin-type core design as an alternative and are confirming the capability of burning TRU and minor actinides. Design of the safety system is guided by probabilistic methods and involves developing a decay heat removal system for accidents, shutdown, and refueling; improving emergency power, such as microturbines or fuel cells; and integrating both active and passive means of shutdown assurance to preclude an anticipated transient without scram (ATWS). Researchers will optimize the final design for integration with a high-temperature steam electrolysis process for hydrogen production and they will conduct an economic assessment to estimate costs. Overall, this project will provide a sufficient basis for assessing this type of GFR among the other candidate Generation IV designs being evaluated for final selection.

Research Progress

The current status of the plant design, incorporating all changes implemented during the first 20 months of the project's efforts, is summarized in Table 1. Following is a summary of the noteworthy developments.

Figure 1 illustrates the overall plant layout coupling the reactor to supercritical CO_2 Brayton power conversion units.

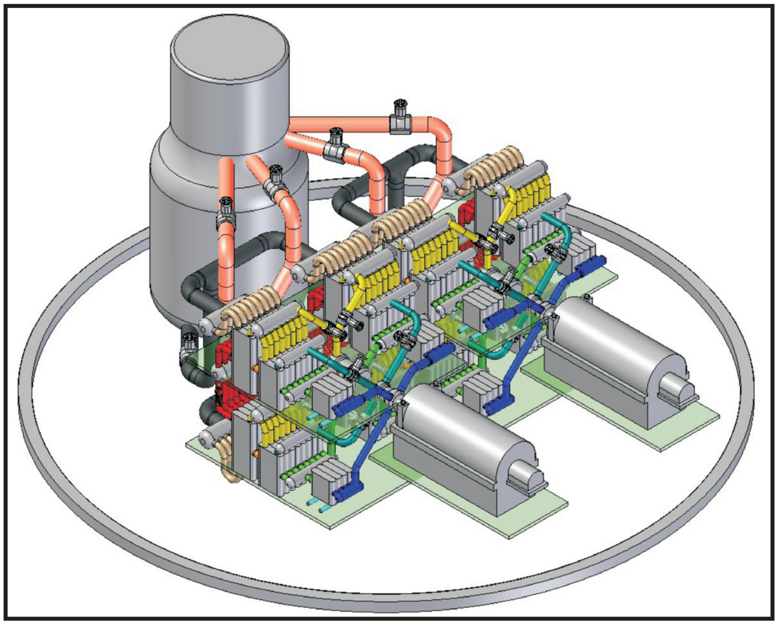


Figure 1. Arrangement of reactor and power conversion units.

Subsystem	Features	Comments
Core		
Fuel	UO$_2$ + BeO	LWR TRU fissile ± MA
Clad	ODS-MA956, or HT-9	SiC a long range possibility
Configuration	tube-in-duct fuel assemblies, “hexnut” pellets, vented, orificed	pin-type core as fallback
Thermal-Hydraulics	axial peaking factor ≤1.3 radial peaking factor ≤1.2 power density ~ 85 W/cc	Vary BeO fraction to flatten power. Lower than GA GCFR of 1970s @ 235 W/cc
Burnup	≥120 MWd/kg (avg)	In single batch no-reshuffle core, 17-yr lifetime
Safety Systems		
Auxiliary Loops	combined shutdown & emergency, 4 x 50% capable, forced convection; natural convection supplemented water boiler heat sink	Based on MIT/CEA/ANL INERI project design. For P≥0.7 MPa natural convection alone may suffice
Emergency Power	Fuel cells to supplement diesels	Projected to be more reliable than diesels alone in long run
Plant		
Power Conversion System (PCS)	supercritical CO$_2$ Brayton direct 2 x 600 MWe loops=1200MWe; 650°C core exit/turbine inlet, pressure: 20 MPa	AGRs in UK use CO$_2$ coolant at 4 MPa and have T~650°C
Reactor Vessel	PCIV	Vessel houses loop isolation and check valves plus shutdown cooling heat exchangers
Containment	PWR type, steel liner reinforced concrete 0.7 MPa design capability, 70,000 m^3 free volume filtered/vented	CO$_2$ can be added to adjust pressure. Internally insulated
H$_2$ production by steam electrolysis	Separate water boiler loops (4) @ 10% of reactor power Recuperation of H$_2$ & O$_2$ heat allows cell operation at 850°C	Water boiler loops can also serve for self-powered decay heat removal

Table 1. Current status of GFR plant features.

The arrangement shown fits inside a conventional 54 m inner-diameter PWR-type containment building.

Researchers developed a final version of a tube-in-duct assembly core and presented the results at PHYSOR 2006. A unique feature was the use of radial reflector assemblies as conduits for the CO$_2$ coolant. This, plus the use of beryllium oxide (BeO) diluent in the fuel, yielded a core having a negative coolant void reactivity over its burnup lifetime without significant penalties to other performance criteria. An improved flow-levitated absorber was developed, and a prototype was tested in the laboratory which provides a passive means to ensure reactivity insertion during loss of coolant accident (LOCA) or loss of flow (LOF) events. The basis for core self-protection, however, remains the incorporation of integral fast reactor-type inherent reactivity feedbacks (e.g., Doppler, expansion, etc.) to ensure quasi-static compensation. Significant progress was made on both steady state and transient/accident thermal-hydraulic analyses. The results were published as a major topical report.

Researchers have developed a steady-state core design that utilizes an innovative, high-fuel-volume fraction, vented, tube-in-duct fuel assembly. After performing an extensive series of iterative calculations, researchers used RELAP5-3D to evaluate the natural circulation performance of an active/passive hybrid Shutdown/Emergency Cooling System (SCS/ECS). The routes were identified by which significant post-LOCA core bypass could occur and degrade the decay heat removal performance. Moderately sized blowers were shown to be capable of overcoming even extreme core bypass routes. A highly reliable active SCS/ECS was thus adopted for the reference design.

The loss of external load event was analyzed and a bypass valve scheme recommended that prevents shaft overspeed and excessive core coolant mass flow rate. Researchers selected a large, dry pressurized water reactor (PWR) containment building that has a free volume of 70,000 m^3 and a peak design pressure of 7 bar for this design based on a 100 in^2 cold duct break. During this same cold leg LOCA, the depressurization time was in excess of 10 minutes. No action needed to be taken by the SCS/ECS blowers before this time to prevent core damage. After this time, a total blower power less than 90 kW is sufficient to cool the core out to 10,000 seconds. A loss of flow transient in which a primary loop is instantaneously isolated and no mitigating action is taken (i.e., no reactor scram) is also shown not to cause core damage.

Researchers concluded that a large S-CO_2-cooled GFR coupled to a supercritical Brayton power conversion system can withstand the thermal hydraulic challenges posed by the usual menu of severe accident scenarios.

The final major development was devising an approach for optimally coupling the supercritical CO_2-cooled GFR to a high-temperature steam electrolysis (HTSE) plant for hydrogen production. This involves the use of four parallel self-powered loops, each removing about 2.5 percent of reactor thermal power. The steam discharged from the loop's high-pressure turbine normally flows to the HTSE cell via recuperators, which recover thermal energy from the product hydrogen and oxygen gases. This allows the cell to operate at a higher temperature than the reactor, sustained by the ohmic heating produced by the electricity supplied by the reactor's large power conversion loops.

In normal operation and most shutdown scenarios, the turbine drives the CO_2 loop circulator and generates excess electricity for plant or emergency system use. The reversible motor-generator can also power the blower using on- or off-site emergency electric power. This arrangement has several advantages. The water boiler loops eliminate the need for separate shutdown and emergency cooling loops and are always on, which increases the probability that they will be available for SCS/ECS service (no fail-to-start sequences and constant diagnostic signals). The loops are oversized for SCS/ECS service with a required total water boiler energy rating that allows for four 100 percent capacity shutdown cooling system loops, versus the four 50 percent loops specified in the current all-electric design. This yields a major improvement in safety assurance. Although devised for a GFR, the same approach will work for other Generation IV reactor concepts.

Planned Activities

Following is a summary of activities planned for the next fiscal year.

- Continue RELAP5-3D transient thermal hydraulic analyses to confirm the capability of the overall plant design to tolerate severe transient events, such as loss of coolant, flow, or load.
- Optimize a pin-type core design and finalize down-selection between pin and tube-in-duct designs. Also assess minor actinide burning.
- Continue probabilistic risk assessment studies to help determine the best balance between passive and active safety assurance features and capabilities.
- Devise a final balance-of-plant direct cycle arrangement for the supercritical power conversion system, taking into account the experience developed under a separate Generation IV contract for indirect cycle analyses. This will serve as the basis for an updated, overall cost-of-electricity estimate.

NUCLEAR ENERGY RESEARCH INITIATIVE

On-Line Fuel Failure Monitor for Fuel Testing and Monitoring of Gas-Cooled Very High-Temperature Reactors

PIs: Ayman I. Hawari and Mohamed Bourham, North Carolina State University (NCSU)

Collaborators: None

Project Number: 05-054

Project Start Date: January 2005

Project End Date: December 2007

Research Objectives

The primary objective of this project is to devise an accurate approach for detecting failures of TRISO (tristructural isotropic) fuel based on measurements of fission gas activity released into the effluent stream. In the gas-cooled very high-temperature reactor (VHTR), the fuel is made up of TRISO microspheres composed of a uranium-carbide (UCO) kernel surrounded by a porous graphite buffer, an inner graphite layer, a silicon carbide (SiC) coating, and an outer pyrolytic graphite layer. The kernel's coating system acts as the containment and main barrier against the environmental release of radioactivity. However, due to hostile in-core conditions during reactor operation (e.g., high temperature and fast neutron flux), some TRISO microspheres will fail. To ensure compliance with radiological and safety requirements, it is essential to detect any fuel failure at the earliest stage possible.

This project will develop techniques for detecting a single failed TRISO particle per testing capsule. Researchers believe that fuel failure rates on the order of 10^{-5} are detectable and that the detection method will provide insight into the failure mode. They will study various detection methods to differentiate the minute fission product signal from the background.

As part of the VHTR fuel development program, researchers will conduct fuel failure experiments at Idaho National Laboratory's (INL) Advanced Test Reactor (ATR). Methods and instrumentation developed by this project may be applied to on-line fuel failure monitoring of VHTRs.

Research Progress

The team continued work to understand the gamma-ray signal generated by the krypton (Kr) and xenon (Xe) fission gases released from failure of TRISO fuel. Researchers have studied several theoretical models that describe this release and performed detailed Monte Carlo (MCNP) simulations of the German II, JAERI (Japanese), General Atomics (GA), and British models. All of these models are based on the Booth diffusion formula and yield the release-to-birth (R/B) ratio for a particular fission gas species based on steady-state conditions.

The JAERI and GA models account for gas release due to recoil effects and introduce correction factors for burnup and precursor effects. Figure 1 shows the predicted gamma-ray spectra measured by a high-purity germanium (HPGe) detector using both of these models. The simulations considered release due to both uranium contamination in the graphite matrix and the failure of a single TRISO particle.

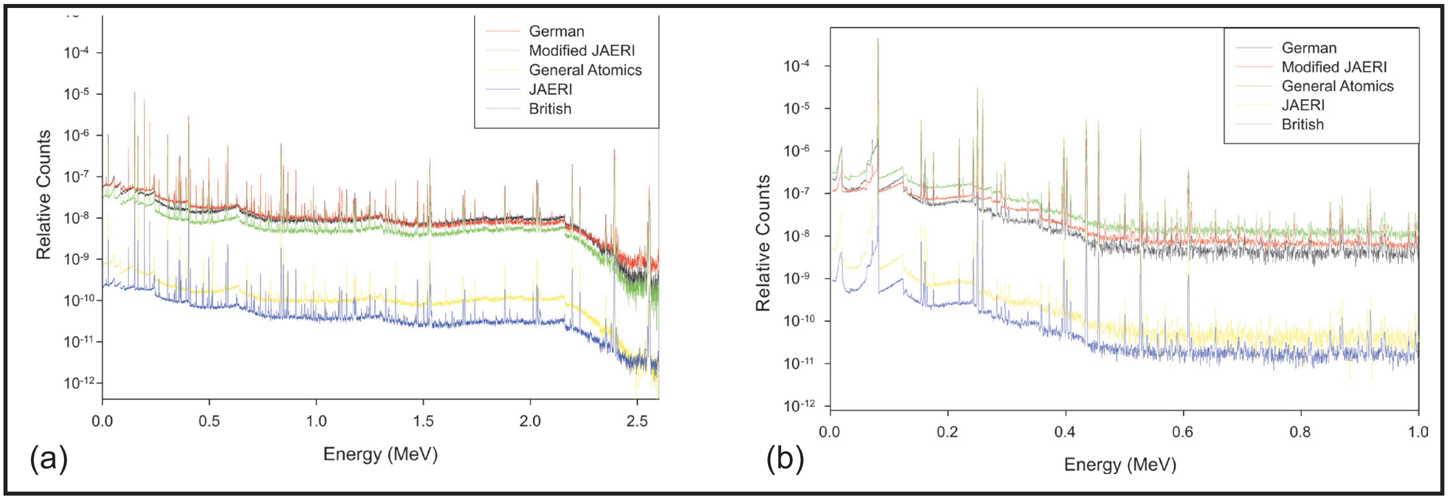


Figure 1. Predicted gamma-ray spectra from an HPGe detector for Kr release (a) and Xe (b). The Modified JAERI model does not include release through a graphite compact (if one exists).

Researchers received a cerium-doped lanthanum bromide (LaBr$_3$(Ce)) scintillation detector, considered a high-resolution instrument at room temperature. To test its performance, they conducted a detailed study of resolution as a function of energy. Figure 2 shows measured gamma-ray spectra using cobalt (Co-60), barium (Ba-133), cesium (Cs-137), europium (Eu-152), and thorium (Th-228) sources. The information derived from these spectra was processed for use in the MCNP detector models.

In addition, researchers examined the applicability of room temperature cadmium-zinc-telluride (CZT) detectors for the gamma ray spectral analysis of failed TRISO fuel. They measured several different test sources with a 15 x 15 x 10 mm CZT detector, using both digital and analog spectrometry systems. This detector has improved inherent resolution compared to both LaBr$_3$(Ce) and a previously reported high-purity xenon (HPXe) detector.

Researchers have assembled and tested the gas extraction system and electro-ionizer cell. The complete assembly, as shown in Figure 3, includes the following:

- T-shaped test cell
- Ring outer electrodes coupled to a 13.56 MHz radiofrequency generator
- Helmholtz magnet coils with a stabilized DC current power supply
- Gas manifold system with helium main flow and krypton and xenon controlled flow
- Vacuum gauge, pump, metering valves, and structure

The magnet system, composed of two coils in Helmholtz geometry, provides a uniform 830 gauss field with 15 amp current. The system was designed to deflect and focus fission gas ionized products (Kr+ and Xe+) into the detector location. The trajectories of Kr and Xe ions

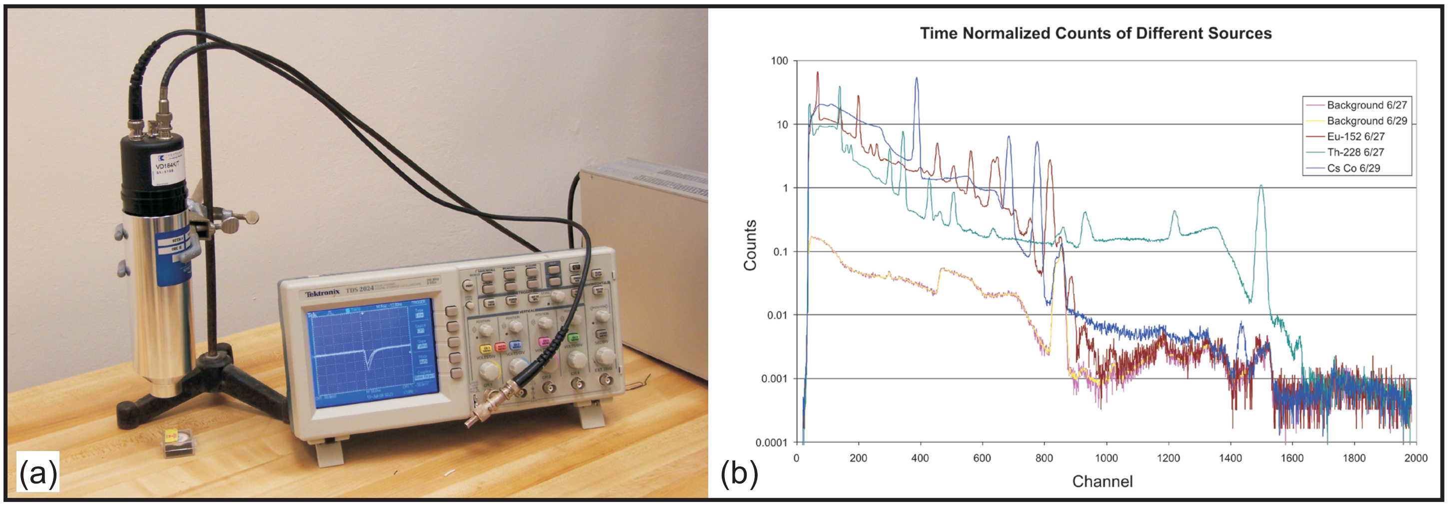


Figure 2. (a) The LaBr$_3$(Ce) detector and (b) the measured energy spectra using various gamma-ray sources. Background spectra are shown, including the inherent background of this type of detector.

Figure 3. The electro-ionizer assembly and Helmholtz magnet coils.

are well into the detection window and are separated by one centimeter for a 100 gauss magnetic field. A test of the cell's capability and the effect of the magnetic field was conducted using the spectral intensity of selected Kr+ and Xe+ lines (Figure 4) with no magnetic field and field intensities of 277 and 553 gauss (5 and 10 amps, respectively). The results show that line intensity increases with increased applied magnetic field, indicating higher focusing of Kr and Xe ions towards the detection window.

The intensity of the 465.89 nm KrII line is 5x10^{-3}, 1.5x10^{-2}, and 3.1x10^{-2} μW/cm^2–nm, corresponding to magnet currents of 0, 5, and 10 amps, respectively. For the 472.36 nm XeIII line, these values are 0.59x10^{-3}, 2.38x10^{-3} and 4.76x10^{-3} μW/cm^2–nm, respectively, clearly indicating the effectiveness of the magnetic field in focusing ionic species of fission gas products.

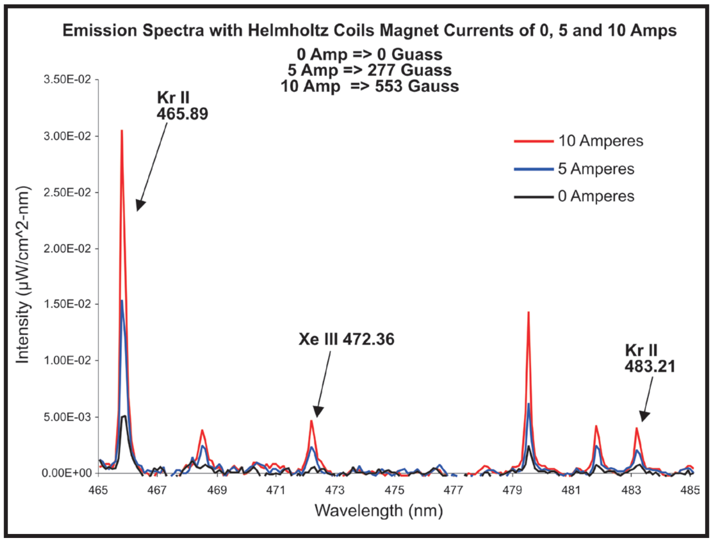


Figure 4. Spectral intensity of Kr and Xe lines with increasing magnetic field intensity.

Planned Activities

Researchers plan to study various gamma-ray spectral analysis techniques for low-resolution detectors that may be implemented in this work. The team will propose a general benchmark methodology of the R/B ratio that utilizes the fundamental information that can be derived from a given spectrum. In addition, they will examine the feasibility of irradiating TRISO fuel in the NCSU PULSTAR reactor to evaluate different R/B ratio models for failed TRISO particles.

Coordination will continue with INL staff to explore transferring the extraction and detection system for testing at the ATR test loop. This will provide a combined gamma-ray spectrometry/mass spectrometry system to perform detailed quantitative analysis of the released signal upon the failure of a TRISO microsphere.

Development of High-Temperature Ferritic Alloys and Performance Prediction Methods for Advanced Fission Energy Systems

PI: G. R. Odette, University of California-Santa Barbara

Collaborators: Oak Ridge National Laboratory (ORNL), University of California-Berkeley, Illinois Institute of Technology

Project Number: 05-074

Project Start Date: March 2005

Project End Date: March 2008

Research Objectives

The primary objective of this project is to develop a new high-temperature alloy class for use in advanced nuclear reactor systems. These nanostructured ferritic alloys (NFAs) have remarkable creep strength, excellent ductility, show good fracture toughness potential, and may mitigate radiation damage.

The team will address the combined effects of high temperatures (>900°C) and high radiation dose on commercial alloys, especially MA957. They will conduct model alloy experiments to better understand NFA thermo-kinetics and structure-property relations in order to optimize processing paths and the balance of properties. Researchers will also collect data and conduct thermal aging experiments on 9Cr tempered martensitic steels (TMS) to assess embrittlement and high-temperature stability-aging limits. The major objectives of this project are to:

- Develop a comprehensive mechanical property and microstructural database of MA957, other NFAs, and TMS, emphasizing the effects of irradiation on deformation and fracture; semi-empirical constitutive models, including high-temperature creep; and a master fracture toughness-temperature curve method for applying NFAs
- Conduct experiments on nano-microstructures and mechanical properties to optimize processing paths, properties, and service lifetimes; conduct thermal aging studies; and perform post-irradiation examination and data analysis of irradiation experiments
- Investigate advanced solid-state welding and diffusion bonding techniques for joining MA957 and other NFAs that maintain beneficial micro-nanostructures
- Develop models of precipitation thermo-kinetics and high-temperature thermal and irradiation stability of nm-scale precipitates in NFAs, transport fate and consequences of helium, and compare results of thermal aging and irradiation experiments to predictions

Research Progress

Database and Physically Based Constitutive and Fracture Toughness Models. The researchers continued developing a large 9Cr TMS database to support models of irradiation hardening and embrittlement and their underlying constitutive behavior. They used an assessment of irradiation effects up to 500°C to develop a preliminary composite model of embrittlement due to irradiation hardening and non-hardening mechanisms leading to weakened grain boundaries and intergranular fracture. Figure 1 provides an example of the model predictions for three loading rates at the high helium-to-displacement per atom ratio (100 appm/dpa) pertinent to Advanced Fuel Cycle R&D applications.

Data collected to test model predictions at higher dpa are very encouraging. Researchers analyzed 1) a dynamic yield stress database from 158 unirradiated and 610 irradiated specimens by Schneider et al., and 2) a static tensile database based on a $\sigma(\varepsilon,\varepsilon',T)$ dislocation dynamics constitutive model. These analyses showed that a two-component yield stress model with a thermally activated component of the yield stress, $\sigma_{th}(\varepsilon',T)$, adding to the athermal contribution applies over a wide range of strain for 17 unirradiated 9 Cr TMS alloys. The model calibrated to unirradiated data provides a reasonable fit to irradiated data; however, there is a small, but systematic deviation, especially at higher temperatures. These differences in flow dynamics are likely caused by short-range dislocation obstacles introduced by neutron irradiation.

The post-yield strain-hardening behavior to a necking instability point has also been derived from the tensile tests of Cr-W and Cr-Mo steels irradiated up to 2 dpa at 300°C. Reduced strain hardening rate and higher flow stress result in immediate necking for yield stress levels above 700 MPa. Contrary to previous understanding, the higher yield stress and small increase in hardening at low strains result in higher maximum flow stresses in alloys irradiated to high dpa levels. Researchers are analyzing the strain-hardening database with a model based on dislocation-dynamics.

Work has continued on the mechanical properties and a microstructure database for NFAs, adding information from 93 papers. Current efforts focus on developing a deformation mechanism map and a dislocation dynamics-based constitutive model. Analysis of the database clearly demonstrates the superior strength of NFAs over a wide range of temperatures. As seen in Figure 2, the data also show the critical contribution of yttrium (Y) and titanium (Ti) towards high-temperature strength.

Processing and Alloy Stability Modeling Database for TMS and NFA. Researchers mechanically alloyed Fe-14Cr-3W-0.4Ti-0.3Y2O3 and successfully consolidated two samples at 1,000°C and 1,150°C using hot isostatic pressing (HIP). They characterized the alloys' microstructure and mechanical properties using optical microscopy, transmission electron microscopy (TEM), density measurement, hardness, and fracture toughness tests. The alloys are essentially pore-free, have nearly 100 percent theoretical density, and exhibit a bimodal distribution of fine and coarse ferrite grains. While microhardness decreases with increasing HIP temperature, researchers observed similar fracture toughness/temperature behavior for both processing conditions. Small-angle neutron scattering (SANS) measurements confirmed the presence of nanoscale features.

Researchers also conducted extensive microstructure analysis and mechanical property testing of MA957 (aged for 3,000 hours at 900°C to 1,000°C) using a variety of techniques: optical metalography, TEM, SANS, electron-probe microanalysis, scanning electron microscopy (SEM), electron backscattering diffraction (EBSD), and microhardness. As shown in Figure 3, the ferrite grains, dislocations, and nanofeatures are all stable at 900°C. The nanofeatures coarsen slightly at 950°C, showing additional growth and a significant increase in porosity at 1,000°C.

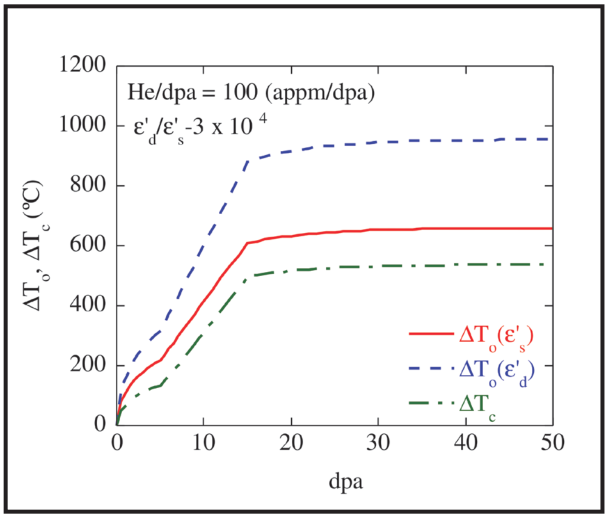


Figure 1. Composite model prediction of irradiation embrittlement in TMS irradiated at 300°C.

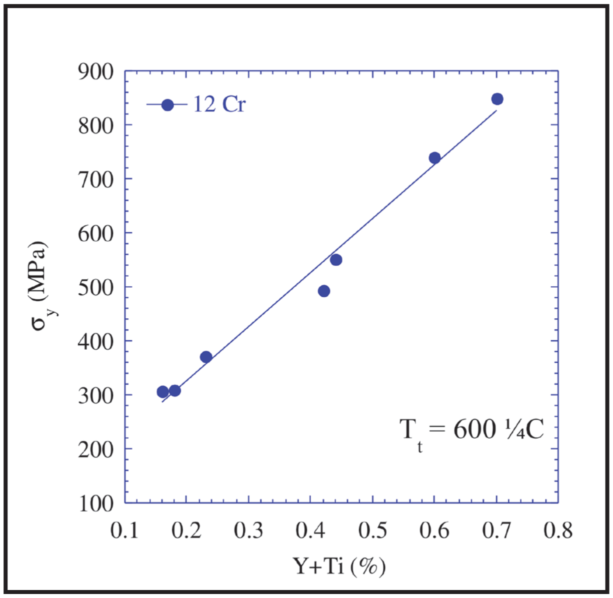


Figure 2. Y and Ti effects on high-temperature yield stress of NFAs.

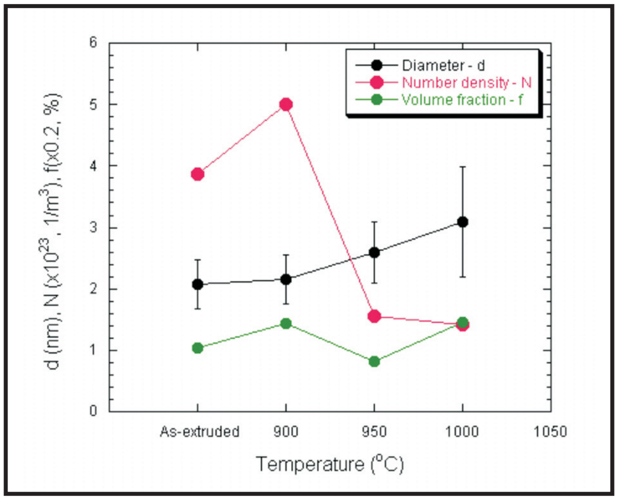


Figure 3. Evolution of NSP in MA957 aged for 3,000 hr at 900-1,000°C.

The room temperature microhardness is essentially unchanged at all temperatures. This research was reported at the 8th International Workshop on Spallation Materials Technology and will be submitted for publication.

One of the most significant issues facing the development of NFAs is understanding the character and consequences of the nanofeatures, especially at the smallest sizes. Results of extended X-ray absorption fine structure (EXAFS) studies using the Advanced Photon Source at Argonne National Laboratory will be reported in the near future.

Other Activities. Researchers prepared two specimen capsules for the two-year STIP-V irradiation in the SINQ target at the Paul Sherrer Institute in Switzerland. The goal is to characterize the transport, fate, and consequences of helium combined with varying levels of irradiation hardening in advanced alloys. The capsules will experience peak doses of approximately 20 dpa at helium levels up to 1,000 appm. However, controlling specimen temperature presents a major challenge due to very high, variable beam heating. The capsules were specifically designed to mitigate the consequences based on the following principles:

1) Provide specimen heat transfer paths with circular symmetry
2) Minimize interfaces between the sample and capsule wall
3) Use press fit contacts between specimen and capsule wall to minimize thermal resistance uncertainties
4) Use a variable "gear" like pattern to control the overall contact resistance
5) Perform detailed 3-D ABAQUS finite element (FEM) thermal analyses to optimize the design and quantify temperature distributions, accounting for thermal expansion
6) Reduce minimum design temperature to avoid annealing during higher heating rates

Researchers conducted a preliminary post-irradiation examination from a novel *in-situ* experiment for MA957 NFA specimens implanted with 400 appm helium at 500°C and irradiated to 10 dpa at the ORNL High Flux Isotope Reactor (HFIR). The experiments used existing test reactor irradiations to simulate the high helium levels that are pertinent to fusion and accelerator-based nuclear systems. The results clearly show that helium is trapped in MA957 within a very high density of tiny bubbles at the nm-scale precipitates. In contrast, a companion experiment on a 9Cr TMS alloy (Eurofer 97) irradiated to the same helium and dpa levels showed much larger bubbles, primarily on dislocations. These studies offer proof-in-principle of the management of high helium levels by trapping in nm-scale NFA features; preliminary results were presented at a conference and have been submitted for publication. The team is continuing to evaluate a large matrix of alloys under a wide range of conditions.

Researchers have begun developing a new non-destructive technique for measuring constitutive properties. Combined analysis of the load-displacement curves and the pile-up geometry (measured by confocal microscopy) is used in an iterative process to determine yield-stresses and strain-hardening rates based on extensive FEM simulations. Applying this technique to a range of materials (e.g., simple ferritic model alloys, low-alloy steels, TMS, and NFA) provides yield stress values within about 5 percent of measurements. Researchers will use this method to efficiently measure the constitutive properties of alloys over a wide range of temperatures.

Planned Activities

Over the next fiscal year, researchers will continue updating TMS and NFA databases, emphasizing microstructural characterization. They will use the databases to build physically based constitutive and fracture toughness models, including irradiation effects. They will use Kocks-Mecking type dislocation dynamics evolution models, combined with hardening superposition laws, to analyze unirradiated and irradiated stress-strain curves.

Researchers will construct a deformation mechanism map for NFA based on the updated tensile and creep database and will conduct low- and high-temperature deformation tests for further model development. These experiments will include large deformation and strain mapping characterization experiments analyzed with FEM simulations to derive self-consistent constitutive and plasticity laws.

Researchers will also continue characterizing the nanofeatures of existing and commercial NFAs, along with new model alloys being developed. The goal is to resolve issues of uniformity and grain size distribution using a suite of advanced methods: TEM, SANS, EXAFS, and three-dimensional atom probe tomography (APT). In addition, they will develop an alloy stability database from long-term aging experiments of MA957 and other NFAs aged for 10,000 hours at 800–1,000°C and TMS alloys (including T91, HT-9, Eurofer 97, and F82H) aged for 8,000 hours at 550–700°C. They will conduct interim examinations of microstructural and mechanical property changes in 3,000 hour increments. Finally, they will continue post-irradiation examination of HFIR-irradiated TMS and NFA materials (including He-implanted MA957) over a range of temperatures, dpa, and helium levels.

NUCLEAR ENERGY RESEARCH INITIATIVE

Development and Analysis of Advanced High-Temperature Technology for Nuclear Heat Transport and Power Conversion

PI: Per F. Peterson, University of California at Berkeley (UCB)

Collaborators: Oak Ridge National Laboratory (ORNL), Sandia National Laboratories (SNL)

Project Number: 05-079

Project Start Date: April 2005

Project End Date: April 2008

Research Objectives

This project is studying advanced high-temperature heat transport and power conversion technology in support of the Nuclear Hydrogen Initiative and Generation IV. Researchers will focus on the fundamental and applied problems associated with high-temperature heat transport using different gases (e.g., helium) and liquids (e.g., clean liquid salts).

The project makes contributions in four areas:

1) Design options for the 50 MW(t) Next Generation Nuclear Plant (NGNP) intermediate heat exchanger (IHX) system, exploring the major tradeoffs among high-pressure helium, intermediate-pressure helium, and liquid salt (LS) as heat transport fluids for hydrogen production.
2) Scaled integral experiments to study high-temperature heat transport, heat exchange, and fluid mechanics with simulant fluids for liquid salts to generate experimental data for model development and code verification.
3) Multiple-reheat helium Brayton power conversion studies to evaluate its suitability for liquid-cooled, high-temperature systems such as the modular lead-cooled fast reactor (LFR), advanced liquid-salt-cooled very high-temperature reactor (LS-VHTR), and the molten salt reactor (MSR). Brayton cycles are expected to increase efficiency 5 to 10 percent and roughly double the power density.
4) Advanced high-temperature reactor (AHTR) design analysis to extend initial design studies of the LS-cooled AHTR as a potential high-temperature heat source for electricity and power production. Figure 1 compares the liquid-salt-cooled AHTR with the gas-cooled Pebble Bed Modula Reactor (PBMR).

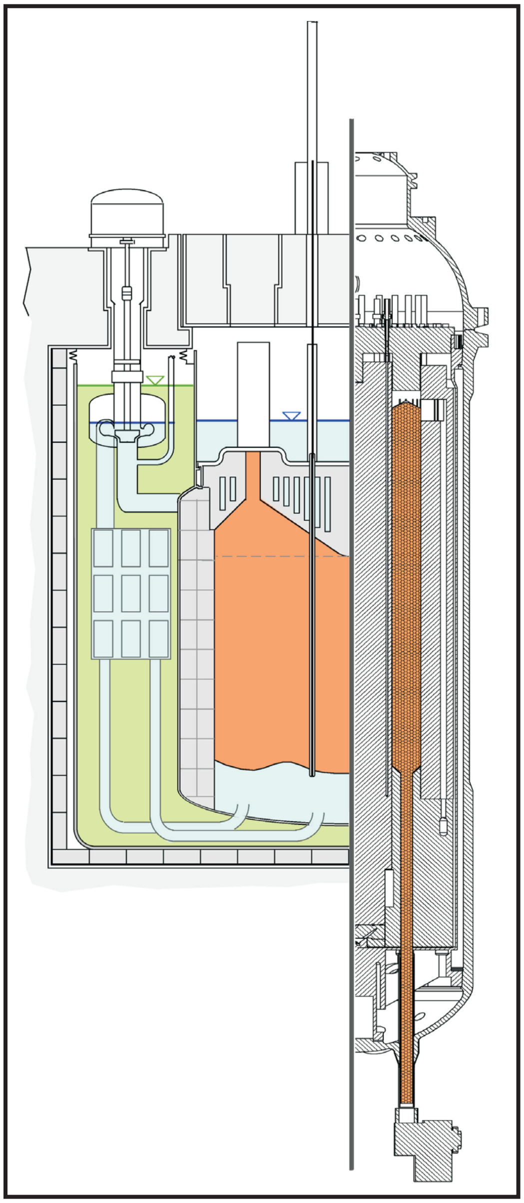


Figure 1. Scaled comparison of the 2,400 MW(t) AHTR-MI and the 400 MW(t) PBMR reactors.

Research Progress

Over this previous year, researchers focused on analyzing the NGNP intermediate heat exchanger and intermediate loop and on designing and analyzing experiments on the liquid-salt-cooled advanced high-temperature reactor (LS-AHTR). They redirected some work towards developing design options for prismatic and pebble bed reactor refueling. The closed-loop primary configuration recommended by UC Berkeley, called the Advanced High-Temperature Reactor using Metallic Internals (AHTR-MI), has been adopted as the national baseline.

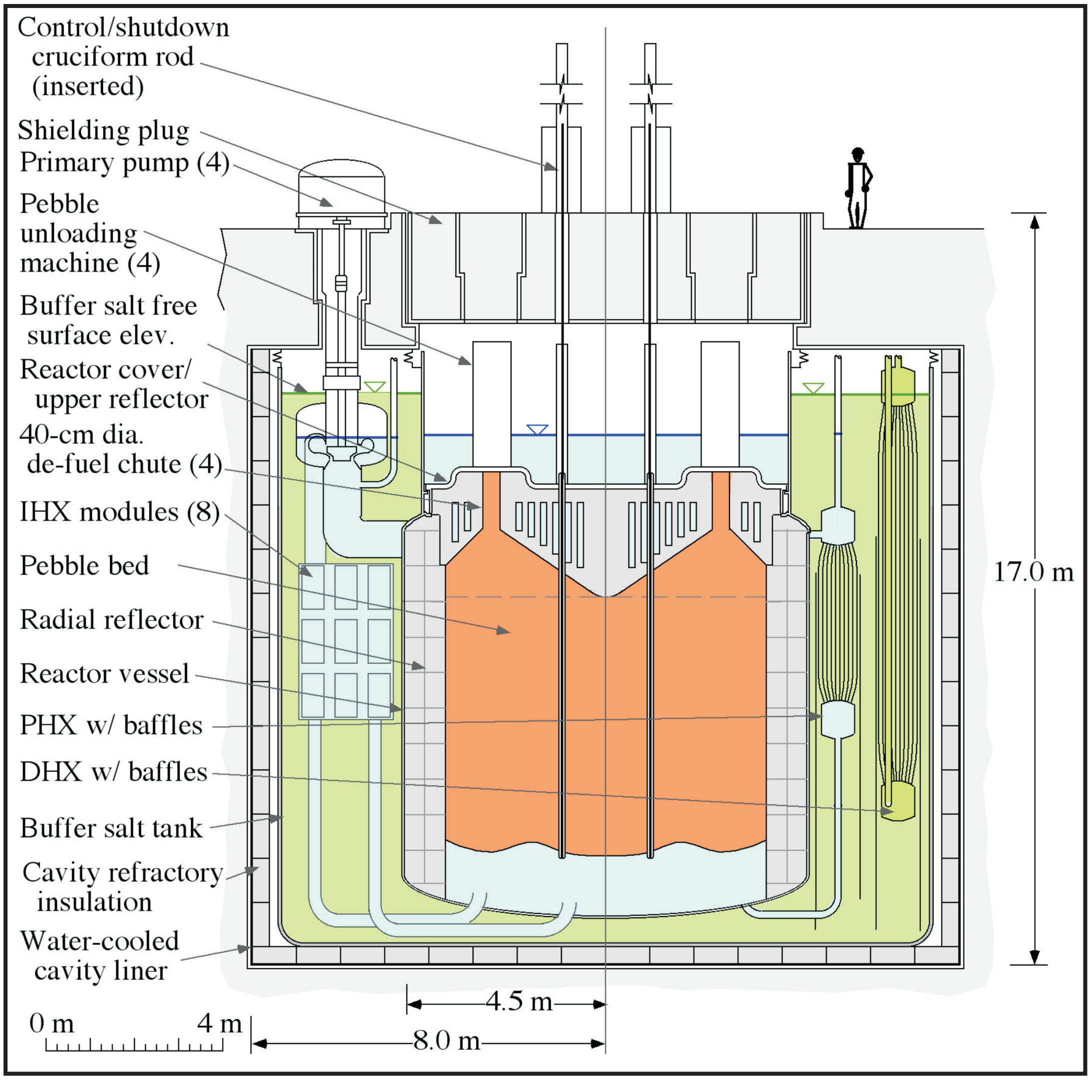


Figure 2. Elevation view of the AHTR-MI.

The major benefit of the new closed primary loop design, shown in Figure 2, is that it greatly limits the number of major metallic components that are exposed to the core outlet temperature under normal and accident conditions. The tri-isotropic (TRISO) coated fuel used in the AHTR-MI has large thermal inertia, as in gas-cooled reactors, but this design also derives additional thermal inertia from the high volumetric heat capacity of its primary salt coolant and from the effective natural-circulation heat transfer attributed to a larger mass in a buffer-salt tank.

Effective natural circulation allows the AHTR-MI to use a cylindrical core geometry and higher power density (10.2 MW/m^3), compared to the 6.6 MW/m^3 limitation of the annular core geometry required for passively cooled HTGRs. This largely increases power output, as shown by the scaled comparison in Figure 1 contrasting the 400 MW(t) PBMR reactor vessel and the 2,400 MW(t) pebble-bed AHTR.

Besides implementing the major design evolution for a closed primary loop and separate buffer salt tank, researchers developed preliminary designs for all major primary loop components. They also developed refueling methods for both the prismatic and pebble fuel versions, along with the third stringer fuel option. Neutronics analysis performed on the pebble bed version provided information on temperature reactivity coefficients and discharge burnup. The team developed a preliminary Phenomena Identification and Ranking Table (PIRT) and RELAP-5 model for the loss of forced cooling transient (LOFC). As seen in Figure 3, the very large thermal inertia and effective mixing in the AHTR-MI gives rise to a very small temperature increase during LOFC.

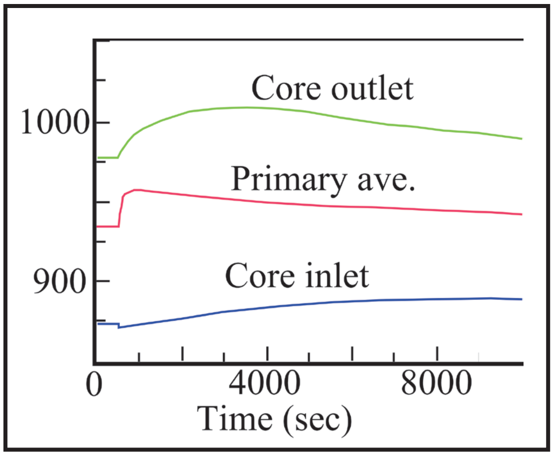


Figure 3. RELAP-5 simulation of transient response of AHTR-MI to LOFC.

In addition to design and simulation work, the team built and operated two scaled thermal hydraulics experiments. The Scaled High-Temperature Heat Transfer Experiment (S-HT2) used heat transfer oil to match non-dimensional parameters – Reynolds Number (Re), Froude Number (Fr), Prandtl Number (Pr), and Grashof Number (Gr) – for liquid salt to study upward heated mixed convection flow. Similarly, the integrated pebble recirculation experiment, PREX-1, shown in Figure 4, used water to match Re, Fr, and the pebble-to-salt density ratio, and provided the first integrated demonstration of the viability of all aspects of pebble injection, pebble bed dynamics, and pebble extraction for the AHTR-MI. Because pebbles have a small positive buoyancy in the liquid salt, they float and are removed from defueling chutes located in the top reflector of the reactor.

Figure 4 The Pebble Recirculation Experiment (PREX-1).

Planned Activities

Researchers are on track for completing the full work scope of this NERI project. Work during the coming year will include PIRT development and design analysis, including transient analysis, for the NGNP IHX, with related experiments. Further design work will also be performed on the AHTR-MI design, including neutronics analysis to determine the maximum achievable depletion with pebble fuels, and RELAP-5 transient analysis of the loss of forced circulation (LOFC) and other accidents. PREX-1 and S-HT2 experiments will also be conducted.

NUCLEAR ENERGY RESEARCH INITIATIVE

Development of Risk-Based and Technology-Independent Safety Criteria for Generation IV Systems

PI: William E. Kastenberg, University of California at Berkeley (UC Berkeley)

Collaborators: None

Project Number: 05-080

Project Start Date: March 2005

Project End Date: February 2008

Research Objectives

The objective of this project is to develop quantitative safety goals for Generation IV nuclear energy systems. These safety goals will be risk based and technology independent. Researchers will develop a new operational definition of risk. They will also lay the foundation for a new approach to risk analysis that will 1) quantify performance measures, 2) characterize uncertainty, and 3) address a more comprehensive view of safety as it relates to the overall system.

Safety criteria are necessary for managing risk prudently and cost effectively. Results of this study will prove valuable to those government agencies charged with assuring the health and safety of the public as they manage, review, and approve these advanced reactor designs.

Research Progress

During the past fiscal year, researchers focused on three of the top-level Generation IV goals: 1) cost/benefit analysis of sustainable nuclear fuel cycles, 2) physical protection, and 3) optimum deployment of future nuclear energy systems. Following is a synopsis of progress made under each of these areas.

Cost/Benefit Analysis of Sustainable Nuclear Fuel Cycles. In this work, researchers are conducting cost/benefit analyses of various sustainable nuclear fuel cycles. The approach is derived from the axioms of sustainability as laid out by Chichilnisky and Heal. They are addressing a primary barrier to sustainability in nuclear fuel cycles, i.e., waste disposal. The team will model the consumption of waste disposal space at a facility, such as Yucca Mountain, using the Chichilnisky criterion. This criterion departs from the conventional utilitarian approach by including an undiscounted long-run average utility in the objective function. With this approach, it is also possible to include utility from consumption as well as conservation of stock for the future. Therefore, it is possible to rank various fuel cycles according to sustainability.

Physical Protection. This project examines the question of how to optimize the allocation of limited physical protection resources at a nuclear power plant. Ongoing work at UC Berkeley has shown that traditional risk analysis techniques can misallocate defense resources when compared to game theory methods that model the interaction between strategic actors, e.g., the plant defender and a terrorist group.

In this project, researchers will use probabilistic risk analysis techniques to model the response of a nuclear facility and physical protection system to an initiating event caused by a strategic adversary. They will also apply a game theory approach to model the interaction between two strategic actors, identifying equilibrium strategies for both of them. Based on this model, researchers will employ nonlinear mathematical programming techniques to find the optimal allocation of resources for physical protection.

Optimum Deployment of Future Nuclear Energy Systems. Researchers are modeling the substitution of nuclear energy systems within the nuclear energy enterprise to find optimal deployment paths for future systems. The goal is to balance sustainability, waste minimization, proliferation resistance, and economics of a design with systemic constraints, such as energy demand, repository limits, and uranium/plutonium resources.

Researchers developed a simple physical model to consider two archetypical nuclear energy systems: 1) a light water reactor with an open fuel cycle and 2) a fast breeder reactor with a closed fuel cycle. They will track a limited number of materials through their corresponding fuel cycles using a multi-objective and multi-period mathematical programming model to describe the decision-making process over time. The researchers defined simple metrics as proxies for the various risks posed by a system and will employ a multi-attribute utility function to resolve the tradeoffs among these risks. The optimal solutions that maximize utility under the constraints will identify the number and type of reactors that should be deployed over time.

Researchers will perform an adjoint sensitivity analysis around the optimum solutions. This will identify the parameters that heavily influence the optimal deployment path. An important element of the planning process is to reduce uncertainties in these parameters. Techniques for finding the space of efficient solutions could be applied to find robust deployment strategies and reduce the dependence on a multi-attribute utility function.

Planned Activities

Researchers plan to accomplish the following activities during the next year:

- Complete a trial set of quantitative safety goals, considering:
    - ◇ Risk to the general public
    - ◇ Nuclear Regulatory Commission safety goals for commercial reactors
    - ◇ Department of Energy safety goals for defense facilities
    - ◇ Safety goals for other hazardous industries
    - ◇ Radioactive exposure information
- Formulate risk in absolute, incremental, and relative terms
- Develop a licensing strategy for Generation IV systems
- Create an operational definition of risk, based on recent advances in network theory, which accounts for the complexity, uncertainty, and ambiguity of Generation IV systems
- Create a nodal model for a nuclear energy system and numerically simulate loss of bulk materials, particulate and gaseous release, and waste materials to characterize risk
- Apply the safety goals and risk definition to a gas-cooled thermal reactor and a liquid-metal-cooled fast burner reactor

Development of Modeling Capabilities for the Analysis of Supercritical Water-Cooled Reactor Thermal-Hydraulics and Dynamics

PI: Michael Z. Podowski, Rensselaer Polytechnic Institute

Collaborators: The Royal Institute of Technology (KTH), Sweden

Project Number: 05-086

Project Start Date: March 2005

Project End Date: March 2008

Research Objectives

This project will develop an experimental database for heat transfer in tubes and channels cooled by water at supercritical pressures. Researchers will design mechanistic models of local turbulence-driven heat transfer in forced-convection flows of supercritical fluids experiencing strong variations of physical properties. The fluids under consideration include water and carbon dioxide (CO_2). The proposed models will be consistent with current computational capabilities of reactor system codes. They will include a mechanistic approach to detailed flow and heat transfer phenomena and new non-dimensional correlations based on sound physical concepts applicable to supercritical water-cooled reactors (SCWRs) over a well-defined range of conditions.

Researchers will implement the new models in the NPHASE computational fluid dynamics (CFD) computer code and conduct testing and validation against experimental data. They will apply the models to demonstrate the applicability of the new models to SCWR thermal-hydraulics based on both system codes and CFD codes. Finally, they will perform numerical simulations of supercritical water system dynamics based on the NPHASE code. The purpose of these simulations is to investigate flow and heat transfer conditions during 1) transients associated with power and flow variations, 2) system depressurization from supercritical to subcritical pressure, and 3) transition from forced to free convection.

Research Progress

Supercritical Water Test Loop (SCWTL). Researchers are reassembling the test loop at its new location (Royal Institute of Technology). Initial tests include checking individual loop components and developing a strategy for future tests with "cold" supercritical water flowing through 6-8 mm ID tubing. They will be followed by runs in which the tubing is gradually heated until it passes the pseudo-critical point (the pipe temperature limit is 600°C). Researchers will measure the pipe temperature distribution and pressure drop during all runs.

Computational Models of Supercritical Fluid Properties. The team has almost completed developing new models for all major properties of water (i.e., density, viscosity, specific heat, thermal conductivity, and Prandtl number) as a function of temperature and pressure, for pressures varying between 23.5 and 25 MPa. The new models have been converted into non-dimensional form based on the ratios of actual-to-critical pressure and actual-to-critical temperature (using the absolute temperature scale). In parallel, similar models are under way for carbon dioxide (CO_2). The new models are being validated for fixed pressures, then the effect of pressure will be accounted for as an independent variable in a manner similar to the model of water properties at supercritical pressure.

Correlations and Scalable Models of Coolant Flow and Heat Transfer. Researchers will use these models in the thermal-hydraulic and safety analyses of SCWRs. The main focus has been the effect of turbulence modeling on flow and heat transfer in supercritical fluids. Researchers have analyzed two models of turbulence: 1) high-Reynolds number k-ε and 2) low-Reynolds number k-ε. Also, they have investigated effects of variable fluid properties on the turbulent viscosity and turbulent thermal conductivity.

Future plans include modifying the existing local models of turbulence by explicitly including the effects of, first, variable density and, next, variable specific heat.

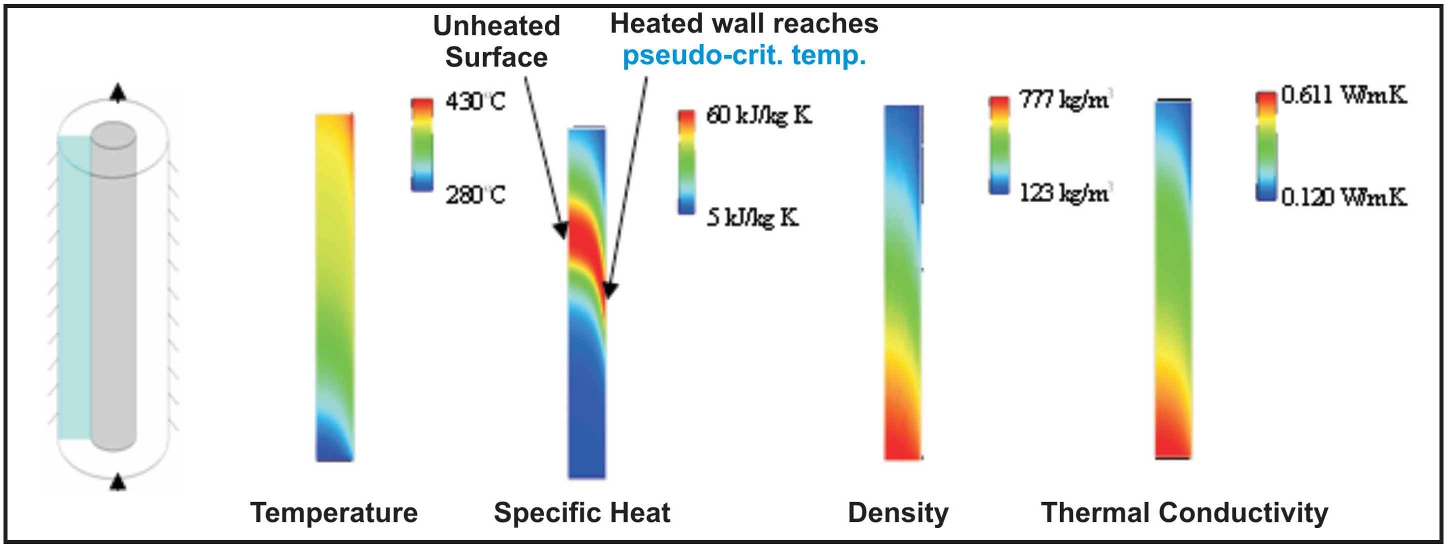


Figure 1. Heated channel geometry and contour plots of various parameters of water at 25 MPa.

Multidimensional CFD Simulation using NPHASE. The team has conducted testing and validation of the proposed multi-dimensional model of flow of heat transfer for both supercritical water and CO_2 as coolants. Typical results are shown in Figures 1 and 2. The overall results are numerically consistent and in reasonable agreement with experiments. Analysis of observed differences between the predictions and data has already provided useful insight into the critical modeling issues.

Planned Activities

Following is a synopsis of the tasks the team plans to conduct over the next period:

- Complete the experiments at the SCWTL facility and use the results of measurements to develop a database for future predictions of flow and heat transfer in water at supercritical pressures
- Complete the development of new mechanistic multi-dimensional models of turbulence and forced convection heat transfer for both water and CO_2 at supercritical pressures
- Encode the new models in the NPHASE code and perform model testing and validation for both water and CO_2 using experimental data
- Use the NPHASE code to perform numerical simulations of supercritical water systems corresponding to the anticipated designs of SCWR
- Develop scalable correlations and simple models for application in system codes

Team members expect to participate in related international collaborations (I-NERI) with Sweden and the Republic of Korea, and possibly Canada and France. Topics for the proposed collaboration include 1) reviewing and analyzing experimental data for supercritical CO_2, 2) cross-comparing computer simulations for selected operational conditions, 3) developing improved turbulence models for supercritical fluids, 4) sharing results of SCWTL experiments, and 5) identifying simulation benchmark problems.

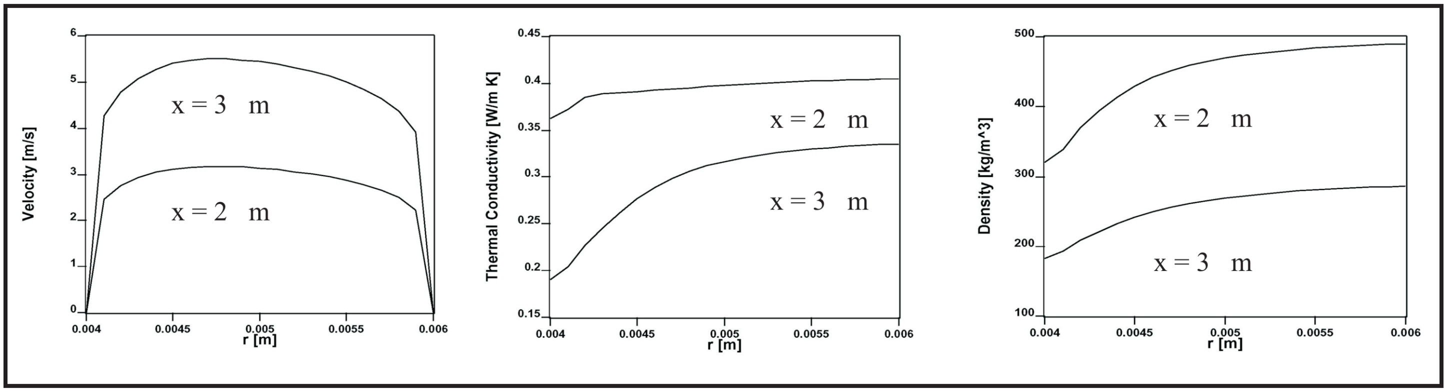


Figure 2. Radial plots at two axial locations along a 4 m heated channel at 25 MPa.

Novel Processing of Unique Ceramic-Based Nuclear Materials and Fuels

PI: Hui Zhang, State University of New York at Stony Brook

Collaborators: Brookhaven National Laboratory, Oklahoma State University (OSU)

Project Number: 05-110

Project Start Date: April 2005

Project End Date: April 2008

Research Objectives

The primary objective of this project is to develop high-temperature refractory ceramic materials for the fuel, in-core components, and control elements of Gas-Cooled Fast Reactors (GFRs). Refractory-based ceramics such as carbides, borides, and nitrides display a number of unique properties, including extremely high melting points, high hardness, high thermal and electrical conductivity, and solid-state phase stability. These unique properties make them potential candidates for a variety of high-temperature nuclear reactor components.

In this research effort, the team will demonstrate the feasibility of a novel process for fabricating mixed-carbide refractory composite materials based upon pyrolysis of a mixture of preceramic polymers and submicron/nano-sized metal particles of uranium, zirconium, niobium, and hafnium. It will be carried out in a conventional oven under an inert atmosphere. This processing technique involves much lower energy requirements compared to hot isostatic sintering. It also provides the capability of fabricating net-shaped components and does not suffer from component size limitations, as does the chemical vapor deposition method.

This project will establish manufacturing processes for fabricating a variety of unique high-temperature ceramic materials and fuels, including metal ceramic carbides, mixed metal carbides, and unique metal silicon-carbides. The resulting materials can be graded and will have a controlled microstructure (at both micron and nano levels), fiber-reinforced configurations, and a wide range of compositional control.

Research Progress

The research activities are broken into three primary tasks: 1) materials processing, 2) process modeling, and 3) nuclear transport. Each of these tasks is described below.

Material Processing. During FY 2006, the team focused on two primary aspects of the materials processing task: 1) generation of kinetics data and structure-property relationships for precursor-derived silicon carbide (SiC) and 2) fabrication of silicon carbide – uranium carbide (UC) materials for nuclear fuel applications. They conducted a detailed characterization of precursor-derived silicon carbide using X-ray diffraction (XRD), transmission electron microscopy (TEM), infrared spectroscopy (FTIR), and nanoindentation. They observed that the parent silicon carbide matrix exhibits a nano-crystalline microstructure with super-hardness and high modulus. The highest hardness and modulus values, 67 and 450 GPa respectively, were obtained for material processed to 1,400°C, with a crystallite size of about 3.6 nm. Figure 1 shows a typical TEM micrograph and a selected area electron diffraction (SAED) for nanocrystalline SiC.

Researchers have fabricated the following ceramic composite pellets, incorporating uranium compounds into four different silicon-carbide matrices: U_3O_8-SiC, UO_2-SiC, UC-SiC and U-SiC. All materials were fabricated into cylindrical pellets using a novel processing technique based on polymer infiltration and pyrolysis (PIP). In all cases, the initial starting composition was controlled to result in a final uranium density of 5 g/cc, as identified by previously reported burn-up calculations. Material fabrication using uranium powder involved hydriding a uranium block to generate flakes that could be easily ball-milled into the liquid polymer precursor. Similar schemes

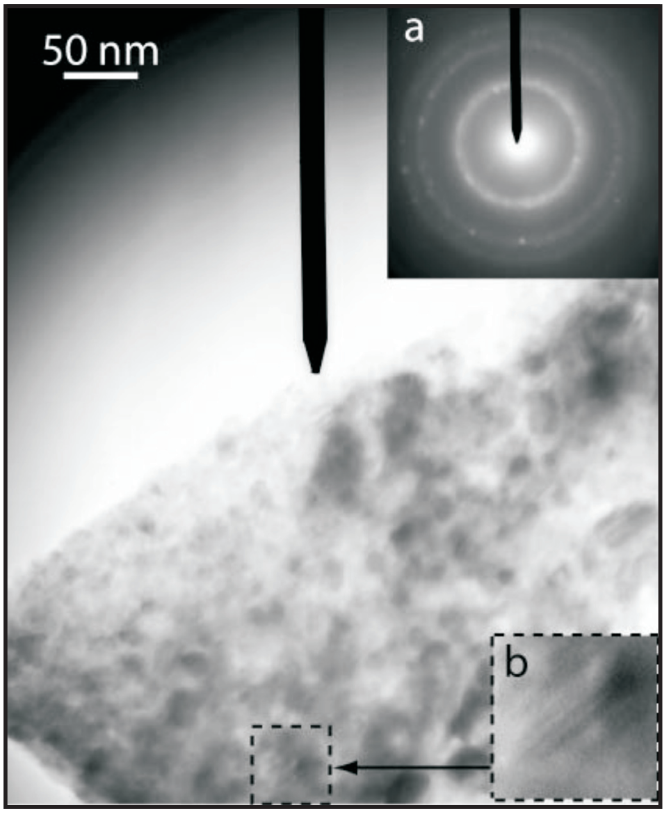


Figure 1. (a) TEM micrograph for SiC processed at 1,650°C, SAED pattern showing rings and specks. (b) Stacking faults.

have been used to generate both uranium and plutonium powders in the past by other researchers. This procedure leads to *in-situ* reactions between the polymer precursor and the uranium powder to form a U-Si-C ceramic. The fabricated plugs are characterized to quantify density, porosity, and mechanical properties as a function of processing temperature and infiltration cycles. Typical open porosities were determined to be about two percent after eight reinfiltration cycles. Figure 2 shows a typical SEM micrograph of the U_3O_8-SiC material.

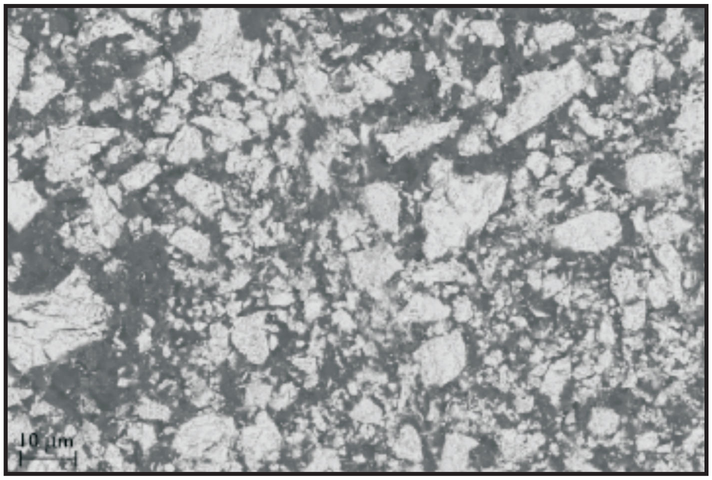


Figure 2. Uranium ceramic composite after eight reinfiltration cycles.

In the latter half of FY 2006, the project underwent an organizational change and the materials fabrication facilities were transferred to OSU. The team acquired new equipment with university funds to enable the fabrication of materials at ultra-high temperatures, while minimizing oxidation issues that had occurred with the original equipment.

Process Modeling. For this task, researchers developed a macroscale global model that describes polymer pyrolysis and uranium/hafnium/zirconium ceramic material processing. The model includes heat transfer, polymer pyrolysis, silicon carbide crystallization, chemical reactions, and species transport of a porous mixture of preceramic polymer and filler particles such as uranium oxide. The model is capable of accurately predicting the polymer pyrolysis and chemical reactions of the source material and the effects of transport processes such as heat-up, polymer decomposition, and volatiles escape. In addition, the model can obtain the yields of multiple components. The model is capable of simulating pyrolysis and sintering of a sample with any geometry according to fuel pellet design requirements. The team has also investigated the effects of heating rate, particle size, and volume ratio of metal and polymer on reaction rates.

In addition, the group developed a microscale local model based on the smoothed particle hydrodynamics (SPH) method. The microscale model applies to repetitive units in the macroscopic global model and describes transport phenomena in a micro-unit, e.g., reaction rates, heat and mass transfer, and composition changes of different components. Thermal boundary conditions are from the macroscopic global model. The microscopic local model (Figure 3) considers shrinkage and bulk translational motion of the filler particles. The model is used to study the effects of filler particle materials, sizes, concentrations, and distributions on the microstructures and material properties of the final product.

Nuclear Transport: Material Composition and Fuel Configuration. The researchers have developed a simplified model for a fuel pin (271 per fuel element) and its associated coolant volume. The maximum pin temperature is estimated assuming the implied power density (400 watts/cc) and standard values for material conductivities as a function of coolant velocity. The pressure drop across the core can then be estimated for each value of coolant velocity. Although these estimates are approximate at this stage, they are sufficiently accurate to indicate whether or not it is necessary to re-configure the core.

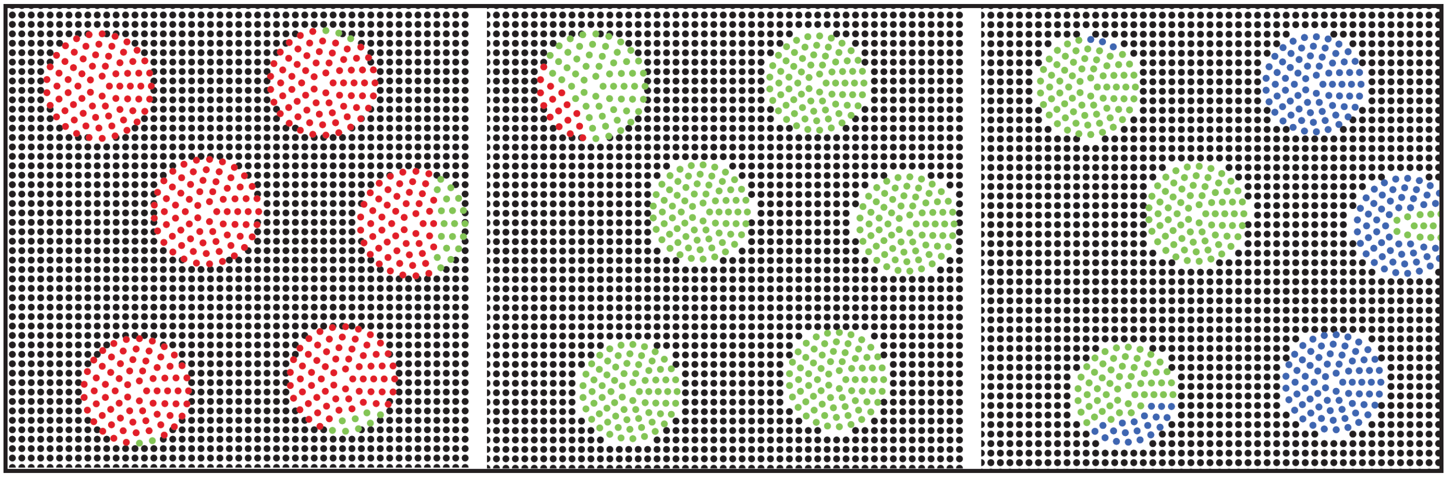


Figure 3. Microstructure evolution of filler particles in the baseline case. The black solid circle, grey solid circle, black hollow circle, and black triangle represent SiC, U_3O_8, UO_2, and UC, respectively.

In order to determine the proper coolant velocity, researchers performed a more detailed analysis of the core using the Monte Carlo code MCNP. In this analysis, they determined heat generated in individual pins. Using this information, they assembled a computer-drafted version of the core using Star Design, which forms input for use in the commercial computatinal fluid dynamics (CFD) code STAR CCM+. Currently, they are gaining familiarity with the CFD code and its limitations. The team is also using parameters from previous and current MCNP calculations to estimate the temperature distributions in the core. Using this CFD code provides them with better insight into the benefit of increasing the clad surface roughening and by how much the roughening should be increased. In addition, they are investigating the type of surface roughening. This study is based on previous work carried out in connection with the gas-cooled fast breeder reactor (GCFBR). In this task, the team determined that increased surface roughening would increase heat transfer coefficient. However, the core pressure drop also increased simultaneously.

Planned Activities

For the material fabrication tasks, the team will continue to focus on fabricating carbide and silicon-carbide composite plugs for uranium, hafnium, zirconium, and niobium as various fuel and in-core materials. Additionally, they will generate reaction kinetics data for the polymer precursor containing uranium, hafnium, and other materials that are of interest in this investigation.

For the process modeling tasks, the team will investigate mesoscale uncertainties and stochastic characteristics of macroscale permeability. They will further improve the integration of microscopic local and macroscopic global models and use this model to optimize the material fabrication process.

Researchers must determine core coolant operating parameters—such as maximum allowed pressure drop, velocity, and temperature—and examine the core intake and outlet design to eliminate hotspots. Although the power density of the current core has been reduced approximately 50 percent, cooling requirements and pressure drop will have to be optimized.

Establishing a thorough understanding of various geometry effects on core temperature and coolant flow rate is important to evaluate both operating costs and the potential for use within a thermo-chemical hydrogen production cycle.

NUCLEAR ENERGY RESEARCH INITIATIVE

Real-Time Corrosion Monitoring in Lead and Lead-Bismuth Systems

PI: James Stubbins, University of Illinois at Urbana-Champaign

Collaborators: Los Alamos National Laboratory, Lawrence Livermore National Laboratory

Project Number: 05-114

Project Start Date: April 2005

Project End Date: March 2008

Research Objectives

The primary focus of this project is to address major corrosion issues associated with using lead (Pb) and lead-bismuth (Pb-Bi) liquid metals as working fluids in advanced nuclear systems. The approach to mitigate corrosion is to develop a persistent oxide film on the surface of internal structural components. The researchers will study material alloying and surface treatment approaches to form these protective films. If properly formed and maintained, the films can provide a useful barrier to inhibit the corrosive attack of liquid metal.

A central objective of this project is to further develop impedance spectroscopy (IS) for characterizing and monitoring corrosion in liquid metal systems. The researchers will use IS corrosion monitoring techniques to measure the kinetics and thermodynamics of the formation of oxide films on reactor structural materials. Use of this advanced real-time corrosion monitoring method to study scale formation on selected alloys will support the development of new corrosion-resistant alloy compositions and surface treatment techniques. Because the IS technology can measure oxide film formation in real time and is sufficiently compact, it can be deployed at numerous locations in an operating system to directly monitor local corrosion processes.

This project was designed to accomplish three major goals:

1) Develop the IS technique for lead and lead-bismuth systems
2) Use enhanced IS techniques to measure the kinetics of oxide scale formation for a variety of materials and oxygen pressures at temperatures ranging from 400–700°C
3) Develop improved surface treatments and alloy compositions for enhanced corrosion resistance

Research Progress

Researchers have performed a number of IS scans during this year. The impedance responses were obtained by periodically scanning each sample over a range of signal frequencies from 100 kHz to 100 mHz. Figure 1 shows the impedance response of a typical sample of 316 stainless steel that was preoxidized for 48 hours. Part (a) is a complex plane plot, commonly called a Nyquist plot, which shows the imaginary impedance (reactance) versus real impedance (resistance). What is plotted is actually the negative of the imaginary impedance, since only capacitance, not inductance, is important for this project. Parts (b) and (c) are Bode plots, showing the magnitude and phase angle, respectively, of the impedance versus signal frequency. Parts (a) through (c) present the same data in various formats, and the curves are, therefore, color-coded for easy comparison. Plotting impedance responses at several different times, spanning an exposure period of nearly 10 days, provides an indication of how the duration of sample immersion affects its impedance response. The different curves in Parts (a) through (c) represent impedance scans at successive times, beginning with red and moving toward blue, with a varying time difference between curves. Part (d) shows the impedance at a single frequency—in this case, 1 Hz—plotted as a function of time. This provides a better picture of the effect of sample immersion time. The ability to collect "real-time" corrosion information is apparent. Researchers conducted extensive additional tests, all with similar time-dependent results.

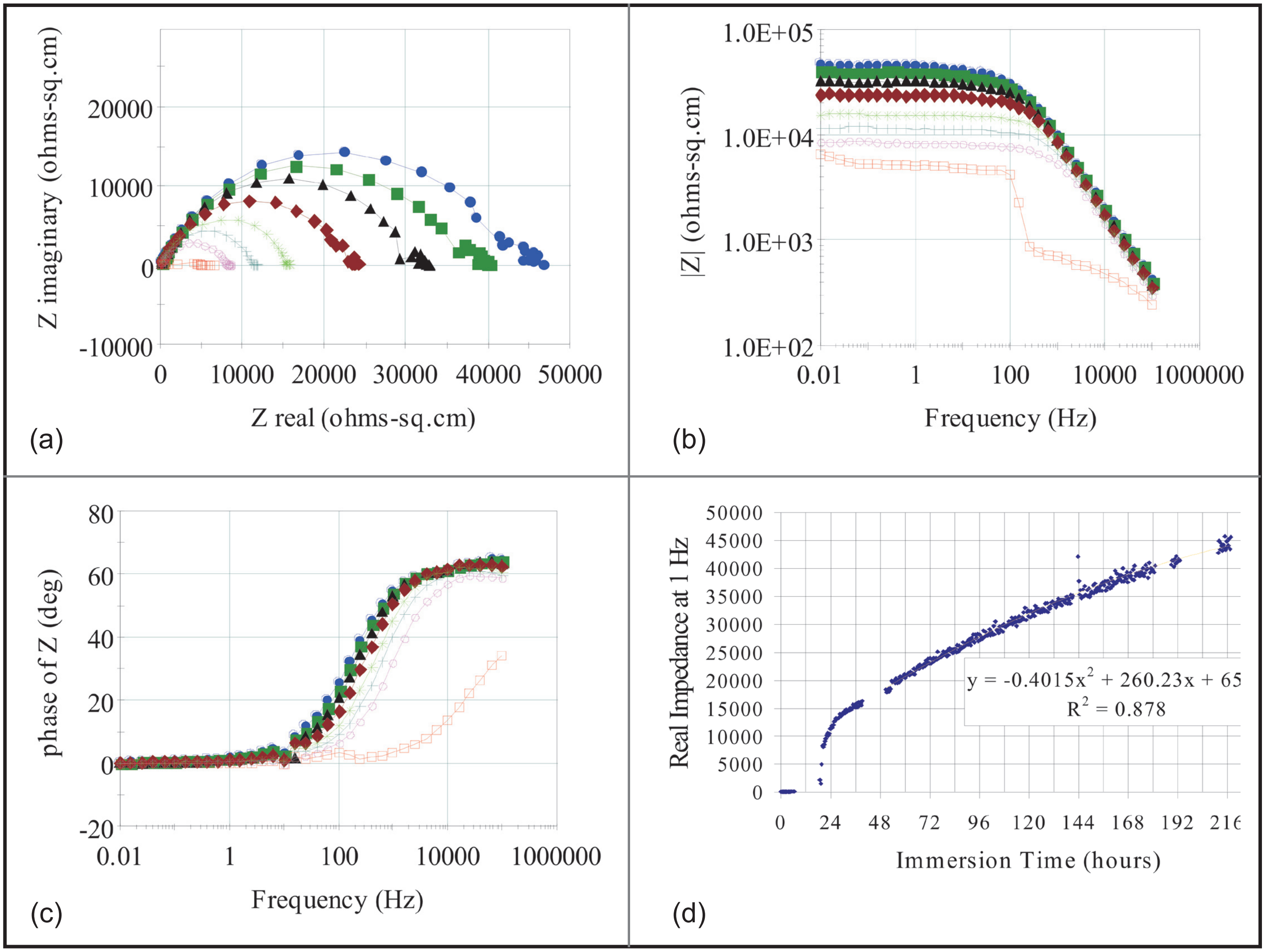


Figure 1. IS results for a single preoxidized sample of 316SS in LBE at 200°C: (a) Nyquist Plot, (b) Bode impedance magnitude plot, (c) Bode impedance phase angle plot, and (d) Real impedance versus corrosion time plot.

As can be seen from the Bode phase plot, (c) the impedance at low frequencies is almost pure resistance. The Bode magnitude plot, (b) shows that resistance is nearly constant in the low-frequency region. In other words, the DC resistance and the low-frequency impedance are practically the same (especially at overall low impedance magnitudes). Since the highest impedance occurs at low frequencies, plotting the low-frequency impedance as a function of time shows how the overall response changes with time.

Part (d) shows that a sample typically has very low impedance when first immersed in the Pb-Bi eutectic (LBE). This condition occurs despite the fact that the sample is preoxidized and is, therefore, completely covered with an adherent oxide layer. Another feature of the time-dependence of the impedance response is that the rate of increase of the impedance is not constant but can vary. In Part (d), a fit to the data after the initial jump shows that the impedance has a parabolic dependence on time. Other samples do not show such a parabolic relationship and may increase linearly or in some other manner. Even within a single sample, the rate can spontaneously change for no apparent reason. More work needs to further characterize these rates, especially at longer immersion times.

The responses also resembled those simulated from a Randles equivalent-circuit model of the physical system, which can be used to fit the experimental results. At overall large impedance magnitudes, however, the fit of the Randles model worsens, indicating that other, unknown electrochemical and physical processes may be taking place. Experimental investigation and corresponding model development may lead to fruitful scientific understanding of oxidation processes.

Planned Activities

Over the next fiscal year, the team plans to continue work on three research efforts: 1) verification and extension of a point defect model to liquid LBE corrosion, 2) experimental verification that heating and quenching the incoming gas can work around the kinetic limitations of oxygen control by gas dynamic equilibrium, and 3) experimentation to quantitatively determine the effect of mechanical integrity defects on the impedance response of oxide layers.

Successful completion of these activities will provide a strong base of confidence in the subsequent efforts to develop new IS probes; to characterize and analyze the IS responses of various materials; and to develop new alloys, surface treatments, and coatings to mitigate liquid-metal dissolution corrosion.

NUCLEAR ENERGY RESEARCH INITIATIVE

The Effect of Hydrogen and Helium on Irradiation Performance of Iron and Ferritic Alloys

PI: James Stubbins, University of Illinois at Urbana-Champaign

Collaborators: Los Alamos National Laboratory; Lawrence Livermore National Laboratory; Argonne National Laboratory; University of Michigan; Idaho State University; Washington State University; Belgian Nuclear Research Centre (SCK/CEN); Hokkaido University, Japan

Project Number: 05-116

Project Start Date: May 2005

Project End Date: April 2008

Research Objectives

The goals of this research project are to 1) develop a fundamental understanding of irradiation-induced defects on ferritic alloys and 2) understand the roles of hydrogen and helium in damage evolution. Researchers will extend this knowledge to increasingly complex iron alloy materials, which are the prime choice for structural and component applications in several advanced reactor and accelerator-based system concepts. This class of alloy has relatively high irradiation resistance and retains good structural properties in temperatures ranging from 400 to 700°C. However, the existing irradiation performance database represents fast fission neutron spectra, as it was developed for the fast breeder program.

This research will be applied to the development of more radiation-resistant alloys through a combination of experiments and modeling. The project will encompass substantial new developments in experimental analysis and high-speed computational modeling to simulate the formation and evolution of defects in ferritic metals and alloys during radiation exposure.

In this work, researchers will also focus on the influence and possible synergistic effects of hydrogen and helium during defect production, clustering, and extended damage structures during irradiation. They will examine the evolution of point defects and defect structures as a function of radiation exposure, irradiation temperature, and hydrogen/helium production in increasingly complex materials. These materials range from the simplest single-crystal iron, to polycrystalline iron and iron alloys, through advanced ferritic/martensitic steels.

The work scope consists of the following two tasks:

1) Perform microstructural and microchemical analyses for a set of irradiation exposure conditions using ion irradiation to accurately control hydrogen and helium levels and radiation dose (materials include single crystal iron and increasingly complex binary, ternary, and commercial alloy systems)
2) Perform large-scale molecular dynamics and kinetic lattice Monte-Carlo simulations to understand the effects of irradiation on material properties and damage processes

Research Progress

The initial objective of the research was to conduct and analyze proton and helium irradiation in single crystal, body-centered cubic (BCC) iron and to extend the work to iron-chromium (Fe-Cr) alloys. During the first year, researchers completed both the proton and helium irradiations of single crystal BCC iron. They analyzed these specimens with positron annihilation spectroscopy and transmission electron microscopy to understand the effects of hydrogen and helium on the damage microstructure. They also performed simulations emulating the experimental conditions in order to follow the defect evolution processes. Currently, the team is preparing specimens of single crystal Fe-14Cr for ion irradiation in a matrix similar to that used for the single crystal BCC iron specimens.

The researchers used LAMMPS, a large-scale molecular dynamics code, to conduct cascade simulations with the Fe-Cr potential. A new model developed at LLNL generalizes many-body classical potentials for incorporating complex formation energy curves in alloys. Researchers used this model, which correctly predicts the order versus segregation tendency in the Fe-Cr system, to carry out the displacement cascade simulations.

Figure 1 shows preliminary results for cascades done in pure iron and Fe-20%Cr, generated by a 25 keV primary knock-on atom in crystal lattices at room temperature. Compositions of interest lie in the range between 8 and 20 atomic-percent chromium, which was chosen because both the atomistic model and experiments show precipitation of the alpha-prime phase in alloys with approximately 12 atomic-percent chromium. More cascades need to be done in order to examine the effect of Cr concentration on the damage evolution in the early stages of damage. Researchers will conduct analyses to identify the types and concentration of the resulting point defects as well as to characterize the effect of chromium on cluster development and migration.

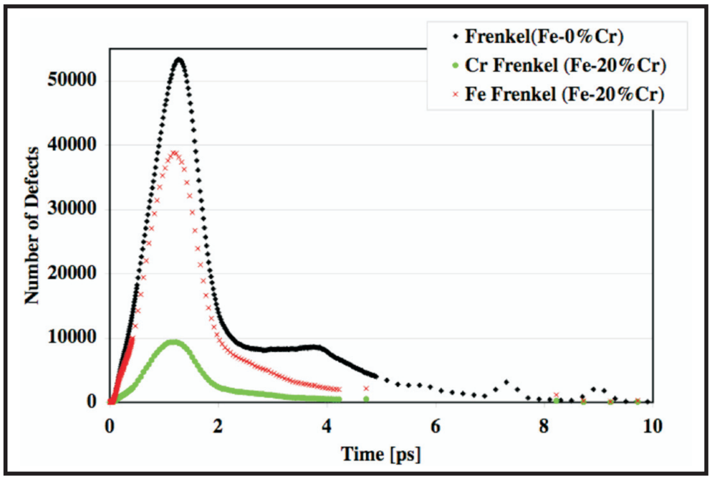


Figure 1. Number of Frenkel pairs versus time for pure iron and Fe-20%Cr.

During this period, the team continued examining the mechanical properties behavior of Fe-Cr alloys. This work included modeling the approach to plastic instability due to the presence of second-phase and grain reorientation (i.e., texture development) during post-yield deformation. They are using electron backscattered diffraction techniques to understand the influence of grain structure reorientation during deformation. The results will later be applied to understanding the influence of irradiation at various temperatures on the deformation dynamics in this class of alloys.

Planned Activities

During the next fiscal year, this project will focus on the microstructural evolution caused by radiation damage in iron alloys and conclude the work being performed on single-crystal Fe.

The research in pure iron will continue on both the experimental and computational sides, including additional molecular dynamics and kinetic Monte Carlo modeling of helium and hydrogen in BCC iron. To identify and quantify defects, researchers will use transmission electron microscopy and positron annihilation spectroscopy.

The work with Fe alloys will examine how the alloying elements (i.e., chromium and carbon) affect the microstructural evolution when the system is exposed to proton irradiation and the presence of helium. Researchers will use both experimental and computational techniques and compare the results to that of pure iron to understand the effects of the alloying elements.

To fully understand the effect of chromium on the damage structure evolution, researchers will conduct irradiations on the Fe-Cr single-crystal materials (Fe-14Cr and Fe-18Cr) at two different temperatures—573 and 723 K. After irradiation, they will analyze the samples using positron annihilation spectroscopy (PAS) measurements, positron annihilation lifetime spectroscopy (PALS), and transmission electron microscopy (TEM).

NUCLEAR ENERGY RESEARCH INITIATIVE

Alloys for 1,000°C Service in the Next Generation Nuclear Plant

PI: Gary S. Was, J. Wayne Jones, and Tresa Pollock, University of Michigan

Collaborators: Special Metals, Inc., Idaho National Laboratory (INL), Oak Ridge National Laboratory (ORNL)

Project Number: 05-143

Project Start Date: January 2005

Project End Date: December 2007

Research Objectives

The objective of this project is to define strategies for improving alloys used for structural components in high-temperature helium reactors, such as the intermediate heat exchangers and primary-to-secondary piping. Specifically, the project will investigate oxidation/carburization from helium impurities, microstructural stability, and impact on creep behavior at temperatures between 900 and 1,000°C. The aim is to better understand the synergism among these critical processes and to provide data for long-term prediction of properties.

The design of the very high-temperature reactor (VHTR) proposed for the Next Generation Nuclear Plant project calls for outlet gas temperatures of up to 1,000°C. These are extremely challenging conditions for operating the metallic components in the intermediate heat exchanger and primary-to-secondary piping. Inconel 617, an advanced nickel-based alloy, has been identified as a leading candidate for such applications. However, its material properties in a high-temperature, impure helium environment are not sufficiently understood to qualify this alloy for service. Therefore, this study will also investigate alloy and microstructure modifications needed to enhance Inconel 617 properties.

Research Progress

Researchers have completed and validated the controlled-purity helium flow system designed to provide a target gas mixture using pre-mixed gas bottles and a series of mass flow controllers. Sensitivity tests have been conducted to ensure signal stability for testing over several hundred hours. An initial set of tests was conducted at 1,000°C for 500 hours in a carbon monoxide (CO) environment mixed with small amounts of carbon dioxide (CO_2) ranging from 0.092 to 0.380 percent.

Figure 1 is a plot of the square of weight change of the samples versus time. A linear behavior on this plot indicates parabolic kinetics and the slope gives the parabolic rate constant. As is evident from the plot, ideal parabolic behavior was not observed in any of the gas compositions for a 500 hour exposure duration test. Oxidation kinetics increases with increasing CO/CO_2 ratio.

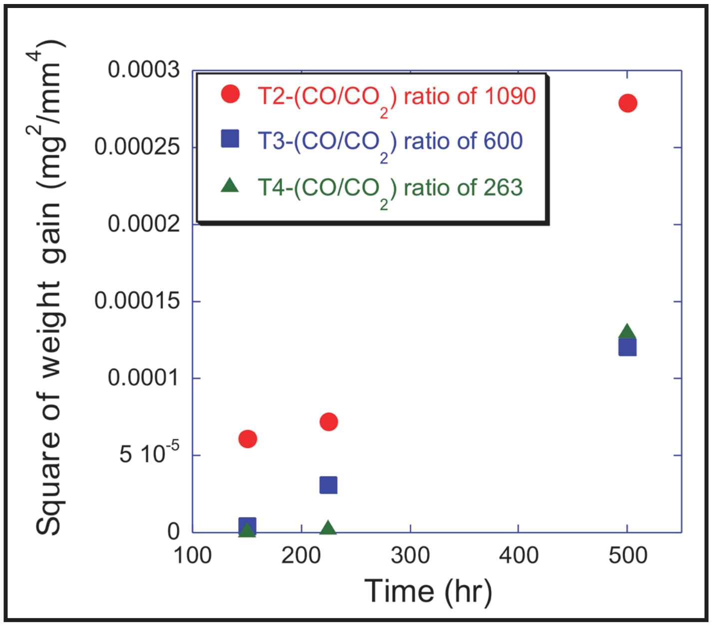


Figure 1. Plot of square of weight change vs. time for alloy 617 exposed to He + CO/CO_2 mixtures for 500 hours at 1,000°C.

Figure 2 contains an SEM image and a set of X-ray maps of a cross-section of the alloy 617 sample after exposure to a CO/CO_2 ratio of 600 for 500 hours at 1,000°C. These show that a surface oxide scale rich in chromium and oxygen has formed. Finger-like internal precipitates of Al_2O_3 also formed as the internal oxidation product of aluminum.

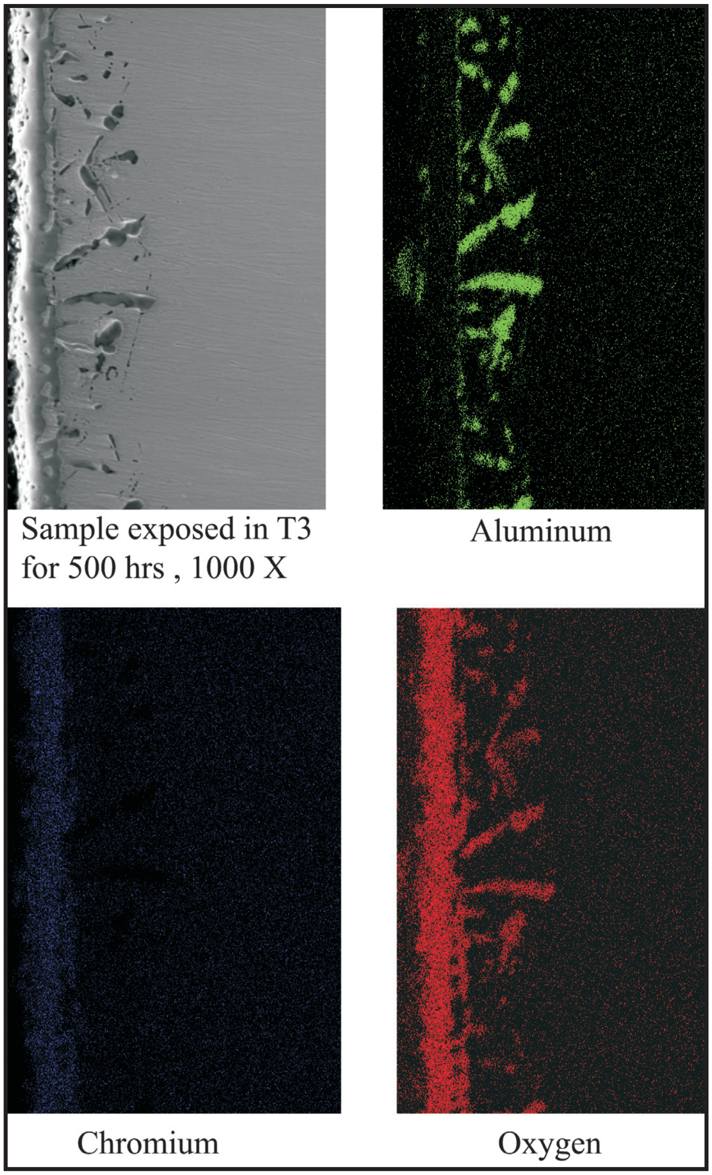


Figure 2. X-ray map of alloy 617 exposed to a CO/CO_2 ratio of 600 for 500 h at 1,000°C.

A major consideration in the screening studies is that any new alloys must ultimately be subject to fabrication via commercial hot working routes. Accordingly, researchers have collaborated with Special Metals on the design of new alloys, discussing in detail the constraints for processing alloys into sheet form. It was established that the company has conducted no prior investigations into the alloy composition domain of interest for this program.

Calculations were conducted using the Thermocalc code for the initial set of alloys in Table 1 (J1 – J5). These alloys were melted, homogenized, and subjected to creep experiments in compression at 1,000°C and 20 MPa. Wrought 617 alloy was also subjected to creep under the same conditions to establish a reference.

	Ni	**Cr**	**Al**	**C**	**W**	**Re**
J1-1	84		6.5		9.5	
J1-2	72.95	12	3	0.05	12	
J1-3	82.95	6	3	0.05	8	
J1-4	76.95	6	3	0.05	8	6
J1-5	79.95	6	3	0.05	8	3

Table 1. Candidate alloys.

Figure 3 shows the results of creep experiments on the alloys in Table 1. Note that the J1 alloy is stronger than 617 due to the presence of γ′ precipitates at the test temperature. While these precipitates provide substantial strengthening, they would be expected to be morphologically unstable for long periods of exposure. Therefore, researchers have focused to a greater degree on alloys that do not contain these precipitates in the temperature range of 900°C to 1,000°C; alloys J2 – J5 are single phase at these temperatures. Although alloys J2 and J4 have creep properties that are somewhat inferior to 617, it is important to note that the microstructure and higher order alloying additions are not optimized. Higher creep resistance in the experimental alloys is associated with high levels of tungsten (W) and rhenium (Re), with a particularly strong effect of the former.

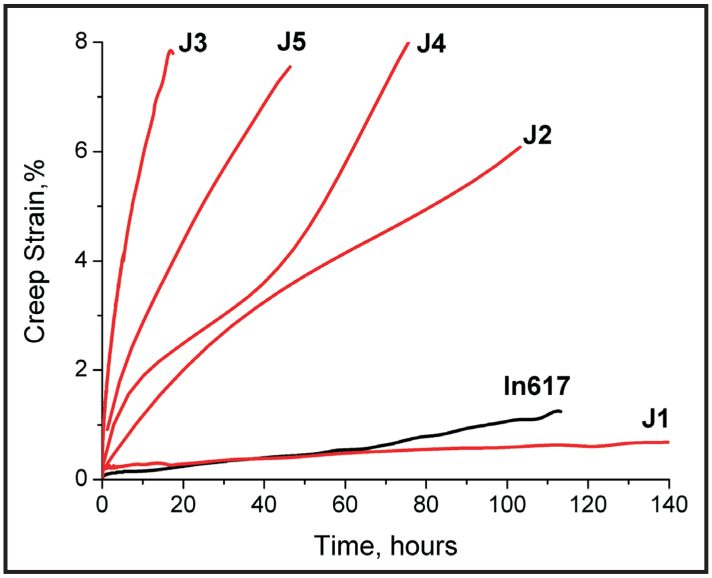


Figure 3. Results of compression creep tests at 1,000°C and 20 MPa.

Planned Activities

The controlled He flow system will be used in a set of exposure tests of alloy 617 at temperatures of 850, 900, and 950°C in a He-CO-CO_2 environment with six different CO/CO_2 ratios. This set of tests will provide information on the role of CO/CO_2 ratio and temperature on the oxidation rate and the mode of degradation: oxidation or carburization.

With the information from the first five alloys, an additional six are currently under investigation. The new set of alloys contains high levels of W and Re as well as molybdenum and cobalt additions. These alloys are currently being subjected to microstructural investigations and to high-temperature mechanical screening tests. Based on the outcome of the microstructural and mechanical tests, researchers will select compositions for two or three scale-up heats of 50 lbs, to be fabricated at Special Metals.

Researchers are completing a custom tensile creep system designed for creep experiments in controlled He at temperatures up to 1,000°C. Following exposure tests, researchers will perform experiments on creep behavior.

NUCLEAR ENERGY RESEARCH INITIATIVE

Heat Exchanger Studies for Supercritical CO_2 Power Conversion System

PI: Akira Tokuhiro, University of Missouri-Rolla (UMR)

Collaborators: Argonne National Laboratory (ANL)

Project Number: 05-146

Project Start Date: January 2005

Project End Date: December 2007

Research Objectives

A gas turbine Brayton Cycle utilizing supercritical carbon dioxide (CO_2) working fluid is being considered for some Generation IV nuclear energy systems. This advanced power conversion technology is expected to increase efficiency and significantly reduce plant cost, size, and complexity. An added benefit is high-temperature operation suitable for hydrogen cogeneration. While such benefits derive from the unique thermo-physical properties of supercritical carbon dioxide, these same properties also present technical challenges for the design of a regenerative heat exchanger.

To maximize the usefulness of the supercritical CO_2 (S-CO_2) power conversion system, researchers must design a compact heat exchanger and develop its basic performance data. The objectives of this project are to 1) establish heat exchanger performance under design conditions, 2) estimate performance for beyond design-basis accidents, and 3) compare different heat exchanger design options. The project will conduct the following activities:

- Design, construct, and operate an experimental facility for performance testing of compact heat exchangers for the supercritical CO_2 Brayton cycle recuperator/cooler application
- Obtain heat transfer and pressure drop data to evaluate performance of selected compact heat exchanger designs (e.g., printed circuit heat exchanger or PCHE)
- Develop fluid flow and heat transfer simulation models and tools to support the evaluation of heat exchanger designs

Research Progress

Researchers are testing two different compact heat-exchangers designs using the new S-CO_2 loops at ANL: 1) a low-pressure S-CO_2/water loop and 2) a low-pressure S-CO_2/high-pressure S-CO_2 loop. The objectives of the tests are to:

- Check the performance of the heat exchanger unit under design conditions, notably flow rate, pressure, and temperature
- Estimate the performance beyond design-basis such that the performance data can serve as a basis for model development and design optimization
- Compare the performance of PCHE (and/or compact heat exchange of similar design) to that of a reference heat exchanger design (e.g., shell-and-tube, helical coil, etc.)

A schematic of the low-pressure S-CO_2/water loop is shown in Figure 1 along with the solid model of the apparatus in Figure 2. Figure 3 shows a schematic of the high-and low-pressure S-CO_2/S-CO_2 loop.

The initial series of CO_2/water heat exchange tests has proceeded as scheduled. However, after the pump used to circulate CO_2 failed, researchers learned that all component materials in contact with the supercritical CO_2 must be carefully selected. Because the exact internal heat exchanger flow configuration is proprietary, the team reconfigured the test loop for water/water heat exchange testing and friction factor measurements in order to establish that the printed circuit flow pattern on the primary and secondary sides was similar. They confirmed a similar flow configuration, so heat transfer coefficients at identical Reynolds numbers can be assumed similar for CO_2/water heat transfer tests.

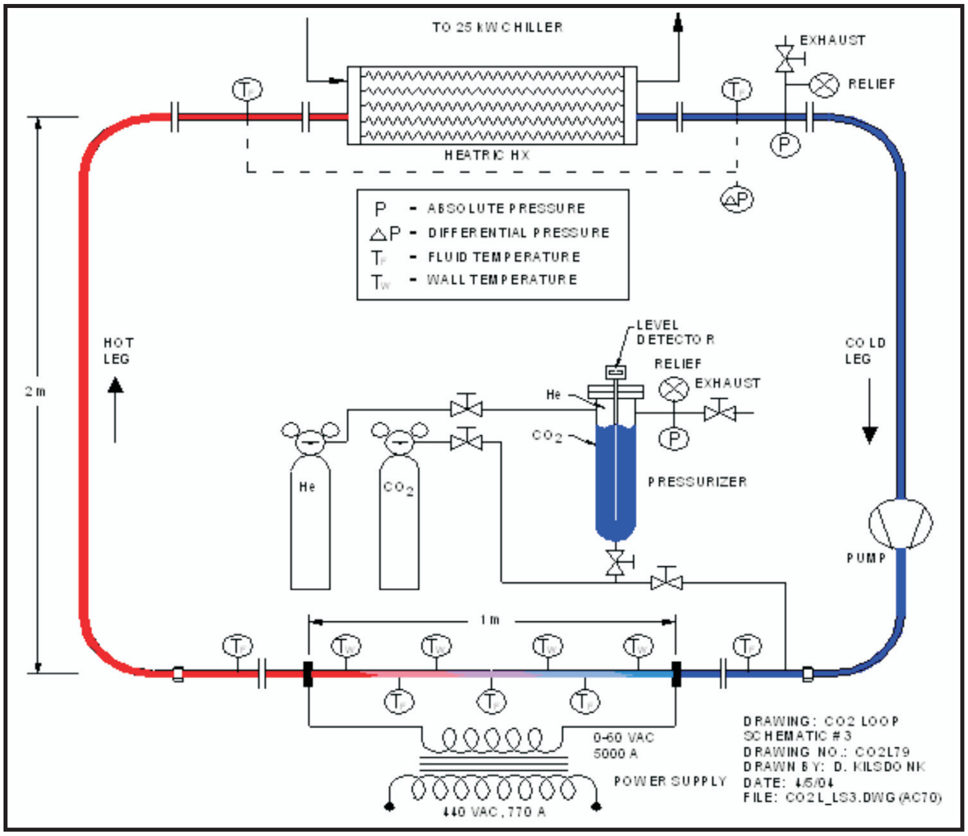


Figure 1. Schematic of the water/supercritical CO_2 test loop.

Because the loop requires fine control to maintain supercritical conditions, the researchers retrofit four resistance temperature detectors (RTDs) for enhanced accuracy of the hot and cold side differential temperatures and installed a 25 kW tankless heater to increase the attainable secondary side temperature from 45°C to 90°C. Figure 4 shows the heat transfer coefficient versus the average hot-side Reynolds number.

Although Tests A and B were both at 7.5 MPa, their outlet Prandtl numbers are different. The team is investigating why the heat transfer coefficients are nearly the same. Results from Tests A and C, conducted at 7.5 and 8.5 MPa, respectively, depict a relative increase in the heat transfer coefficient near the pseudocritical point with increasing pressure. An explanation of results requires consideration of a number of factors, since small changes in a variable such as temperature dramatically affects the thermophysical state of S-CO_2. Researchers are extending data to 8.0, 9.0, and 9.3 MPa under various temperatures surrounding the critical temperature.

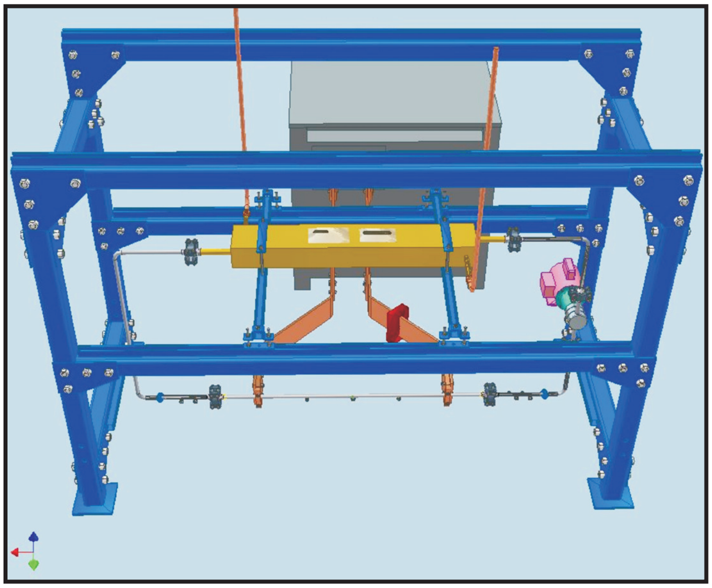


Figure 2. Front view of the water/supercritical CO_2 loop with the PCHE shown in brown.

Figure 5 shows a representative plot of the heat transfer coefficient and specific heat at pressures of 7.5 MPa and 8.5 MPa. The heat transfer coefficient exhibits a striking peak as bulk fluid reaches the critical temperature for the corresponding pressure. Further, the peak heat transfer coefficient at 7.5 MPa is slightly higher than that at 8.5 MPa—a trend observed from other studies, including single tube investigations. There is evidence that two factors influence the heat transfer parameters: 1) the zigzag flow configuration of the PCHE and 2) the characteristic channel diameter, depending on location of the pseudocritical point in the heat exchanger. In order to investigate these factors, researchers are developing a computational model of the PCHE in layers using STAR-CD for comparison with experimental data. They will also analytically calculate the local heat transfer and temperature distribution.

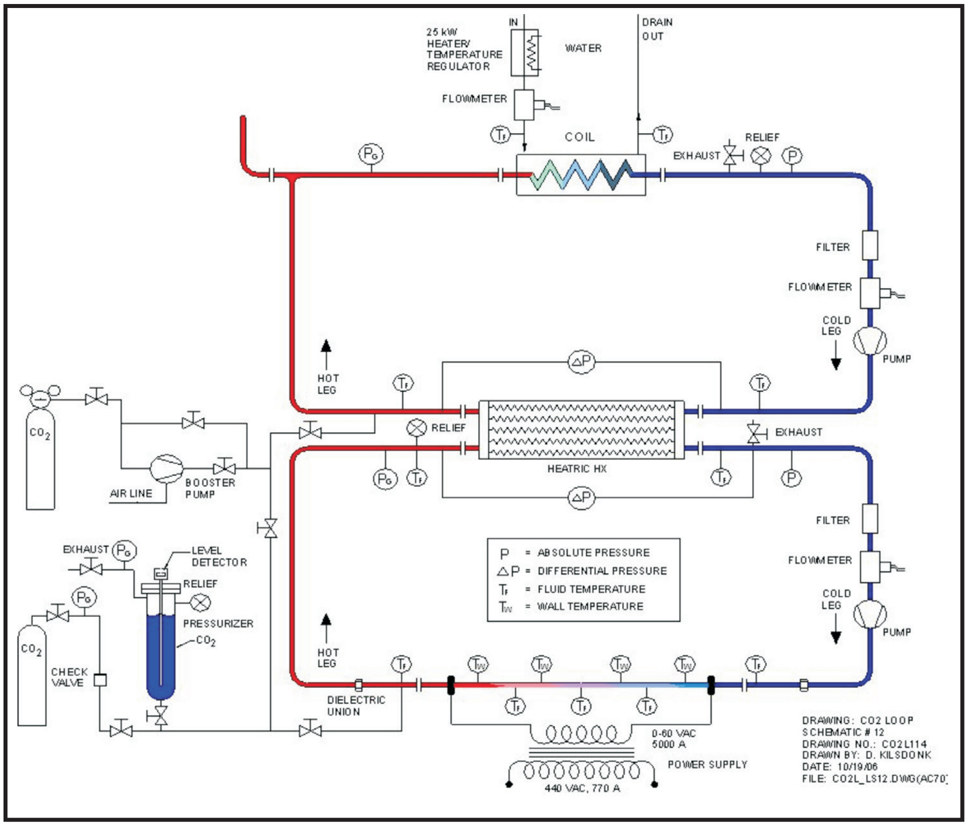


Figure 3. Schematic of the high and low pressure supercritical CO_2.

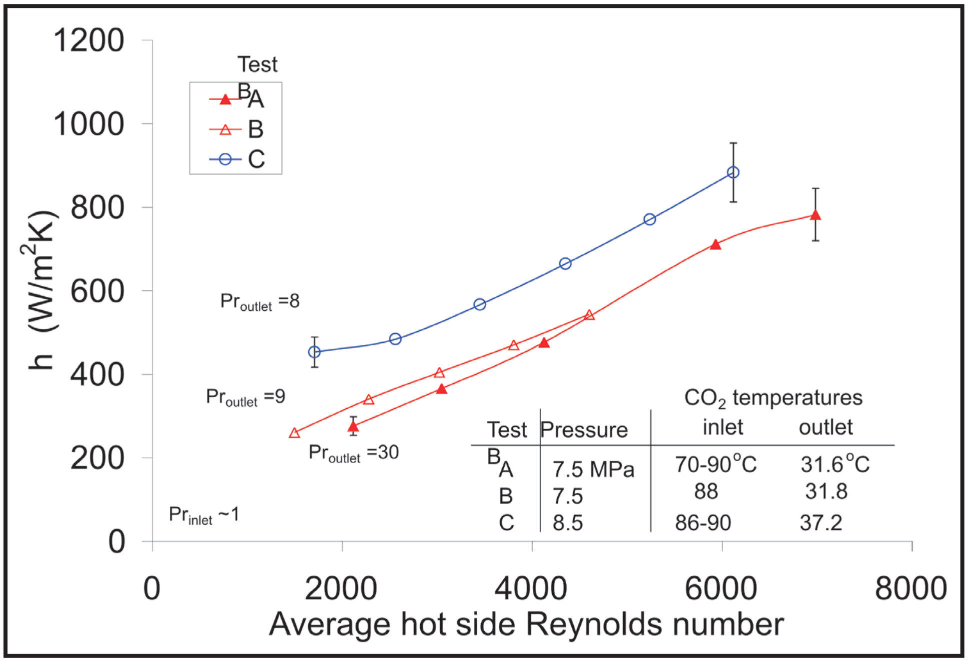


Figure 4. Average hot side heat transfer coefficient for cooler conditions.

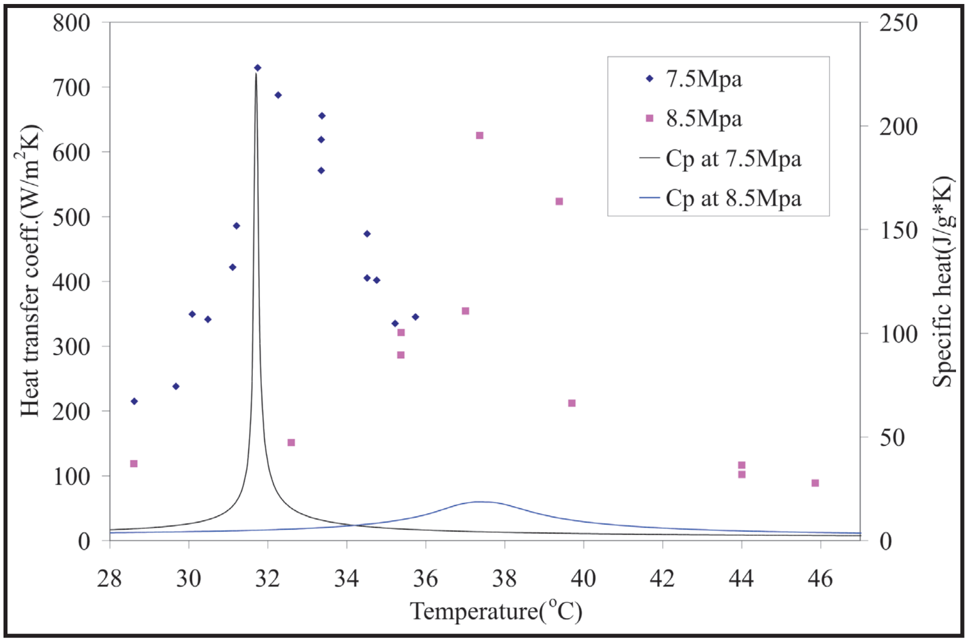


Figure 5. Heat transfer coefficient measured in the small temperature intervals.

Planned Activities

Following is a summary of the planned activities.

- Complete PCHE testing for CO_2/water heat exchange.
- Fabricate the high-pressure CO_2 loop. Adapt the SNAC test loop for low-pressure CO_2. Assemble the test facility for CO_2/CO_2 heat exchange by combining the low-and high-pressure loops via the PCHE. Evaluate PCHE or similar heat exchanger for procurement and installation.
- Conduct PCHE testing for CO_2/CO_2 heat exchange, simulating the low-temperature recuperator for the CO_2 Brayton cycle (85°C to 150°C, at 74 bar primary side, 200 bar CO_2 on secondary side). Conduct performance testing of modified PCHE for Brayton cycle low-temperature recuperator conditions.
- Assess test data for development of an improved heat exchanger model for accurate sizing of the recuperators and coolers. Model development for heat transfer of supercritical fluids in small channels.
- Evaluate results of PCHE (and/or equivalent) performance testing and identify needs for improving the supercritical CO_2 Brayton cycle application.
- Develop an approach and tools to evaluate the performance of compact heat exchanger designs using computational fluid dynamics (CFD) and heat transfer simulation, considering enhancement and modeling schemes. Heat exchanger model development is underway using a commercial CFD code and will be completed during the final research year.

NUCLEAR ENERGY RESEARCH INITIATIVE

Candidate Materials Evaluation for the Supercritical Water-Cooled Reactor

PI: Todd Allen, University of Wisconsin-Madison

Collaborators: University of Michigan

Project Number: 05-151

Project Start Date: March 2005

Project End Date: March 2008

Research Objectives

The supercritical water-cooled reactor (SCWR) system is being evaluated as a Generation IV concept. This system builds on currently proven light water technology by providing higher thermal efficiency and plant simplification. Supercritical water presents unique challenges to the long-term performance of engineering materials. Therefore, developing, testing, and selecting suitable materials for cladding and internal components are central to designing this reactor.

The objective of this project is to investigate degradation of materials in the supercritical water environment. First, researchers will study representative alloys from the important classes of candidate materials to analyze their corrosion and stress-corrosion cracking resistance in supercritical water. This analysis will include ferritic/martensitic (F/M) steels, austenitic stainless steels, and Ni-based alloys. Corrosion and stress-corrosion cracking (SCC) tests will be conducted at various temperatures, exposure times, and water chemistries. Second, emerging plasma surface modification and grain boundary engineering (GBE) technologies will be applied to modify the near surface chemistry, microstructure, and stress-state of the alloys prior to corrosion testing. Third, researchers will examine the effect of irradiation on corrosion and stress-corrosion cracking of alloys in the as-received and modified/engineered conditions by irradiating samples using high-energy protons and then exposing them to supercritical water.

Research Progress

Researchers conducted corrosion testing of the candidate alloys, including F/M steels, austenitic steels, and nickel-based alloys in both subcritical and supercritical water at temperatures of 360°C, 500°C, and 600°C for times to 1,026 hours. The effect of oxygen concentration on the corrosion behavior was also investigated. Researchers also applied surface modification and GBE treatment on selected materials and investigated the corrosion response.

Figure 1 compares the weight gain for most materials tested over a range of temperatures. Weight gain due to oxidation in supercritical water is typically smaller but less predictable in austenitic stainless steels than in F/M steels. Ni-based alloys show a fairly good corrosion resistance in supercritical water environment and have the lowest weight gain in all tested materials. Among the F/M steels, 9Cr oxide dispersion strengthened (ODS) shows the lowest weight gain.

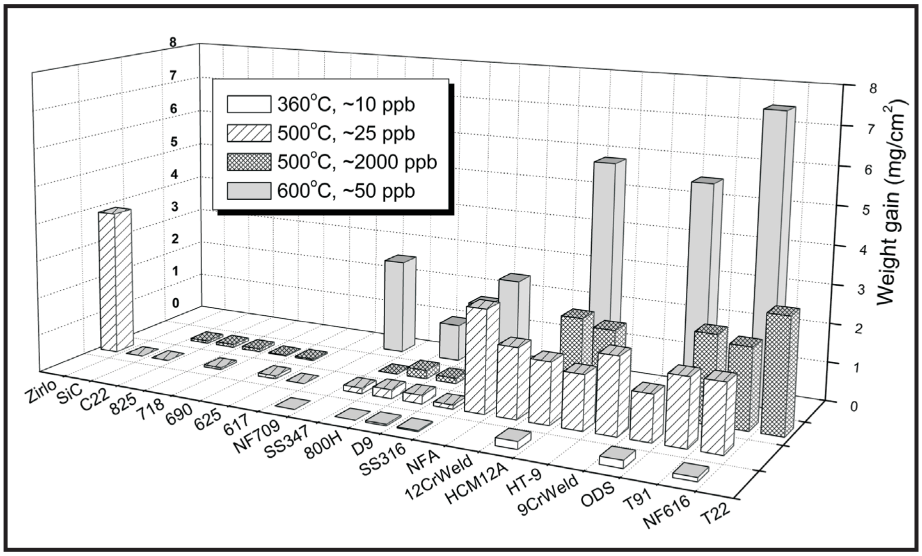


Figure 1. Comparison of weight gain data for the candidate materials after exposure to subcritical/supercritical water with different oxygen concentrations for ~333 hours.

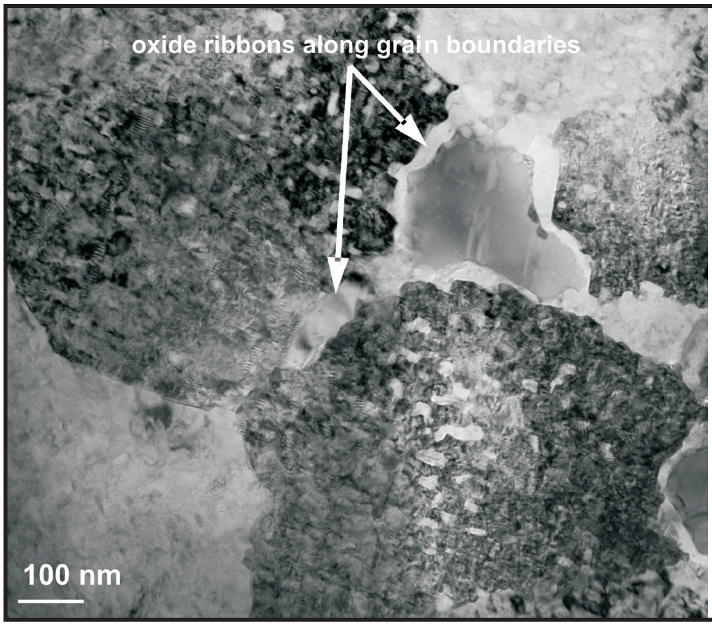


Figure 2. TEM image showing the morphology of the grains and grain boundaries in the internal oxidation layer formed in the 9Cr ODS steel after exposure to SCW at 500°C for 1,026 hours.

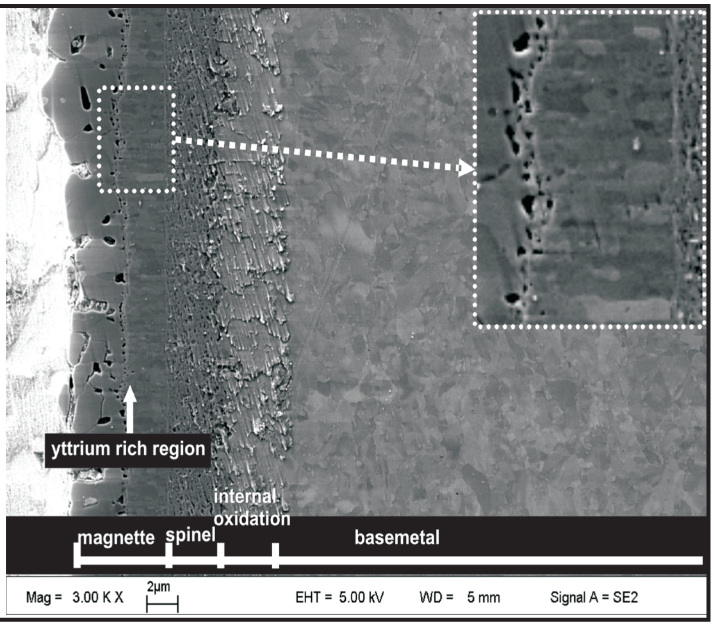


Figure 3. SEM image showing the microstructure of the formed magnetite layer in 9Cr ODS steel coated with a thin yttrium film after exposure to SCW at 500°C for 667 hours.

As shown in Figure 2, there is significant oxidation at the grain boundaries in the internal oxidation zone of the ODS steel, which researchers believe changes the mechanism of the outward growth of the oxide scale. Furthermore, yttrium segregated to the grain boundary area in the internal oxidation layer may retard the diffusion of cations and improve the corrosion properties in SCW.

For a sample surface modified by adding a layer of yttrium, the cross sectional image in Figure 3 shows an Y-rich, Y-Fe-O oxide layer formed on the Y-coated F/M steel after exposure to SCW at 500°C. The yttrium-rich layer separates the magnetite layer in two, each with different microstructures. The existence of the Y-Fe-O layer influenced the diffusion of cations and anions, significantly improving on the corrosion resistance.

Austenitic alloy 800H showed low weight gain in supercritical water; however, it also suffered the spallation of its outer magnetite scale. One approach to solve the spallation issue is GBE treatment. As shown in Figure 4, the scale on the GBE-treated alloy 800H became compact and continuous as compared to the scale on the control sample. The grain boundary character distribution of

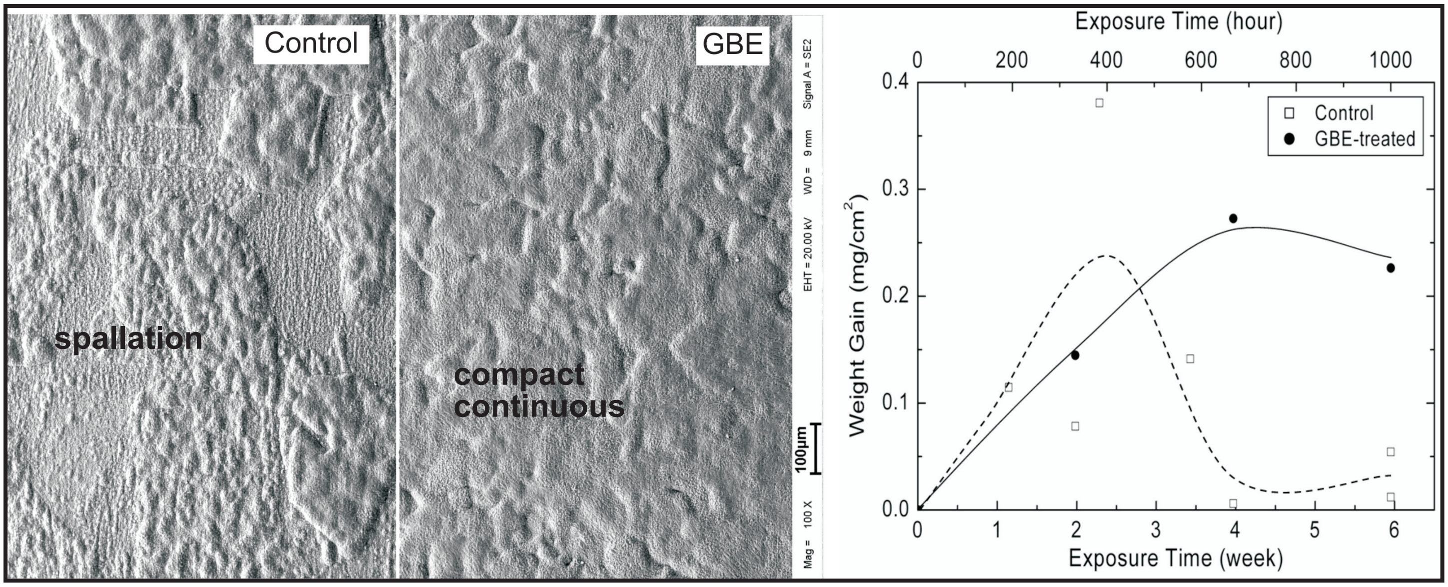


Figure 4. Effect of GBE treatment on the corrosion resistance of the austenitic alloy 800H after exposure to SCW at 500°C.

the base metal was optimized with increase of fraction of low-Σ coincidence site lattice boundaries, leading to the improvement of oxide stability.

Researchers irradiated alloys 316L and 690 with 3 MeV protons to a dose of 7 dpa at 400°C and 500°C. SCC experiments were conducted under 25 MPa of pressure at the same temperatures. The deaerated condition resulted in a dissolved oxygen concentration below 10 ppb and conductivity in the outlet water was maintained below 0.1 µS/cm for all tests. The specimens were strained at a nominal rate of 3×10^{-7} s^{-1} using a stepping motor.

The measure of the extent of cracking for all samples tested is crack length per unit area, as shown in Figure 5. At 400°C, the cracking susceptibility of 316L irradiated to 7 dpa is 1.1 times higher than that of an unirradiated sample. The susceptibility of alloy 690 at 400°C increases 2.8 times. At 500°C, the increase of cracking with irradiation is much greater. Irradiated alloy 316L had a crack length per unit area six times greater than on its unirradiated side. This difference was even higher for alloy 690, as a 7 dpa irradiation increased the amount of cracking by a factor of 48.

The irradiated microstructure is dominated by small (7 nm) faulted Frank loops at 400°C, larger Frank loops (25 nm), and voids at 500°C. Irradiation hardening is greater at 400°C than at 500°C, in agreement with hardening produced from the microstructure according to the dispersed barrier-hardening model. Irradiation hardening is greater in 316L than alloy 690 at both temperatures. Irradiation results in grain boundary chromium and iron depletion and nickel enrichment, with the extent of segregation increased with dose. Radiation-induced segregation (RIS) is slightly greater at 500°C than at 400°C. However, neither RIS nor hardening can satisfactorily account for the changes in SCC susceptibility with irradiation temperature.

In order to improve the cracking behavior of alloys 316L and 690, grain boundary engineering was used to enhance the coincident site lattice boundary (CSLB) fractions. The reference condition designated "as-received" or "AR" was hot rolled between 1,800 and 2,100°F (982 - 1,149°C) and then annealed at a temperature between 1,900 and 2,000°F (1,038 – 1,093.3°C). Due to the presence of chromium carbides in the AR condition, it was necessary to perform a short, 5 minute anneal at 1,100°C to dissolve the carbides. The resulting structure had a CSLB fraction of approximately 76 percent. Given this very high value of CSLB fraction, the decision was made to reduce the CSLB fraction. This was done by compressing the sample by 66 percent and then recrystallizing at 1,100°C for 2 hours to homogenize the grain size. The specimen was then compressed another 5 percent and annealed at 1,000°C for 7.5 minutes, reducing the CSLB fraction to between 32 and 37 percent. The sample with a reduced CSLB fraction will provide an excellent means to test the effect of the CSLB fraction on the cracking behavior of the alloys. The two conditions selected for testing have CSLB fractions that are about a factor of two different (35 vs. 76 percent). Side-by-side images of these two conditions are shown in Figure 6. Note that the grain sizes of both conditions are very similar.

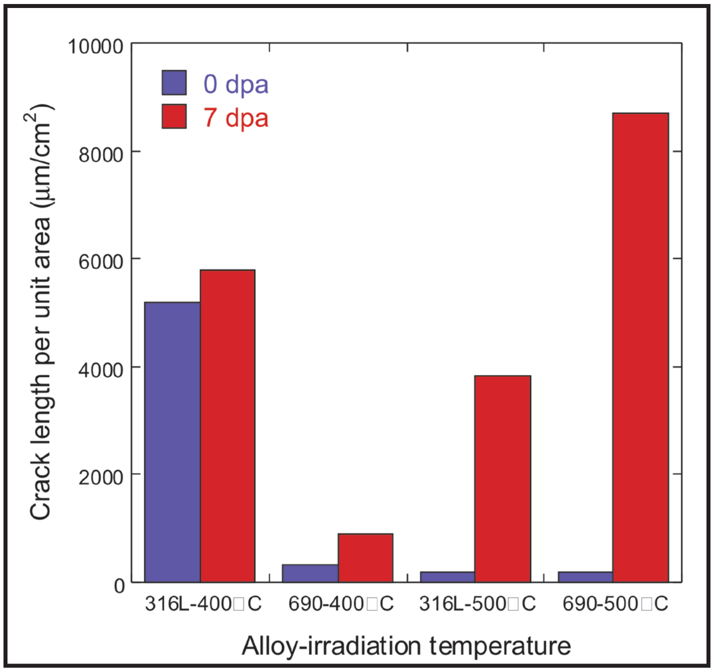


Figure 5. Influence of irradiation on the cracking susceptibility of alloy 316L and 690 in 400°C and 500°C SCW.

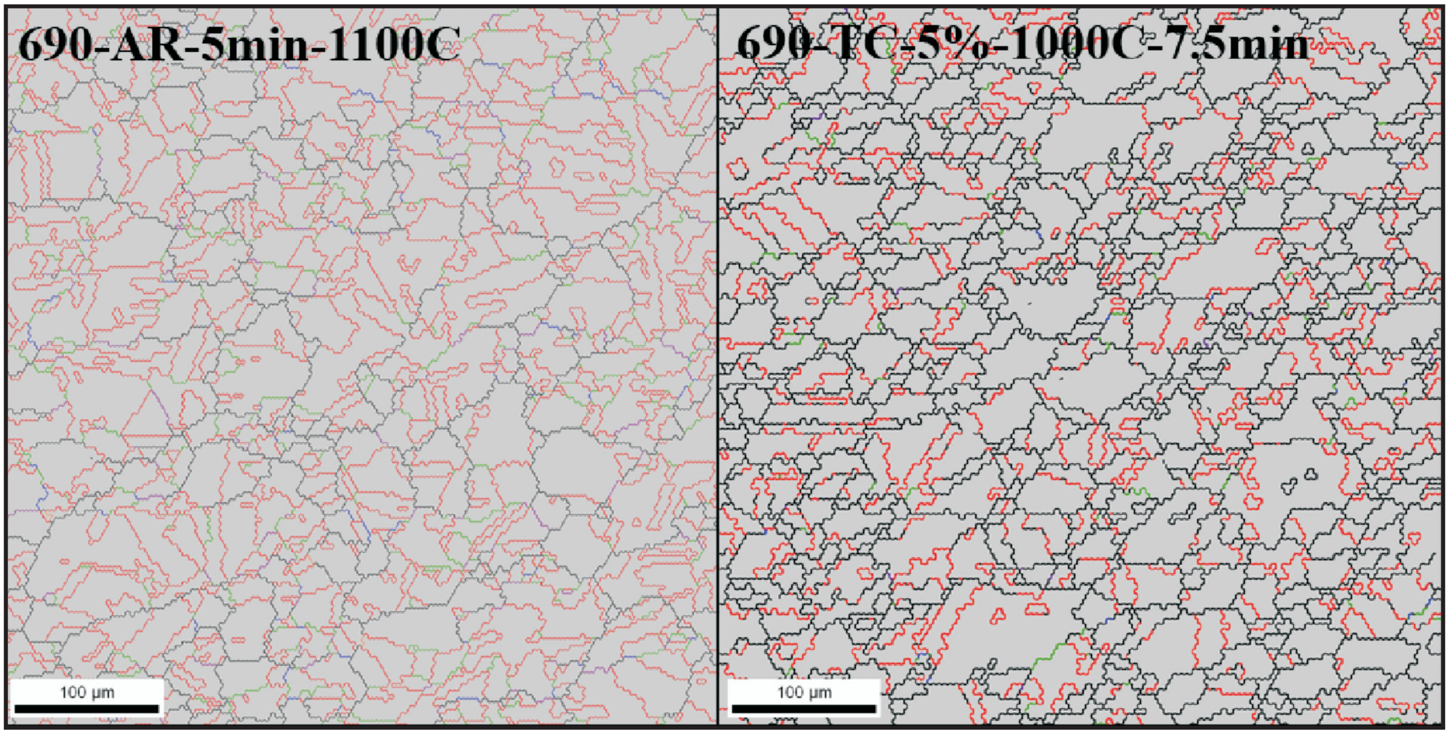


Figure 6. Comparison of the two conditions of alloy 690 showing large differences in the CSLB fraction. Image on the left has a CSLB fraction of 76% while the image on the right has a CSLB fraction of 32%.

Planned Activities

In the corrosion studies, researchers will screen new candidate materials, investigate water chemistry effects and the effect of radiation on oxidation, and investigate the long-term stability of oxides. They will examine continued efforts to optimize corrosion performance through surface modification and grain boundary engineering. Additionally, researchers will investigate the efficacy of pressurized tubes to study stress corrosion cracking.

For the stress corrosion cracking studies, alloys 316L and 690 will be irradiated at 500°C over a range of doses, providing the opportunity to determine the dose and temperature dependence of SCC of these alloys. Alloys D9 and 800H will be irradiated to 7 dpa at 400°C and 500°C to provide complementary data on these alloys. Also, researchers will complete CSLB optimization of alloys 690 and 316L and conduct SCC tests on unirradiated and irradiated samples to assess the effectiveness of CSLB enhancement in retarding IGSCC.

NUCLEAR ENERGY RESEARCH INITIATIVE

Validation and Enhancement of Computational Fluid Dynamics and Heat Transfer Predictive Capabilities for Generation IV Reactor Systems

PI: Robert E. Spall, Utah State University

Collaborators: Idaho National Laboratory (INL); Fluent, Inc.

Project Number: 05-160

Project Start Date: April 2005

Project End Date: April 2008

Research Objectives

There are two primary approaches for computational fluid dynamics (CFD) modeling of reactor systems: 1) thermal/hydraulic analysis codes such as RELAP, which model the entire plant using coarse nodes but cannot predict small-scale flow details, and 2) traditional CFD codes such as FLUENT, which are adept at detailed flow and temperature predictions, but only over specific regions. There are many unanswered questions regarding the ability of traditional codes to accurately model and predict complex flow patterns inherent in nuclear reactors, particularly turbulence. Turbulence is modeled either through direct numerical simulation (which is not practical for engineering design), large eddy simulation (LES), or Reynolds-averaged Navier-Stokes (RANS) equations. Because no single model can handle all geometries, research is needed to validate, modify, and improve CFD predictive capabilities.

This project will validate and improve CFD predictive methods for Generation IV nuclear reactor systems. Researchers will assess the ability of large eddy simulation and RANS closure models, which are available in the FLUENT code, to predict flows for specific, fundamental geometries inherent in advanced reactors. Based on the results of the assessment, researchers will modify the closure models to improve predictive capabilities and obtain experimental data for relevant geometries to support code validation.

Research Progress

RANS Solutions. Using the general purpose CFD solver FLUENT, the team solved the steady-state, three-dimensional RANS equations for the annulus/spacer geometry. They applied boundary conditions representing periodicity and symmetry conditions, where appropriate, to reduce the model cell count. The fine grid discretized model consisted of approximately 900,000 cells. Results were computed using five different turbulence models: 1) standard k-epsilon, 2) realizable k-epsilon, 3) shear stress transport (SST), 4) k-omega, and 5) $\upsilon^2 - f$. All turbulence models were integrated to the wall using a two-layer approach for the k-epsilon models. Comparisons between experimental data and numerical results were made at locations 32, 80, 200, and 320 mm downstream of a grid spacer (periodic with spacing of 440 mm and length of 40 mm).

Figure 1 shows the mean axial velocity profiles at streamwise location 32 mm. These results indicate that the k-epsilon and realizable k-epsilon models do a better job of predicting the experimental data than the other three models. In particular, the k-omega, SST, and $\upsilon^2 - f$ models each show a tendency to over predict velocities in

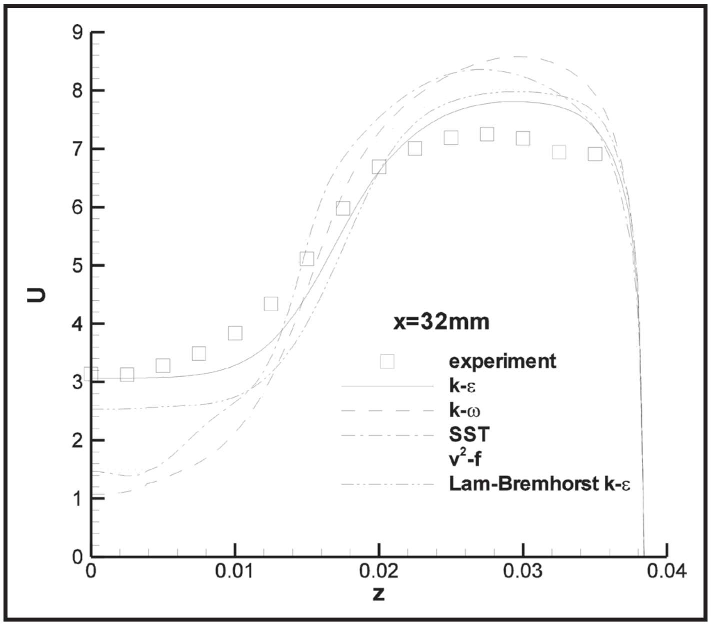


Figure 1. Axial velocity results on ymax plane between cylinders.

the narrow gap between the parallel cylinders and to over predict the length of the wake behind the spacer.

LES Solutions. Researchers have completed results for three Shehata/McEligot large eddy simulation runs and evaluated the following fluent models:

- Smagorinsky-Lilly
- Dynamic Smagorinsky-Lilly
- Wall-Adapting Local Eddy-Viscosity (WALE)
- Dynamic Kinetic Energy Subgrid-Scale

The Smagorinsky-Lilly model compares least favorably with other LES models and the experimental data. The predicted temperatures of the LES models, as shown on Figure 2, fall somewhat below the measured data, indicating excessive heat transfer at the wall. The results are an improvement over most two-equation turbulence models, but are not as good as the $\upsilon^2 - f$ model. Further, the LES approach requires an order of magnitude more computational time than the RANS solutions. The Smagorinsky-Lilly model will not be used in other LES calculations because of its predictive capabilities in the Shehata/McEligot runs.

Experiments. Work on the cylinder array is complete and a paper is currently under review with the *Journal of Fluids Engineering*. Researchers determined that turbulence is found in the flow at very small Reynolds number (< 2,000), and that the boundary layer transitions between 2,500 and 15,000. The team is currently constructing two other experiments. The first is the heated array of parallel jets. Considerable time and effort has gone into the design that must produce well-mixed, high- temperature air with low turbulence exiting into a quiencesent, room temperature air seeded with oil droplets for particle image velocimetry (PIV) measurements. The second experiment is a rounded exit jet made of quartz for use in the INL Matched Index of Refraction (MIR) facility. The model is complete and will be installed in the MIR facility in July 2007.

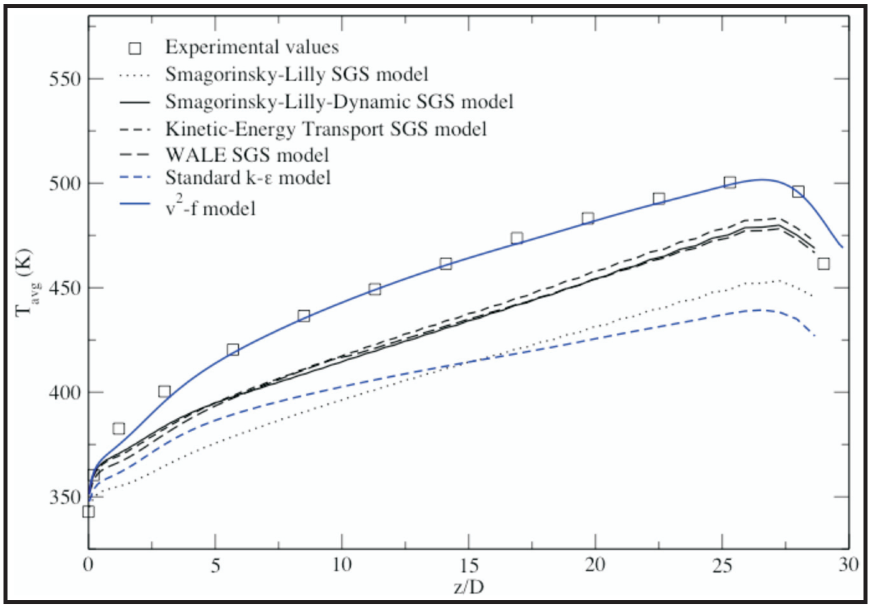


Figure 2. Wall temperature of four LES models, k-epsilon, and $\upsilon^2 - f$ RANS model.

Planned Activities

RANS. In terms of RANS solutions, researchers plan to complete results for the parallel jets case. In particular, results for parallel heated and unheated jet configurations will be obtained for several two-equation and second-moment closure turbulence models. Researchers will compare solutions with experimental results and make recommendations on which models have the capability to accurately predict these buoyancy-dominated flows.

LES. The cylinder array simulations have been started. Solutions at two different Reynolds numbers will be compared with the experimental results. In addition, work has begun to improve the LES models in FLUENT. Currently, the heat transfer model is based on a constant turbulent Prandtl number. Researchers are implementing a dynamic model in which the Prandtl number is dynamically computed from the filtered quantities, similar to the approach for calculating tubulent viscosity in the Smagorinksy model. They will then test if this approach can improve the heat transfer prediction for the LES models in FLUENT using constant and temperature-dependent properties.

Experiments. Researchers will perform 3-D, time-resolved PIV measurements of a strongly heated array of jets. Initally, they will take 2-D measurements in the streamwise plane. Once the nature of the flow is well established, 3-D measurements will be made in a cross stream plane. This will allow the researchers to examine the interaction between jets in real time.

The researchers will begin measuring the flow of a jet with a rounded and beveled exit at the MIR facility. They anticipate that the modified boundary condition will result in reduced steadiness of the jet and that this will be a strong function of Reynolds number for the rounded exit. This facility will allow the acquisition of 3-D, time-resolved data inside the rounded exit.

NUCLEAR ENERGY RESEARCH INITIATIVE

Ab-Initio-Based Modeling of Radiation Effects in Multi-Component Alloys

PI: Dane Morgan, University of Wisconsin–Madison

Collaborators: None

Project Number: 06-006

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The objective of this project is to develop a highly accurate, thermokinetic model for austenitic stainless steels based on fundamental quantum mechanical calculations. The model will incorporate the true temperature- and composition-dependence of the diffusion constants and provide missing information on interstitial motion.

In order to establish the critical data and computer programs to build the model, researchers will pursue the following specific objectives:

- Perform initial *ab-initio* calculations of atomic-scale properties in pure elements and alloys
- Develop iron-chromium-nickel (Fe-Cr-Ni) radiation-induced segregation (RIS) simulation and validation/refinement based on semi-analytic expressions for diffusion constants
- Develop Fe-Cr-Ni RIS simulation methods based on Monte Carlo techniques
- Perform validation/refinement by comparing analytical results to experiments
- Extend calculations and simulations to a preliminary ferritic Fe-Cr model

Research Progress

Over the past fiscal year, researchers focused on two aspects of the Ni-Cr binary alloy: 1) the thermodynamics of Ni-Cr, of which the most important property is the phase diagram, and 2) the kinetics of Ni and Cr hopping in a nickel-rich alloy environment. Following is a synopsis of the progress made in each of these areas.

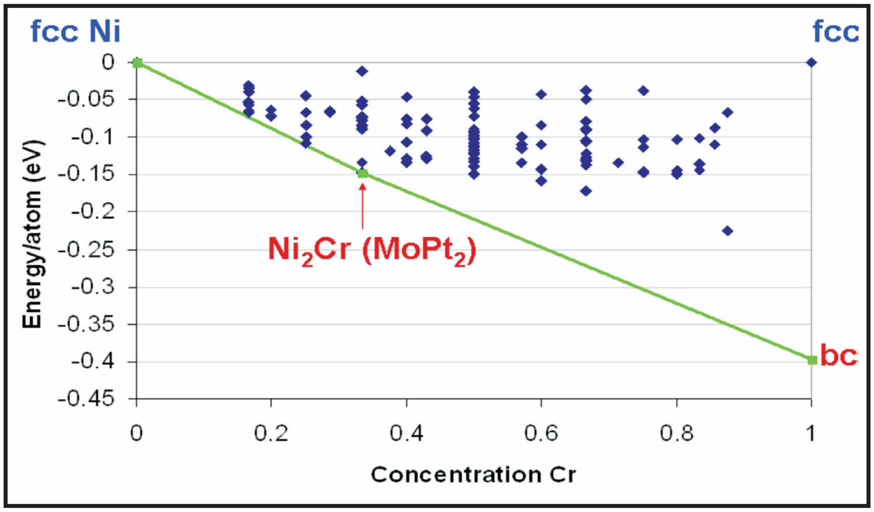


Figure 1. Formation energies for different configurations of Ni-Cr on an fcc lattice. Negative values demonstrate the strong ordering tendency. The convex hull with respect to bcc Cr shows that the correct MoPt$_2$ structure is predicted.

Thermodynamics. The first step to building a thermodynamic model is to determine the energetics of Ni-Cr alloys as a function of configuration. Researchers calculated over 100 different configurations, starting each with a ferromagnetic structure. Figure 1 shows that all the structures have a negative formation energy with respect to face-centered cubic (fcc) chromium, which demonstrates that Ni-Cr is a strongly ordered system on the fcc lattice. The chemical interactions between Ni and Cr will create ordering-type short-range-order, even in the high-temperature solid solution phase, giving a greater than random chance for Ni and Cr to be neighbors. When considering phase stability, the formation energies are more properly referenced to body-centered cubic (bcc) chromium, which is more stable than fcc Cr by about 0.4 eV.

The figure also shows that when bcc Cr is used as the end-member structure, the convex hull predicts that the system will have one ordered fcc phase—the $MoPt_2$ structure. This is very encouraging because experimental data also suggest that one fcc ordered phase with composition Ni_2Cr forms in the $MoPt_2$ structure. These energies will form the basis of a cluster expansion, which researchers will use with Monte Carlo to predict the full thermodynamics of the system.

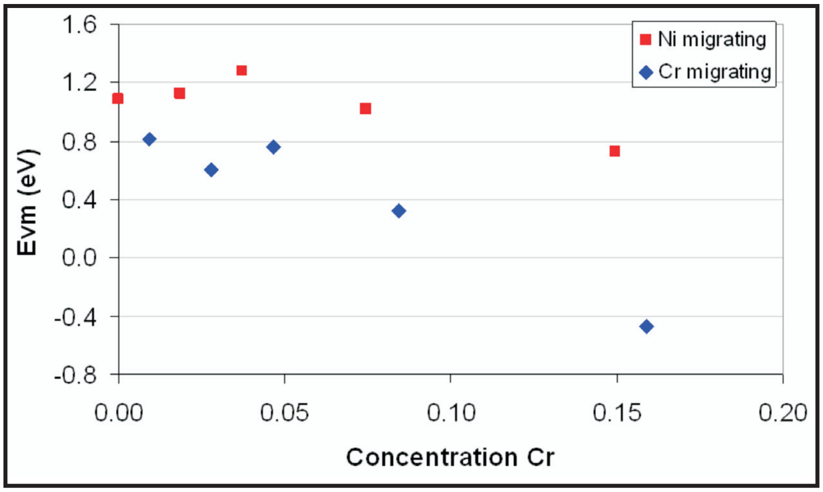


Figure 2. Energies of activated states for Ni and Cr in a Ni host with increasingly chromium-rich environment. Negative values due to an fcc lattice instability at high Cr content.

Kinetics. The first step in building the kinetics model is to determine the activation barriers to hopping as a function of local hopping environment. Barriers are found by comparing the energy of the hopping atom in an activated state half-way through the hop to the energy when the atom is on a lattice site. Researchers have found a number of barriers for different local environments and discovered very unexpected and complex behavior, as shown in Figure 2. These first results for Ni and Cr in a pure nickel environment (leftmost barriers) show that a barrier for Cr hopping is about 0.25 eV lower than for Ni, which suggests that major revisions to previous RIS models are necessary.

Researchers performed further calculations to explore how increasing the Cr concentration around the hopping atom can influence the barriers. The additional barriers in Figure 2 are for Ni and Cr hopping in environments that locally contain 2, 4, 8, and 16 Cr neighbors. As shown in Table 1, the Cr neighbors occupy the nearest-neighbor (NN) shells for the hopping atom activated state. The barriers show a noticeable decrease, particularly for Cr. In fact, the Cr activated state energy is actually negative for the most chromium-rich local environment. This does not indicate a negative hopping barrier, but that some instability has occurred that makes the Cr in the activated state more stable than on the usual fcc lattice.

Cr Neighbors	NN Shell Occupied
2	Part of 1st
4	All of 1st
8	All of 1st and 2nd
16	All of first three

Table 1. Nearest neighbor (NN) shells for hopping atom activated state.

Researchers believe that this dramatic change in energetics is due to the instability of chromium in the fcc structure. When the local environment is very Cr-rich, the system effectively behaves like Cr and tries to form some more stable structure than fcc. This effect occurs in pure fcc Cr as well. While such Cr-rich local environments are not expected experimentally, these studies demonstrate that the local chemistry can have a major impact on the hopping barriers. Researchers will use additional barrier calculations to fit a cluster expansion, which they will apply with analytic methods and Kinetic Monte Carlo (KMC) codes to predict the full kinetics of the system.

Planned Activities

Over the next fiscal year, researchers will continue this work with Ni-Cr to develop a semi-analytic model for diffusion constants to use in RIS modeling. This will be based on approximations of dilute solution in the Ni host and/or non-interacting solid solution models. They will then add in Fe and perform basic RIS simulations to refine the model and suggest further calculations. They will also begin to develop KMC codes and cluster expansions of the on-lattice and hopping energetics.

Through the remainder of the project, they will obtain full and accurate cluster expansions, complete the KMC codes, and combine them to derive improved diffusion constants. The temperature and composition-dependent diffusion constants will be used to study RIS in the Fe-Cr-Ni alloy.

Finally, researchers will further refine the models through extensive comparison to RIS simulations, using the results to explore the effects of RIS on voids through void growth modeling. If time permits, they will extend their approach to Fe-Cr ferritic model systems.

NUCLEAR ENERGY RESEARCH INITIATIVE

Managing Model-Data Introduced Uncertainties in Simulator Predictions for Generation IV Systems via Optimum Experimental Design

PI: Paul J. Turinsky, North Carolina State University

Collaborators: Argonne National Laboratory (ANL), Idaho National Laboratory (INL)

Project Number: 06-046

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The objective of this project is to understand and manage the uncertainties in modeling and simulation software that are caused by uncertainties in the underlying physical data in the software used to model and simulate the nuclear core of a proposed Generation IV reactor. In this project, researchers will optimize experiments by determining and quantifying the uncertainties of key design attributes and using INL's Zero Power Physics Reactor (ZPPR) facility as a test basis to reduce model data uncertainties. The team will then complete a pseudo-ZPPR experiment for the optimum design via simulation to determine observable values and use these values to obtain adapted nuclear data.

The goal of this project is to produce the following methodologies and results, each of which has merit as a stand-alone method or can be used collectively to optimize experimental design:

1) A methodology to determine covariance matrices for responses of a complex engineering system and an experimental system
2) A methodology to interpret experimental system results via adaptive simulation
3) A methodology to optimize the experimental configuration most economically appropriate for reducing the uncertainties of the complex engineering system
4) A covariance matrix originating from nuclear data uncertainties for the key design attributes of a Generation IV nuclear core
5) Optimum experimental system properties for a ZPPR experimental facility which are most appropriate for reducing the uncertainties of the key design attributes of a Generation IV nuclear core

Research Progress

During this reporting period, the researchers obtained the fast reactor system analysis codes MC2 and REBUS/DIF3D. They tentatively selected ANL's Advanced Burner Test Reactor (ABTR) core for analysis and have reestablished the ANL models for both the REBUS/DIF3D and MCNP codes. Researchers studied ANL core simulation software and sodium-cooled fast reactor design, obtaining additional insight into key design limiting responses by reviewing General Electric's S-PRISM documentation and a preliminary ABTR design report. They also reviewed past experimental data from the ZPPR facility to adjust cross section values.

Work has progressed on efficiently generating the homogenized few-group cross section covariance matrix from ENDF/B data, and to utilize these results to constrain adaptive simulation through few-group cross section adjustments. A side project addressed the design of an ABTR to minimize the power rating of the core, which will reduce ABTR total cost.

Planned Activities

Researchers will continue investigating the free design parameters and instrumentation options for a ZPPR core and will establish a neutronic model that will provide evaluation capabilities. They will also develop cost models for Generation IV core margin and ZPPR experiments, which will require the cooperation of the participating national laboratories and industry. The team will also develop the capability to evaluate the sensitivity coefficients and covariance matrix of the key design limiting responses of the Generation IV core.

NUCLEAR ENERGY RESEARCH INITIATIVE

Uncertainty Quantification in the Reliability and Risk Assessment of Generation IV Reactors

PI: Karen Vierow, Texas A&M University (TAMU)

Collaborators: The Ohio State University

Project Number: 06-057

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The goal of this project is to develop practical approaches and tools for dynamic reliability and risk assessment techniques, which can be used to augment the uncertainty quantification process in probabilistic risk assessment (PRA) methods for Generation IV reactors. The objectives of the project are 1) to develop practical approaches and computationally efficient software to test event tree completeness for Generation IV reactors, 2) integrate a reactor safety code with PRA, and 3) assess and propagate plant state uncertainties in the PRA analysis.

This project involves generating a practical dynamic event tree tool and assessing and quantifying uncertainty propagation. In Phase 1, current software for Dynamic Event Tree generation will be modified and linked to a best-estimate computer code (MELCOR for demonstration purposes). Key modeling uncertainties will be identified via the Phenomena Identification and Ranking Table (PIRT) technique. The integrated software package will be tested on selected, high-risk initiating events. In Phase 2, the computational efficiency will be improved by coupling the Dynamic Event Tree generation software with sampling software developed by Sandia National Laboratories. Finally, the new software will be tested for selected initiating events.

Research Progress

A computational infrastructure has been developed outside this NERI project that supports the generation of multiple dynamic event trees (DETs) on a distributed computing architecture composed of a heterogeneous collection of computational and storage nodes. The DET generation is managed by a Driver that 1) determines when branching is to occur, 2) initiates multiple restarts of system code analyses, 3) determines the probabilities of scenarios, 4) determines when a scenario can be terminated, and 5) combines similar scenarios to reduce the scope of the analysis.

A plant simulator (the MELCOR code for demonstration purposes) is used to follow the transient along each branch. Branches are pruned based on user-specified criteria to prevent numerical errors. Following are some significant features of the computational scheme:

- The scheme is designed for a distributed computing environment. The scheduler can track multiple branches simultaneously.
- The scheduler is modularized so that the branching strategy can be modified.
- A distributed database system manages data from the simulation tasks running on different computational nodes and stores the Accident Progression Event Tree (APET) structure. The database management system also allows any simulator output variable to be plotted during the run and enables construction of the APET during or after the runs.

Figure 1 provides a schematic overview of the infrastructure. Following an initiating event (or at any user-specified starting point during an accident progression), the Distributed Database Management System provides initiating conditions as well as the duration of the simulation (time parameters) to the Plant Simulator (SIM). The Driver runs the simulator until a stopping condition is reached. The Scheduler decides whether to branch or not depending on the information received from: 1) the Plant Simulator on setpoint crossing or equipment demand in general and 2) the Probability Module on the branch probability.

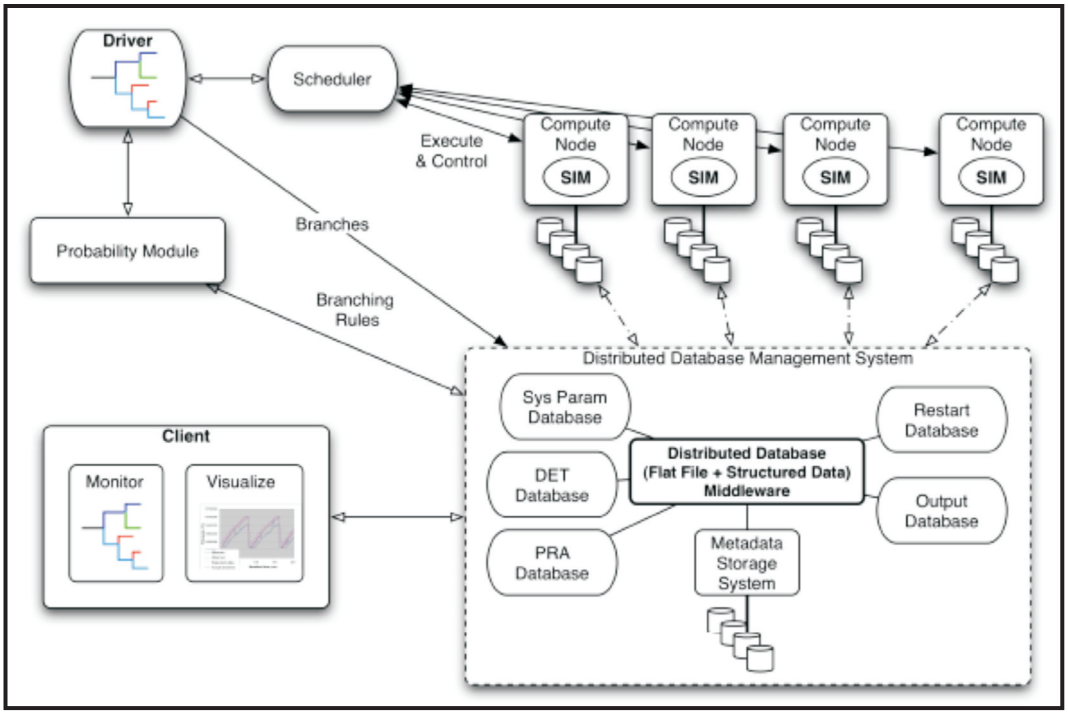


Figure 1. A schematic overview of the computational infrastructure.

The PRA Database contains data to quantify the likelihood that branches will be generated upon meeting certain branching criteria (e.g., crossing set points). The database can consist of minimum cut sets for the Top Events relevant to the branch in the form of binary decision diagrams for fast pre-processing or simply contain probabilities based on operational failure data. The branching probabilities (possibly obtained through preprocessing) are passed on to the Probability Module. If branching is initiated, the Scheduler then spawns a process to follow the branch. If the Scheduler receives other demands on equipment from the Plant Simulator while this process is running and decides on branching using the criteria above, then it can spawn as many processes as needed to follow the subsequent branches. The resulting tree structure, branch probabilities, and simulation results are sent to the Distributed Database Management System for possible post-processing and/or load distribution in a distributed computing environment.

The interface to the plant simulator (e.g., MELCOR) is abstracted to allow the use of different plant simulators with different computational models. The plant simulator needs to interface with the run-time system both 1) during execution for task branching and migration and 2) before and after execution to load and store its state and results.

The Driver communicates with the Distributed Database Management System to retrieve and store the necessary input and output files. That is, the Driver stages the necessary input files before executing the plant simulator. After completing the execution, the Driver stores the output files generated by the plant simulator on the Distributed Database Management System. The storage nodes of the distributed database do not need to be different than the compute nodes.

Key uncertainties in Generation IV modeling of reactor events are being identified via the PIRT technique. The Depressurized Loss of Forced Cooling (DLOFC) scenarios may present some of the most significant uncertainties with respect to fuel modeling, although the PIRT process is in the beginning stages.

A MELCOR input deck for a Pebble Bed Modular Reactor was developed outside of this NERI project. Additional uncertainties were identified during the deck development process but they were not quantified. These uncertainties are being further considered, including heat transfer coefficients in pebble beds, fuel properties, and boundary conditions.

Planned Activities

- Install the computational infrastructure on TAMU clusters
- Develop a graphical user interface (GUI) for on-line management of DET generation
- Complete determination of key modeling uncertainties
- Model key uncertainties for a representative Generation IV plant through best estimate code input
- Link computational infrastructure and input deck
- Test the software integration to consist of validation and verification exercises
- Prepare documentation for the user's manual
- Quantify modeling uncertainties for a reference Generation IV reactor
- Discuss software coupling with best estimate codes other than the demonstration code

An Advanced Neutronic Analysis Toolkit with In-line Monte Carlo Capability for VHTR Analysis

PI: William R. Martin, University of Michigan

Collaborators: Studsvik of America, Idaho National Laboratory, Los Alamos National Laboratory, General Atomics, Oak Ridge National Laboratory, and TransWare Enterprises, Inc.

Project Number: 06-068

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The goal of this project is to develop a lattice physics code for very high-temperature reactor (VHTR) neutronic design and analysis. This approach takes advantage of the highly developed capabilities available for light water reactor (LWR) neutronic analysis, in which lattice physics codes generate effective cross sections at the assembly level. Researchers can use these cross sections in nodal codes to efficiently calculate global flux/power distributions and effective multiplication (k_{eff}) as a function of fuel depletion and temperature.

This project will establish “proof of principle” by incorporating the nodal Monte Carlo capabilities of the MCNP5 code directly into the lattice code, CPM-3. The team will accomplish code linkage through an interface that also enables extension to other cross-section generation codes. This will be demonstrated by linking MCNP5 to CASMO-4. The final package will incorporate the substantial downstream capabilities of CASMO-SIMULATE, such as cross-section generation for global nodal analysis and depletion, systematic preparation of cross-section sets for accident analysis, and efficient fuel cycle analyses and assessment of alternative fuel management schemes. The final result will be a validated neutronics methodology for VHTR design and analysis, including cross-section generation, global reactor analysis, depletion, and fuel management.

The primary objectives are listed below:

- Develop an application program interface (API) to couple a collision probability code (CPM-3) and MCNP5 for analyzing VHTR configurations
- Demonstrate "proof of principle" of the coupled CPM-3/MCNP5 methodology by implementing and testing on a suite of selected benchmark problems
- Apply the coupled CPM-3/MCNP5 methodology to a Deep Burn configuration and assess its capability to treat low-lying resonances of plutonium isotopes; adapt the methodology as needed to handle these important resonances
- Demonstrate the capability of using the API with a production lattice physics code by coupling MCNP5 and CASMO-4 and evaluating with the test suite
- Verify and validate the coupled CPM-3/MCNP5 methodology for simple VHTR configurations, critical experiments, and startup/operational data from Fort St. Vrain and Peach Bottom
- Assess the applicability of the coupled methodology to analyze pebble bed configurations

Research Progress

The research team has made progress toward meeting all three of their first-year objectives:

- Design the API
- Modify CPM-3 to accommodate the API
- Determine the validation test suite for the modified version of CPM-3

Following is an overview of their specific accomplishments.

Application Program Interface. Researchers have designed a basic architecture for coupling a CPM-3 and MCNP5 using a master process to organize the communications. An input file, including metadata intended for non-CPM-3 parts of the system, will be read

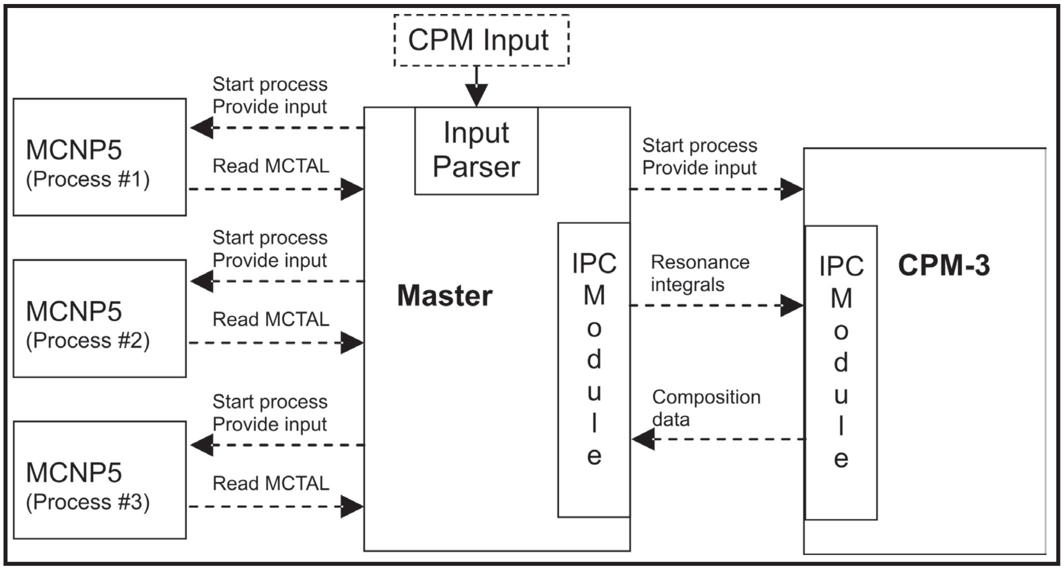


Figure 1. Application program interface.

by a parser module that creates the data structures needed to write CPM-3 input and an MCNP5 input deck that models the same cell geometry. Although specific to CPM-3, the parser can be replaced ones for other collision probability codes. Figure 1 is a schematic of the basic architecture for coupling CPM-3 and MCNP5.

The modified CPM-3 code will contain a module to compute the resonance integrals and other group data, calling back to the master process through an interprocess communications channel. The modification to the collision probability code is limited to the routine needed to compute the resonance integrals at each burnup step. This involves a lightweight interprocess communications protocol that transmits nuclide-by-nuclide composition change data back to the master process and receives the MCNP5 computed resonance integrals in response.

The master process receives the data at each burnup step and generates MCNP5 input needed to perform accurate cell calculations. The master can start several MCNP5 processes in a parallel environment to perform this calculation and read an MCTAL file to collect the data needed to compute the resonance integrals. These data are then transmitted to the waiting CPM-3 process for the next burnup step.

Modification of CPM-3. Researchers have examined the CPM-3 code and manuals, as well as the documentation for NJOY, to decide the most promising approach for integrating with MCNP5 to analyze VHTR configurations. The following coupling approach will be taken:

- CPM-3 will perform its calculation of the VHTR geometry assuming homogenized TRISO fuel. Since the resonance self-shielding is important, this calculation will be performed by MCNP5.
- MCNP5 will simulate the same geometry as CPM-3 and will predict the resonance group absorption rate, denoted R_{ig}^{res}. The TRISO fuel will be modeled explicitly, accounting for the microspheres. MCNP5 will also tally the fine group flux ϕ_g for group g.
- The microscopic absorption cross section for resonance group g and resonance isotope i is then computed using the MCNP5 results:

$$\sigma_{ig} = \frac{R_{ig}^{res}}{\phi_g}$$

These microscopic cross sections will account for TRISO fuel self-shielding and may be used directly for the remainder of the CPM-3 calculation during the current depletion step.

Verification and Validation. General Atomics will provide data regarding their modular helium reactor (MHR) design and the Fort St. Vrain plant, including predicted results and few-group cross sections. This data will be compared with coupled MCNP5/CPM-3 results.

Researchers are developing several VHTR benchmark cases, including full-core geometries with homogeneous and heterogeneous fuel blocks. This will test the methodology for handling the double heterogeneity of TRISO fuel.

Researchers have almost completed benchmarking MCNP5 for Windows and Mac G5 platforms. The latter may be needed for full-core depletion runs with MCNP5, at least the benchmark calculations for comparison to the coupled methodology being developed by this project.

Planned Activities

Researchers plan to accomplish the following activities in the next period:

1) Before developing the API, simulate its functions by hand, modifying CPM-3 to read resonance integral data from an external source for a single burnup step and run MCNP5 by hand to compute the needed resonance integral data. Since CPM-3 is an LWR code, the first benchmark attempt will use a LWR lattice, including pin cell and assembly configurations, comprising a "sanity check" for the approach.
2) Test the hexagonal geometry option in CPM-3 with a simple homogeneous hexagonal fuel block geometry and compare the results to MCNP5.
3) Repeat the "hand approach" for a hexagonal configuration, using both homogeneous fuel and heterogeneous fuel, and compare the results to MCNP5.
4) Initiate development of the API following the "hand approach" effort.
5) Compare coupled methodology using the API to the results of the "hand approach."
6) Initiate discussions with Studsvik-Scandpower regarding use of CASMO-4 as the lattice physics code.
7) Set up validation test problems with General Atomics' assistance and perform MCNP5 benchmark calculations of these problems.
8) Set up and run VHTR benchmark cases with MCNP5 and the coupled methodology.

Improving Corrosion Behavior in SCWR, LFR, and VHTR Reactor Materials by Formation of a Stable Oxide

PI: Arthur T. Motta, Pennsylvania State University

Collaborators: Westinghouse Electric Company, Los Alamos National Laboratory, University of Wisconsin, University of Michigan

Project Number: 06-100

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The objective of this project is to establish a technical basis for corrosion protection of candidate materials for three different types of reactors: 1) the supercritical water reactor (SCWR), 2) the lead-fast reactor (LFR), and 3) the very high-temperature reactor (VHTR). Researchers will study ferritic-martensitic steels, austenitic alloys, and nickel-based alloys. In order to understand the mechanisms for corrosion behavior in these materials, they will conduct a systematic study on the nature of protective films formed during corrosion tests in simulated reactor environments.

The overall objective is to understand why certain alloys exhibit better corrosion behavior than others by examining the oxide microstructure. Alloys that resist corrosion develop a protective oxide layer that limits the access of corrosive species to the underlying metal, leading to stable oxide growth. The differences between a protective and a non-protective oxide are determined by the alloy chemistry and microstructure. Very small changes in microstructure can significantly affect corrosion rate.

Researchers will use two techniques to study the oxide microstructure: 1) microbeam synchrotron radiation (X-ray) diffraction and fluorescence, and 2) cross-sectional transmission electron microcopy (TEM) on samples prepared with a focused ion beam. X-ray diffraction and fluorescence examination, using the synchrotron X-ray beam, can resolve the crystal structure, texture, and composition of oxide layers at the sub-micron level. By complementing this examination with transmission electron microscopy, researchers will precisely determine the structure of these layers and their impact on the corrosion behavior of the alloys.

Research Progress

During the first year, researchers examined oxide layer samples using various techniques, including microbeam synchrotron radiation diffraction and fluorescence from the Advanced Photon Source (APS) at Argonne National Laboratory. Figures 1–3 show preliminary examples of the results of these measurements. Figure 1 is a metallographic cross section of an oxide formed on 9Cr oxide dispersion strengthened steel (ODS) during exposure to supercritical water, showing four distinct layers. Figure 2 shows the X-ray fluorescence intensities obtained by rastering a micro X-ray beam (0.2 micron) from the metal to the outer surface of the oxide. It is clear that the diffusion layer in the metal is depleted in chromium (Cr), the inner layer is Cr-enriched, and the outer layer is almost pure iron (Fe).

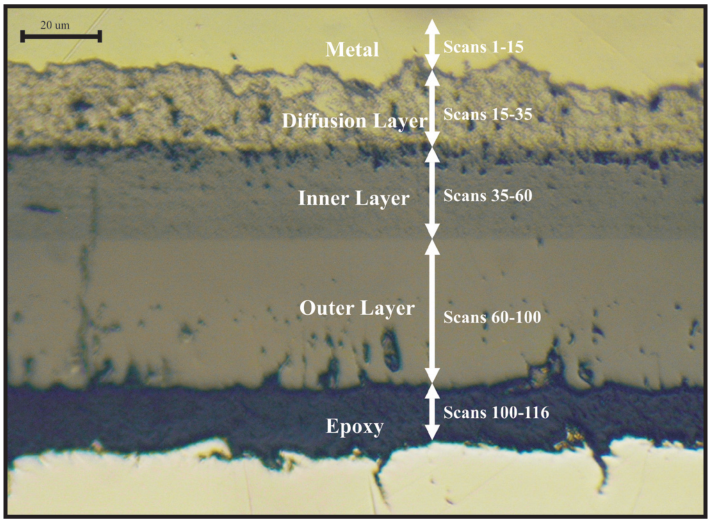


Figure 1. Metallographic cross section of oxide formed on 9 Cr ODS steel when exposed to supercritical water, showing four distinct layers.

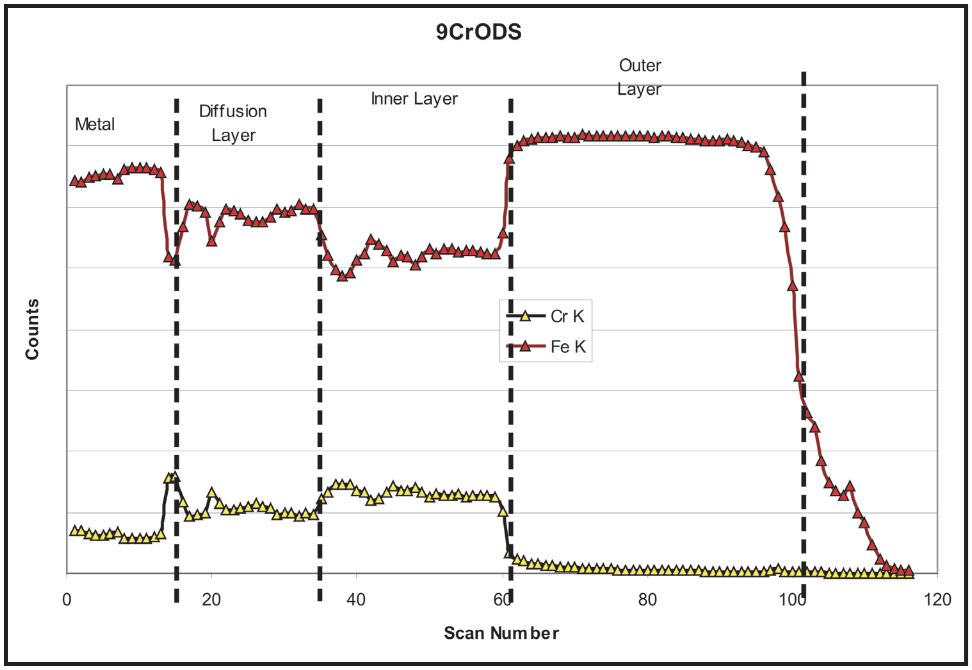


Figure 2. Iron and chromium K_α fluorescence intensity versus position in the oxide (for the layers shown in Figure 1) obtained using microbeam synchrotron radiation and fluorescence at APS.

While conducting the fluorescence measurements, researchers simultaneously obtained diffraction patterns for each location. Figure 3 shows a few of the 200+ diffraction patterns obtained for this oxide layer sample—different colors represent each of the four layers. The indexing of the peaks reveals that only body-centered cubic (bcc) Fe peaks are visible in the metal layer and in the diffusion layer. Some oxide intensity starts to appear towards the end of the diffusion layer, nearer the inner oxide interface.

These oxide peaks can be indexed as the spinel ($FeCr_2O_4$) phase in the inner layer, and as magnetite (Fe_3O_4) in the outer layer. These results agree with previous examinations of similar oxide layers.

Planned Activities

For the next year, researchers will continue to analyze the oxide layers using both microbeam synchrotron radiation diffraction and fluorescence and transmission electron microscopy. They are preparing cross-sectional TEM samples using focused ion beam to examine microstructure details in these oxide layers. Further examinations will be performed using microbeam synchrotron radiation diffraction and fluorescence. Using these techniques, they will determine the phases present, chemical composition, grain sizes, etc., in the oxide layers formed on various alloys in the three environments being considered (i.e., supercritical water, lead-bismuth, and the very high-temperature reactor). They will analyze these results and correlate them to the corrosion behavior to understand the mechanisms for protecting and forming stable oxide growth.

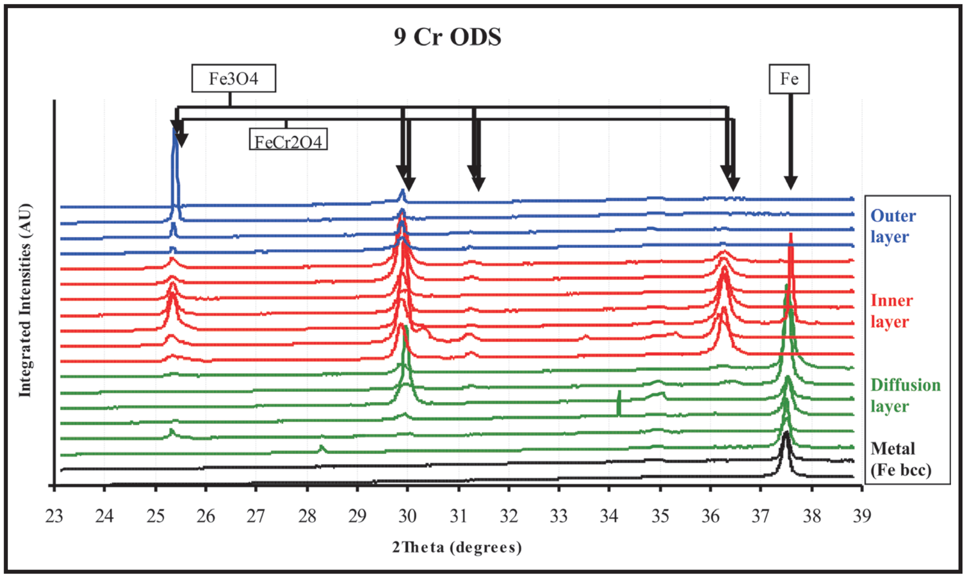


Figure 3. Diffraction intensity versus two-theta angle for oxide layer formed on 9 Cr ODS steel exposed to supercritical water. The scans are: *black*–base metal; *green*–diffusion layer in the metal; *red*–spinel rich oxide inner layer; and *blue*–outer oxide layer. The diffraction peaks are indexed as shown.

Multi-Scale Modeling of the Deformation of Advanced Ferritic Steels for Generation IV Nuclear Energy

PI: Nasr M. Ghoniem, University of California, Los Angeles (UCLA)

Collaborators: California State University, Northridge (CSUN)

Project Number: 06-109

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The objective of this project is to use the multi-scale modeling of materials (MMM) approach to develop an improved understanding of the effects of neutron irradiation on the mechanical properties of high-temperature materials at elevated temperatures of 650-700°C, compared to the current 550°C limit. To date, there are no physically based models for high-temperature, in-reactor deformation of advanced ferritic/martensitic steels. The objective of this project is to develop such a model.

Empirical potentials are not well developed for alloys and cannot easily adapt to local changes in chemistry caused by impurities. In this project, researchers developed a hybrid *ab-initio* continuum model to describe the core of dislocations in iron. The model allows researchers to study the dislocation of core structures in steels, without *ad hoc* assumptions of interatomic forces. This model will be applied to determine the core structure of screw dislocations in iron (Fe) and the interaction between dislocations and oxide and carbide precipitates, which control the ductility and high-temperature strength of steels. Dislocation Dynamics models simulate the mechanical properties of radiation-damaged steels as a function of the neutron dose.

Researchers will also develop single dislocation interaction with nano-voids, precipitates, and self-interstitial atom (SIA) clusters during irradiation. This information will be used in a comprehensive rate theory model of radiation damage and in-reactor deformation. Predictions will be made for in-reactor deformation, with full microstructure information linked with the deformation field.

Research Progress

Ab-Initio Modeling. At low temperatures, plasticity in body centered cubic (bcc) Fe is governed by low mobility screw dislocations with Burgers vector **b**= 1/2a<111>. It is generally believed that the core structure of these dislocations in bcc metals is a controlling factor of their mobility. For the non-magnetic bcc tantalum (Ta), theoretical studies have led to two types of core structures: asymmetric core and symmetric core. To date, the dislocation core structure of bcc Fe has not been studied, except by using empirical interatomic potentials which cannot accurately capture the additional complication arising from the presence of magnetism. Furthermore, the interaction between dislocations and solute atoms is of great interest since it determines one of the important strengthening mechanisms in ferritic steel alloys, the so-called "solid solution hardening" (SHH).

Researchers are carrying out a comprehensive investigation of the 1) dislocation core structure in Fe and 2) the effect of impurities on the dislocation core properties using a hybrid approach based on the Peierls-Nabarro model for non-planar core, which couples continuum linear elasticity and first principles electronic structure calculations. As a first step, the dislocation core of a screw dislocation can be described by the displacement of the atomic rows along the dislocation line. The interatomic row potential is assumed to be a function only of the relative atomic positions, u, and composed of the first and second terms in the Fourier expansion:

$$\Phi(u)=\frac{\Phi_0}{(1-4\alpha)}\left(\cos\left(\frac{2\pi u}{b}\right)-\alpha\cos\left(\frac{4\pi u}{b}\right)+\frac{1}{2}(1-\alpha)\right) \quad (1)$$

where b is the Burgers vector, and the parameter Φ_0 is determined by the magnitude of the potential at u=0 and $\alpha=0$. The parameter α describes the deviation of Φ(u) from a sinusoidal form. The average variation under the atomic row shift along <111>, $\Delta E_{row} = 3[\Phi(u - 1/3) + \Phi(u + 1/3)]$, may be calculated using high-accuracy, first-principles, electronic structure methods.

Researchers have carried out total-energy calculations using the VASP code with the generalized gradient approximation (GGA) for the exchange-correlation potential. The atomic row displacement energies were calculated for a shift of a single atomic row along the <111> direction using super-cells consisting of 5 layers and 8 atoms with vectors $\mathbf{a}_1 = (2, -2\sqrt{2}, 0)a$, $\mathbf{a}_2 = (1,\sqrt{2},0)a$, and $\mathbf{a}_3 = (0, 0, 4\sqrt{2})a$, where a is the lattice constant.

Figure 1 shows that the energy changes for displacement of a single atomic row along <111> were calculated for molybdenum (Mo) and Fe. Interestingly, the atomic row energy decreases from Mo to Fe and changes the curve toward sinusoidal. Both of these effects can result in a significant reduction of the Peierls stress itself and even in a transformation from isotropic to anisotropic (degenerate) core structures.

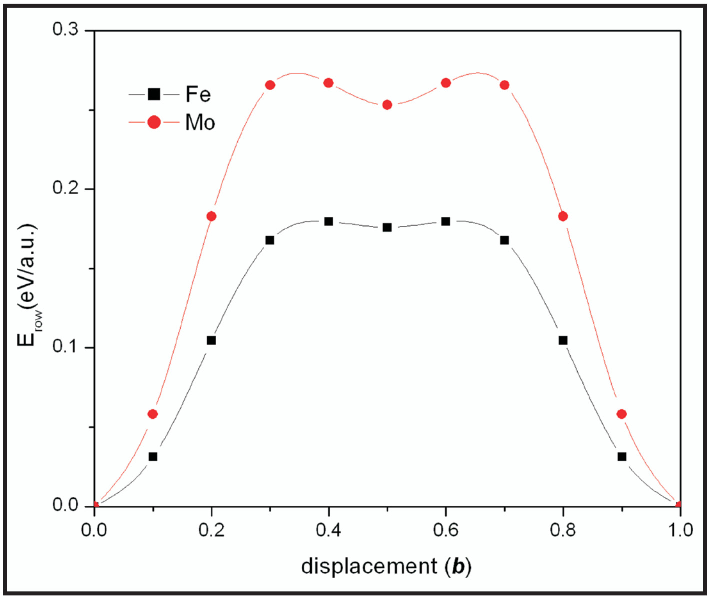


Figure 1. The atomic row energies for a shift of the atomic row along the <111> versus displacement in units of the Burgers vector ½<111> for Mo and Al.

Dislocation Dynamics Modeling. This part of the research investigates fundamental aspects of the dynamics of dislocation interaction with radiation-induced defect clusters, specifically with both glissile and sessile SIA clusters in defect clouds formed along grown-in dislocations. Researchers developed kinetic Monte Carlo (KMC) simulations that describe the formation of SIA cluster clouds during neutron irradiation in bcc Fe and their evolution kinetics. The main thrust of these simulations is to determine the size and space distribution of SIA clusters in the cloud region at a variety of displacement damage doses, taking both edge and screw dislocations into account. These results will be used as input to Parametric Dislocation Dynamics (PDD) simulations to determine the mechanisms and the critical stresses of dislocation unlocking from defect atmospheres.

The motion and interaction of SIA clusters can lead to the formation of rafts of small dislocation loops and decoration of dislocations. The multiplication and movement of these free dislocations and the resulting dislocation-dislocation interactions lead to work hardening as plastic deformation continues. Researchers first considered the models that involve the interaction between an edge dislocation and a number of SIA clusters. A computational cell of 300a × 300a × 300a (a = 0.2867 nm, the lattice constant of iron) was used with periodic boundary conditions. An edge dislocation with **b** = a/2[-111] lying on a (101) plane was inserted in the simulation box.

Researchers also performed KMC simulations for microstructure evolution in pure iron irradiated at 300K to displacement dose in the range of 2×10^{-4} - 2×10^{-3} dpa. A fixed initial number of SIA clusters with a size distribution obtained from molecular dynamics (MD) simulations and corresponding to damage dose levels of 2×10^{-4}, 4×10^{-4}, 0.001, and 0.01 dpa, respectively, were introduced randomly into the simulation cell. Figure 2 shows a comparison between the experimentally measured yield stress and the equivalent uniaxial tensile stress, computed from the present simulations. Researchers obtained general agreement between their simulations and experimental results.

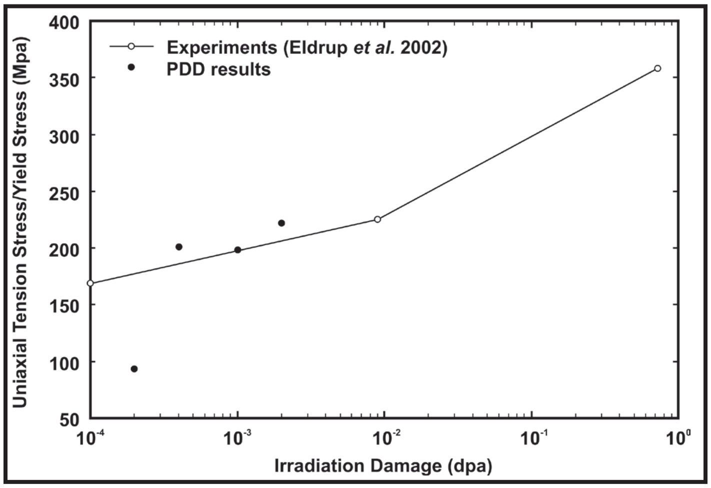


Figure 2. Equivalent uniaxial tension stresses calculated from the results of the PDD simulations and yield stresses obtained by experiments by Eldrup et al.

Constitutive & Crystal Plasticity Modeling. This task will develop an understanding of the mechanical behavior and dislocation microstructure evolution of single and polycrystals, and delineate between the physical and mechanical origins of spatially localized plastic deformation. Traditional approaches to the study of plastic instabilities have either been based on kinematics considerations, such as finite strain effects and geometric softening, or physics-based concepts. In this study, researchers are developing a framework that combines both approaches.

A rate-independent crystal plasticity model was developed to incorporate micromechanics, crystallinity, and microstructure into a continuum description of finite strain plasticity. A comprehensive dislocation density model based on rate theory was employed to determine the strain hardening behavior within each plastic slip system for the face centered cubic (fcc) crystal structure. Finite strain effects and the kinematics of crystal plasticity are coupled with the dislocation-density-based model via the hardening matrix in crystal plasticity. ABAQUS/CAE is employed as a finite element method (FEM) solver, and several user subroutines were developed to model fcc crystals with 2 and 12 slip systems. The developed material models were applied to study single and polycrystal deformation behavior of copper. Interfaces between the ABAQUS user's subroutine Umat and the ABAQUS main code were developed to allow further extension of the current method. Simulations carried out for polycrystals clearly illustrate the heterogeneous nature of plastic strain and the corresponding spatial heterogeneity of the mobile dislocation density. The origins of the spatial heterogeneities are essentially geometric, as a result of constraints on grain rotation (finite strain effects), geometric softening due to plastic unloading of neighboring crystals. The physical origins of plastic instabilities manifest themselves in the coupling between the dislocation densities and the localized kinematically induced softening.

Planned Activities

Following is a summary of activities planned for the next fiscal year.

1) *Ab-Initio* Modeling
    - Determine the core structure and Peierls Stress for pure Fe
    - Determine the effect of impurities on the core structure
    - Construct the two-dimensional Peierls potential
2) Dislocation Dynamics Modeling
    - Determine the dynamics of moving dislocations and static SIA cluster atmospheres in bcc iron
    - Determine the dynamics of moving dislocations and mobile SIA cluster atmospheres in bcc iron
    - Conduct DD simulations of the collective motion of large numbers (over several thousand) SIA clusters and move dislocations to investigate SIA cluster patterns in irradiated iron
    - Determine the effective velocity of dislocations as they interact with SIA cluster clouds
3) Constitutive & Crystal Plasticity Modeling
    - Further develop a rate theory model for dislocation populations in irradiated Fe
    - Include spatial gradient effects in the rate theory model of dislocation populations
    - Develop a crystal plasticity framework that includes dislocation populations in the FEM solutions
    - Apply the crystal plasticity model to single and bi-crystals

NUCLEAR ENERGY RESEARCH INITIATIVE

An Advanced Integrated Diffusion/Transport Method for the Design, Analysis, and Optimization of Very High-Temperature Reactors

PI: Farzad Rahnema, Georgia Institute of Technology

Collaborators: Idaho National Laboratory

Project Number: 07-003

Program Area: Generation IV

Project Description

The main objective of this research is to develop an integrated diffusion/transport method to substantially improve the accuracy of nodal diffusion methods for the design and analysis of very high-temperature reactors (VHTR). Because of the presence of control rods in the reflection regions in the Pebble Bed Reactor (PBR-VHTR), traditional nodal diffusion methods will not accurately model these regions, within which diffusion theory breaks down in the vicinity of high neutron absorption and steep flux gradients. The proposed IDT method will use a local transport solver based on a new incident flux response expansion method in the controlled nodes. Diffusion theory will be used in the rest of the core. This approach will improve the accuracy of the core solution by generating transport solutions of controlled nodes while maintaining computational efficiency by using diffusion solutions in nodes where such a treatment is sufficient. The transport method will initially be developed and coupled to the reformulated 3-D nodal diffusion model in the PEBBED code for PBR core design and fuel cycle analysis.

This method will also be extended to the prismatic VHTR. It is expected that the new method will accurately capture transport effects in highly heterogeneous regions with steep flux gradients. The calculations of these nodes with transport theory will avoid errors associated with spatial homogenization commonly used in diffusion methods in reactor core simulators.

Work Scope

This project will accomplish the following primary objectives:

- Develop a 2-D cylindrical integrated diffusion/transport (IDT) method
- Extend the IDT method to whole core calculations in 3-D cylindrical geometry for the pebble bed design option of the VHTR
- Develop a new 2-D response function transport method for coupling to the reformulated diffusion method in hexagonal geometry for the prismatic design option of the VHTR
- Develop 2-D/3-D VHTR benchmark problems

NUCLEAR ENERGY RESEARCH INITIATIVE

Implications of Graphite Radiation Damage on the Neutronic, Operational, and Safety Aspects of Very High-Temperature Reactors

PI: Ayman I. Hawari, North Carolina State University

Collaborators: Idaho National Laboratory, Oak Ridge National Laboratory

Project Number: 07-011

Program Area: Generation IV

Project Description

This project entails experimental and computational investigations to study the radiation effects of graphite in very high-temperature reactors (VHTR). Researchers will use molecular dynamic and *ab-initio* molecular static calculations to 1) simulate radiation damage in graphite under various irradiation and temperature conditions, 2) generate the thermal neutron scattering cross sections for damaged graphite, and 3) examine the resulting microstructure to identify damage formations that may produce the Wigner effect.

In both the prismatic and pebble bed VHTR designs, the graphite moderator is expected to reach exposure levels of 10^{21} to 10^{22} n/cm^2 over the lifetime of the reactor, resulting in damage to the graphite structure. However, studies of irradiated graphite show changes in the thermal conductivity and heat capacity at fluences less than 10^{21} n/cm^2. These properties depend on the behavior of atomic vibrations (phonons) in the graphite solid. Therefore, it can be expected that any alterations in phonon behavior that would produce changes in these properties would impact thermal neutron scattering, with implications for the neutronic and safety behavior of the VHTR. Another important phenomenon pertains to published data showing that a high-temperature (>1,200°C) Wigner-like effect may exist in graphite. If confirmed, this effect would have direct implications on the safety behavior of VHTRs.

Work Scope

The primary objectives will be accomplished through the following tasks:

- Simulate atomic collision cascades in graphite using a realistic VHTR neutron spectrum
- Study damage cascades using the calculated PKA spectrum and molecular dynamics and kinetic Monte-Carlo simulations
- Calculate dispersion relations and obtain vibrational (phonon) frequency distributions
- Calculate thermal neutron scattering cross sections of imperfect graphite
- Determine the stored energy of irradiated graphite samples using differential annealing measurements and compare to simulated values
- Assess phonon density of states
- Perform structure studies, comparing irradiated and unirradiated graphite samples
- Use analysis codes to assess the neutronic, operational, and safety aspects of the VHTR

Advancing the Fundamental Understanding and Scale-up of TRISO Fuel Coaters via Advanced Measurement and Computational Techniques

PI: Muthanna Al-Dahhan, Washington University

Project Number: 07-017

Collaborators: None

Program Area: Generation IV

Project Description

Defect-free tri-isotropic (TRISO) fuel particle coating is critical for the future use of nuclear energy produced by advanced gas reactors (AGRs). The quality of coating applied to the fuel kernels is impacted by the hydrodynamics, solids flow field, and flow regime characteristics of the spouted bed coaters, which are influenced by design parameters and operating variables. This work is to advance the fundamental understanding of the hydrodynamics of TRISO fuel particle spouted bed coaters by investigating the effect of design and operating variables, evaluating the reported dimensionless groups as scaling factors, and establishing a reliable scale-up methodology that accounts for the effects of particle-particle interactions and thermal expansion of the gas phase. Researchers will also develop a non-invasive measurement technique based on gamma ray densitometry that can be used for coater process monitoring to ensure proper performance and operation and to facilitate the developed scale-up methodology.

To achieve the objectives, researchers will measure critical parameters of the spouted bed using gamma ray computed tomography and computer automated radioactive particle tracking, as well as gas dynamic measurement techniques, optical probes, and pressure transducers. These measurements will be used as benchmark data to evaluate and validate the computational fluid dynamic (CFD) models two-fluid and discrete particle models and their closures. The validated CFD models and closures will be used to develop a methodology for scale-up, design, and hydrodynamic similarity and to further optimize the process performance of TRISO coaters under different conditions.

Work Scope

This project will perform the following primary tasks:

- Develop on-line and non-invasive techniques for process monitoring and measurement
- Conduct Gamma Ray Computed Tomography (CT), pressure drop fluctuation, and optical probe measurements and investigation
- Perform Computer Automated Radioactive Particle Tracking (CARPT) measurements
- Perform gas dynamic measurements and investigations
- Conduct computational fluid dynamics (CFD) studies
- Simulate real TRISO fuel particle coaters using CFD
- Investigate mimic TRISO fuel particle coaters using the above techniques and models

Fission Product Transport in TRISO-Coated Particle Fuels: Multi-Scale Modeling and Experiment

PI: Izabela A. Szlufarska, University of Wisconsin-Madison

Collaborators: None

Project Number: 07-018

Program Area: Generation IV

Project Description

The objective of this project is to develop a multi-scale computational model of transport of fission products through tri-isotopic (TRISO)-coated particles. This model will be capable of predicting diffusion constants and concentration profiles based on experimental images of the coating's microstructure. Researchers will employ this model to discover mechanisms underlying fast diffusion of silver through silicon carbide layer, which is a primary barrier for fission products.

Previous models did not take into account the details of the underlying silicon-carbide (SiC) microstructure. The pathway of silver (Ag) transport in the SiC layer is likely to be governed by grain boundary diffusion, which researchers will by model through the molecular dynamics (MD) technique. Simulated microstructures will be benchmarked against experimental results. The MD-derived diffusion constants will be compared to diffusion constants calculated from kinetic Monte Carlo and based on energy barriers estimated in full *ab initio* calculations for select microstructures. The diffusion constants will be optimized based on both of these methods and incorporated into diffusion equations, which will be then employed to predict silver concentration profiles in experimental structures derived from transmission electron microscopy (TEM) images. In order to validate the model, predicted concentration profiles will be compared to experimental profiles determined by means of electron backscatter diffraction (EBSD). This approach will provide a reliable model for transport based solely on the fuel microstructure, with little reliance on historical measurements of diffusion.

Work Scope

This project consists of the following primary tasks:

- Set up atomistic models of SiC bulk and grain boundaries (MD simulations)
- Perform *ab initio* calculation of diffusion in bulk crystalline SiC
- Fit Ag-SiC potential (*ab initio*, MD) and implement into MD code
- Build diffusion couple apparatus and perform initial EBSD characterization of SiC
- Initiate diffusion equation framework
- Conduct MD simulations of diffusion pathways and activation energies
- Perform *ab initio* calculations of activation energies for diffusion along grain boundaries
- Develop KMC model
- Perform heat treatments and initial EBSD characterization on diffusion couples; continue diffusion equation framework
- Develop KMC model and perform simulations of diffusion along grain boundary
- Complete EBSD characterization and perform TEM examinations of selected samples
- Set up SiC specific diffusion equations and calculate diffusion profiles in experimentally derived structures

NUCLEAR ENERGY RESEARCH INITIATIVE

Emissivity of Candidate Materials for VHTR Applications: Role of Oxidation and Surface Modification Treatments

PI: Kumar Sridharan, University of Wisconsin-Madison

Collaborators: None

Project Number: 07-020

Program Area: Generation IV

Project Description

In this project, researchers propose to: 1) Evaluate emissivities of candidate ferritic and austenitic alloys for the reactor pressure vessel (RPV) and internal components of the very high-temperature reactor (VHTR) in air and helium environments at 300 to 900°C; 2) study the effects of surface treatments on the oxidation resistance of alloys by applying emerging and commercial surface treatments to candidate alloys and evaluating emissivities after exposure in air and helium environments at elevated temperatures; 3) develop a comprehensive understanding of the relationships between emissivity, oxide characteristics, and surface treatments by characterizing surface oxides that form on untreated and modified alloys after elevated temperature exposure; and 4) develop an integral separate-effects emissivity database for potential candidate materials and surface modification treatments.

The thermal radiation of heat from the outer surface will partially cool the RPV and internal components of the VHTR. With an unexpected increase in temperature, thermal radiation becomes a significant mode of heat dissipation because of its fourth power temperature dependence according to the Stefan-Boltzmann equation. Since oxidation will inevitably occur at these higher temperatures, it is clear that material emissivity is intricately related to the chemical, physical, and mechanical characteristics of the oxide scales that form on the surface, including their chemical composition, grain morphology, topography, and porosity. The growing field of surface modification provides opportunities for achieving high emissivities at high temperatures by changing topography and grain orientation or inducing controlled surface compositional changes.

Work Scope

This project consists of the following primary tasks:

- Emissivity measurements of potential candidate materials before and after elevated temperature exposure in air and impure helium environments
- Characterization of oxide layers and the effect of oxide layer characteristics on emissivity
- Surface modification of alloys
- Emissivity testing and characterization of as-surface modified alloys and elevated temperature exposure in air and impure helium environments
- Emissivity measurements and surface characterization of surface modified alloys after high-temperature exposure to air and impure helium environments

Materials and Design Methodology for Very High-Temperature Nuclear Systems

PI: James Stubbins, University of Illinois

Project Number: 07-024

Collaborators: Stress Engineering Services

Program Area: Generation IV

Project Description

The objective of this research project is to address major materials performance and methodology issues for the design and construction of high-temperature and very high-temperature nuclear systems. This work will provide a synergy between the development of simplified, but robust, design rules for high-temperature systems and materials testing, along with performance and improvement of these systems. Such systems will have to deal with time-dependent materials properties (creep, creep-fatigue, high-temperature corrosion) in components with complex stress states, long intended service lives, and aggressive operating environments. Routine mechanical properties data and current high-temperature design methodology do not provide adequate information for long-term, robust system design. This project will address these issues. In addition, high-temperature materials testing in relevant corrosive environments (low oxygen, partial pressure with substantial carbon activities) will be performed to support further code qualification of existing alloys and the development of emerging alloys.

Work Scope

This project will consist of the following tasks:

1) High-Temperature Design Methodologies
    - ASME and European code assessment
    - Simplified high-temperature rules and design approaches
    - Creep-fatigue-crack-corrosion design
    - Constitutive behavior
2) Materials Mechanical Testing
    - Inert testing
    - Creep-fatigue, thermal fatigue testing
    - Microstructural analysis
3) Materials Mechanical/Corrosion Testing
    - HT gas corrosion facilities reconstruction
    - Corrosion exposure/testing
    - Creep-fatigue, thermal fatigue testing
    - Microstructural analysis

Experimental and CFD Analysis of Advanced Convective Cooling Systems

PI: Victor M. Ugaz and Yassin A. Hassan, Texas Engineering Experiment Station

Collaborators: None

Project Number: 07-058

Program Area: Generation IV

Project Description

The objective of this proposed work is to study the fundamental physical phenomena in the Reactor Cavity Cooling System (RCCS) of very high-temperature reactors (VHTR). One of the design objectives is to assure that RCCS is the ultimate heat sink capable of maintaining thermal integrity of the fuel, vessel, and equipment within the reactor cavity for the entire spectrum of postulated accident scenarios. Researchers will perform a series of experiments to obtain the complex flow patterns in the cavity volume using state-of-the-art particle image velocimetry and laser-induced fluorescence techniques. Accurate numerical simulation of the flow and temperature in the cavity will be performed using advanced turbulence models to simulate the complex conditions of flows in critical zones of the cavity. These turbulence models will be validated, verified, and implemented into commercially available computational fluid dynamics (CFD) codes.

A key outcome of this work will be to establish a versatile platform for the experimental and computational characterization of RCCS designs that will significantly advance the state of knowledge in both liquid-cooled and gas-cooled (e.g., sodium fast reactor) reactor technology. This study will extend the measurement to the micro-scale levels not obtainable in large-scale test facilities, thereby complementing the existing infrastructure.

Work Scope

The proposed project will have the following products and deliverables:

1) Computer Codes
    - Develop improved turbulence model to predict behavior of the complex RCCS flow structure
    - Deliver details of the LES subgrid model and implement in commercial codes through user-defined subroutines
2) Experimental Data
    - Scaling, preliminary analysis, test plan, calibration, and initial measurements
    - Temperature measurement under various flow conditions
    - Fluorescence seeding for air flow
    - Measurements for various flow and geometry in key convective zones

NUCLEAR ENERGY RESEARCH INITIATIVE

Establishing a Scientific Basis for Optimizing Compositions, Processing Paths, and Fabrication Methods for Nanostructured Ferritic Alloys for Use in Advanced Fission Energy Systems

PI: G. Robert Odette and Takuya Yamamoto, University of California-Santa Barbara

Collaborators: None

Project Number: 07-069

Program Area: Generation IV

Project Description

The objective of this research is to develop high-performance fuel cladding, duct, and internal structural material systems for a variety of future fission reactors, including advanced fast burner reactors envisioned in the Global Nuclear Energy Program (GNEP). This research will focus on an emerging alloy class—nano-structured dispersion strengthened ferritic alloys (NFAs)—that has shown a very high promise of achieving the necessary objectives.

Researchers will develop a deformation processing database using a science-based approach to address limitations in directionally worked product forms in NFAs which have anisotropic microstructural and strength properties. They will construct a database over a wide range of conditions to map re-crystallization regimes that lead to more isotropic behavior. They will examine strain and temperature regimes that may allow superplastic deformation resulting in fine, stable grain structures that can be optimized for creep strength and properties. Researchers will assess severe deformation paths to solid state joining and map regimes of efficient diffusion bonding, guided by an understanding of the thermal stability of NFA microstructures. Through a semi-combinatorial approach, they will optimize NFA compositions to enhance a variety of performance indices (e.g., corrosion resistance) and explore utilizing austenite to martensite phase transformations for achieving equiaxed microstructures that reduce strength and fracture toughness penalties associated with oxide dispersion strengthened martensitic steels. Identification and optimization of the NFAs fills a missing element in alloy design, namely their basic character, thus providing a basis of understanding for property optimization. In the final task, researchers will provide additional low-cost information of the use of NFAs in severe nuclear environments.

Work Scope

The following tasks comprise the primary work scope of this project:

- Deformation processing database
- Solid state joining
- Alternative alloys and alloy optimization
- Identification and optimization of the NFAs
- Target of opportunity irradiations, exploratory mechanical testing and modeling

6.2 ADVANCED FUEL CYCLE RESEARCH AND DEVELOPMENT

There are 42 NERI research projects currently being performed that closely relate to the research goals of the Advanced Fuel Cycle R&D (AFCR&D) program: 17 awarded in FY 2005, 13 awarded in FY 2006, and 12 newly awarded projects in FY 2007.

As described in Section 3, AFCR&D is a wide-ranging research and development program whose mission is to develop and exhibit technologies that facilitate the conversion to an environmentally, socially, politically, and economically acceptable advanced fuel cycle. The chief goals are to achieve a significant reduction in the amount of toxic and heat producing high-level radioactive waste requiring geologic disposal, to significantly reduce accumulated plutonium in commercial spent fuel, and to extract more useful energy. This will be accomplished by developing advanced fuel, cladding, waste forms, separations, and disposal technologies that separate long-lived, highly radiotoxic material and facilitate their recycle, allowing the recovery of valuable energy from the spent fuel.

During FY 2006, a number of research projects targeted the separation of actinides and lanthanides by several techniques (aqueous process with redox, aqueous process with soft donor atoms, and UREX+). Much work is taking place in the advanced fuel development area. Projects involve conducting analytical studies and modeling techniques, developing and optimizing materials, developing fuel processing and fabrication techniques, and improving fuel coatings. Transmutation projects are targeting alloys for the advanced burner reactor (ABR), TRU transmuters, and minor actinide recycling with boiling water reactors. Systems analysis projects are developing and optimizing computer models for fuel cycle analysis, using those codes to evaluate different scenarios, and conducting fuel cycle economic evaluations. Two new projects are improving SFR simulation methodology and measurement techniques.

Beginning in FY 2007, the program is being refocused to support R&D on the most promising technologies developed to date. Under the Global Nuclear Energy Partnership (GNEP), DOE will test the UREX+ separations process and design an Advanced Fuel Cycle Facility for R&D on advanced separations and fuel manufacturing technologies. Over the coming year, NE will collaborate with international and private parties to refine GNEP and gauge interest in a demonstration of sodium-cooled reactor technology, which would serve as the fast ABR. Planned NERI research efforts under the AFCR&D program will focus on the following areas:

- Separations
- Fuels
- Transmutation
- Systems analysis

An index of the research being performed under this program follows, along with a summary of each project.

Project Summaries and Abstracts

FY 2005 Project Summaries

FY 2006 Project Summaries

FY 2007 Project Abstracts

NUCLEAR ENERGY RESEARCH INITIATIVE

Determination of Basic Structure-Property Relations for Processing and Modeling in Advanced Nuclear Fuels: Microstructure Evolution and Mechanical Properties

PI: Pedro D. Peralta, Arizona State University

Collaborators: Los Alamos National Laboratory (LANL)

Project Number: 05-001

Project Start Date: March 2005

Project End Date: March 2008

Research Objectives

The objective of this project is to investigate a strategy for fuel development based on experimental work on surrogate materials. Fuel development under the Advanced Fuel Cycle Research and Development (AFCR&D) Program will rely heavily on modeling physical mechanisms to predict performance, rather than on conducting direct experimentation on nuclear materials or on empirical relationships derived from experimental data. In this project, researchers will study the structure-property relationship of nitrides and oxides in solid solutions using surrogate elements in order to simulate the behavior of inert matrix fuels, emphasizing zirconium-based materials. The goal is to 1) provide insight into processing fuel that has better performance and greater structural reliability during manufacturing and service and 2) develop structure-property relations that can be used as input for fuel performance models.

Researchers will explore three key aspects of these materials: 1) microstructure, measured through global texture evolution and local crystallographic variations; 2) mechanical properties (including fracture toughness, compression strength, and hardness) as a function of load and temperature; and 3) structure-property relations. This research will use crystallographic information to evaluate fuel performance and incorporate statistical variations of microstructural variables into simplified models of the mechanical behavior of fuels.

Following are the primary tasks of this project. In conjunction with these activities, the research team will also carry out work with actual fuel materials.

- Develop processing procedures for pellet fabrication and characterize their properties
- Establish appropriate plutonium surrogates, fabricate samples, and optimize processing
- Translate techniques from surrogate processing to actual fuel; fabricate and characterize
- Establish models for high-temperature behavior, characterize properties, perform testing and analysis

Research Progress

During the second year of this project, researchers continued to focus on studies for optimizing the microstructure and mechanical properties of sintered zirconium nitride (ZrN) and (Zr,Ti)N as surrogates for plutonium nitride (PuN) and (Pu,Zr)N, respectively. This was accomplished via characterization, mechanical testing, and computer simulation. They investigated the effects of sintering atmosphere on the kinetics of ZrN pellets, characterizing identically prepared samples sintered in eight combinations of environment and temperature. Researchers found a significant difference in hardness measurements, ranging from approximately 100 kg/mm^2 for samples sintered in 1,300°C nitrogen (N) to 1,000 kg/mm^2 for samples sintered in argon (Ar) at 1,600°C.

All samples consistently showed a clear correlation between increasing porosity and decreasing hardness. While argon samples had similar texture orientation patterns to those sintered in nitrogen, the development of this texture was more advanced and showed local orientation density peaks and larger grain size—suggesting that the grain growth kinetics of the nitrogen-sintered samples was limited somehow. Samples with 6 percent hydrogen added to the sintering environment showed a decrease in hardness, increased intergranular cracking, increased variability in grain size, and had a larger fraction of high angle grain boundaries compared to samples sintered without hydrogen. These results suggest that hydrogen may be interacting with grain boundaries either directly or by forming hydrides that precipitate at grain boundaries.

Researchers examined the microstructure and mechanical behavior of small-diameter (4 mm) sintered ZrN and (Zr,Ti)N pellets via electron microscopy and compression tests to establish structure-property relations in the solid solutions and to compare with the behavior observed in larger diameter (12 mm) pellets. Results indicate that "solid solution" pellets do not form a single-phase solid solution; rather, two phases are present, one rich in zirconium (Zr) and the other rich in titanium (Ti). This is attributed to slower kinetics due to the mismatch in atomic size between zirconium and titanium.

Uniaxial compression tests showed that solid-solution pellets had only slightly lower compression strength as compared to pure ZrN pellets sintered under identical conditions, despite their lower densities. Solid-solution pellets had a higher specific strength, which was attributed to their smaller grain size and higher porosity. The larger number of grain boundaries and pores in the solid solution will provide additional sites for energy dissipation, via crack deflection and pore collapse, thus allowing for more damage accumulation before catastrophic failure. This could be aided by an increase in strength in the solid solutions as compared to pure ZrN.

Fractography of the broken samples indicates that fracture tends to be transgranular, since the fracture surface shows flat facets suggestive of cleavage (Figures 1-2). The examination of fracture surfaces of solid solution samples using energy dispersive spectroscopy (EDS) indicates a tendency for fracture along the Zr-rich phase. A comparative illustration of Zr concentration on a fracture surface and a polished surface is shown in Figure 3.

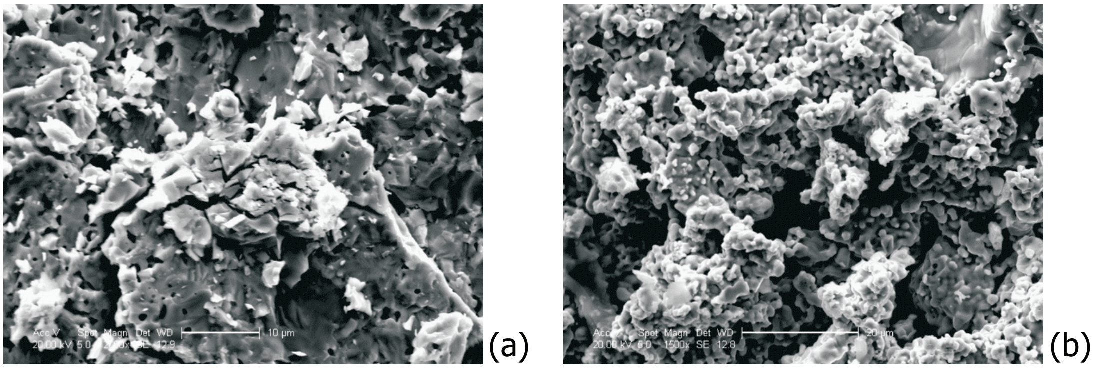


Figure 1. Fracture surface of (Zr,Ti)N: (a) 1,475°C @ 2,000x, 10 µm scale; (b) 1,600°C @ 1,500x, 20 µm scale.

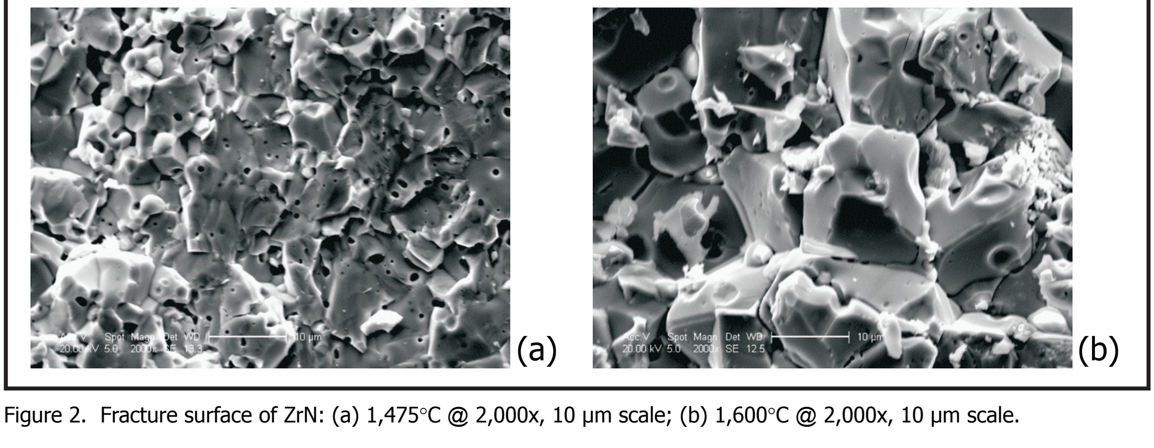


Figure 2. Fracture surface of ZrN: (a) 1,475°C @ 2,000x, 10 µm scale; (b) 1,600°C @ 2,000x, 10 µm scale.

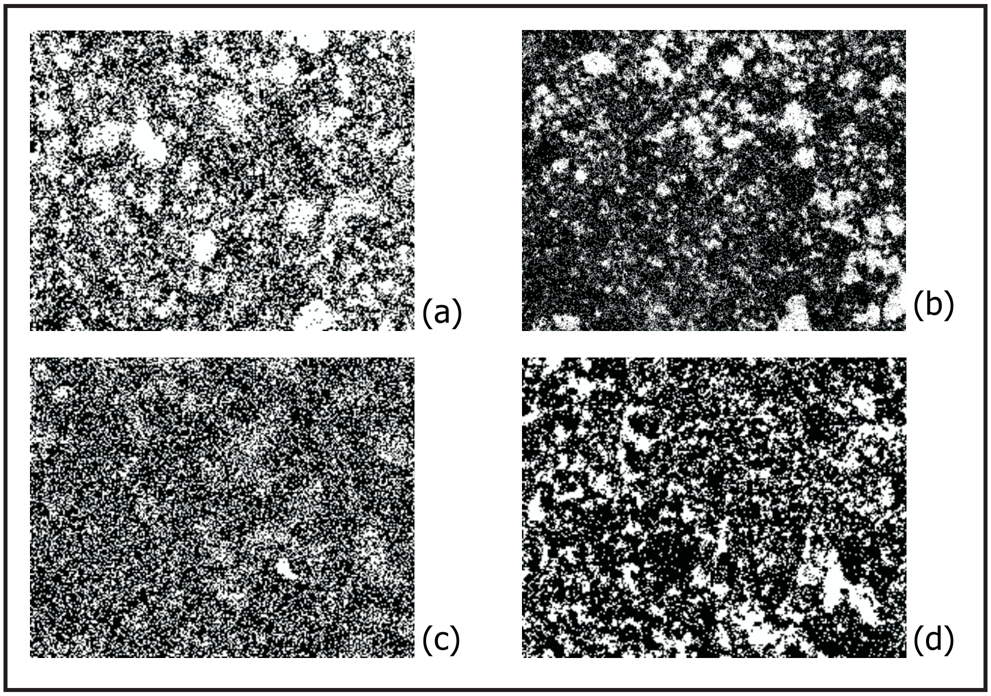


Figure 3. Zr distribution (black) in (Zr,Ti)N samples: (a) 1,375°C smooth surface, (b) 1,375°C fracture surface, (c) 1,600°C smooth surface, (d) 1,600°C fracture surface.

Researchers constructed two-dimensional models of both a low-density and a high-density ZrN pellet using finite elements that accounted for the actual microstructure. For the low-density pellet, they developed methodologies to 1) identify each phase using scanning electron microscope (SEM) micrographs and 2) import the geometry into software able to generate a finite element mesh. For the high-density pellet, they processed an orientation imaging microscopy (OIM) map to create a model that accounted for geometric and crystallographic variability of the microstructure and the anisotropy of the mechanical properties at the microscale.

They determined that the shape and variability of pores along with preferential and crystallographic orientation of the grains can lead to anisotropy in the value of the Effective Young's modulus. Simulations show that high stress concentrations in high-density samples are found at the interfaces between grains and intergranular pores (Figure 4). In low-density samples (Figure 5), stresses showed higher variability and were affected by local pore geometry and the presence of interfaces among the different phases considered (dense clusters, low density porous matrix, and voids).

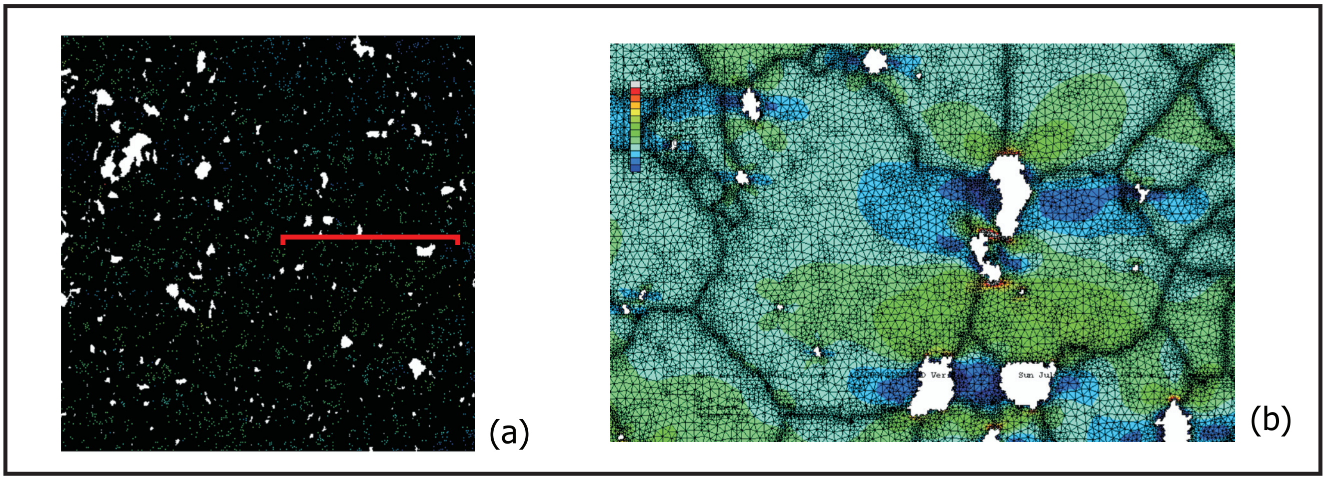


Figure 4. Von Mises stress in high-density sample: (a) general view; (b) local maximum.

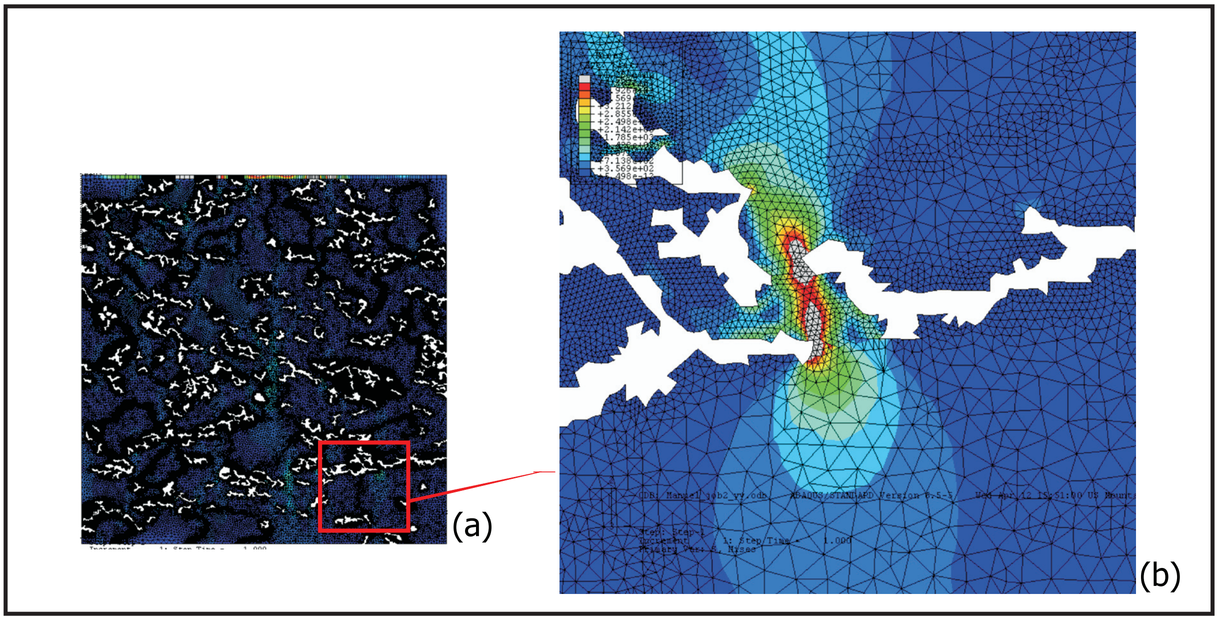


Figure 5. Von Mises stress: (a) General view; (b) local maximum.

Planned Activities

The mechanical testing activities planned for the third year of this project will focus on elevated temperature testing of ZrN, (Zr,Ti)N, and ZrO_2 pellets. Researchers will correlate microstructural characterization with mechanical property measurements including fracture toughness and compression strength (at both 800°C and 1,700°C). They will initiate compression creep experiments (tested at approximately 1,700°C) using a furnace and mechanical testing setup recently acquired for this purpose. They will also perform ambient temperature fracture toughness and compression tests *in situ* in an SEM. The team will evaluate deformation and failure mechanisms on samples used for mechanical testing using scanning and transmission electron microscopy, atomic force microscopy (AFM), and OIM. The results will be used to propose basic structure–property relations in ZrN with emphasis on mechanical behavior.

Among the phenomena that occur in a nuclear fuel element under irradiation, the behavior of xenon and krypton fission products is one of the most challenging. If these fission gases are retained in the fuel, they precipitate as bubbles which leads to swelling of the fuel. Swelling and thermal expansion adversely affect fuel performance because it promotes fuel-cladding contact, and the resultant stress on the cladding can shorten its lifetime. In addition, the bubbles of low-conductivity gas decrease the thermal conductivity of the fuel and lead to fuel temperatures higher than exhibited by fully dense fuel at the same heat rating. One of the primary objectives of the upcoming year is to incorporate thermal expansion and swelling in thermoelastic finite element models that are microstructurally explicit. This will allow the quantification of stress variability in fuel pellets due to microstructural heterogeneity, which can lead to better models of structural reliability of fuel materials.

The Application of Self-Propagating High-Temperature Synthesis (SHS) to the Fabrication of Actinide-Bearing Nitride and Other Ceramic Nuclear Fuels

PI: John J. Moore, Colorado School of Mines

Collaborators: Idaho National Laboratory (INL)

Project Number: 05-013

Project Start Date: January 2005

Project End Date: December 2007

Research Objectives

The major objective of this project is to produce dense americium-bearing ceramic fuel materials. Researchers will first determine the fundamental, self-propagating, high-temperature synthesis (SHS) processing parameters using manganese (Mn) as a surrogate for americium (Am) to produce dense zirconium-manganese-nitrogen (Zr-Mn-N) ceramic compounds.

In addition, they will generate fundamental SHS processing data for the synthesis of two plutonium (Pu) and uranium (U) ceramic fuel compounds: 1) Pu-Am-Zr-N and 2) U-Pu-Am-N. As before, surrogate materials will first be substituted to establish the process. The sequence for SHS synthesis of these ceramic fuels, and the proposed surrogates, are as follows:

Pu-Am-Zr-N, using cerium (Ce) as the surrogate for Pu and manganese as the surrogate for Am:

1) $(Ce_{0.5}Mn_{0.5})N$
2) $64wt\%[(Ce_{0.5}Mn_{0.5})N]-36wt\%ZrN$

U-Pu-Am-N, using depleted uranium (DU) for uranium, Ce as the surrogate for Pu, and Mn as the surrogate for Am:

1) $(DU_{0.5}Mn_{0.5})N$
2) $(DU_{0.5}Ce_{0.25}Mn_{0..25})N$

Once sufficient fundamental data have been determined from these three surrogate systems, the team will synthesize Zr-Am-N, Pu-Am-Zr-N, and U-Pu-Am-N ceramic fuels.

Earlier difficulties experienced during laboratory-scale production of metal alloys containing Am have led researchers to abandon compact powder sintering methods and investigate other synthesis methods, such as SHS. The high vapor pressure of Am and americium-nitride (AmN) resulted in retention problems of Am during sintering, adversely affecting the ability to synthesize a consistent ceramic nuclear fuel product with desirable properties.

Research Progress

During this fiscal year, researchers produced zirconium (Zr), manganese (Mn), and nitrogen (N) compounds and began quantifying the manganese loss using an Induced Coupled Plasma (ICP) process—they expect minimal to no manganese loss. They are also investigating the use of lanthanide-nitrides as surrogates for actinide-nitrides, considering praseodymium (Pr) as a potential surrogate for americium, cerium (Ce) for plutonium (Pu), and depleted uranium (DU) for uranium (U). A preliminary densification process using a Gleeble 1500 will be utilized before the induction hot press.

The researchers also produced manganese nitride (Mn_3N_2) powder by employing an auto-ignition combustion synthesis method using low-cost reactants of manganese nitride and urea. This powder will then be fabricated into dense nitride pellets. Further work is being conducted to optimize and expand the process in order to produce lanthanide-nitrides as surrogates for actinide-nitrides using the elements stated above.

Planned Activities

Following is a synopsis of the tasks the team plans to conduct over the next period:

- Initiate additional surrogate studies using Pr and dysprosium (Dy)
- Optimize auto-ignition combustion synthesis (AICS) of Mn-N, Pr-N, and Dy-N powders
- Optimize SHS-consolidation of dense Zr-Mn-N compounds
- Optimize Am-N and Zr-Am-N SHS systems
- Conduct differential thermal analysis (DTA) of Am-N and Zr-Am-N SHS systems
- Optimize SHS consolidation of the Zr-Am-N system

NUCLEAR ENERGY RESEARCH INITIATIVE

Minor Actinide Doppler Coefficient Measurement Assessment

PI: Nolan Hertel, Georgia Institute of Technology (Georgia Tech)

Collaborators: Education, Research and Development Association of Georgia Universities, Los Alamos National Laboratory (LANL)

Project Number: 05-024

Project Start Date: April 2005

Projected End Date: May 2007

Research Objectives

The objective of this project is to assess the viability of measuring the Doppler coefficient of reactivity in minor actinides. Using a series of calculations, the researchers will estimate the change in reactivity resulting from a change in the operating temperature of small quantities (approximately 1-10 g) of pure minor actinides. The team will use this data to design experiments for measuring Doppler coefficients.

As part of the Advanced Fuel Cycle R&D (AFCR&D) program, transmutation of waste using advanced fast reactors and accelerator-driven systems have shown the ability to reduce the amount of plutonium and transuranic materials for disposal. In order to conduct safety assessments of transmutation systems for fuel with a significant minor actinide content, researchers require the Doppler coefficients for each isotope. Several isotopes of plutonium (Pu), neptunium (Np), americium (Am), and curium (Cm) will be studied, including Np-237, Pu-239, Pu-238, Pu-241, Am-242m, Am-243, Am-241, and Cm-244.

Using the radiation transport code MCNP5, researchers will perform extensive scoping calculations as a function of five parameters: 1) isotope, 2) sample quantity, 3) operating temperature, 4) critical assembly, and 5) data library. With these calculations, they will determine the quantity of minor actinide material needed to cause a 10^{-5} change in reactivity due to a 200°C change in sample temperature (e.g., from 800 to 1,000°C). They will use the resulting data to develop experiments for measuring the Doppler coefficient of each isotope. For this work, the team will use the FLATTOP and COMET assemblies at the LANL Critical Experiments Facility.

Research Progress

Researchers have obtained information on the critical assemblies, types of experiments possible, and the MCNP5 models for the FLATTOP assembly and the ZEUS critical experiment using COMET. They modified the KCODE output from MCNP5 to print out the effective multiplication factor (k_{eff}) and the associated statistical uncertainty data. They used this data to determine differences in the k_{eff} values on the order of 10^{-5}, which was needed to look for the expected reactivity changes. After completing the code modification, they created MCNP5 cross-section files at 800°C, 900°C, 1,000°C, and 1,100°C from the ENDF, JEFF, and JENDL tapes for each isotope using the NJOY computer code.

Using these cross-section files, the researchers created 480 input files in order to perform initial calculations for 10 g samples of each isotope in the FLATTOP MCNP5 model. Of these 480 cases, 160 have been completed, consisting of an entire set of isotope and temperature cases for the ENDF cross-section library. Each calculation requires 1,500 KCODE cycles with 6×10^6 neutrons per cycle, taking approximately three and a half days per calculation on the multiple computer clusters at Georgia Tech. In order to speed up the calculations, researchers requested computing time on the thousand-processor computer system at LANL. Results of these calculations were used to determine five different masses for each isotope. For Np-237 and Pu-239, the masses ranged from 6 to 22 g; for the other six isotopes, masses ranged from 2 to 18 g. Table 1 shows the calculated change in k_{eff} resulting from a 200°C temperature increase for each isotope.

Isotope	Δ k_{eff}	Std Dev
Np-237	6.100E-06	1.770E-05
Pu-238	1.020E-05	1.700E-05
Pu-239	3.600E-06	1.700E-05
Pu-241	3.130E-05	1.710E-05
Am-241	2.460E-05	1.690E-05
Am-242m	-1.410E-05	1.620E-05
Am-243	1.720E-05	1.710E-05
Cm-244	2.670E-05	1.700E-05

Table 1. Calculated change in k_{eff} resulting from temperature increase from 800 to 1,000°C for 10 g samples of various actinides.

After analyzing the data, researchers were unable to identify a clear trend to permit interpolating the amount of each isotope needed to create a Δk_{eff} of 10^{-5}. The inability to obtain meaningful data was due to the fast neutron spectrum present in the FLATTOP assembly. This complication rules out using the FLATTOP assembly for these experiments.

Planned Activities

Researchers decided to limit the scope of the project to allow them to complete the research in the remaining time period. They will focus on determining if the Doppler coefficient measurements can be accomplished on the COMET assembly. The first step is to identify a configuration of fuel and scattering material on the COMET assembly that results in a neutron spectrum resembling that of the proposed Advanced Burner Test Reactor (ABTR). Currently, researchers are working to determine the proper configuration of the COMET assembly to replicate the neutron spectrum in the ABTR.

After identifying the configuration, they will run Doppler coefficient calculations using the latest resonance cross-section data available for Pu-239, Pu-241, Np-237, and Am-241 at each of the four temperatures for 2-3 different masses. The objective is to determine the mass of each isotope resulting in a Doppler coefficient of 10^{-5}. These calculations will use the latest resonance cross-section data available. As time permits, the team will complete additional calculations of the remaining four isotopes from the original eight.

NUCLEAR ENERGY RESEARCH INITIATIVE

Plutonium Chemistry in the UREX+ Separation Processes

PI: Alena Paulenova, Oregon State University

Collaborators: University of Nevada at Las Vegas, Argonne National Laboratory

Project Number: 05-062

Project Start Date: April 2005

Project End Date: March 2008

Research Objectives

The objective of this project is to examine the chemical speciation of plutonium in the UREX+ (uranium/tributyl phosphate) extraction processes for advanced fuel technology. The researchers will perform the following tasks:

- Analyze the change in speciation of plutonium in aqueous and organic phases and incorporate kinetic and thermodynamic data into existing computer modeling codes
- Examine the different oxidation states of plutonium to determine the relative distribution between the aqueous and organic phases under various conditions, such as different concentrations of nitric acid (HNO_3), total nitrates, acetohydroxamic acid (AHA), or actinide ions
- Apply several spectroscopic techniques, including X-ray absorbance spectroscopy and small-angle neutron scattering, to determine plutonium and uranium speciation in all separation stages

Research Progress

Researchers performed experiments to study the effect of acetohydroxamic acid on the speciation and extraction of hexavalent and tetravalent plutonium (Pu) and uranium (U) in the nitric acid/TBP-n-dodecane system. They performed extended characterization studies of uranyl-AHA species in both the aqueous and organic phases using (Vis-NIR and IR) spectroscopy techniques. The team initiated an investigation of possible AHA-TBP solvates, extraction of nitric acid, and speciation of TBP-HNO_3. The initial results obtained with UO_2^{2+} will form the basis for further plutonium experiments. Besides Pu and U, researchers are also investigating several other metals present in the dissolved spent nuclear fuel: neptunium (Np), molybdenum (Mo), thorium (Th), zirconium (Zr) and cerium (Ce). Additionally, they have begun a spectroscopic investigation of the metal speciation in both the aqueous and organic phases.

Speciation of Pu using a 1 meter liquid core waveguide (LCW). Acetohydroxamic acid is a salt-free reductive/complexing agent tested for the use in UREX under a wide range of aqueous matrix and temperature conditions. It is a strong chelator binding actinide metals. Formation of the complex chelate ring stabilizes the hydroxamic acid against acidic hydrolysis.

To investigate the reactivity of AHA, an accurate and prompt determination of the valence state of actinides is necessary. The separation process of plutonium and neptunium from uranium(VI) is based on the redox-complexation reaction of AHA with these actinides. Researchers found that the reduction of hexavalent Pu and Np with AHA is a rapid process (Equation 1), followed by disproportionation and a slow reduction to Pu^{3+}.

$$2PuO_2^{2+} + 2CH_3CONHOH \leftrightarrow 2PuO_2^{+} + N_2 + 2CH_3COOH + 2H^{+} \qquad \textbf{(1)}$$

The plutonium speciation in aqueous phase, excluding NO_3^-, is described by Equation 2:

$$\Sigma[Pu]_{aq} = [Pu(VI)] + [Pu(V)] + [Pu(IV)] + [Pu(III)] + [Pu(IV)AHA)_x]^{4-x} + Pu(III)AHA)_y]^{3-y} + Pu(VI)AHA)_z]^{2-z} + Pu(V)AHA)_w]^{1-w} \qquad \textbf{(2)}$$

The most common redox-speciation extraction method for low concentrations of actinide uses extractants specific to the desired oxidation state. However, redox-speciation extraction schemes withhold information about formation of different complexes for selected actinide oxidation states in the aqueous phase. In that case, spectroscopic techniques (VIS-NIR) are necessary, but these methods require a higher chemical concentration of the species for a sufficient absorbance signal.

Researchers solved this problem by using the 1 meter liquid core waveguide (LCW) with a high-resolution spectrometric system, which allows scanning and monitoring the chemical reaction kinetics. The LCW measures very low chemical concentrations (~10^{-6} M) in minimal sample volumes (~0.3 mL).

Figure 1 (black line) displays spectra of a Pu(IV) and Pu(VI) mixture (4×10^{-5} M in 2.2 M HNO_3), showing characteristic peaks at 475 nm and 831 nm, respectively. After adding acetohydroxamic acid, Pu(VI) was reduced and Pu(IV) was complexed by the AHA almost immediately (red line). The absorbance of the Pu(IV)-AHA complex drops with time due to reduction of Pu(IV) by hydroxylamine formed in the system as an AHA hydrolysis product. After 24 hours, most plutonium present in the sample appeared in the trivalent state Pu(III) accompanied by a small portion of Pu(IV) that either remained unreduced or was re-oxidized (blue line).

Speciation of metal-AHA complexes in the aqueous and organic extraction phases. Researchers observed an evident change in the color of aqueous uranium solutions in the presence of AHA. Although increasing nitric acid concentration suppressed the chelation of uranyl with AHA, the ternary complex $UO_2(AHA)(NO_3)$ formed even for 1M HNO_3, as shown in Figure 2. After prolonged agitation of 30 percent tributyl phosphate (TBP), with the aqueous phase containing U, AHA, and HNO_3, the organic phase turned slightly orange-yellow, confirming the presence of AHA. Researchers investigated the nature of uranyl-AHA species in the TBP phase using several analytical techniques and identified the bi-solvate adduct $UO_2(AHA)(NO_3)$.2TBP in the extraction organic phase. Infrared spectroscopy (FTIR) results confirmed that the uranyl cation is coordinated with two oxygen atoms of the CONHO group (Figure 3). This method also established the presence of acetic acid (the hydrolysis product of AHA) in the organic phase.

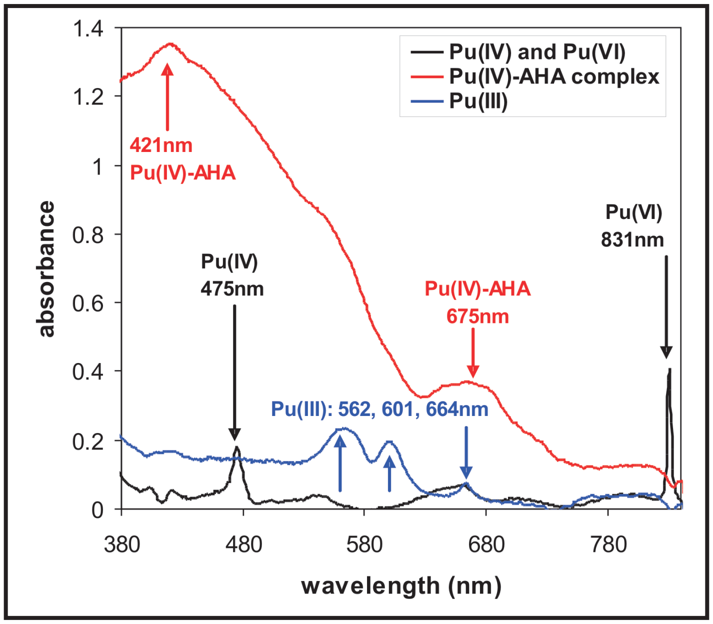


Figure 1. Absorption spectra of Pu(IV) and Pu(VI) mixture in 2.2 M nitric acid and 0.4 M acetohydroxamic acid (AHA) recorded using LCW.

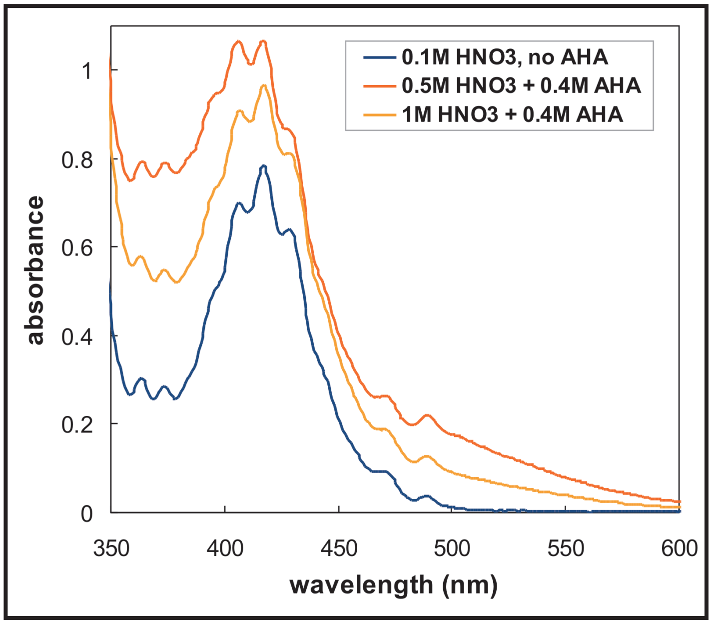


Figure 2. Absorption spectra of 0.1 M uranyl nitrate in nitric acid and 0.4 M AHA.

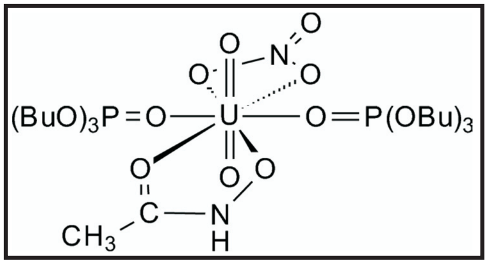


Figure 3. FTIR results of uranylcation.

The researchers are investigating the effect of zirconium (Zr) and molybdenum (Mo) fission products on AHA equilibrium in UREX+ extraction processing. Speciation of hexavalent molybdenum is complex and depends strongly on the concentration of acid. UV-VIS spectroscopy applied to two extraction systems identified similar solvates of ternary complexes for Mo(VI): Mo-AHA-NO3 with CMPO/TBP and Mo-AHA-Cl with TBP. Colorimetric studies of zirconium in the AHA-HNO_3-TBP system are underway.

The research team has submitted three articles for publication in peer-reviewed journals and have given numerous presentations at conferences.

Planned Activities

In the next period, researchers will:

- Investigate plutonium and neptunium speciation in both the aqueous and organic phases for different concentrations of AHA and nitric acids, using UV-Vis-NIR, FTIR, Raman, and ESI-MS spectroscopy
- Continue the extraction and titration experiments with Pu (Np, U) and measure distribution of actinides between aqueous and organic phase under various conditions, such as different concentrations of nitric acid, total nitrates, or actinide ions
- Examine the redox kinetics and complexation speciation of actinides (Pu and Np) with various concentration of nitric acid and nitrates, utilizing SQUAD modeling software (equilibrium) and GlobalWorks (kinetics)
- Determine plutonium and uranium speciation in all separation stages using techniques such as Raman, X-ray absorbance spectroscopy, and small-angle neutron scattering

Development of an Engineered Product Storage Concept for the UREX+1 Combined Transuranic/Lanthanide Product Streams

PI: Sean M. McDeavitt, Purdue University

Collaborators: Texas A&M University, Argonne National Laboratory

Project Number: 05-066

Project Start Date: April 2005

Project End Date: March 2008

Research Objectives

The U.S. Department of Energy's Advanced Fuel Cycle R&D program is developing next generation processing methods to recycle uranium and transuranic (TRU) isotopes from spent nuclear fuel. Future deployment of an advanced fast reactor designed for burning TRU will provide a long-term disposal solution for these isotopes, but realization of this plan is decades away.

The objective of this project is to develop near-term options for storing TRU oxides isolated through the uranium extraction (UREX+) process. Candidate storage forms include powder storage, monolithic ceramics, and a manufactured metal matrix composite, or cermet. This research work will focus on the cermet option because it has the ability to enable direct TRU burning after the intermediate storage period ends. The storage "lifetime" is estimated to be 50 to 60 years before a fast burner reactor will become available, so the design requirement for this project considers approximately 500 years of storage.

The goals of this research are to:

1) Develop the processing steps required to transform the effluent TRU nitrate solutions and the spent Zircaloy cladding alloy into a zirconium matrix cermet storage form
2) Evaluate the impact of phenomena that govern durability of the storage form, material processing, and TRU utilization in fast reactor fuel

Research Progress

Over the past fiscal year, the team conducted research in the areas of computational simulations and experimental process development. Following is a synopsis of the progress made under each of these research areas.

For the computational research, researchers are evaluating TRU cermet fuel performance in a fast reactor system. They have conducted two evaluations of a preliminary core design and the results are in good agreement. The initial effective multiplication factor (k_{eff}) of the simulated core is greater than 1.122, indicating that it is feasible to design a fast reactor that runs exclusively on the TRU cermet fuel. Further details will be reported next year.

Cermet fabrication entails three steps: 1) conversion of TRU-bearing solutions to oxide powder or microspheres, 2) recovery of Zircaloy cladding to form the cermet matrix, and 3) cermet fabrication using hot extrusion. As described below, researchers began mixed oxide fabrication experiments using uranyl nitrate and cerium nitrate precursors with the sol-gel and direct denitration methods developed at Oak Ridge National Laboratory. Development of the Zircaloy recovery process is nearly complete and the design of a bench-scale device is underway.

Zircaloy recovery consists of a hydride-milling-dehydride process designed to embrittle the alloy by 1) converting it to zirconium hydride (ZrH_2), 2) milling it to fine powder, and 3) decomposing the hydride powder to metal. This process is used to convert a portion of the Zircaloy cladding from spent fuel into a powder to generate the cermet matrix.

During this fiscal year, researchers examined the kinetics of hydride formation. Figure 1 illustrates the hydride formation progress versus time for a Zircaloy tube with a mass of 5 g under flowing Ar-5%H_2 at approximately 560°C. This experiment represents a diffusion-controlled scenario which requires almost 10 hours to convert 90 percent of the Zircaloy into ZrH_2. Researchers measure the percent hydride by monitoring the mass increase and correcting for *in-situ* oxidation. The experiments form

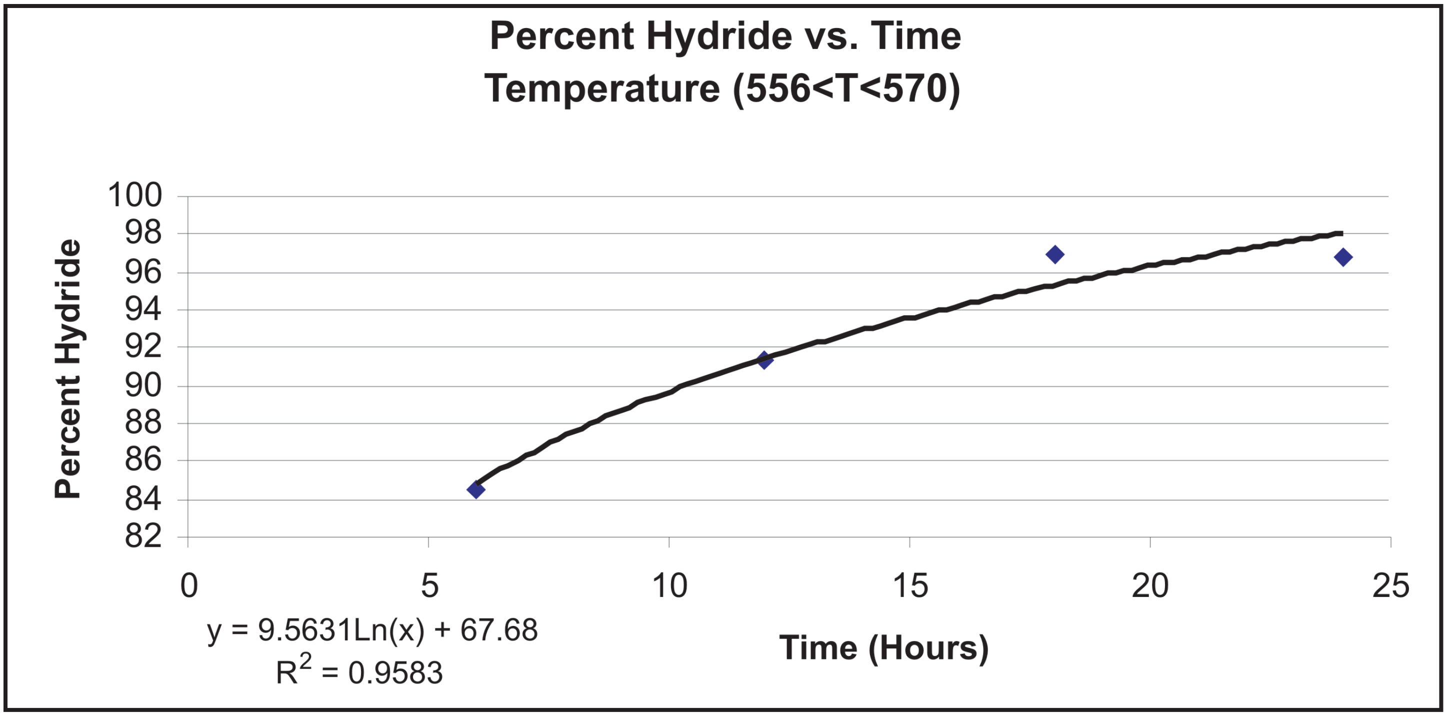


Figure 1. Hydride formation vs. time for Zircaloy (5 g tube) under flowing Ar-5%H_2.

Zircaloy products that are in the form of large flakes of brittle hydrides which can be easily ground into a fine powder.

The next steps are to 1) complete the parametric studies on the hydride and dehydride processes and 2) construct an all-in-one device designed to hydride, mill, and dehydride the Zircaloy in a single operation. Researchers are currently reviewing conceptual designs and will complete a system demonstration next year.

The research team established a powder metallurgical hot extrusion system to fabricate prototypic cermet samples using zirconia powders to simulate TRU microspheres and zirconium metal powder (nominal particle size = 44 μm). They first formed green billets by mixing the powders and sealing them in a copper canister. The powders were weighed and mixed inside of an argon atmosphere glovebox. After heating the tooling and billet to their respective process temperatures ($T_{tool} \approx 540^\circ C$ and $T_{billet} \approx 800^\circ C$), they used a dual-acting, 90 ton hydraulic press to apply the extrusion pressure.

Initial experiments used dies with a high reduction ratio (R=9) between the die entrance area to exit area. These trials experienced destructive radial cracks in the cermet pins that caused extensive matrix failure and significant oxide particle damage. Tests performed with R=2.66 and a lower oxide loading produced pins with far less damage. Figure 2 shows a typical cross section from an R=2.66 extruded product. Particle damage may be reduced by increasing the pre-extrusion inter-particle spacing and reducing the flow stress in the deformation region of the die. Researchers are redesigning the extrusion setup to optimize the die angle and reduction ratio and to increase the extrusion temperature. They will perform experiments on bare powders (i.e., no copper canister) at approximately 800°C using an extrusion method developed for uranium metal powders. The necessary back-pressure will be provided by a pre-compacted disk of Zr metal at the die face.

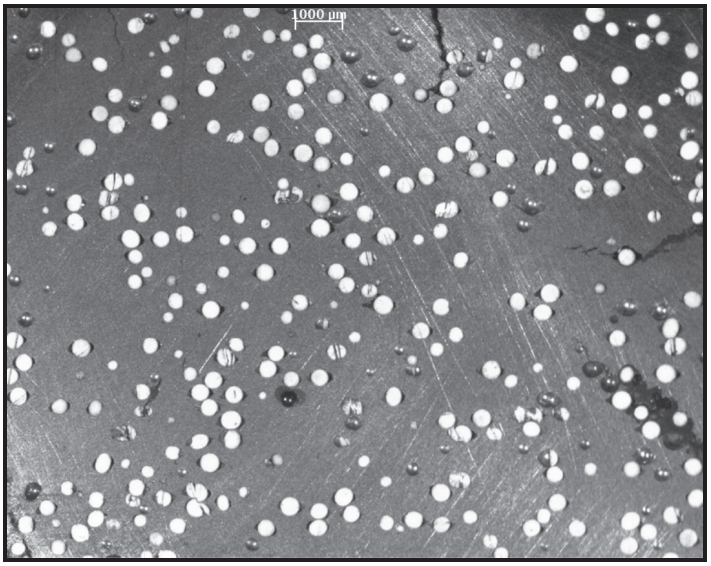


Figure 2. Particle damage in extruded billet passing through R=2.66 die.

Planned Activities

In the final year of the project, researchers will finalize the processing parameters and conduct further computational simulations. Following is a summary of planned activities:

Process Development

- Continue the hydride and dehydride experiments to optimize process variables and to characterize the rate-controlling mechanisms
- Design an all-in-one Zircaloy recycle system to hydride, mill, and dehydride spent cladding into Zircaloy powder
- Continue cermet fabrication experiments by hot extrusion using the bare extrusion design
- Continue sol-gel and direct denitration experiments to understand the process for generating mixed TRU-uranium oxide formation

Computational Simulation

- Complete models for heat generation and helium buildup (from α-decay) within the storage form
- Complete the system simulations to evaluate the TRU burnup effectiveness for cermet and MOX fuels in a fast reactor

NUCLEAR ENERGY RESEARCH INITIATIVE

Selective Separation of Americium from Lanthanides and Curium by Aqueous Processing with Redox Adjustment

PI: Dr. Kenneth L. Nash, Washington State University (WSU)

Collaborators: Idaho National Laboratory (INL)

Project Number: 05-082

Project Start Date: January 2005

Project End Date: February 2008

Research Objectives

The objective of this project is to investigate oxidation state adjustment and control methods to achieve selective partitioning of americium (Am) from lanthanides and curium (Cm) using conventional aqueous separations methods and materials. Increased application of mixed oxide (MOX) fuels and longer burnup times of conventional fuels will produce greater amounts of the transplutonium actinides Am and Cm in spent nuclear fuel. Because the half-lives of the americium isotopes (433 years for ^{241}Am and 7,370 years for ^{243}Am) are significantly longer than the half-lives of Cm, berkelium (Bk) and californium (Cf), isolating americium is a rational approach to integrating transmutation into advanced nuclear fuel cycles. In addition, the selective separation and transmutation of Am isotopes from other actinides and lanthanides could significantly reduce the long-term radiotoxicity of the residues from spent fuel or from spent fuel reprocessing.

The chemistries of trivalent lanthanides and actinides under aqueous processing conditions are similar, making selective separation of Am extremely challenging. Trivalent ion-recognition techniques are unlikely to provide an adequate thermodynamic basis for separation in an acceptable number of contacts. Therefore, this project is investigating oxidation state adjustment (and control) methods to achieve selective partitioning of Am from lanthanides and Cm using conventional aqueous separations methods and materials. Oxidized Am species are not expected to be inherently stable, but transient stability may be adequate for isolating Am.

The goal of this research is to develop strategies for adjusting the oxidation state and demonstrating a successful separation based on the oxidation of Am. Detailed studies will be conducted on the most promising candidate process identified. The work scope is defined by the following three tasks:

1) Investigate application of conventional aqueous separation processes to Am in non-standard oxidation states
2) Develop methods and operational conditions under which the upper oxidation states of Am can be stabilized for a period of time adequate to isolate it from Cm and lanthanides
3) Investigate use of unconventional media like room temperature ionic liquids and organic or inorganic micellar/colloidal media (e.g., non-ionic surfactants or polyoxometallates) as media for Am oxidation state adjustment and control

In the first task, researchers will gain insight from studying the chemical separations behavior of redox stable analog ions like thorium (Th^{4+}), neptunyl (V) (NpO_2^{+-}), and uranyl (VI) (UO_2^{2+}). The second task will emphasize the influence of kinetics and the use of chemical oxidants to maintain oxidized Am species long enough to allow the separation. Task three will focus on reducing the influence of readily oxidizable reagents on Am instability while considering the need for short contact times.

Research Progress

The researchers received actinide isotopes from the Pacific Northwest National Laboratory. In response to restrictions imposed by the WSU Radiation Safety Office and the state of Washington, the team is commissioning new facilities dedicated to conducting research with macroscopic concentrations of actinide ions. A sample of ^{248}Cm has also been transferred from Lawrence Livermore National Laboratory to the INL in support of this project. Minor equipment acquisitions funded from other sources (such as a diode array spectrophotometer) have been completed. Researchers have elected to postpone the purchase of the ozone generator, needed for clean preparation of oxidized Am species, until they have commissioned the milligram actinide laboratory. They have also upgraded glovebox facilities for actinide handling and inert atmosphere operations.

Researchers conducted initial studies on the effect of nonionic surfactants on actinide chemistry and are re-examining the latest literature on ionic liquids to determine the best path forward. On the question of room temperature ionic liquids (RTILs), they have ruled out a simple solvent-substitution approach because other work has established that this system is too complex to provide a workable solution to the problem. However, the electrochemical properties of RTILs would make them an attractive medium for investigating facile preparation of oxidized Am species. The nonionic polyelectrolyte approach has a number of positive features to recommend it for further studies. Researchers are exploring a connection between electrochemical oxidation of Am in an RTIL with subsequent selective isolation of the oxidized Am from the RTIL phase. Ionic liquids could play an important role as a medium that could facilitate oxidation of Am(III). A convenient connection to an industrial supplier of extractants and less expensive ionic liquids has been made. Researchers have also conducted exploratory studies of polyoxometallate systems and of lanthanide/actinide separations in carbonate/bicarbonate media.

Planned Activities

During the next quarter, researchers will shift their focus to study the chemistry of actinides in the upper oxidation states in carbonate and bicarbonate solutions as they continue to investigate the nonionic surfactant systems. The carbonate chemistry approach is seen as a means of increasing the lifetime of oxidized Am species to that regime suitable for conventional aqueous separations techniques. This line of investigation is unconventional, but could develop a variety of new options for selective separation of Am with variation in redox control parameters. A principal advance that could arise from this line of research would be improved radiation stability in the separation system.

The initial experiments provided encouraging evidence that this approach could provide an important breakthrough in Am-lanthanide separations efficiency. Several reports in the literature indicate that alkaline solutions could have a useful impact on creating and retaining oxidized Am species. Researchers can significantly advance this activity through studies of redox stable species of uranium and neptunium, such as U(VI) and Np(V). They are also examining the chemistry of plutonium, in the form Pu(VI), as a spectrophotometric probe of the hexavalent oxidation state.

One limitation is gaining the assent of the WSU Radiation Safety Office for conducting work with higher concentrations of these materials. Recent discussions have established a framework for this portion of the project and researchers are expecting significant advances in the coming quarter. The planned acquisition of an ozonizer will enable the production of oxidized Am species and for clean oxidation of other actinide ions as needed. Researchers are also investigating a variety of novel separations techniques like Cloud Point Extraction, a technique that does not involve conventional organic solvents, as a means of improving options for mitigating the effects of radiolytic degradation of reagents and materials.

NUCLEAR ENERGY RESEARCH INITIATIVE

Selective Separation of Trivalent Actinides from Lanthanides by Aqueous Processing with Introduction of Soft Donor Atoms

PI: Kenneth L. Nash, Washington State University (WSU)

Collaborators: Pacific Northwest National Laboratory (PNNL)

Project Number: 05-083

Project Start Date: January 2005

Project End Date: February 2008

Research Objectives

A closed loop nuclear fuel cycle requires mixed oxide (MOX) fuels containing plutonium. The use of MOX fuel, combined with longer irradiation times, increases the production of trans-plutonium actinides, most significantly isotopes of americium and curium. Because the presence of these isotopes significantly impacts the long-term radiotoxicity of high-level waste, it is important to develop effective methods for their isolation and/or transmutation. Whether by thermal reactor, fast spectrum reactor, or accelerator irradiation, transmutation is most efficiently done in the absence of lanthanide fission products, as some of the lanthanides are significant neutron poisons.

Lanthanide content is 100-fold higher on a molar basis than americium or curium (Am/Cm) in freshly dissolved spent fuel; therefore, it is very important to develop effective procedures for their mutual separation. The most useful and versatile separations of these species are accomplished using reagents containing donor atoms that are "softer" than oxygen (O) and interact more strongly with actinides than lanthanides. Nitrogen (N) and sulfur (S) are particularly suited and the chloride ion (Cl^-) has been used as well. Reagents that have been advanced in recent years show promise, but suffer various weaknesses, many relating to their instability in a radiation field or strongly acidic solutions.

This project investigates new chemical methods (and improvement of existing methods) for selective separation of transplutonium actinide isotopes from fission product lanthanides using the proven technique of aqueous processing—specifically those processes that employ soft donor atoms (N, Cl^-, and S). The overall work scope for this project includes the following elements:

- Investigate selective partitioning of trivalent americium and curium from fission product lanthanides using ammonium thiocyanate and concentrated chloride solutions
- Adapt the basic philosophy of the TALSPEAK process (using water soluble aminopolycarboxylate complexants) to these extractant systems in various classes of solvent extraction systems
- Explore radiation protection methods based on the removal of radiolytic degradation products (largely free radicals, introducing radical scavengers) from the extractant or the aqueous phase.
- Design ligands for selected new classes of reagents (lipophilic analogs of EDTA and thio polyamide/polyamine derivatives)—essential features of these systems include rapid complexation kinetics, high selectivity measurable radiation stability, and good phase compatibility (solubility)

Research Progress

Research initially focused on 1) solvent extraction studies from thiocyanate media using conventional extractant molecules and 2) the design, synthesis, and characterization of polyaza-extractants. Researchers also conducted some electrochemistry studies designed to characterize lanthanide complexes with new complexants. At the present, the team has suspended activities on chloride and thiocyanate systems in favor of a more focused effort on the TALSPEAK system. They have examined the literature describing TALSPEAK-relevant separations and studied the kinetics of lanthanide interactions with aminopolycarboxylate complexants in lactate media.

Researchers are repeating selected experiments in this area in preparation for completing at least one publication based on this work. However, kinetic features of TALSPEAK may limit or alter the process development parameters. Results indicate that kinetic limitations in process chemistry must result from chemistry occurring in the interfacial region of the phase transfer system rather than in the aqueous phase. This knowledge could direct a different engineering solution to this particular problem. Researchers have also completed a detailed pH profile of the performance of lactate-based TALSPEAK on lanthanide extraction.

Researchers have received actinide isotopes from the Pacific Northwest National Laboratory and improved their infrastructure to enable the safe handling of these materials at the milligram level. The delivery of isotopes was delayed unexpectedly by additional paperwork required by the State of Washington Department of Health regarding airborne release permitting for the research facility. Researchers have worked out some materials handling issues with the WSU Radiation Safety Office (RSO) and are presently commissioning new laboratory space to conduct these studies. An equipment grant from the DOE Office of Basic Energy Sciences will be used to modernize the instrumentation in this special-purpose laboratory.

Researchers have also synthesized several new polyaza extractant molecules and are presently evaluating their coordination chemistry and separations potential. The ligands that have been targeted for synthesis are polyaza donor systems, which are expected to be inherently resistant to radiolytic degradation. The polyaza extractant synthesis studies have progressed from investigating a combination amine-amide donor system to investigating a multiple amine donor extraction system. These extractant species employ some degree of preorientation of donor groups to enhance interaction strength and emphasize conditions for actinide selectivity.

Planned Activities

Researchers are currently planning studies with millimolar concentrations of actinides. They have received the desired supplies of isotopes, and are working through the final details of operational parameters with the RSO. The alpha-emitting nuclides used by this project have challenged the experience-base of RSO personnel as they gain familiarity with the demands of working with radioactive materials in amounts above the radiotracer level. Waste management and recovery of precious actinide isotopes are an integral part of the team's standard research practice, requiring efficient work with alpha emitters and recovery of actinides from complex mixtures. Researchers are designing intelligent synthesis procedures for the target extractant molecules.

The research team will continue to investigate the chemical details of the TALSPEAK process, profiling the temperature dependence of this process. Adjusting the temperature of this extraction system has not been previously reported, and perhaps represents the most facile approach to solving kinetic limitations that plague this process in lab-scale tests with actual dissolved spent fuel and simulants. These investigations are designed to assist the team in optimizing the operational characteristics of TALSPEAK.

NUCLEAR ENERGY RESEARCH INITIATIVE

Development of Nanostructured Materials with Improved Radiation Tolerance for Advanced Nuclear Systems

PI: Xinghang Zhang and K. Ted Hartwig, Texas A&M University

Collaborators: Los Alamos National Laboratory (LANL)

Project Number: 05-088

Project Start Date: April 2005

Project End Date: April 2008

Research Objectives

This project explores the mechanisms through which interfaces in the nanolayered structures and grain boundaries of bulk nanomaterials attract and eliminate point defects and unwanted foreign species. Candidate materials include nanostructured multilayer composites synthesized by magnetron sputtering (a bottom-up approach) and structural bulk nanomaterials produced by severe plastic deformation, equal channel angular extrusion (a top-down approach). Researchers will induce interfaces and grain boundaries in nanomaterials and design structural nanomaterials for advanced nuclear reactors.

This project will have a profound and broad impact on understanding the fundamental science behind improving nanomaterial radiation resistance. Data will be used to estimate defect capture rates and lifetimes of multilayered structures and bulk nanomaterials in conditions that would seriously degrade conventional microstructures.

Research Progress

ECAE processed alloys. Researchers have processed a series of alloys, including bulk 304, 316L stainless steel, HT-9 alloys, 9Cr-1Mo steel, and EP823, using equal channel angular extrusion (ECAE). Some of these materials are very special (such as HT-9, 9Cr-1Mo, EP823) and are not commercially available. The microstructures of as-processed T91 alloys have been characterized using transmission electron microscopy (TEM). The grain size of T91 has been briefly reduced from a few microns in the as-received alloy to around 200-300 nm after ECAE processing. Researchers have also observed dislocation walls in these grains. An example of such fine microstructure is shown in Figure 1.

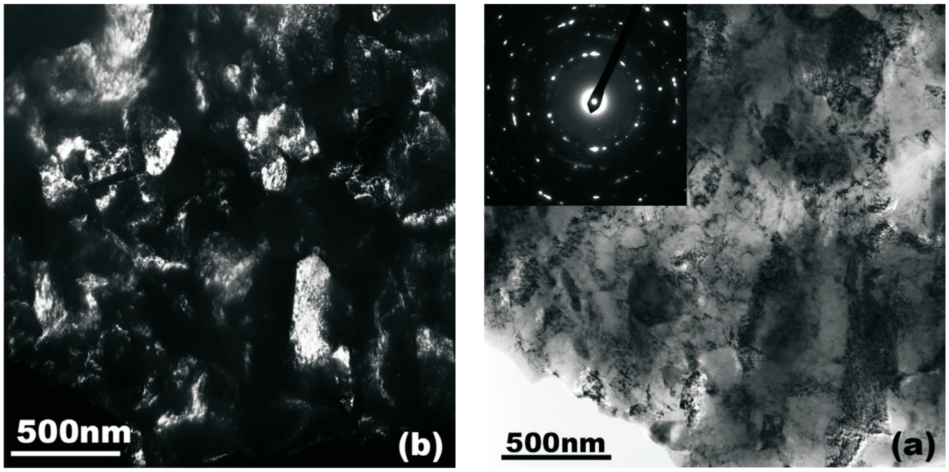


Figure 1. TEM micrograph of T91 alloys processed at 700°C for 2 passes. The average grain size has been refined dramatically down to ~ 250 nm with a large increase in dislocation density. (a) bright field TEM (b) corresponding dark field TEM micrographs.

Processing ferritic/martensitic steels using ECAE has rarely been explored. The relatively high strength of these materials makes ECAE processes very challenging. The hardnesses of T91 alloys measured using Fischerscope 2000 XYp are plotted as a function of $d^{-1/2}$, where d is the average grain size, as shown in Figure 2. Hardness increases from about 2.5 GPa (as received) to about 4 GPa after ECAE processing. A linear fit of the experimental data indicates that the hardening in ECAE-processed T91 is dominated by grain boundary mediated dislocation activities. This is typically known as the Hall-Petch model, which describes strengthening due to dislocation pile-ups within grains.

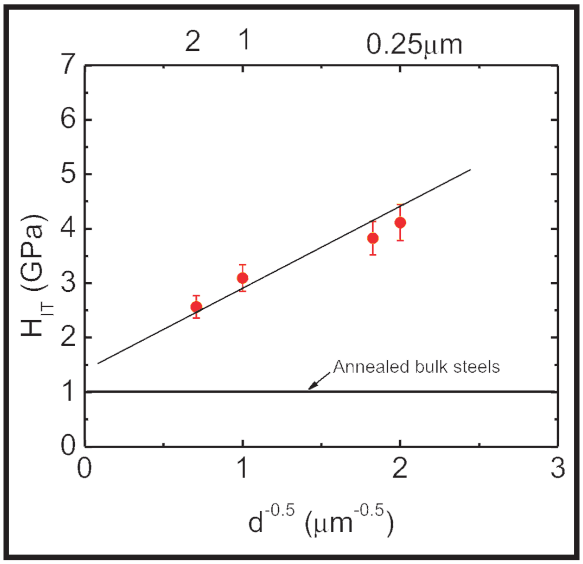


Figure 2. Indentation hardness (H_{IT}) plotted vs. $d^{-0.5}$, where d is the average grain size of T91 alloys. A linear increase of H_{IT} with $d^{-0.5}$ indicates that strengthening is primarily attributed to Hall-Petch dislocation pile-up mechanism.

Researchers have recently processed another batch of bulk T91, HT9, 316L, 316L powder, and 304 alloys. Extrusion temperatures varied from 500 to 700°C. Most of these materials were extruded well and will be tested for corrosion studies or in hot cells at LANL. An optical micrograph of extruded 316L powder is shown in Figure 3. Shear localization was observed, indicating that the powder is fully consolidated.

Figure 3. Consolidation of 316L powder at 700°C using a route of 2Bc. The specimens, 1-inch square in cross-section, exhibit obvious shear localization, a typical indication of complete consolidation of powders.

Sputter-deposited nanolayer films with improved ion irradiation tolerance

Fe/W nanolayer films before and after ion irradiation

Researchers at LANL performed helium ion implantation on 5 and 50 nm iron/tungsten (Fe/W) multilayer films, at 150 keV with a total dose of $10^{17}/cm^2$, corresponding to a few dpa at peak concentration. Figure 4 shows the cross-sectional TEM micrograph (XTEM) of Fe/W 5 nm in a heavily ion-irradiated region. Ion irradiation introduced 1–2 nm diameter helium bubbles in these very fine multilayer films. Layer interfaces seem to be rather stable, although significant intermixing is expected due to the miscibility between Fe and W. Neither TEM nor XRD studies show the generation of new phases.

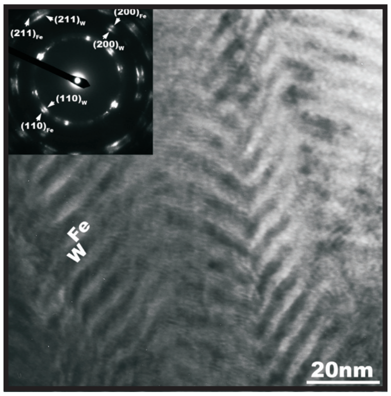


Figure 4. Cross-sectional TEM micrograph of ion irradiated Fe/W 5 nm multilayer films. Irradiation induces bubbles with an average diameter of approximately 1-2 nm. Ion irradiation did not change the film texture (110)Fe and (110)W. There is no indication of the formation of new phases after ion irradiation.

The microstructure of ion-irradiated Fe/W multilayer films remains similar to as-deposited films, as shown in Figure 5a. The under-focused TEM micrograph, Figure 5b, clearly shows that He bubbles around 1–2 nm in diameter have formed in both the Fe and W layers, with a larger bubble concentration along the Fe/W interfaces. The formation of He bubbles is a result of high dose He ion irradiation. Helium bubbles align along grain boundaries and layer interfaces, as indicated by arrows. Interface and grain boundaries seem to play an important role in accumulating He bubbles.

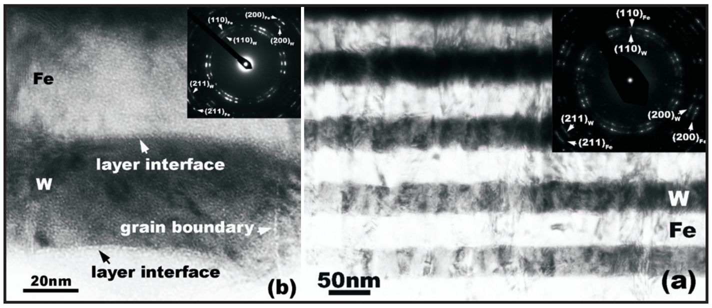


Figure 5. Microstructure of Fe/W 50 nm films after He ion irradiation. (a) 800 nm underneath film surface. Low magnification TEM micrograph (b) He bubbles 1–2 nm in diameter can be seen in both Fe and W layers.

The hardness of ion irradiated Fe/W multilayer films are compared with that of as-deposited multilayer in Figure 6. Current experiments indicate that radiation-induced hardening is less significant in the thinner multilayer films (Fe/W 5 nm) as compared to the thicker films (Fe/W 50 nm). Reduced hardening due to irradiation could be due to the reduced number of defects generated by irradiation.

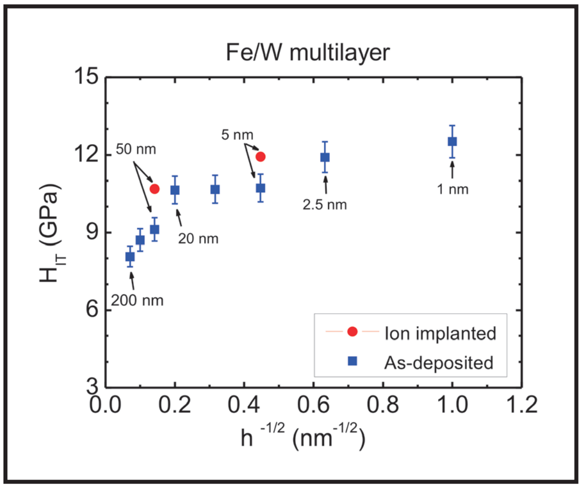


Figure 6. Indentation hardness (HIT) plotted vs. $h^{-0.5}$, where h is the thickness of each individual layer. Hardness increases with decreasing layer thickness. Blue squares stand for hardness of as-deposited Fe/W multilayers, whereas red solid circles stand for hardness measured from the two sets of ion-implanted Fe/W multilayer films.

Synthesis of Al/Nb Nanolayers for ion-irradiation studies

Aluminum/niobium (Al/Nb) was chosen because Al coatings can be corrosion-resistant in lead-bismuth (Pb-Bi)-cooled nuclear reactors with the introduction of an oxide layer. The microstructure of as-deposited Al/Nb 5 nm multilayer films is shown in Figure 7.

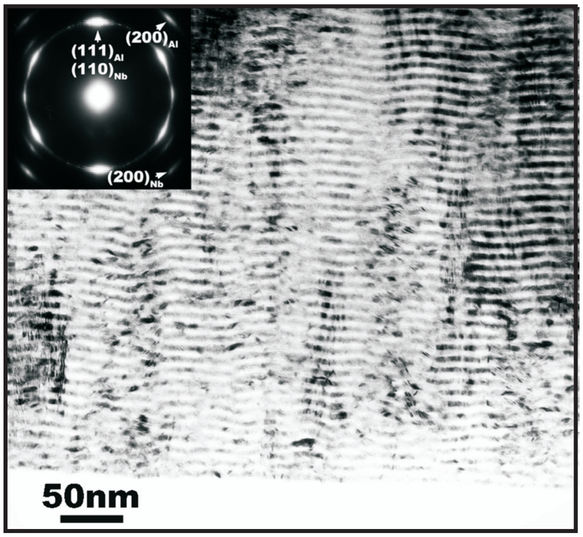


Figure. 7. TEM micrograph of as-deposited Al/Nb 5 nm multilayers with Kurdjumov-Sachs orientation relationship. Film has strong {111} Al and {110} Nb texture shown by the inserted SAD pattern.

The film has clear and unmixed layer structure, as shown in Figure 7. The inserted selected area diffraction pattern indicates a strong Kurdjumov-Sachs orientation relationship between bcc Nb and fcc Al (body-centered cubic and face-centered cubic, respectively). The film has strong {111} Al and {110} Nb texture, as shown by the inserted SAD pattern.

Al/Nb films have been subjected to He ion irradiation at 150 keV with a total dose of $10^{17}/cm^2$ corresponding to a few dpa at peak concentration in Al/Nb multilayer films. Such ion implantation conditions are identical to that of Fe/W multilayer systems. An under-focused TEM micrograph of ion irradiated Al/Nb 50 nm multilayers is shown in Figure 8. The bubble size in Al is approximately 2 nm, whereas it is about 1 nm in Nb. The SAD of Al/Nb 50 nm multilayer shows no obvious texture and no indication for the formation of new phases. The larger bubble size in Al could be due to the lower elastic modulus of Al than that of Nb. It is anticipated that radiation-induced defects in Al are more significant than that in Nb.

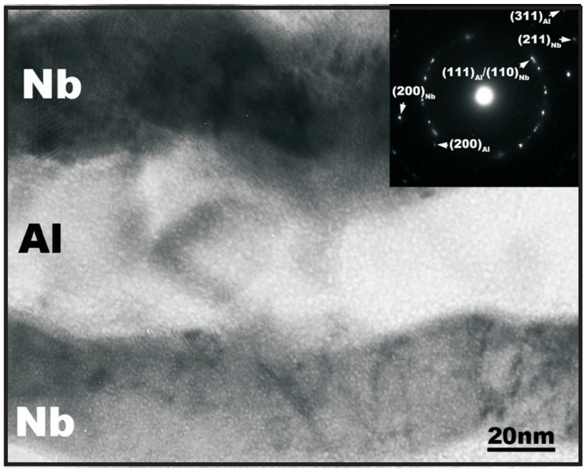


Figure 8. Cross-sectional TEM micrograph of Al/Nb 50 nm multilayers after He ion irradiation with a dose of $1017/cm^2$ at 150 keV. He bubbles can be seen in both Al and Nb. The bubble size in Al is approximately 2 nm, whereas it is about 1nm in Nb. The SAD of Al/Nb 50 nm multilayer shows no obvious texture and no indication for the formation of new

Planned Activities

Researchers will investigate the influence of grain size on irradiation-induced defects in ECAE-processed T91, HT-9, and 316L SS alloys. ECAE-processed specimens will be subjected to radiation test in hot cell and corrosion tests at LANL. Researchers will also examine the density of consolidated 316P in more detail via cross-sectional SEM measurement. Furthermore, the porosity, if it exists, can be indirectly reflected from premature failure during tensile tests. The microstructure and mechanical behavior of consolidated 316P will be examined in more detail.

Researchers will also investigate the influence of interface in annihilation of radiation-induced defects in more detail. For instance, radiation-induced hardening in Fe/W and Al/Nb have opposite trends. Researchers will also examine the chemistry along layer interfaces with scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) techniques. Ion radiation experiments have been planned for more Fe/W and Al/Nb specimens with different layer thicknesses. These studies will provide valuable information on the role of different interfaces (fcc/bcc versus bcc/bcc) in interaction with radiation-induced defects.

Utilization of Minor Actinides as a Fuel Component for Ultra-Long-Life VHTR Configurations: Designs, Advantages, and Limitations

PI: Pavel V. Tsvetkov, Texas A&M University

Collaborators: None

Project Number: 05-094

Project Start Date: March 2005

Project End Date: March 2008

Research Objectives

The objective of this project is to assess ultra-long life very high-temperature reactor (VHTR) configurations utilizing minor actinides (MAs) as a fuel component. Researchers will compare the capabilities of pebble-bed and prismatic core designs with advanced actinide fuels. The ultimate goal is to operate the reactor for its lifetime (limited by material considerations) without intermediate refuelings. Systems will focus on control, dynamics, safety, and proliferation-resistance to support autonomous operation. The suggested approach offers consistent analysis of the advanced configurations.

This work will provide a comprehensive assessment of the VHTR's passive safety design and operation. The researchers will conduct code-to-experiment benchmarks to confirm the models and analytical results obtained. Success of the project will be determined by its ability to demonstrate (or refute) the possibility, advantages, and limitations of achieving ultra-long-life VHTR configurations by utilizing MAs as a fuel component.

Researchers will also evaluate ex-core fuel cycle segments and study the impact of increasing burn-up levels on the generated radioactivity. Use of advanced actinide fuels could reduce the long-term radiotoxicity and heat load of high-level waste sent to a geologic repository and enable recovery of the energy contained in the spent fuel. Since both the pebble bed and prismatic block core designs permit flexibility in component configuration, fuel utilization, and fuel management, it is possible to improve the fissile properties of minor actinides by neutron spectrum shifting through configuration adjustments. Consequently, small reactivity swings will yield high levels of burnup. The principal mechanism for achieving ultra-long VHTR life is enhanced involvement of self-generated fissile compositions based on spent light water reactor fuel.

The ultra-long core life approach reduces the technical need for additional repositories and should improve VHTR marketability worldwide. Figure 1 illustrates potential relations between the VHTR with MAs and other designs within the current nuclear technology framework.

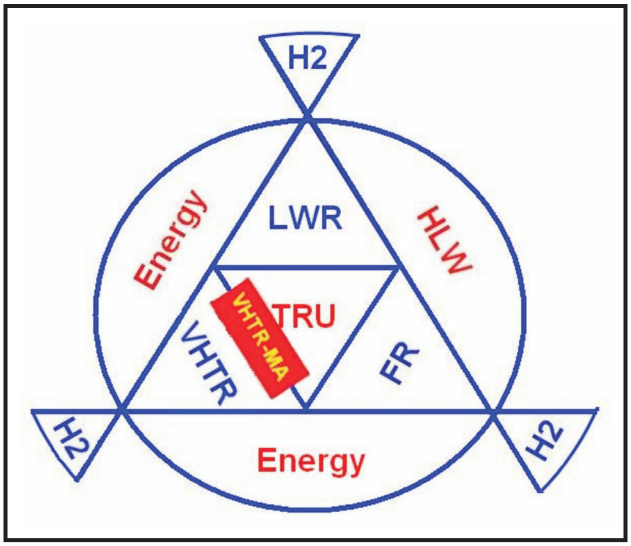


Figure 1. VHTRs with MAs and the nuclear technology framework.

Researchers have adopted a hybrid methodology for coupled neutronics-thermal hydraulics design studies of VHTRs that combines Monte Carlo and deterministic approaches. They are developing realistic 3-D coupled neutronics and thermal-hydraulics models with multi-heterogeneity treatments, performing experimental/computational benchmarks for model verification and validation, and analyzing uncertainty effects and error propagation. The results describe performance of the entire power unit and allow conclusions regarding feasibility, performance, and possible directions for further development.

Research Progress

Researchers performed a literature survey to develop a database of actinide fuels and materials properties in order to establish realistic VHTR configurations with advanced materials. The major thrust in FY 2006 has been on analyzing configuration variation capabilities to achieve ultra-long operation without refueling, to maximize burnup, and to minimize reactivity swings. Using 3-D whole-core/system models, researchers developed a variation analysis methodology and applied it to studies of VHTR geometry and material variations. Figure 2 illustrates parametric variations for pebble-bed cores; similar variations were performed for prismatic cores.

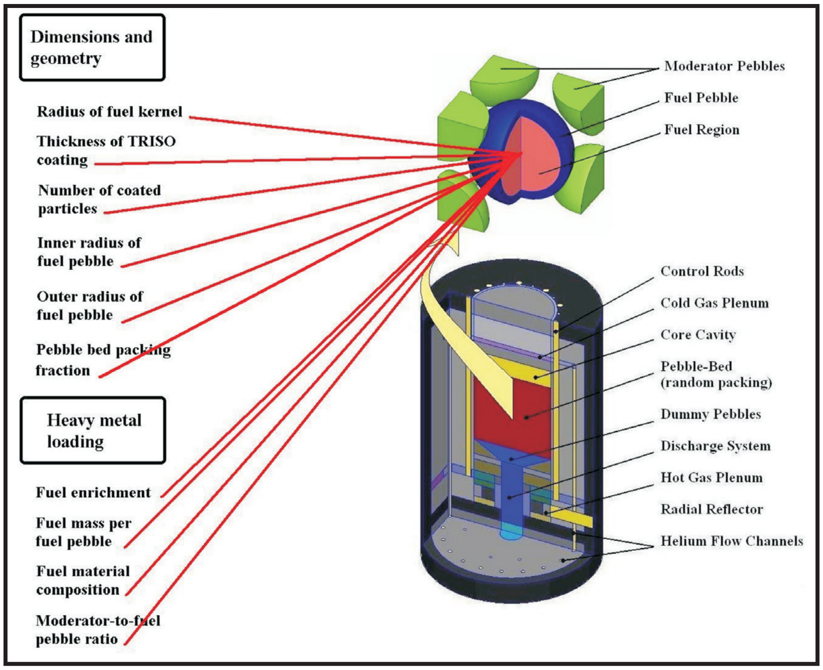


Figure 2. Geometry and material variations in the pebble-bed layout.

Researchers have completed the analysis of existing uncertainty effects on VHTR performance characteristics, focusing on the effects of nuclear data and design parameters. This was followed by a reliability evaluation of VHTR modeling.

The team developed code systems to link the applied suite of neutronics and thermal hydraulics codes and the generalized codes for universal sensitivity analysis, calibration, and uncertainty evaluations into a single framework. The project tools include MCNP, SCALE, auxiliary tools to account for double heterogeneity, HeatWave suite, and statistical analysis packages and modules. Generalized codes for universal sensitivity analysis, calibration, and uncertainty evaluations are represented by the UCODE-2005 code system and its post-processors.

Researchers developed coupling methodology and applied tools that account for multi-heterogeneity of the VHTR configurations and allow whole-core/system 3-D modeling. To assure comprehensive and realistic assessment, they compiled model benchmark sets based on the LEU-HTR PROTEUS, HTTR, and HTR-10 experimental programs. Results of model validation and verification and sensitivity/uncertainty analysis agree with available data and confirm the validity of the approach.

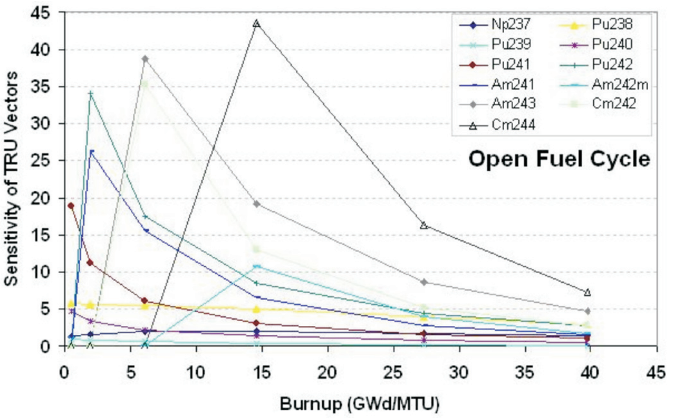
If further generalized, the methodology will be suitable for multi-parametric design optimization. As an example, Figure 3 illustrates ongoing sensitivity/uncertainty studies: dimensionless sensitivity indicators for fluctuations of TRU/MA vectors and for criticality fluctuations in VHTR configurations due to variations of the isothermal core temperature.

Prismatic Core

T_{core} (K)	δ_k	δ_T	$S_{k,T}$ (%)
300.0	-0.0042	40.0	-3.1
380.0	-0.0121	40.0	-11.6
460.0	-0.0027	20.0	-6.4

Pebble-Bed Core

T_{core} (K)	δ_k	δ_T	$S_{k,T}$ (%)
300.0	-0.0180	93.0	-5.0
393.0	-0.0100	80.0	-4.3
473.0	-0.0107	50.0	-9.0



TRU vectors in the open fuel cycle

Core temperature fluctuations

Figure 3. Sensitivity/uncertainty analysis of the VHTR configurations with MAs.

The sensitivity/uncertainty analysis is the basis of ongoing studies of configuration variation capabilities. Researchers are evaluating methods to optimize a physically achievable system lifetime, taking advantage of self-sustainable fuel compositions with higher actinides. The design target is an autonomous operation with minimized required control interventions.

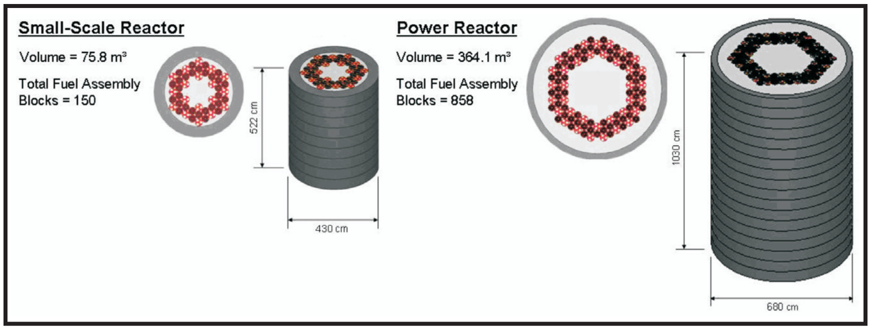


Figure 4. Examples of small-scale and power reactor layouts.

Researchers chose the HTTR and HTR-10 model configurations with fully withdrawn control rods as the prototypes to represent prismatic block and pebble bed core designs, respectively. Due to inherent safety characteristics of annular configurations, the whole-core 3-D models were adjusted from the original cylindrical cores to annular, considering both small-scale and large power reactor layouts. Figure 4 shows both layouts taking the prismatic core design as an example.

As part of the initial safety analysis, researchers evaluated the isothermal temperature coefficient of pebble-bed and prismatic core layouts for each fuel loading case. Figure 5 illustrates the results obtained and presents core configurations with different fuel loadings for comparison.

Based on the results obtained, researchers have updated and re-validated the VHTR models to account for the increased accuracy requirement. Despite some technical limitations and challenges, the studies suggest promising performance of VHTRs with MAs and the possibility to achieve prolonged operation.

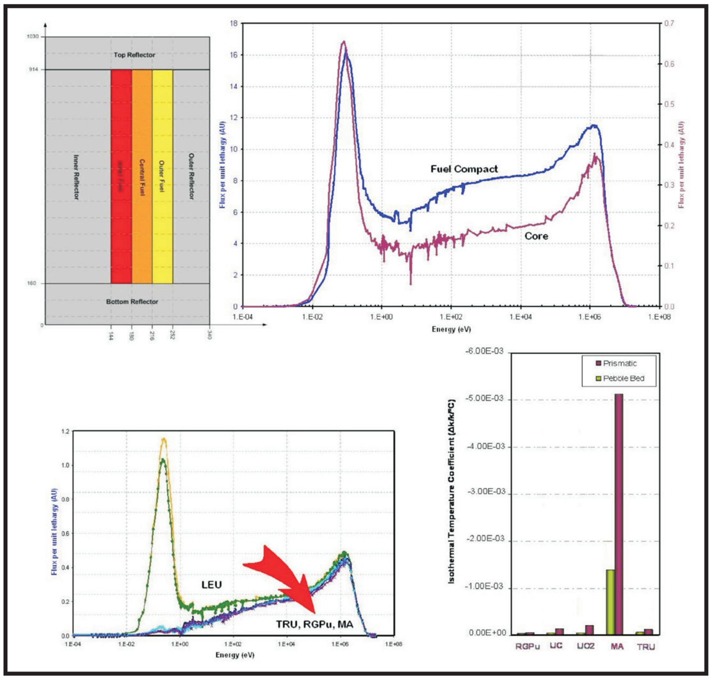


Figure 5. Power reactor model structure and selected performance characteristics.

Planned Activities

In the third and final year, the following subtasks will be completed, fulfilling the objectives of the project:

- VHTR optimization to achieve ultra-long life
- Feasibility of ultra-long-life VHTRs with MAs
- Ultra-long-life VHTRs and transmutation
- Dynamics, safety, and control of VHTRs with MAs
- Fuel cycle of ultra-long-life VHTRs with MAs
- Proliferation-resistance of ultra-long-life VHTRs

NUCLEAR ENERGY RESEARCH INITIATIVE

Ambient Laboratory Coater for Advanced Gas Reactor Fuel Development

PI: Duane D. Bruns, University of Tennessee (UTK)

Collaborators: Idaho National Laboratory, Oak Ridge National Laboratory (ORNL), Iowa State University

Project Number: 05-118

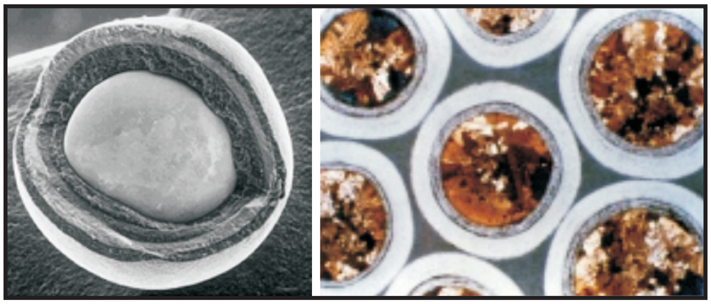
Project Start Date: January 2005

Project End Date: December 2007

Research Objectives

The objective of this project is to develop a physics-based understanding of the spouted bed coaters presently used to coat **Tris**tructural-**iso**tropic (TRISO) nuclear fuel particles. The goal is to scale up the coaters from research scale (50 mm ID) to production dimensions (>150 mm). To achieve this goal, the team will use a combination of intensive experimental efforts and detailed model development to guide (and accelerate) the scale-up program.

The physical characteristics and properties of the particles, bed, and fluidizing gas interact, affecting the hydrodynamics in the fluidization processes. The hydrodynamics drive the heat, mass, and momentum transfer both locally and globally in the unit operation. Presently, there are no reliable design procedures to scale-up the fluidization process, let alone specialized spouted bed reactors.



Researchers are collecting experimental measurements from four coaters operating at temperatures up to 500°C (50, 83.5, 95, and 150 mm), a 50 mm hot surrogate coater, a 50 mm uranium coater, and a 150 mm BWXT coater. The latter has more sophisticated distributors than the typical conical bottom. The data collected includes the high-speed (1,000 Hz) differential pressure time series of the fluidizing gas from the bed inlet to exit.

Researchers will use fast response sensors to capture dynamic behavior, such as a 3-D positioning system with feedback control and pitot tube to measure average local velocities. They control relative humidity to mitigate electrostatic effects. If the coater provides optical access, the team will record digital images for later analysis. The time scale of the bed dynamics is such that visual observation provides insight into the physics of the process.

The advanced computational fluid dynamics tools for granular flow simulations in MFIX allow researchers to interactively conduct experiments and simulations. The excellent overall agreement between experiments and simulations provides additional insight into the complex interactions between the gas and particles in the spouted beds and is expected to reduce the development and optimization time. Researchers have reported that existing correlations for minimum spouting velocity give poor values. Therefore, this project's new correlations should be of immediate value.

The research includes:

- Design and fabricate fluidized beds with changeable nozzles and distributors
- Develop LabVIEW software for operation, data collection, and feedback control
- Study parameters important to scale-up and develop correlations for minimum fluidization velocity, minimum spouting velocity, bed pressure drop, and spout shape in shallow spouted beds with high density and spherical particles
- Collect high-speed pressure measurements and images and conduct image analysis; develop new measurement techniques for flux and momentum distributions
- Support instrumentation and control and measurements in coating temperatures to 2000 K
- Apply chaos and nonlinear dynamics concepts for feedback control

Research Progress

These coaters are highly nonlinear, sensitive to boundary conditions, and exhibit idiosyncratic behaviors such as complex transients, unstable hydrodynamics, and chaos, which contribute to scale-up issues.

The images in Figure 1 show the profiles produced by 53.9 g of 500 μm zirconium oxide (ZrO_2) particles in the 50 mm spouted bed with a 60° cone at four different flow rates. Simulated local gas velocities track the experimental values taken with a small Prandtl tube. Figure 2 shows the experimental gas velocities plotted for eight different heights from the cone inlet. The model output compares well dynamically to lab data in terms of the Power Spectral Density (Figure 3). These plots generally show transitions from one spout pinching or modulating amplitude peak to two peaks, which indicates both spout pinching and entering "bubbles" and then to one "bubbling" or pockets of fluidizing gas entering the bed amplitude peak as the gas velocity is decreased from a high to low flow rate. This demonstrates that bifurcations occur in the chaotic process. This result has major implications for operation of coaters and deserves additional investigation.

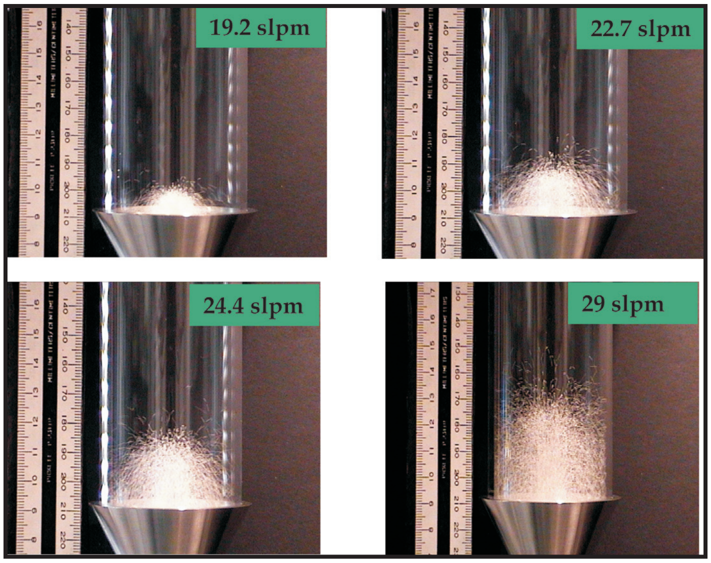


Figure 1. High-speed photographs of ZrO_2 particles in 60° cone, 50 mm spouted bed.

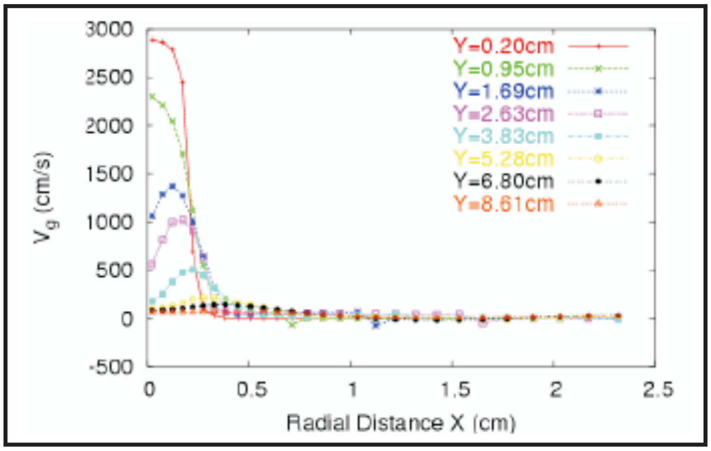


Figure 2. Experimental gas velocities as a function of radial distance and height.

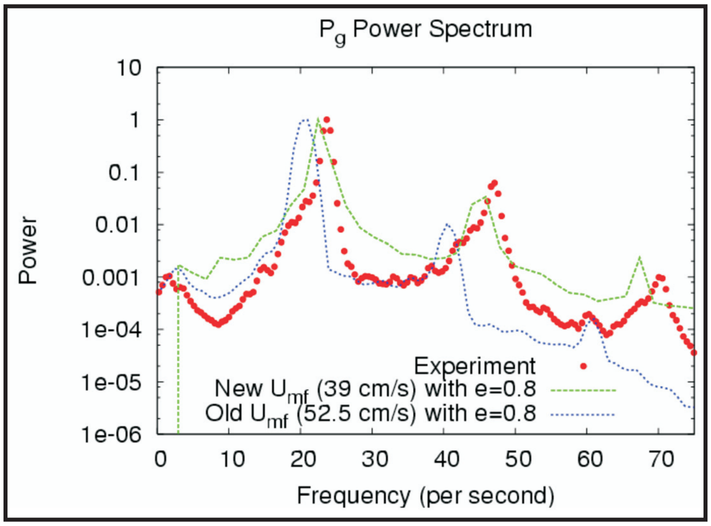


Figure 3. Experimental versus model power spectral density.

The methodology for extracting quantitative spout height and diameter is illustrated in the series of images shown in Figure 4. The image on the left is single frame, the center is an average over many contiguous experimental frames, and the right-hand frame shows a time-averaged MFIX simulation for a vertical cross section through the center of the bed. The time-averaged images from the experiment and MFIX model agree very well.

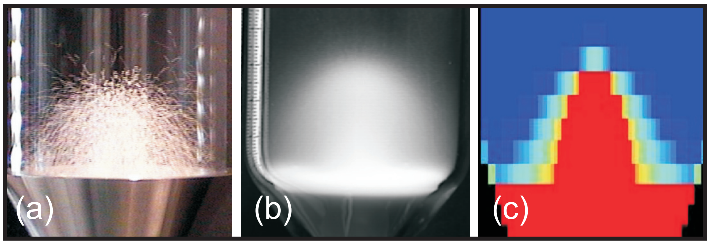


Figure 4. Methodology for extracting spout parameters: (a) 1/30th second, single-frame image; (b) average over many contiguous frames; (c) MFIX simulation.

Quantitative Definition of U_{ms}. The procedure to measure the minimum spouting velocity (U_{ms}) is similar to that for determining minimum fluidization velocity (U_{mf})—except visual observations are used. Starting from a fully spouting state, the gas flow rate is slowly decreased; U_{ms} has been reached when the observed particle movement stops.

Researchers have developed a new quantitative technique to define U_{ms}. Lowering the gas flow rate in discrete steps while measuring differential pressure (ΔP) yields a smoothly decreasing ΔP curve until it reaches a minimum value. Then, it increases sharply as gas flow is lowered further. The velocity corresponding to this minimum point is U_{ms}. Figure 5 shows an example for 53.9 g of 0.5 mm ZrO_2 in a 60° spouted bed. Here, U_{ms} occurs at a flow rate of 12.0 SLMP. This method is more reproducible than visual observations; generally, the particles appear to have stopped moving slightly before reaching the minimum ΔP.

Hydrodynamic Correlations. The spouted beds used for nuclear fuel particle coating are very different from those published in fluidization literature, as the nuclear coaters have very shallow beds (ratio of particle height to bed diameter < 1) and very dense particles (U specific gravity ≈ 13; ZrO_2 ≈ 7). However, the very narrow particle size distribution and nearly spherical shape make the process ideal for modeling.

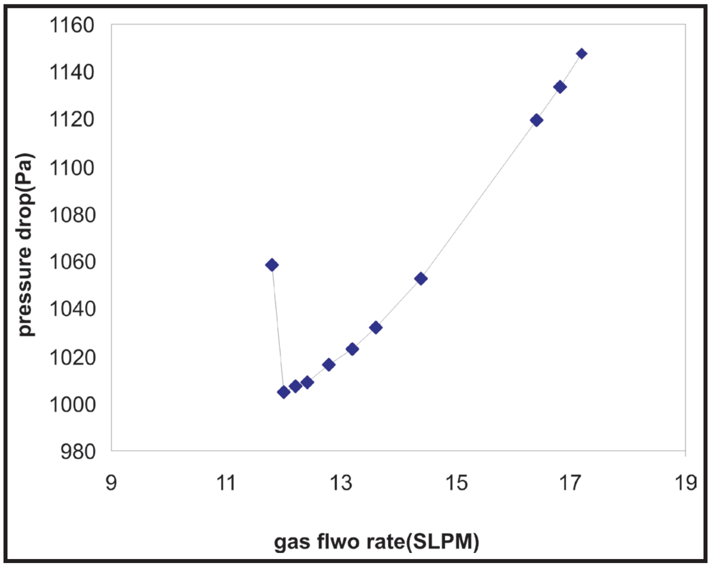


Figure 5. Quantitative measurement of Ums for 53.9 g of 0.5 mm ZrO_2 in a 60° spouted bed.

The experimental matrix covers the following set of variable parameters: 1) ZrO_2 particle diameters (Dp) from 300–1000 μm; cone angles (γ) from 15–75°; static particle height $0.5<H_o<1.1$ and less than cone height; fluidizing gas velocity $0.9 < U/U_{ms} < 2.5$. Fixed conditions include a 500 mm bed column diameter (Dc), 0.04 mm throat diameter (Dt), and use of ambient air at 35 percent relative humidity as the fluidization gas. Measurements of U_{mf} for ZrO_2 particles agree very well with predictions. The U_{ms} correlation is: $Re_{ms} = 0.0015\ Ar^{0.86}\ (Ho/Dc)^{0.59}\ \tan(\gamma/2)^{0.87}$.

The gas pressure drop across the spouted bed fluctuates around its mean value. Figure 6 illustrates the time series for a sample case (53.9 g of 500 μm ZrO_2 in 60° bed at $U/U_{ms} = 1.5$). The average ΔP is obtained by averaging data collected at 1,000 Hz over one minute.

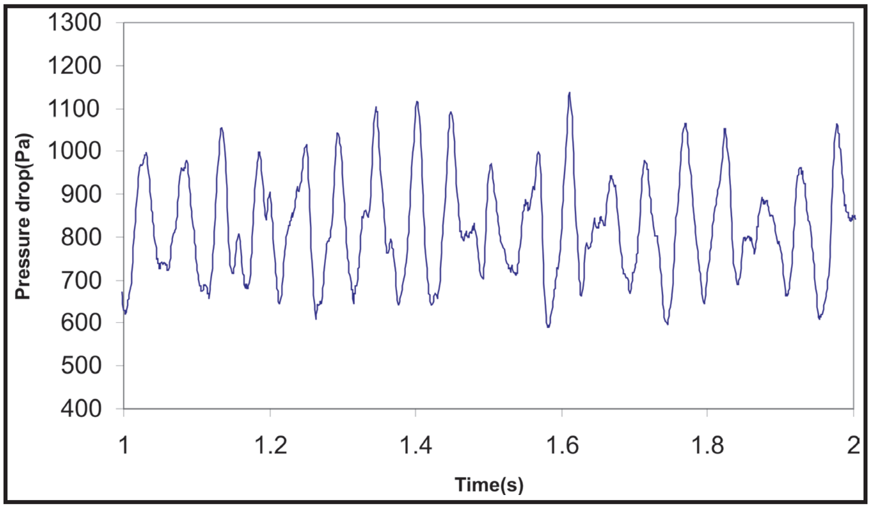


Figure 6. Fluctuations in pressure drop measured across spouted bed.

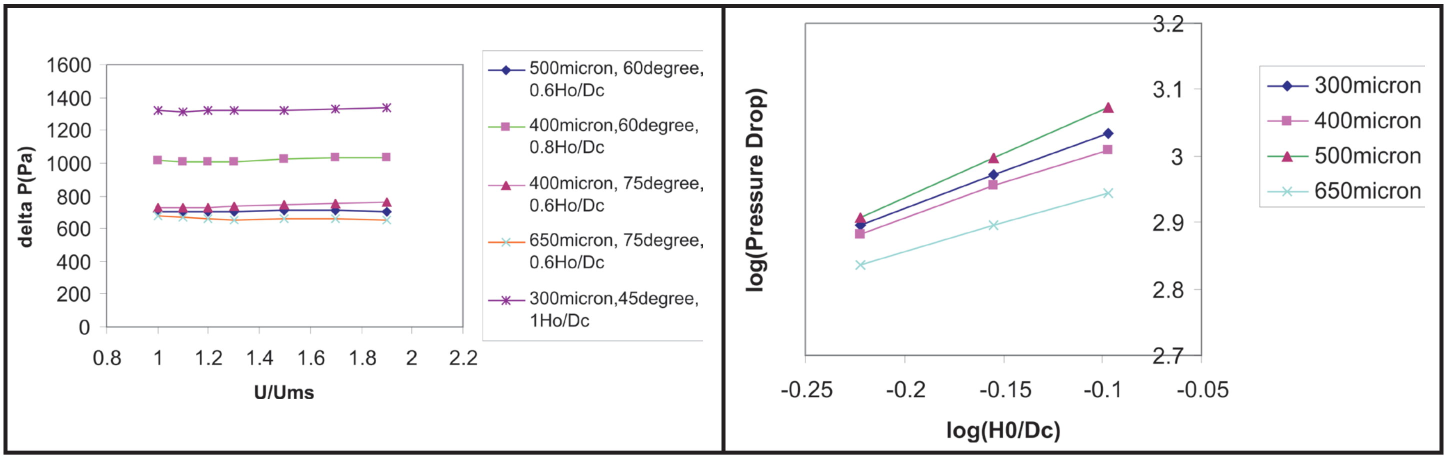


Figure 7. Pressure plots as a function of input parameters (e.g., particle size, spout angle, velocity).

Researchers studied the effect of all parameters in detail for the example problem. Figure 7 shows plots of ΔP versus U/U_m and log(ΔP) versus $\log(H_0/D_c)$. The resulting ΔP correlation is:

$$\frac{\Delta P_s}{\rho_p H_0 g} = 0.15\left(\frac{D_p}{D_c}\right)^{-0.208}\left(\frac{H_0}{D_c}\right)^{0.02}\left[\tan\left(\frac{\gamma}{2}\right)\right]^{-0.039} \qquad r^2 = 0.99$$

The hydraulic bifurcations related to "pinching" and "bubbling" are found with respect to most process inputs. This is an important key to controlling spouted bed coaters.

Planned Activities

The team plans to conduct the following activities during the next fiscal year:

- Construct 84.5, 95, and 150 mm beds. The selected distributors will utilize the Coater Scale-up Plan, PLN-1975, and MFIX modeling results.
- Develop spout height and diameter correlation.
- Demonstrate the particle flux and momentum sensor, ideally in a hot coater.
- Determine particle statistics for passage through a plane or a local volume; local particle velocities, flux, and void fraction; and wall boundary conditions from images of the 50 mm bed. The boundary conditions can be used in the numerical models.
- Develop equations to provide insight into spouted bed behavior by identifying the important physical nonlinearities and process parameters. This can be used for model-based control to improve long-term coater operation.
- Evaluate differential pressure of hot coater (400 K); collect additional data to develop physical understanding of the differences from the ambient coater.

NUCLEAR ENERGY RESEARCH INITIATIVE

Uncertainty Analyses of Advanced Fuel Cycles

PI: Laurence Miller, The University of Tennessee

Collaborators: Argonne National Laboratory (ANL)

Project Number: 05-123

Project Start Date: March 2005

Project End Date: March 2008

Research Objectives

The overall objective of this project is to quantify uncertainties associated with the sustainability of power generated by nuclear energy. Researchers will evaluate various fuel cycle options and strategies with the versatile DANESS computer program developed by ANL. This code has capabilities to calculate numerical values of parameters that relate directly or indirectly to specified outcomes. Uncertainties in parameters are propagated through dynamic and equilibrium fuel cycle models to determine distributions of values for the desired results. Thus, the quality of results can be evaluated and understood, and the gaps in knowledge that contribute to the uncertainty of the results can be identified. This permits one to understand where improvements in knowledge are needed and where additional resources should be invested. Some of the activities that are required to accomplish these objectives are as follows:

1) Design and analyze advanced fuel cycles for light water reactors (LWRs)
2) Determine the effect of nuclear data and technological uncertainties on fuel cycle analyses and evaluate the feedback of nuclear data requirements
3) Identify and assess the repository benefits of advanced fuel cycles
4) Determine the effect of uncertainties on repository benefit assessments
5) Conduct dynamic fuel cycle scenario studies to understand the issues in transitioning from thermal reactors to a mixed thermal/fast reactor fleet, or a fleet in which the majority of reactors are fast and/or accelerator-driven
6) Optimize the long-term use of key resources for advanced fuel cycles, e.g., repository capacity and uranium ore
7) Evaluate the optimal use of fast reactors and accelerator-driven systems from both technological and market perspectives

Research Progress

Project staff have made the following significant accomplishments during the past year:

1) Improvements and updates of DANESS
2) Determination of time-dependent isotope-specific decay heat release in a repository
3) Simulations of once-through and mixed oxide (MOX) fuel cycles for LWRs
4) Evaluation of LWR and fast reactor (FRs) fuel cycles
5) Uncertainty assessment of an equilibrium fuel cycle that includes plutonium recycle

The most significant improvements that the team recently implemented into DANESS involve input-output features and time-dependent isotopic inventories. They have also incorporated new features into the database attributes. Instead of having to define each case though the DANESS graphical user interface (GUI), they developed an Excel-based input sheet template that allows uploading case settings into DANESS and running multiple cases in a batch-mode. Although previous versions of DANESS provided the functionality to address isotopic decay in the nuclear fuel cycle, inclusion of the latest iThink 9.0.1 software with specifically developed functions enhances the isotopic evolution model.

The researchers performed reactor physics calculations to extend ranges of burnup and enrichment data available in DANESS for fuel cycle simulations and to obtain isotopic characteristics of spent fuel over a 1,500-year time period. Results from these calculations were used to determine relative energy releases to a repository as a function of delay time for disposition, isotopic composition, reactor type, and burnup. This permitted the determination of integrated heat loads as a function of separation technology, which showed that repository heat load can be reduced by a factor of 100 with optimal management of transuranics and fission products. The study results suggest that minor actinides (MA), such as americium (Am) and curium (Cm), be considered for disposition in thermal reactors and that plutonium (Pu) and neptunium (Np) be utilized in fast reactors. Figure 1 illustrates results of relative energy deposition as a function of delay time for various reprocessing efficiencies.

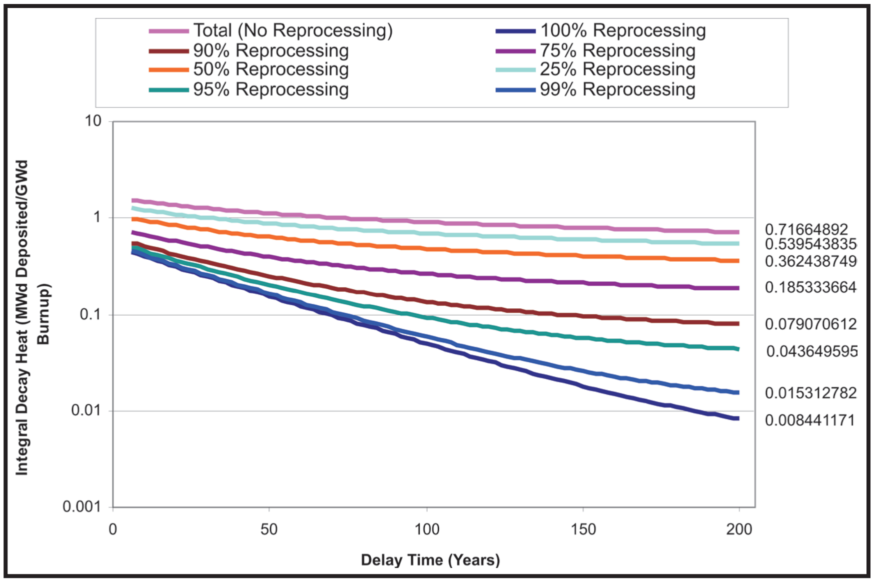


Figure 1. Ratio of energy yield to the repository relative to burnup versus delay time for various reprocessing efficiencies.

Researchers simulated both LWR fuel cycles and mixed fleets of FRs and LWRs. For the LWRs, they simulated once-through and MOX recycle fuel management options to determine their impacts on a repository, considering: 1) burnup from 30 to 100 gigawatt-days per ton, 2) growth rates, 3) time of implementing high-burnup fuel, and 4) fuel enrichment. Results of these simulations indicate that a 30 percent reduction in repository space requirements is achievable. More significant gains in utilization of repository space will require use of separations technology and fast reactors. Simulations of mixed reactor fleets with time-dependent ratios of FRs and LWRs determined plutonium and minor actinide inventories in the overall system and the reactor cores. Results show that plutonium inventories can be significantly reduced through the use of fast reactors with conversion ratios of about 0.5. However, development of fuel cycles to control MA inventories will require additional reactor physics calculations. Simulations that modeled mixed fleets of LWRs and FRs included: 1) fixed and varying numbers of LWRs with three different FR growth rates, 2) three different initial amounts of Pu, and 3) different times of FR introduction. Researchers have prepared time-dependent plots of the results and tabulated Pu and MA inventories at the year 2100.

The team also analyzed equilibrium fuel cycles using a Monte Carlo sampling method to propagate uncertainties through the model, considering: burnup of spent fuel, composition of Pu and MA in spent fuel, requirements for natural uranium, mass flows of Pu and depleted uranium for blending, and the number of FRs to burn Pu and MA produced by LWRs. Parameters in the algebraic equations that model the equilibrium fuel cycles are specified by uniform and triangular distributions. Figure 2 shows the number of fast reactors required to utilize the Pu produced by 100 LWRs.

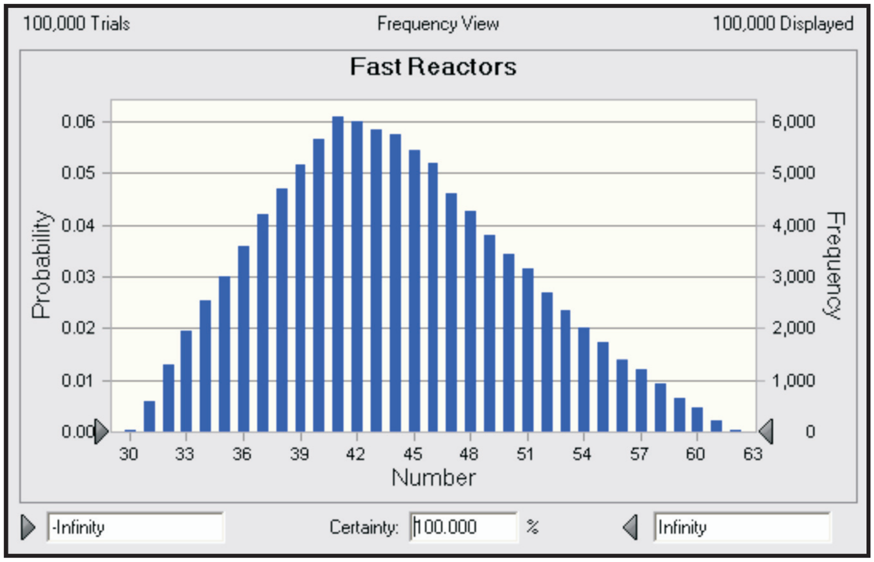


Figure 2. Distribution of the number of fast reactors with a conversion ratio of 0.5 required to utilize the Pu produced by 100 LWRs.

Planned Activities

During the third year, researchers will obtain remaining data required for uncertainty analyses of advanced dynamic and equilibrium fuel cycles, identify repository benefits associated with advanced fuel cycles chosen for further study, and conduct assessments to determine the effects of uncertainties on those benefits. These objectives will facilitate their understanding of issues and uncertainties in the transition from thermal reactors to a mixed thermal/fast reactor fleet. Some of the tasks required to accomplish these objectives include the following:

1) Review relevant reports and publications
2) Conduct conferences to evaluate specific parameters for consideration to obtain a consensus on choices for detailed studies
3) Run sufficient simulations with DANESS to obtain distributions of results to satisfy objectives cited above
4) Perform uncertainty analyses on dynamic fuel cycles selected for study
5) Perform uncertainty analyses on equilibrium cycles selected for study
6) Calculate the fractional contributions to uncertainties due to each parameter that has significant influence on repository requirements, such as repository space required per megawatt-hour of power generated
7) Create a user-friendly data base for evaluating alternatives

NUCLEAR ENERGY RESEARCH INITIATIVE

BWR Assembly Optimization for Minor Actinide Recycling

PI: G. Ivan Maldonado, University of Cincinnati

Collaborators: Exelon Nuclear, Oak Ridge National Laboratory, Los Alamos National Laboratory, Westinghouse Electric Corp.

Project Number: 05-125

Project Start Date: March 2005

Project End Date: March 2008

Research Objectives

The primary goal of this project is to design advanced boiling water reactor (BWR) fuel assemblies for the recycling of minor actinides (MA), applying and extending the latest advancements in light water reactor (LWR) fuel management optimization. Two specific objectives include:

1) Develop a new methodology for the direct coupling between the pin-by-pin control variables and the core-wide (bundle-by-bundle) optimization objectives
2) Extend this new methodology into a new application that includes control variables, objectives, and constraints designed to maximize targeted minor actinide incineration

The first objective is expected to uncover considerable dormant thermal margin, while the second is expected to consume some of this uncovered margin. Therefore, researchers will optimize improvements in fuel cycle efficiency to offset potential losses in efficiency associated with the recycling of minor actinides.

This project implements an Advanced Fuel Cycle R&D program initiative to investigate spent fuel treatment and recycling options for current generation light water reactors, and supports the DOE's technical assessment of a second high-level waste repository. The general work scope entails:

- ***Within-bundle activities***. Define candidate minor actinides; specify control variables, objectives, and constraints at the bundle level; and generate families of lattices and bundles as a function of relevant parameters (exposure, void fraction, etc.).
- ***Core-wide activities***. Define bundle-to-core coupling, generate families of core loadings and corresponding operational strategies (control rod patterns, core flow), and validate diffusion theory analyses via transport theory benchmarks
- ***Global integration of the project***. Verify proper functioning of models and generate optimized advanced BWR bundles and associated fuel cycle strategies

Research Progress

During this reporting period, the results of spiking lattices with americium (Am-241) have provided helpful insights toward understanding the likelihood of efficiently eliminating this MA as a target within a BWR system. In general, the results of loading Am-241 into lattices follow the decreasing trend shown in Figure 1. While it appears viable to eliminate a significant percentage of a preloaded inventory of this MA, the benefits of these reductions need to be carefully contrasted against potentially higher-than-usual accumulations of other minor actinides, particularly curium.

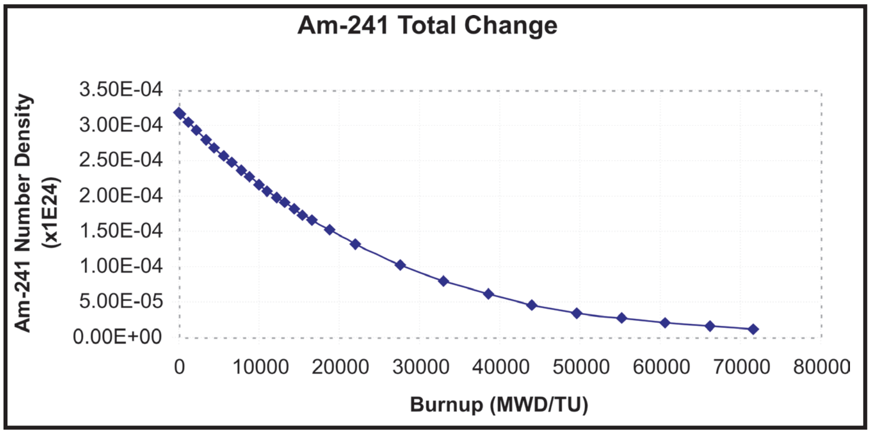


Figure 1. General trend of Am-241 inventory pre-loaded in a BWR lattice.

The practical aspect of these lattice designs has shown that the higher the level of americium content, the more difficult it is to satisfy the local power peaking, especially in the latter part of the cycle. By reviewing the fissile inventory of uranium (U-235), plutonium (Pu-239), and Pu-241, researchers have seen important trends indicating that the inventory of fissile plutonium dramatically increases in these lattices relative to a standard reference lattice without MA pins, potentially creating as much as three times the quantity of Pu-239 and 1.5 times the amount of Pu-241. This shows the possibility of a lower initial U-235 enrichment requirement for Am-spiked bundles and creates a potentially severe peaking problem that needs to be addressed later in the cycle.

Consequently, the team has redirected the research to consider actual lattice loading designs and optimizations by adapting and implementing the FORMOSA-L lattice loading optimization computer program. This code is now operational and the team has used it to help design better lattices and will eventually devise optimization objectives that maximize the elimination of specific minor actinides.

The first few large-scale optimization calculations have confirmed the viability of minimizing the power peaking of Am-241 loaded lattices, while simultaneously constraining their infinite multiplication (k_∞) profiles to remain unchanged relative to a reference (target) lattice. This type of result is illustrated in Figure 2, showing CPM-2 power peaking minimization results for an americium-spiked lattice as a function of optimization history. Recalculation of the lattices with the Westinghouse PHOENIX/POLCA/CM2 code system showed no major changes between the reference and optimized lattices.

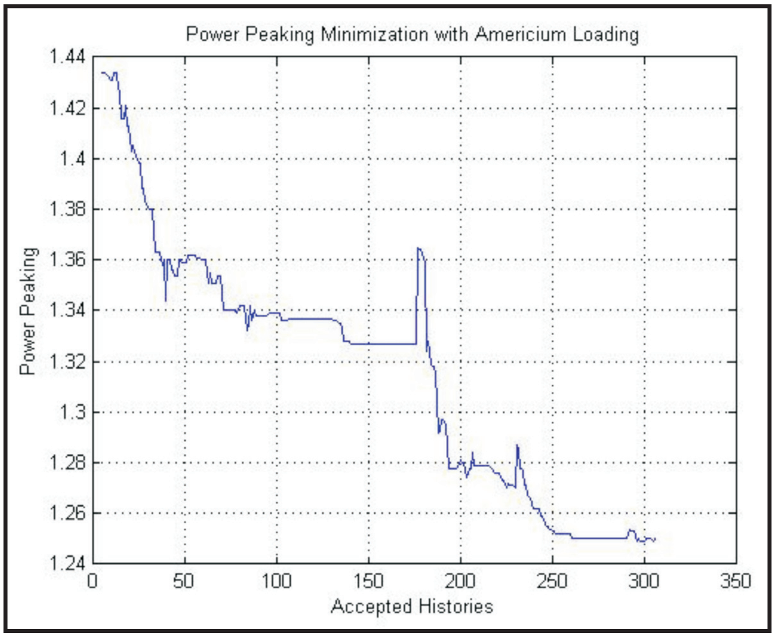


Figure 2. Optimization results for a lattice loaded with Am-241 pins.

PHOENIX is now fully operational so that lattices can be stacked axially into bundles to investigate core-wide and multi-cycle effects.

Planned Activities

Researchers will finalize the direct coupling of PHOENIX-4 to the FORMOSA-L software, an effort that is in progress. During this time, the team will also continue implementing their minor actinide minimization objectives.

Researchers also plan to develop 3-D bundles from the optimized lattices and test them on an in-core environment with the Westinghouse CoreMaster2 package and the POLCA 3-D core neutronics simulator. A recent agreement will enable this research to be carried out using realistic equilibrium models of the Quad Cities 2 nuclear power plant using Optima-2 fuel. This will enable the researchers to scale the lattice optimization studies into core-wide multi-cycle studies that will employ an operational U.S. nuclear power plant as the test bed for research.

Optimization of Oxide Compounds for Advanced Inert Matrix Materials

PI: Juan Nino, University of Florida

Collaborators: Imperial College of Science, Technology, and Medicine (U.K.), Idaho National Laboratory

Project Number: 05-134

Project Start Date: April 2005

Project End Date: March 2008

Research Objectives

The objective of this project is to develop oxide ceramics with optimal thermophysical properties for use as inert matrix fuel (IMF) in the current generation of light water reactors (LWRs). The approach, entailing a combination of computation and experiment, focuses on the materials science of oxide compounds and composites that exhibit minimal radiation swelling, high thermal conductivity, excellent hot water corrosion resistance, and are compatible with the UREX+ process.

An important benefit of using optimized IMF materials, rather than conventional uranium oxide (UO_2) fuel, is their higher thermal conductivity, which will considerably reduce the fuel centerline temperature and minimize the impact of a loss-of-coolant accident. Further, use of an inert matrix will avoid formation of transuranic fission products by neutron capture, thereby allowing higher fuel burnup and reducing waste. Improved corrosion resistance will ensure the IMF is compatible with the coolant under cladding breach accidents.

Research Progress

Researchers are currently conducting composite synthesis and characterization studies. They have completed thermal conductivity measurements on the composites and have determined a number of important processing-property relationships. Increasing the sintering time from four to eight hours increased the thermal conductivity of the *solid state* ball-milled composites at 1,473 K from 1.3 to 1.4 $Wm^{-1}K^{-1}$. Also, raising the sintering temperature of the *sol gel* ball-milled composites from 1,550°C to 1,650°C increased thermal conductivity from 1.1 to 1.4 $Wm^{-1}K^{-1}$. Further, when the volume ratio of magnesium oxide (MgO) increased from 50 to 60 volume-percent, thermal conductivity of the solid state composites rose from 1.4 to 2.0 $Wm^{-1}K^{-1}$ at 1,473 K. Representative thermal conductivity curves are presented in Figure 1.

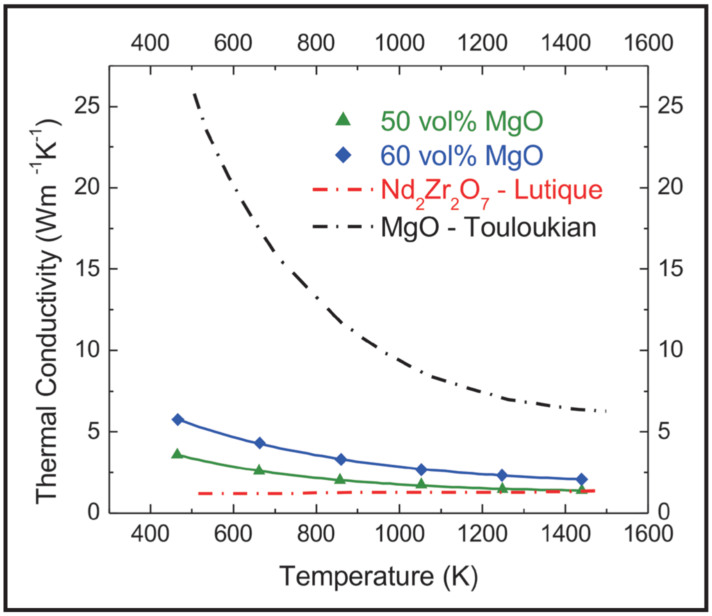


Figure 1. Experimental thermal conductivity of $Nd_2Zr_2O_7$ MgO composites compared with reported values of the end-members (dashed lines).

Microstructural analysis using scanning electron microscopy (SEM) determined that the overall low thermal conductivity of the composites is due to the undesired 3-D connectivity of the neodymium-zirconium-oxide ($Nd_2Zr_2O_7$) phase. Researchers performed water corrosion resistance tests on the composite pellets and proposed the hydration mechanism for the sol gel derived magnesium-neodymium-zirconium (MgO-$Nd_2Zr_2O_7$) composites. Detailed analysis has shown that the corrosion occurs by a series of three mechanisms: 1) hydration beginning at the surface of the pellet, with water diffusion and hydration at MgO grain boundaries; 2) MgO hydration at grain boundaries, which results in magnesium hydroxide ($Mg(OH)_2$) byproduct buildup on the pellet surface; and 3) the neodymium zirconium oxide ($Nd_2Zr_2O_7$) grains remain embedded and randomly dispersed within the hydration product layer. This can be clearly observed in the SEM picture of the corroded pellet presented in Figure 2.

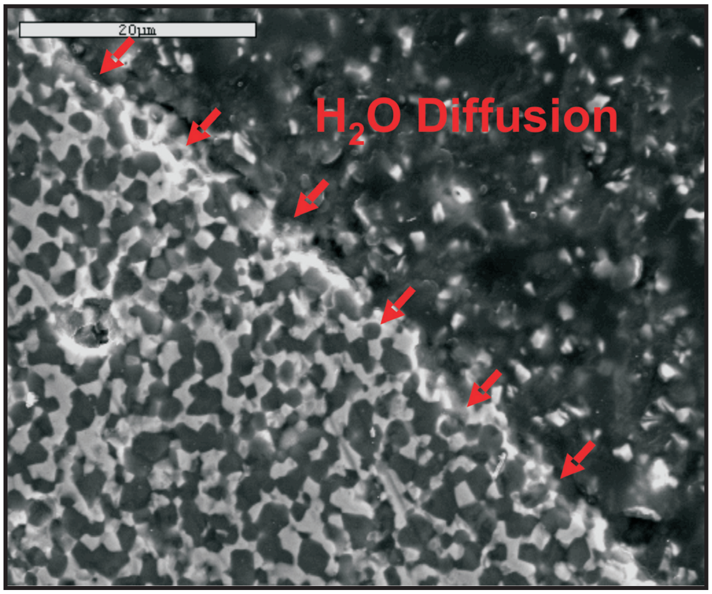


Figure 2. SEM of the MgO pyrochlore composite where the $Mg(OH)_2$ byproduct (dark top right diagonal area) surrounds the pyrochlore phase.

For the reprocessing task, researchers carried out the dissolution of MgO-$Nd_2Zr_2O_7$ composite pellets in a 50 ml acid solution in an ultrasonic cleaning bath at 50°C. The mass loss rate of the pellets exhibited a linear relationship with dissolution time before pellet collapse. Examining the residual power by SEM after dissolution revealed the presence of only the pyrochlore phase. It is important to note that although $Nd_2Zr_2O_7$ could not be dissolved in either nitric or sulfuric acid at 50°C, it did not block the dissolution of the MgO phase.

For the computational simulation, the team used the models for single-crystal structures of magnesium aluminum oxide ($MgAl_2O_4$) spinel that were developed in the previous quarter to calculate the thermal expansion coefficient of the material. Calculated values match very well with the reported experimental values. Also, in the first step toward generating $Nd_2Zr_2O_7$-MgO nanocomposites, researchers have determined the separate thermal conductivity of polycrystalline MgO and $Nd_2Zr_2O_7$.

Planned Activities

In accordance with the project's objectives, researchers are investigating improvements in thermal conductivity of the composites through an alternative processing method using a 3-D planetary dry mixer. In this process, no decrease in the size of the MgO and $Nd_2Zr_2O_7$ particles is expected, and therefore, the connectivity of the MgO phase should improve, significantly increasing the thermal conductivity of the composite. Reprocessing tests using cerium (Ce) as a surrogate for plutonium (Pu) in the composite will be conducted and the dissolution behavior characterized. In addition, they will begin experimental and computational work on a magnesium tin oxide (Mg_2SnO_4) spinel system.

For the computational simulation task, researchers will determine the thermal conductivity of single crystalline spinel, construct a model MgO-$Nd_2Zr_2O_7$ nanocomposites of differing connectivity, and initiate simulations of their thermal-transport properties. Finally, they will investigate the radiation resistance of selected spinel compounds.

Synthesis and Optimization of the Sintering Kinetics of Actinide Nitrides

PI: Darryl P. Butt, Boise State University

Collaborators: University of Florida

Project Number: 05-135

Project Start Date: August 2005

Project End Date: July 2008

Research Objectives

The primary objective of this project is to develop processing models and to perform an economic analysis on the synthesis of nitride-based nuclear fuels. Such fuels, particularly those based on uranium-nitride (UN) and plutonium-nitride (PuN), are candidates for the Advanced Fuel Cycle Research and Development (AFCR&D) program. Nitride-based fuels have a combination of higher uranium loading and higher thermal conductivity compared to other fuel forms, thus lower enrichment can be used. It is also possible to produce inert matrix fuels because of their compatibility with candidate matrices, such as zirconium-nitride (ZrN) and refractory metals. Although several processes have been developed for synthesizing powder and monolithic forms of actinide nitrides, the sintering kinetics and mechanisms are not fully understood. Having a quantitative understanding of the mechanism and kinetics of densification and grain coarsening is critical to ensure both satisfactory product performance and favorable economics of any ceramic fabrication process. Through optimized processing conditions, sintering temperatures and equipment size can be greatly reduced, production rates can be increased, and properties can be improved and more precisely controlled.

In this study, researchers will synthesize actinide and surrogate powders of varying morphologies and particle size. They will thoroughly characterize the powders and press them into fuel forms. Detailed sintering studies will be conducted in order to assess the specific rate equations and kinetics models as a function of time and temperature, grain size, and other processing variables. By applying these fundamental models and combining microstructural characterization, the researchers will determine rate-limiting and process-controlling mechanisms for comparing transport properties (including solid-state diffusion and gas transport). An end result of these studies will be a processing model and economic analysis that will enable fuel processing to be done at lower temperatures, shorter times, and with less costly infrastructure.

Research Progress

The researchers have procured several powders and ingots for use in the project. As nitrides are not available in most cases, they are being synthesized in the laboratory from oxides, hydrides, or pure metals. UN and surrogates are synthesized via amide, iodide, and silazane routes.

The formation of mono-nitrides is important in fuel fabrication due to high actinide density. Therefore, the first surrogate fuel synthesis attempts were to form cerium mono-nitride (CeN) and dysprosium mono-nitride (DyN) as surrogates for plutonium and americium nitride. From published data and previous lab work, the researchers were able to determine initial parameters to synthesize cerium mono-nitride using a hydride-nitride thermal route. Beginning with a 99.9% pure Ce ingot and using the hydride-nitride route, they were able to produce high-purity CeN powder, as confirmed by X-ray diffraction (XRD).

Dysprosium mono-nitride (DyN) was synthesized using various thermal cycles to determine the best cycle for producing a high-purity DyN powder. The starting material was shavings of 99.9% pure dysprosium ingot. A direct nitrification route (not a hydride-nitride route) was used to produce DyN powder. It was estimated from the XRD results that the sample was 90% pure dysprosium mono-nitride. The results of this synthesis route are promising in that the steps and time of manufacturing, and therefore costs, are minimal when compared to other routes. While further work will confirm the validity of direct nitrification

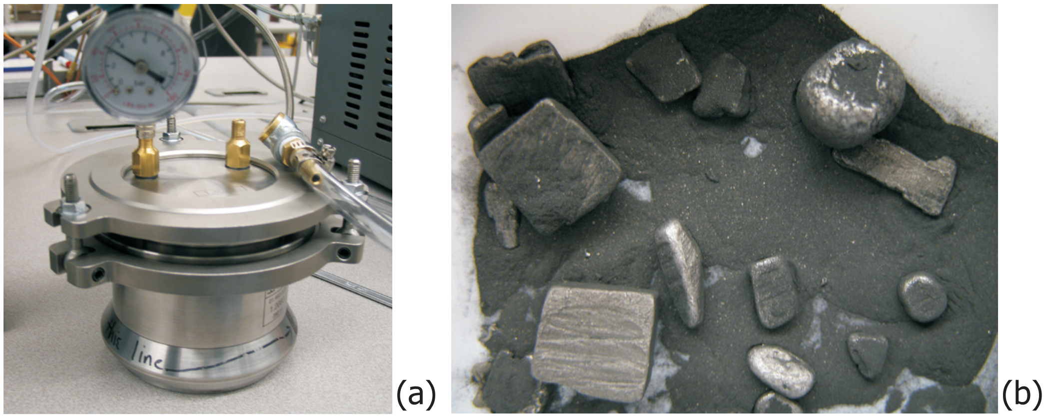


Figure 1. a) Planetary ball mill container used for the synthesis of DyN. This container allows for multiple charges/purges with UHP N_2 during the milling process. b) Photograph of DyN powder produced by mechanically induced gas-solid reaction (ball milling) method with N_2 atmosphere at room temperature.

for synthesizing high-purity DyN, researchers have also synthesized dysprosium mono-nitride from metal shavings by initiating the reaction in a N_2/H_2 mixed gas atmosphere before nitrification in nitrogen gas. Although this route takes longer, it produced a finer DyN powder and yielded a higher quality nitride (>99% pure) as evidenced by XRD.

The mechanically induced gas–solid reaction method (ball milling synthesis route) has been used to synthesize DyN directly (Figure 1b). The dysprosium metal shavings and pieces (used as milling media to decrease the chances of contamination) were placed in the planetary ball mill container (Figure 1a). The container was purged and pressurized with nitrogen prior to milling. During the milling stage, the jar was re-charged with nitrogen periodically to ensure that an excess quantity of nitrogen was present to allow the DyN reaction to proceed to completion. The start-up and overall cost of this method would be negligible.

To better understand the compatibility of these nitrides for an inert matrix fuel application, the team hot pressed a composition range of ZrN-DyN (from 90/10 to 50/50) to determine the sinterability of this binary mixture. Due to the volatility of DyN, the ratio was not increased beyond 50/50. The hot-pressed microstructures indicated that a two-phase solid solution formed. This is an important finding due to the lack of information in the literature regarding the equilibrium conditions for these compounds. Further analyses on these hot-pressed samples are being performed to determine the compositions of these phases.

Planned Activities

The major tasks associated with this project are to fabricate, procure, and characterize a sufficient quantity of powder to begin synthesis and fuel fabrication; fabricate and characterize fuel as a function of temperature, time, and grain size; fully assess the kinetics of sintering; and produce an economic analysis of nitride processing. These tasks are summarized below:

- Powder synthesis and characterization (continue to refine procedures to increase purity levels)
- Fuel fabrication
- Microstructural characterization
- Assessment of atmospheric effects on desification and grain growth
- Model sintering kinetics and assessment of sintering mechanism
- Development of novel routes for nitride powder preparation
- Economic assessment

NUCLEAR ENERGY RESEARCH INITIATIVE

The Development of Models to Optimize Selection of Nuclear Fuel Materials Through Atomic-Level Simulation

PI: Simon Phillpot, University of Florida

Collaborators: Los Alamos National Laboratory

Project Number: 05-136

Project Start Date: April 2005

Project End Date: April 2008

Research Objectives

The objective of this project is to develop an advanced fuel performance calculational platform, based on the FRAPCON code, using databases to provide detailed nuclear material properties input. Currently, all fuel performance codes are based on correlations derived from experimental data. However, these correlations cannot be extrapolated to operating conditions beyond the experimental points on which the correlations are based, nor can they be used for materials lacking experimental data.

Figure 1 provides a schematic of the key tasks of this work. Researchers will evaluate the possibility of extending performance codes to new materials based on databases developed from state-of-the-art electronic-structure, thermodynamic, atomistic, and first principles calculations. They will use these databases to create a prototype of a new generation of advanced fuel performance codes. Pertinent inputs include material composition, temperature, density, closed porosity, surface roughness, fuel grain size, sintering temperature, and fractional cold work of the cladding. The code, based on "first principles," will reduce costs associated with fuel development programs—transforming the current selection process, which relies on costly and time-consuming experimentation, into a process based on modeling, simulation, and analysis that requires only confirmatory irradiation testing.

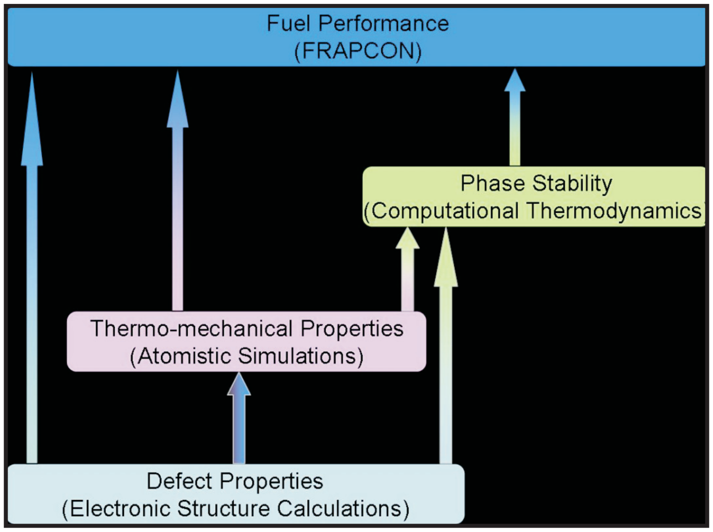


Figure 1. Schematic showing key tasks of the project and connections among them.

Research Progress

Following is a synopsis of the work researchers completed under several research tasks during this fiscal year.

FRAPCON Enhancement. Researchers broke the FRAPCON code into its component modules and wrote a new module that will allow the input of the *ab initio* thermal conductivity. The *ab initio* modeling group began developing a suitable format for their thermal conductivity module to ensure integration with FRAPCON.

Simulation Methodologies. Researchers developed and fully tested all of the required methodologies for the simulation of thermal conductivity in both single crystals and polycrystals. They completed the analysis of pure uranium oxide (UO_2) thermal conductivity, and obtained initial results for polycrystalline UO_2 (shown in Figure 2). They also developed methodologies for simulating radiation damage in UO_2 and obtained initial results.

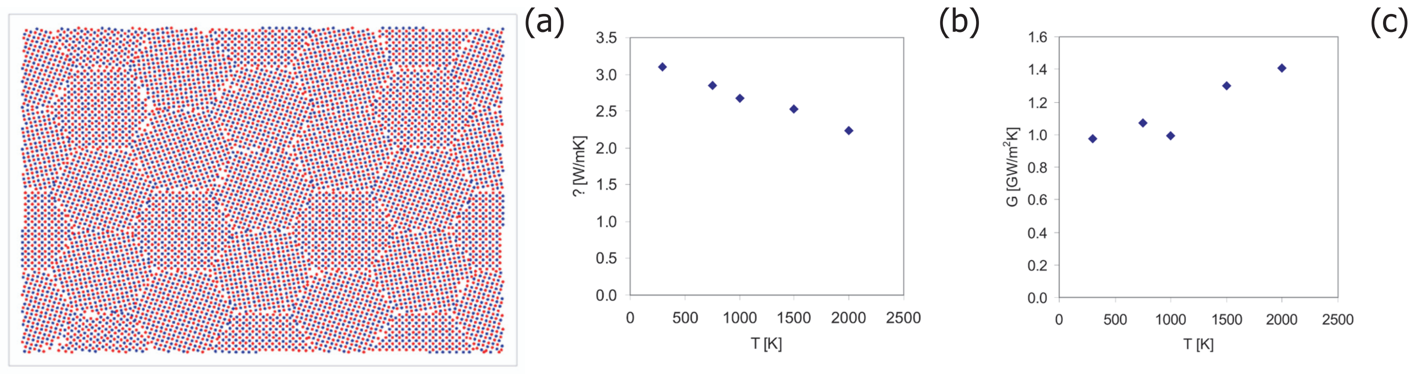


Figure 2. (a) Texture polycrystal of UO_2 with a grain size of ~3 nm. (b) The calculated conductivity decreases approximately linearly with temperature, leading to an interfacial (Kapitza) conductance that increases approximately linearly with temperature (c).

Phase Modeling. The cerium-oxygen (Ce-O) system was thermodynamically optimized using the CALPHAD (CALculation of PHAse Diagrams) approach. The results give crucial information that can be transferred to the phase modeling of the plutonium-oxygen (Pu-O) system, where less data are available. The team critically evaluated numerous experimental data for U- and Pu-based systems (see Figure 3); the resulting system reports are in press.

Electronic Structure. Researchers have identified the VASP code with spin-polarized LDA+U as an appropriate method for calculating electronic structure. This code shows good agreement for the structural parameters and electronic band gap of UO_2, as shown in Figure 4.

Planned Activities

The new FRAPCON code module allows researchers to experiment with various techniques for calculating the heat conduction coefficient. It is critical to establish exactly what data is available to put into the new module, and

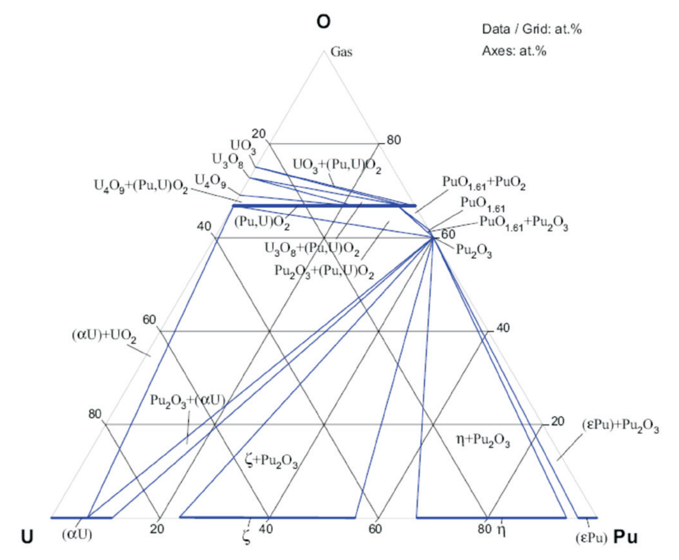


Figure 3. Optimized O-Pu-U isothermal section at 1,000°C, determined from critical assessment of the literature.

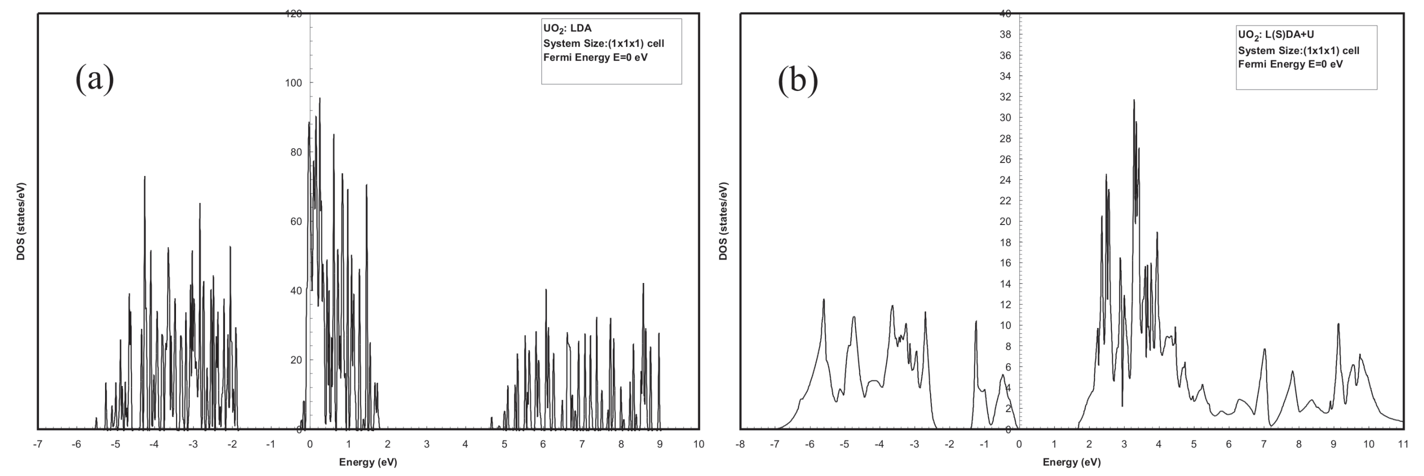


Figure 4. The predicted density of states of UO_2 as calculated with (a) DFT-LDA and (b) DFT-LSDA+U approaches.

what calculations must be performed as they are currently done in FRAPCON. If the data simply consists of tabulated values for a temperature and corresponding conductivity coefficient, a setup similar to that expressed above will be used. However, new ideas for modifying any of the five factors or creating new correction factors can now be incorporated directly. The nature of the data must be known for this new module to become useful for simulating fuel performance for the selection of nuclear materials.

Researchers are also working to elucidate the fundamental mechanisms of radiation damage in UO_2. They will extend this work to polycrystalline UO_2 and establish the effects of grain boundaries on radiation damage. Finally, the team will apply their electronic-structure methods to larger supercells. Using defect energy calculations and a recently developed thermodynamic framework, they will determine how defect energies change with temperature and composition.

NUCLEAR ENERGY RESEARCH INITIATIVE

Development of TRU Transmuters for Optimization of the Global Fuel Cycle

PI: John C. Lee, University of Michigan

Collaborators: None

Project Number: 05-142

Project Start Date: January 2005

Project End Date: December 2007

Research Objectives

The objective of this project is to develop advanced fuel cycles for the transmutation of transuranic (TRU) elements in irradiated nuclear fuel from light water reactors (LWRs). Researchers will use a systematic, integrated approach to evaluate diverse fuel cycles and energy production systems in order to optimize the global fuel cycle.

This project will study deployment of fast-spectrum transmuters, together with LWRs and advanced reactors, to minimize the risks associated with disposing and storing irradiated nuclear fuel in underground repositories. Such risks include radiological toxicity, proliferation, and radiological dose of the irradiated fuel. Researchers will develop an equilibrium fuel cycle methodology to consistently compare LWR transmuter performance with other designs. Key objectives of this research are to:

- Develop an optimization methodology that could systematically optimize core configurations both for LWRs and sodium-cooled fast reactors (SFRs)
- Study synergistic deployment of LWRs and SFRs for global fuel cycle optimization as envisioned in the Global Nuclear Energy Partnership

Research Progress

During the first year, researchers developed an equilibrium search algorithm to systematically compare the performance of diverse fuel cycles in order to conduct global fuel cycle analysis. The algorithm is similar to the REBUS-3 fast reactor methodology, but with macroscopic depletion capabilities typically employed for LWR analysis. To illustrate the usefulness of the LWR equilibrium methodology, and to explore ways to efficiently transmute legacy plutonium in spent nuclear fuel, the researchers studied the use of thorium in an alternate pressurized water reactor (PWR) fuel cycle.

The potential to increase the net destruction of plutonium by eliminating the secondary production of new plutonium led to the development of a thorium-based mixed-oxide (TMOX) configuration. This configuration consists of $(Th,Pu)O_2$ pins loaded on the periphery of a standard 17x17 fuel assembly, with the remaining interior fuel pins loaded with $(Th,{}^{233}U)O_2$. A four-loop PWR core fueled with TMOX assemblies results in significant destruction of plutonium (95 percent depletion of ^{239}Pu and 70 percent of total Pu) in once-through operation. This is comparable to the 98.1 percent depletion rate of ^{239}Pu reported for a deep-burn strategy in the driver fuel of the gas-turbine modular helium reactor (GT-MHR) core.

During the second year, researchers focused on developing an optimization methodology that can account for constraints in the overall fuel cycle. They developed a basic formulation, applicable to both LWR and SFR core configurations, using the calculus of variations. The algorithm consists of five key features:

1) The necessary conditions for optimal control leading to optimal fuel and core configurations are obtained in the form of Pontryagin's maximum principle.
2) A direct adjoining approach is used to augment the fuel cycle objective function and to explicitly and rigorously represent the power peaking inequality constraint.
3) The Euler-Lagrange equations for the adjoint flux are solved in a backward fuel depletion calculation.
4) A conjugate gradient method is used to iteratively converge on the optimal solution that minimizes diverse objective functions.
5) A backwards diffusion theory is implemented as part of the conjugate gradient algorithm to rigorously satisfy the constraints in the final optimal solution.

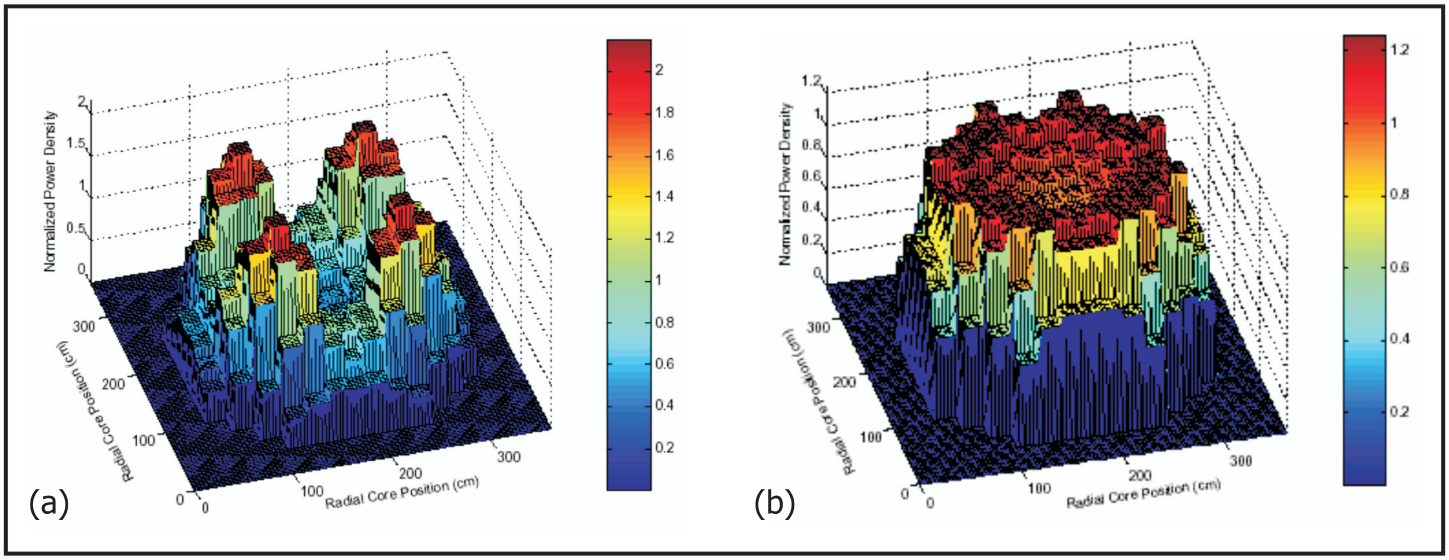


Figure 1. SRO2D optimization of the radial power distribution for the AP600 core: (a) original distribution, (b) optimized.

Researchers have incorporated their new Systematic Reactor Optimization in 2-Dimensions (SRO2D) algorithm for PWR analysis into a two-dimensional, two-group structure of the UM2DB code. Testing of the SRO2D methodology for the Westinghouse AP600 core with a radial power peaking factor design limit of 1.30 yields the same fuel assembly loading pattern and Pyrex burnable absorber (BA) placements as reported in the AP600 Standard Safety Analysis Report (SSAR). Furthermore, with the peaking factor limit reduced to 1.25, SRO2D generates a core configuration that not only satisfies the lower limit but also requires 35 percent fewer BA rods than the Westinghouse design. The optimal core configuration extends cycle length by 3.2 equivalent full power days of operation. These rather surprising results suggest the possibility of 1) increasing the allowable power and energy output for the AP600 design and 2) obtaining cost savings associated with BA rods. Figure 1 illustrates the optimization of a power distribution into a smooth, flattened power profile that satisfies the peaking factor limit of 1.25.

Another test of the SRO2D methodology for a four-loop PWR design addressed the objective of maximizing Pu depletion over a mixed oxide (MOX) fuel cycle. The core configuration is based on the French CORAIL assembly concept, entailing 24 percent MOX loading. In this test case, researchers used the LWR equilibrium cycle methodology developed during the first year to calculate the equilibrium cycle. With the SRO2D optimization formulation, the plutonium inventory at the first recycle discharge was reduced by 6 percent. With an increased Pu consumption in transition cycles, the Pu inventory for the equilibrium MOX cycle was reduced by 7 percent.

Following are several significant conclusions resulting from the successful formulation, implementation, and testing of the new fuel cycle optimization algorithm:

1) The SRO2D code can rigorously account for power peaking factor constraints, while current methods typically use approximations in the form of a penalty function
2) SRO2D accommodates diverse fuel cycle objectives without the need to customize stochastic algorithms for a specific objective
3) Unlike conventional stochastic optimization algorithms requiring a large number of trial fuel depletion calculations, the conjugate gradient algorithm in SRO2D converges within a few iterations

To extend the successful SRO2D methodology to SFR configurations, researchers have begun incorporating the fuel cycle optimization algorithm into the DIF3D/REBUS package. The original SROD algorithm required the use of a 7-dimensional system vector to represent the two-dimensional, two-group diffusion equations, power normalization, and macroscopic depletion equation. In contrast, the optimization algorithm for an SFR core consisting of hexagonal fuel assemblies with a G-group, N-nuclide microscopic depletion structure, requires a $(2G+N+3)$-dimensional system vector. Researchers have completed initial testing of the optimization algorithm with a modified version of the DIF3D/REBUS code for a simplified SFR configuration.

Planned Activities

Researchers will perform the following tasks during the second half of this project:

- Optimize SFR transmuter performance by incorporating heterogeneous core designs and optimal placement of TRU target assemblies using the new optimization algorithm fully developed in a modified DIF3D/REBUS code
- Further test and enhance the SRO2D code, incorporating a thermal-hydraulic feedback model
- Enhance modules in the DANESS/VISION fuel cycle system codes by incorporating the optimal PWR and SFR fuel cycles systematically obtained through the fuel cycle optimization algorithms
- Formulate simplified models to provide physical insights and guidance for evaluating diverse fuel cycles, in parallel with developing optimal cycles

Nuclear Energy Research Initiative

The Adoption of Advanced Fuel Cycle Technology Under a Single Repository Policy

PI: Paul P. H. Wilson, University of Wisconsin-Madison

Collaborators: Argone National Laboratory (ANL)

Project Number: 05-157

Project Start Date: April 2005

Project End Date: March 2008

Research Objectives

This project will develop models to study the impact of a national policy that retains a single spent fuel storage repository at Yucca Mountain. An increasing amount of technology-driven analysis is being done to determine how reprocessing and separation technologies can improve the loading of Yucca Mountain while maintaining the same general design concept and licensing basis. However, little policy-driven analysis has been conducted to study the adoption of new reprocessing and separation technologies assuming that only one repository is constructed. Given the current mismatch between the legislative capacity limit at Yucca Mountain and the expected spent fuel inventory from the existing reactor fleet, a single-repository policy would likely improve the economic attractiveness of advanced fuel cycle technologies. In addition, this project will study the relationship between fuel cycle advances driven primarily by repository performance and those advances necessary for a transition to a sustainable fuel cycle that is both economical and feasible. This project supports the Department of Energy's evaluation of additional geologic repositories for spent nuclear fuel (beyond Yucca Mountain), which is one of the near-term goals of the Advanced Fuel Cycle R&D program.

Research Progress

Using the documents available on the licensing support network for the Yucca Mountain project, researchers performed a literature review to search for existing specifications on waste packages and the analysis methods by which they are determined. They identified performance measures for the repository as a whole and a number of specific criteria for the waste packages; however, most criteria are based on the fact that these packages contain once-through light water reactor fuel.

Previous work by Argonne National Laboratory (ANL) has developed some simple specifications for the allowable heat load for packages emplaced in Yucca Mountain. In order to still meet the currently anticipated licensing basis, there are three simple limits on: 1) the instantaneous decay power at the time forced convection ceases, 2) the total released decay energy over a time period following the end of forced convection, and 3) the instantaneous decay power at the time the package is placed in the repository. These limits are being explored by ANL for use in fuel cycle studies and will be considered in this project also.

In addition to the thermal limits for repository loading, ANL has studied radiological limits. Early indications are that repository loading will be limited by thermal considerations, not radiological. That is, any loading that meets the repository thermal performance limits will have radiological loadings that result in exposures below the stated limits. Changes in radiological exposure limits and regulations during the fiscal year may have an impact on this conclusion.

The concept of embodied energy relates directly to the quantity of fission products in the material stream— since fission products are the only indicator of actual energy generation. This simplifies the modeling of embodied energy necessary to determine the cost per unit energy of different fuel cycle options. However, to best partition the costs of different fuel cycle processes, it may also be necessary to estimate the potential energy remaining in the material.

In general, the term "embodied energy" is used in the energy analysis field to account for the process input energy used to produce a material or item. For example, in a nuclear fuel cycle, the mining, conversion, and enrichment processes would increase the embodied energy of a unit of nuclear reactor fuel due to the energy used in performing these processes. While this quantity is certainly important in a comprehensive fuel cycle analysis, this work will concentrate more on the theoretically available fission energy and the expended fission energy — embodied potential energy (EPE) and embodied delivered energy, (EDE) respectively.

Although many economic quantities are normalized by the delivered value (often converted to electrical energy via thermodynamic conversion efficiency), most fuel cycle study tools track mass/mass flow of materials within a scenario. Understanding both the potential and delivered energy of those materials in economic terms is necessary when performing economic comparisons of different scenarios. The simplest approach is to ascribe roughly 200 MeV of EPE to every remaining actinide atom and roughly 100 MeV of EDE to each fission product atom. This results in approximately 1 megawatt-day per gram (MWd_{th}/g) of EPE for actinides, and a similar quantity of EDE for fission products.

Associating the *available* energy exclusively with actinides and the *expended* energy with fission products preserves economic concepts that will be important for advanced fuel cycles. In particular, recycling of spent nuclear fuel primarily results in a fission product stream with very high specific expended energy. The actinide stream has very low specific expended energy and a high specific available energy. The variable cost of constructing a deep geologic repository is dependent on the length of the tunnels and is independent of the EDE being disposed. By increasing the EDE of the material stored per unit length of tunnel, the economic utilization of the repository resource is improved.

Since different combinations of processes and reactor systems will have a wide array of total costs and energy values for different material streams, it is important to track the economic value of the streams through the use of the specific EDE and EPE quantities. As EDE is most often related to electrical energy, not thermal, it is necessary to track this quantity as a separate material characteristic due to the variety of thermal efficiencies that may exist in a fuel cycle scenario. On the other hand, the thermal efficiency applied to EPE utilization need not be tracked separately, as it is generally not known (or may even be variable) and is directly related to the quantity of actinides in the material, a quantity which is generally tracked already.

Collaborations established with Argonne National Laboratory align the goals of this project with the related research program underway in support of the Advanced Fuel Cycle Research and Development project, including Yucca Mountain repository modeling and fuel cycle scenario modeling with DANESS and DYMOND. Connections were also established with the SINEMA project at Idaho National Laboratory (INL). While the proposal for this project originally considered DANESS as the platform for implementing many of these developments, DYMOND, VISION, SINEMA, or other options may provide the necessary flexibility. Currently, none of the fuel cycle system study tools allow for economic optimization under resource constraints (e.g., repository space), a fundamental capability for this project. Therefore, interactions between this project and SINEMA (or DYMOND/DANESS/VISION) will include support for this type of capability.

The repository models for VISION and DANESS simply track the accumulation of waste mass, whether spent nuclear fuel or high level waste, without considering how different waste streams consume different amounts of space in the repository. While VISION does not quantify repositories by either mass or volume, DANESS offers an interface that suggests finite-sized repositories. This results in the need to construct additional repositories, as for other fuel cycle facilities. However, the default behavior of DANESS does not allow the construction of additional repositories so it simply overfills the available repository. Even after incorporating minor code modifications to allow the construction of new repositories, there is no feedback on the cost (known or assumed) into the total fuel cycle costs.

Conceptual development of a repository capacity model resulted in a proposal for including the model into both DANESS and VISION. It is useful to formulate a repository loading and costing model based on the available space in the repository. However, the total cost of waste disposal is best expressed in units of cost per unit energy. A model that permits both of these goals is proposed in Equation 1:

$$C = \frac{U}{\rho_{limit} \alpha E} \qquad (1)$$

where C is the disposal cost per unit of energy generated [\$/MWh],

U is the unit cost of space per meter of repository tunnel [\$/m],

ρ_{limit} is the limiting waste loading density [kg_{HLW}/m],

α is the fraction of High Level Waste (HLW) composed of fission products [kg_{FP}/kg_{HLW}],

and E is the amount of generated energy per unit mass of fission products [MWh/kg_{FP}].

The limiting waste loading density is calculated for a given repository design and licensing basis from the isotopic composition of the HLW stream. The intermediate result of C/U [m/MWh] allows a system studies tool to determine when a repository will be full based on the amount of tunnel space available, rather than the mass of material being loaded into the tunnel. Both measures may be necessary to satisfy a combination of technical and political limits, as well as the ability to track the initial mass of heavy metal that can be attributed to the HLW stream.

Models to calculate ρ_{limit} for arbitrary waste streams are being implemented conceptually in VISION and then DANESS. The current VISION implementation is based on thermal limits using approximate values derived from previous studies of repository benefit. These limits need to be determined in more detail to accommodate a wider array of possible isotopic compositions.

In concert with the SINEMA/GENIUS effort at INL, researchers have completed an assessment of optimization strategies, focusing on the contrast between "local" optimization that is common among current tools and "global" optimization that can be expected to find idealized policy options. It may be necessary for fuel cycle simulation tools to reduce the degree and complexity of their decision making and feedback algorithms to permit a global optimization approach to be successful. These algorithms are intended to simulate the real decisions made by, and constraints faced by, decision makers in the development of a nuclear enterprise. The result is a set of successive optimizations based on local information that may not lead to a global policy optimum. On the other hand, global optimization evaluates the overall objectives of the system in the absence of these algorithms to identify an ideal development scenario. An interesting combination of these two approaches can be used to design policy instruments: algorithms can be added to the local optimization scheme in an attempt to force the same performance as the global optimum.

In the transition from local to global optimization, the variable space may substantially increase in size. As such, careful consideration must be given to the selection of decision variables and the degree to which some decision-making/feedback algorithms may be determined to always contribute to a global optimum and permit a reduction in the size of the variable space. Researchers have developed an example for the case of reactor construction schedules, showing a substantial savings in the decision variable space arising from an algorithm that maximizes reactor capacity factors at all points in time.

The project team presented two papers at the ANS 2006 Winter Meeting.

Planned Activities

The most important activity in the coming year is to perform calculations with VISION and/or DANESS in which repository capacity is used as a metric rather than mass of waste accumulations. Through simple economic models, this work will provide insights into and conclusions about the economic benefits of reprocessing, considering ultimate disposal costs. After this, researchers can improve repository facility models to allow for construction of new facilities with finite cost. This system will enable the determination of simplistic break-even costs for future repositories and will lead to more sophisticated economic modeling. The project will culminate with the study of different economic/financial models for fuel cycle facilities in order to assess their impact on fuel cycle economic performance.

NUCLEAR ENERGY RESEARCH INITIATIVE

Radiation Stability of Candidate Materials for Advanced Fuel Cycles

PI: Todd Allen and James Blanchard, University of Wisconsin-Madison (UW)

Collaborators: None

Project Number: 06-007

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

This project will use proton irradiation to further understand the microstructural stability of those ceramics being considered as matrix material for advanced fuels. Following are the specific goals for this work:

- To determine the radiation stability of candidate materials in response to proton irradiation at temperatures between 600–900°C. Following irradiation, researchers will examine samples using transmission electron microscopy (TEM) to understand the effect of radiation on lattice stability, phase change, void growth, and other microstructural features
- To determine the effect of radiation on hardness and fracture toughness in response to proton irradiation at temperatures between 600–900°C. Estimates of the relative changes in fracture toughness as a function of radiation will be made using crack length propagation following Vicker's indentation
- To perform structural analysis using finite element analysis to determine the limiting performance of these ceramic fuel matrices, identify promising candidate materials for advanced reactors, and identify pressing data needs

Researchers will test the following materials: titanium carbide (TiC), zirconium carbide (ZrC), titanium nitride (TiN), zirconium nitride (ZrN), and magnesium oxide (MgO). They will also test combinations with zirconium oxides ($MgO-ZrO_2$) and erbium oxides ($MgO-ZrO_2-Er_2O_3$).

Research Progress

To provide a basis for comparing the unirradiated and irradiated microstructures, researchers characterized the as-received materials using scanning electron microscopy with energy dispersive spectroscopy (SEM EDS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and microhardness. The ceramic materials were mounted in copper-filled epoxy and polished to a 1 μm finish for SEM imaging. To reveal the grain structures, the samples were thermally etched at 1,400°C for 2 hours in a vacuum furnace (10^{-5} Torr). EDS was used to identify the inclusions in the materials which could cause localized phase changes during high-temperature irradiation. Results agree well with the elemental compositions measured by NSL Analytical Services.

Researchers used XRD and glancing angle XRD (GAXRD) to characterize the lattice parameters of the investigated materials. The measured lattice parameters of as-received materials agree very well with the values reported by other researchers. The microstructures of unirradiated materials were also characterized using TEM for ZrC, TiC, ZrN, and TiN. The materials are generally free from defects, although ion milling during sample preparation can introduce some damage on the surface of the specimen which can be differentiated from proton irradiation damage based on size and structure. Microhardness tests were performed with a Buehler Micromet 2003 Microtester and indentations will be used for the fracture toughness analysis.

Proton irradiations were performed using the UW Tandem Accelerator Facility and High Temperature Radiation Stage. This accelerator is a 1.7 MV machine capable of accelerating protons up to 3.4 MeV. Samples are irradiated in the form of 3 mm diameter disks coupled to a metallic stage through a graphite foil which can provide enough compliance to ensure that samples of slightly varying thickness are coupled to the stage for adequate temperature control. Fifteen different samples can be irradiated simultaneously and temperature is monitored and controlled through beam heating and stage temperature controller. The rastered irradiation beam is centered on the target via an aperture system with total

Proton Energy		2.6 MeV				
Temperature		800 ± 23°C				
Accumilated Damage	Material	ZrN	ZrC	TiC	TiN	SiC
	Dose (dpa)	1.5	1.5	1.0	1.0	0.6

Table 1. Irradiation parameters and accumulated doses.

beam current measured to provide a measure of the radiation dose. The parameters of the first irradiation as well as the accumulated damage of the specific materials (ZrN, ZrC, TiC, TiN, and SiC) involved are listed in Table 1.

The microstructures of irradiated ZrC and TiC, studied using TEM, mainly consist of a high density of Frank loops. The researchers observed no voids, as displayed in the bright field (BF) and relrod dark field images (Figures 1 and 2). The lattice plane resolution image shows more details about the defect structures. The Frank loop size for both ZrC and TiC is on the order of several nanometers (nm).

The microhardness tests yielded a 14 and 11 percent increase for irradiated ZrC and SiC, respectively, which corresponds well with the high density of dislocation loops observed in samples during TEM studies.

Planned Activities

For the upcoming research year, researchers will perform more proton irradiation experiments at different temperatures and doses. The materials will be extended to cover all seven proposed ceramics or composites. Following radiation, microstructural evolution will be examined using TEM to study the lattice stability, phase change, void growth, and other microstructural features. New TEM characterization techniques will be applied for this study, such as HOLZ (higher-order Laue Zone) for quantifying lattice strain. Ultimately, correlations between the microstructural changes and radiation temperatures and doses for different materials will be developed and related to bulk properties. Researchers will conduct systematic evaluation of the effect of radiation on hardness and fracture toughness in response to different irradiation conditions. They will also estimate the changes in fracture toughness as a function of radiation conditions by measuring the length of cracks produced by hardness indents. Finally, they will use finite element analysis techniques to determine the performance limits of these ceramic fuel matrices.

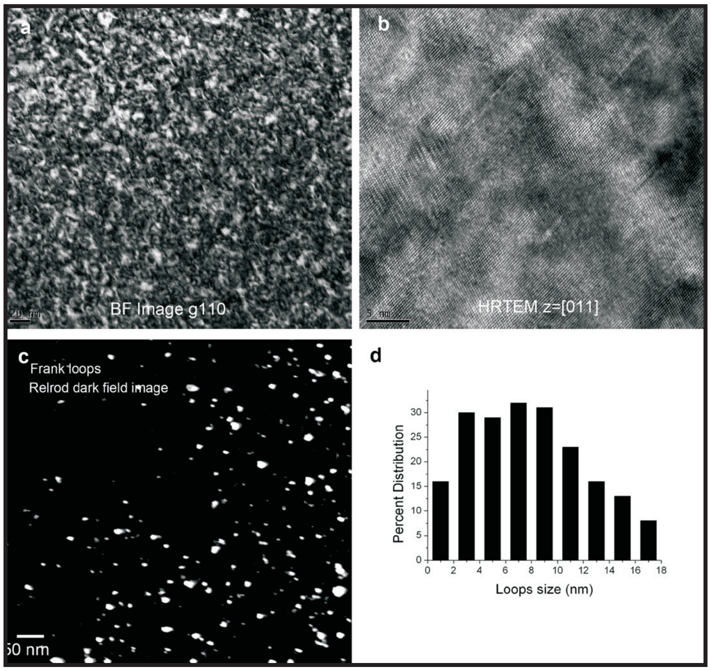


Figure 1. Microstructure of ZrC irradiated with protons at 800°C to 1 dpa.

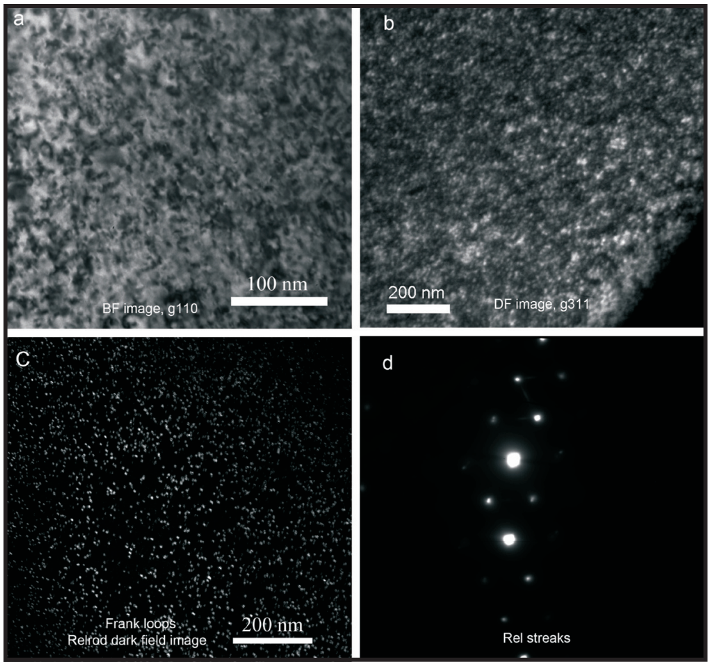


Figure 2. Microstructure of TiC irradiated with protons at 800°C to 1 dpa.

NUCLEAR ENERGY RESEARCH INITIATIVE

Solution-Based Synthesis of Nitride Fuels

PI: Ken Czerwinski and Thomas Hartmann, University of Nevada, Las Vegas

Collaborators: Los Alamos National Laboratory (LANL), Savannah River National Laboratory

Project Number: 06-012

Project Start Date: September 2006

Project End Date: August 2009

Research Objectives

The objective of this project is to develop a solution-phase process for synthesizing actinide nitrides for use in nuclear fuels. The current process for synthesis of nitride fuels entails carbothermic reduction from the oxide to the nitride, based on a stepwise process of solid-phase reactions from the metal oxide, to the carbide, and finally the nitride. This high-temperature, solid-phase synthesis process is plagued by impurities in the final nitride product and difficulties in production, creating major drawbacks in using nitride fuels for advanced reactor designs. Direct synthesis of the nitride by a solution route could eliminate or minimize the impurities and other synthesis problems. The proposed solution route to nitride has the added benefit of providing several adjustable parameters that would allow control over the properties of the final solid product.

Recent work by LANL collaborators has investigated amido reactions in non-aqueous solvents, where An is an actinide fuel (uranium, neptunium, plutonium, or americium):

$$\mathrm{AnI_3(solv)_4 + 3\ NaNR_2 \longrightarrow An(NR_2)_3 + 3\ NaI + solv}$$

From this result, a plausible route for the synthesis of nitride fuels is:

$$\mathrm{AnI_3 \xrightarrow[NH_3(l)]{} AnI_3(NH_3)_4 \xrightarrow[3NaNH_2]{} An(NH_2)_3 \xrightarrow{\Delta,-2NH^3} AnN}$$

The non-aqueous synthetic route based on amido chemistry potentially provides property control over the nitride product similar to the sol-gel methods for actinide oxides. The resulting nitride product should be free of the impurities inherent in the carbothermic reduction technique.

Research Progress

This project was initiated in September 2006. The work performed during this quarter involved preparation and acquisition of laboratory equipment and development of procedures for initial synthesis of uranium compounds. Researchers performed an extensive literature review of amide synthesis and formation of uranium iodide (UI_3) in liquid ammonia. Based on other ongoing research, they initiated characterization methods for uranium nitride (UN) for final product evaluation.

After evaluating existing synthesis equipment and supplies, researchers ordered new equipment and materials for the project and received specific safety training on radiation and handling of liquid ammonia.

Planned Activities

The project is divided into three primary tasks as outlined below:

1) Perform non-aqueous coordination chemistry, involving development of amido coordination with uranium, neptunium, and transneptunium actinides
2) Develop and characterize uranium nitride, neptunium nitride, and transneptunium nitrides from amido species
3) Develop methods for the synthesis of actinide nitrides
    - Identify crucial parameters of the solution-based synthesis of uranium nitride, neptunium nitride, and transneptunium nitride
    - Compare solution synthesis for uranium and neptunium nitride and identify required methods for solid-solution synthesis
    - Perform experiments on the synthesis of uranium-neptunium solid solutions if large variations are identified

NUCLEAR ENERGY RESEARCH INITIATIVE

The Development and Production of Functionally Graded Composite for Lead-Bismuth Service

PI: Ronald G. Ballinger, Massachusetts Institute of Technology

Collaborators: Los Alamos National Laboratory

Project Number: 06-038

Project Start Date: April 2006

Project End Date: April 2009

Research Objectives

The objective of this project is to produce materials that meet both the corrosion and structural requirements of liquid lead and supercritical water systems at temperatures up to 700°C in a neutron flux environment. Use of lead and lead-bismuth (Pb/Pb-Bi) eutectic as coolants in advanced liquid metal cooled fast reactor and transmutation systems is limited by their corrosive effects on fuel cladding and structural materials. In addition, the existing upper temperature limit of approximately 550°C for operation of these systems, dictated by corrosion concerns, is insufficient.

A new series of iron-chromium-silicon (Fe-Cr-Si) alloys provide several advantages: 1) formation of a protective film over a wide range of oxygen potentials; 2) minimal solubility in liquid metals, which may occur in crevices or other oxygen-depleted areas; and 3) resistance to corrosion in Pb/Pb-Bi eutectic at temperatures up to 700°C. Initial testing indicates that these materials are resistant to stress corrosion cracking degradation in supercritical water systems and the formation of a Cr-Si based dual oxide layer provides a high degree of protection.

In this work, researchers will produce functionally graded composites, consisting of a corrosion-resistant layer on a structural alloy, in two forms of tubing suitable for either pipe or fuel cladding applications. Two structural alloy systems will be used for each product form: 1) quenched and tempered and 2) oxide dispersion strengthened (ODS), resources permitting, which will be fabricated using standard commercial practice. The researchers will test the materials produced for corrosion resistance and structural properties. The clad alloy can also be fabricated in the form of welding wire for use as an overlay for more complex shapes.

Research Progress

During this year, the team focused on the following areas:

1) Developing and finalizing the detailed process flow sheet for producing the tubing and pipe forms for the composite system and identifying specific commercial vendors for each step in the process
2) Upgrading and operating the corrosion testing system that will be used to evaluate the behavior of the composite tubing and piping material
3) Developing a program plan for diffusion studies to evaluate the long-term diffusion of Si in T91—the structural material chosen for the project
4) Developing the initial design for a thermal convection loop that will be used to test the tubing and pipe forms produced in the project.

Processing Flow Path. Researchers fixed the composition chemistry for the weld overlay wire at Fe-12%Cr-2.0%Si. They will use T91 tubing as the basis for the quench and tempered material. Vendors have been identified for providing the materials and extrusion billets to be used in the project, as well as processing companies that can machine, extrude, and overlay the materials for the tubing. Figure 1 shows a schematic of the final process flow path. The team is currently developing a detailed timeline for processing.

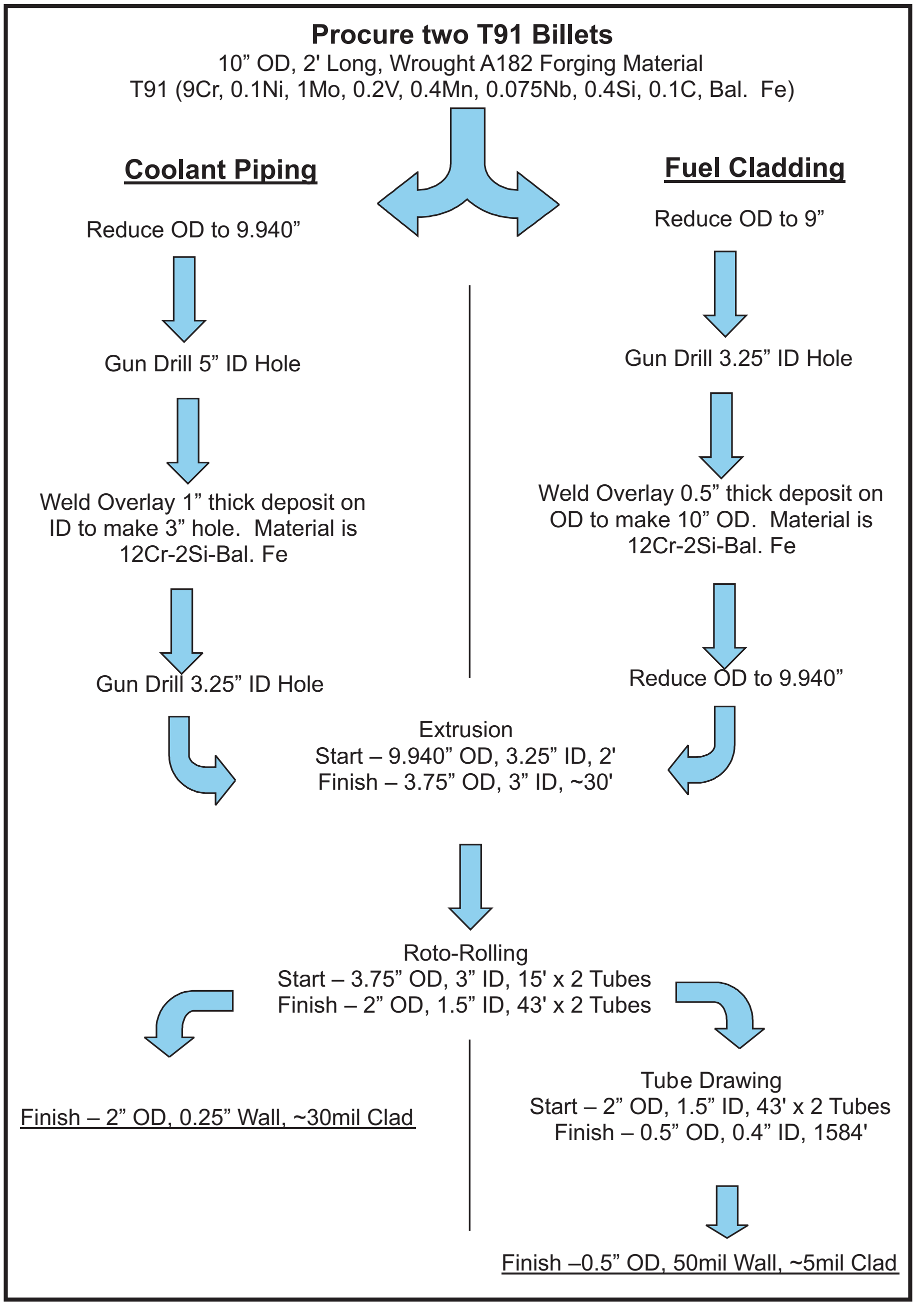


Figure 1. Processing schematic.

Corrosion Testing System. Researchers are preparing the mechanical and corrosion testing systems. They have refurbished the liquid lead-bismuth furnace and calibrated its sensors; a new data acquisition system has been set up to replace an older, more limited system. The system now has the capability to deliver 5 percent hydrogen (H_2) in argon reliably and remove all moisture and oxygen from the stream. Computer controls allow a multiplexed gas analysis system to analyze many streams at once with a single pair of sensors. The supercritical water system is being modified for use in this project.

Corrosion Testing. Corrosion testing and analysis are continuing using archive material from the original Fe-Cr-Si alloy development process. The team is working to identify the nature of the film formed during exposure. There is a clear indication that silicon is participating in the formation of a protective oxide (Cr-Si) layer. Figure 2 shows the results of secondary ion mass spectrometry (SIMS) analysis for an Fe-12Cr-1.25Si sample exposed in Pb-Bi eutectic for 500 hours at 600°C. The surface oxide layer is 12 μm thick and there is a clear enrichment of Si at the metal/oxide interface.

Diffusion Studies. The composite system will achieve its corrosion resistance via the presence of a high Si layer on the surface exposed to the environment. For this layer to remain protective, the Si concentration must be maintained above approximately 1.25 weight-percent. However, the Si concentration of the underlying structural layer will be much less a requirement for radiation damage resistance. At the expected upper operating temperature of 700°C for the fuel cladding product form, there will be a potential for dilution of Si in the protective layer due to mixing by diffusion. Because of this possibility, the team has initiated a task to evaluate the diffusion of Si between the protective layer and the T91 structural substrate material. During FY 2006, researchers designed the overall program (Figure 3).

Modeling of the thermal convection loop has begun, specifically to determine whether the liquid lead requires extra heating sections to start up, and to establish if lead provides natural convective flow or must be a forced convection loop.

Planned Activities

During the coming year, the program will focus on the following areas:

- Producing the composite fuel cladding and pipe forms
- Completing the corrosion testing system and continuing the corrosion testing of both archive and new material from the composite program:
  - ◇ Weld wire used for the overlay
  - ◇ T91 base material
  - ◇ Composite material
- Initiating the diffusion studies program
- Completing the thermally driven loop design
- Commissioning the supercritical water experimental facility

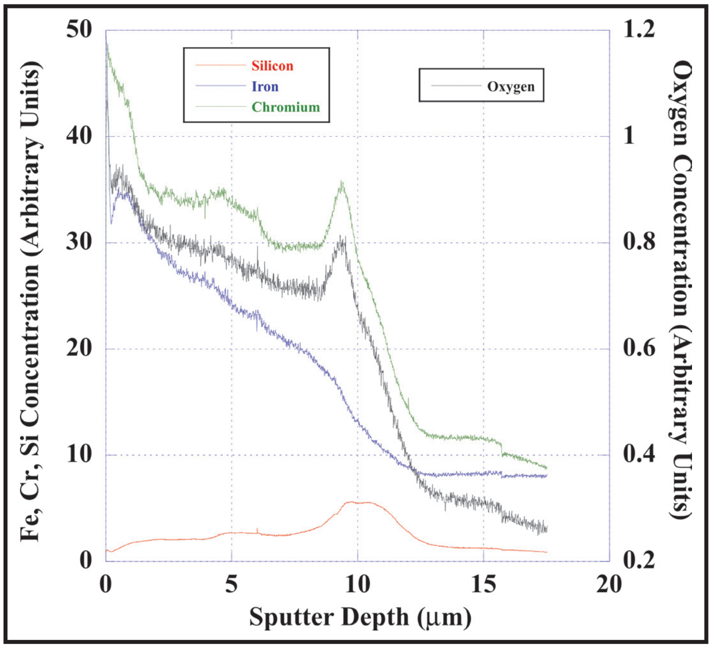


Figure 2. SIMS results for Fe-12Cr-1.25Si exposed in LBE for 500 hours at 600°C.

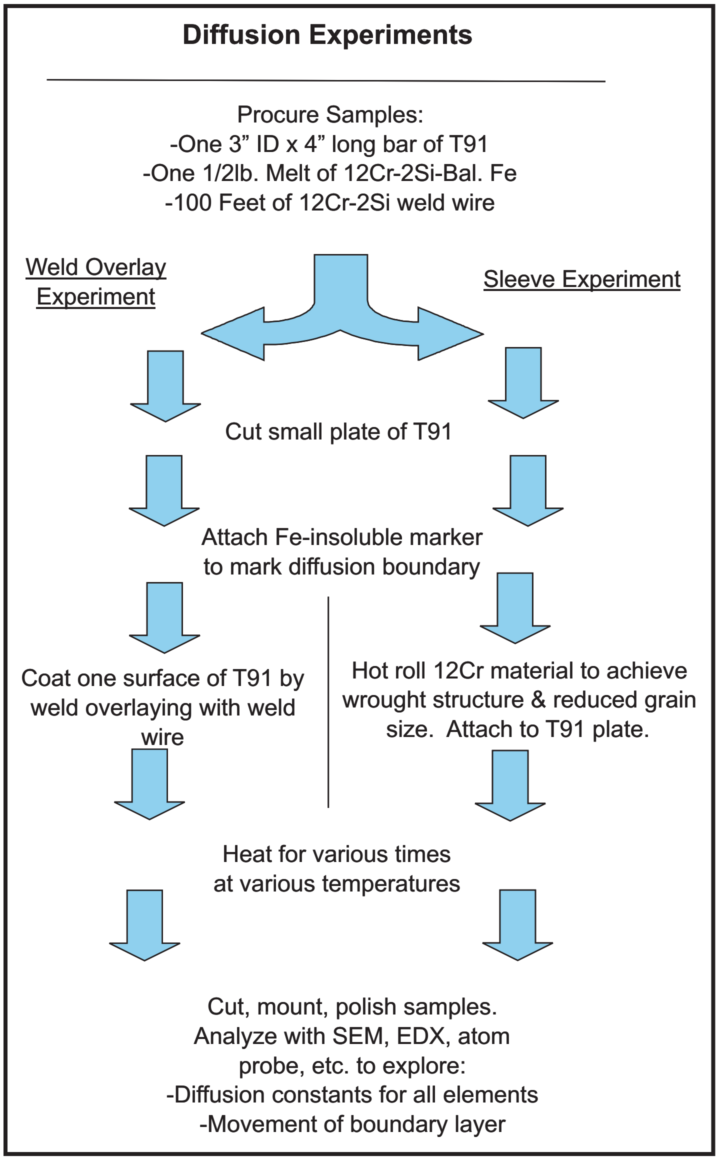


Figure 3. Diffusion testing task flow chart.

NUCLEAR ENERGY RESEARCH INITIATIVE

Flexible Conversion Ratio Fast Reactor Systems Evaluation

PI: Neil E. Todreas and Pavel Hejzlar,
Massachusetts Institute of Technology (MIT)

Collaborators: None

Project Number: 06-040

Project Start Date: March 2006

Project End Date: March 2008

Research Objectives

The objective of this project is to design a flexible conversion ratio fast reactor system that enables time-dependent management of fissile inventories and higher actinides. The goal is to produce a single reactor design capable of being configured to achieve both 1) conversion ratios near zero in order to transmute legacy waste and 2) conversion ratios near unity for operation in a sustainable closed cycle.

A consistent plant rating of 2,400 megawatts (MWt) will be used in both designs and the reactor cores will be cooled by forced circulation during normal operation to achieve high power density of at least 100 kilowatts/liter. To be more economically competitive, power conversion systems will eliminate the intermediate heat transfer loop. Safety and core integrity will be achieved through a self-controllable reactor design that ensures safe shutdown for all key transients. Proliferation resistance will be enhanced by eliminating blankets and using transuranics as fuel without separating plutonium.

Candidate liquid coolant core designs—lead and liquid salt—will be developed and cross-compared against two other reactor designs: 1) the supercritical carbon dioxide cooled reactor and 2) the sodium-cooled reactor. This will help decision makers select the most attractive, large, high-power density fast system for closed fuel cycles in countries with fuel service centers.

Research Progress

During the first five months of the project, researchers focused on lead-alloy-cooled reactor designs. They performed extensive reactor physics analyses using the MCNP4C and MCODE2.2 computer codes to evaluate the feasibility of high power, flexible conversion ratio, lead-cooled cores. Thermal hydraulic analysis focused on determining the maximum achievable power density that could satisfy the cladding and fuel temperature limits and on performance improvement through orificing.

As shown in Figure 1, researchers designed the CR=0 core as a 3-batch core with transuranic and zirconium (TRU-Zr) fuel to accommodate a large reactivity swing. The initial fuel composition of 34 weight-percent TRU and 66 percent Zr matrix resulted in a fuel cycle length of about 550 effective full power days (EFPD), corresponding to 1.7 years of operation at a 90 percent capacity factor. Fuel was driven to a discharge burnup of 400 MWd/kg$_{HM}$. This high burnup was achieved because of a small heavy metal weight fraction in the pins and is not expected to pose a problem for two reasons: 1) the amount of fissions during pin lifetime is comparable to that of a CR=1 core and 2) more Zr diluent in the pins provides more volume which

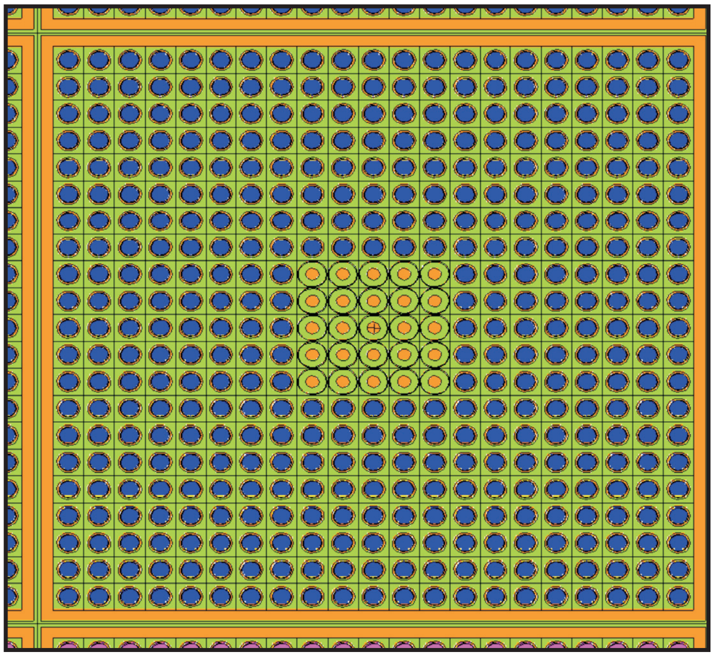


Figure 1. CR=0 core assembly with cans to scale (blue are fuel rods, green and orange are guide tubes with control rods).

can accommodate heavy metal swelling. The CR=0 core has higher power peaking than CR=1, but the proposed fuel management strategy makes it possible to maintain radial power peaking below 1.35.

Reactivity coefficients are all negative except for the coolant temperature reactivity coefficient; however, its value is less positive than the sodium-cooled integral fast reactor (IFR) and is comparable to the CR=1 case. The Doppler coefficient is negative and significantly smaller than for the CR=1 core due to the absence of fertile U-238—easily satisfying the first criterion on self-controllability. The main challenge for the CR=0 core is related to the inadvertent Control Rod Withdrawal accident, which necessitates the use of control rods in every fuel assembly to reduce the reactivity worth of any individual rod. Because reactivity excess to be compensated at beginning-of-life (BOL) is large and even small control rod movements during seismic events could result in unacceptable reactivity insertions, special double-entry control rods that overcome this problem have been devised.

The 1-batch, 3-region CR=1 core uses metallic U-TRU-Zr fuel, where the composition of transuranics corresponds to that of discharged light water reactor fuel at 50 MWd/kg burnup. To maintain low power peaking during core life, researchers took the approach of varying heavy metal loading among different core regions through Zr content adjustment, rather than TRU enrichment grading. Therefore, the core contains three regions, each with different weight fractions of zirconium, uranium, and TRU as indicated in Table 1 (the TRU-to-heavy-metal ratio remains fixed). This allowed maintaining the core radial peaking below 1.2 throughout core life and achieving the target core average burnup of 100 $\mathrm{MWd/kg_{HM}}$. The corresponding cycle length is 2,200 EFPD, equivalent to 6.5 years at 90 percent capacity factor, limited by cladding peak fluence. Only one-third of the assemblies of the CR=1 core are equipped with control rods due to its smaller reactivity swing.

Region	Zr	U	TRU
1	10	74	16
2	15	69.9	15.1
3	19	66.6	14.4

Table 1. Composition of CR=1 core.

Researchers calculated reactivity feedback parameters at BOL using MCNP. The coolant temperature reactivity coefficient was positive, but less than for the sodium-cooled IFR, even though the CR=1 core is significantly larger and has lower leakage. This is due to the use of lead coolant, which exhibits smaller coolant density effects than sodium. Thermal expansion reactivity feedbacks (core radial expansion, fuel thermal expansion) were negative and within the expected range. The Doppler coefficient was negative and slightly larger than for IFR metallic fuel.

Reactivity coefficient ratios fell within the range satisfying the ANL self-controllability criteria, except for the A/B criterion. Although larger Doppler and thermal expansion coefficients contribute, this is primarily caused by a significantly smaller temperature rise of the lead-cooled core (94°C versus 150°C for IFR) which reduces the B coefficient, thus increasing the A/B ratio. This is above the conservative limit, but satisfies the safety limit for uniform core radial power distribution. Because the radial power peaking was very small, it is expected that the transient analyses of unprotected accidents will yield acceptable performance.

The 600°C cladding temperature and 2 m/s velocity limits constrained the core power density to 95.7 and 84 kW/liter for the CR=1 and CR=0 cores, respectively. The volume used in power density calculations included the gaps between the assemblies and can structure. The smaller power density of the CR=0 core was a consequence of a larger radial power peaking. Increasing the coolant velocity limit in the CR=1 core to 4 m/s, while keeping within the 600°C cladding temperature limit, allowed a power density increase to 197 kW/liter; increasing the clad temperature limit to 750°C allows operation at 248 kW/liter.

The same limit increases for the CR=0 core yielded power densities of 140 and 243 kW/liter. Thus, advances in material development are crucial for high-power-density lead-cooled cores. The target power rating of 2,400 MWt at 110 kW/liter power density can be achieved with velocities of 2.45 and 2.9 m/s for the CR=1 and CR=0 cores, respectively. These velocities are expected to be compatible with ferritic-martensitic steels with advanced alloy cladding surface under development.

Researchers selected a three-zone orificing approach for both the CR=1 and CR=0 cores, with a suggested implementation strategy in which orifices are attached to fuel assemblies in the CR=1 core and adjusted to one of three settings during fuel shuffling in the CR=0 core. This orificing scheme would raise the average outlet temperature from the non-orificed core from 552°C to 564°C in the CR=1 core, and from 544°C to 567°C for the CR=0 core, given a clad temperature constraint of 600°C and a coolant velocity constraint of 2 m/s. This allows a one percent increase in plant thermal efficiency.

Planned Activities

For the next year, researchers will complete the lead-cooled reactor and begin designing the liquid salt reactor. Key activities for the lead reactor will be developing an intermediate heat exchanger design and performing RELAP transient analysis. For the salt reactor, researchers must select a liquid salt that meets neutronic, thermal hydraulic and materials constraints and determine the steady state and transient performance.

Since achieving passive decay heat removal from the 2,400 MWt reactor vessel is a main challenge to be overcome, the team will focus on identifying and evaluating the passive decay heat removal system. Finally, researchers will gather information on ANL's sodium-cooled core designs and MIT's fast gas-cooled designs to compare these four coolant types.

NUCLEAR ENERGY RESEARCH INITIATIVE

Development and Utilization of Mathematical Optimization in Advanced Fuel Cycle Systems Analysis

PI: Paul J. Turinsky, North Carolina State University (NC State)

Collaborators: Argonne National Laboratory (ANL), Idaho National Laboratory (INL)

Project Number: 06-047

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The objective of this project is to develop mathematical techniques to optimize deployment strategies for advanced nuclear fuel cycle/reactor/fuel facilities. Researchers will employ a stochastic optimization approach, which will determine the tradeoff surface of this multi-objective optimization problem. The optimization will consider economic, energy, environmental, and nonproliferation resistance metrics of the fuel cycle, which will be modeled using the VISION code.

This project will accomplish several goals:

1) The capabilities developed will assure that optimum deployment strategies are determined with reduced scientist/engineering effort, providing higher confidence in utilizing the results in policy decision making
2) The automated capability should make it possible for less technically sophisticated individuals to utilize fuel cycle simulation capability
3) Determination of the tradeoff surface using multi-objective mathematical optimization, resulting in different optimization deployments strategies as one moves across the surface, will provide quantitative data on such items as relationship of repository capacity to energy costs

Decision makers could use resulting data to establish policies concerning incentives and requirements to encourage the preferred evolution of the commercial nuclear power enterprise.

Research Progress

During this reporting period, researchers obtained the VISION computer code from INL, into which they will incorporate optimization capabilities. The code has been made operational at NC State and researchers are becoming familiar with its capabilities. Preliminary definitions of objectives, decision variables, and constraints have been established during visits to collaborating laboratories. To determine how the VISION code responds, various decision variables have been perturbed by altering input data.

Communications with the VISION development team at INL is ongoing in regard to needs. Researchers plan to issue a specification document shortly indicating input and output needs for decision variables, and will evaluate constraints and objective functions since the optimization engine will be constructed as a "wrapper" around VISION. This will facilitate porting to other system codes if later desired. Researchers have identified the manner of interfacing the optimization engine and the VISION code. They continue to work on determining which heuristic rules currently in the code should be removed to allow spanning of the decision space.

Planned Activities

With the assistance of INL, researchers will complete the modifications of the VISION code to support the optimization engine as required. A single-objective optimization capability using the Simulated Annealing approach will be developed. The optimization capabilities will be exercised for code verification and validation (V&V) purposes and for obtaining useful early results. Researchers will then direct their attention toward developing a single-objective optimization capability using the Genetic Algorithm approach.

NUCLEAR ENERGY RESEARCH INITIATIVE

Engineered Materials for Cesium and Strontium Storage

PI: Sean McDeavitt, Purdue University

Collaborators: Texas A&M University

Project Number: 06-058

Project Start Date: April 2006

Project End Date: March 2009

Research Objectives

Next-generation spent fuel reprocessing methods being developed under the U.S. Department of Energy's Advanced Fuel Cycle R&D (AFCR&D) initiative include solvent extraction schemes to isolate cesium (Cs) and strontium (Sr) from spent nuclear fuel. Isolating these isotopes for short-term decay storage (approximately 300 years) eases the design requirements for long-term repository disposal, since most radiation and decay heat energy in fission product waste comes from Cs-137 and Sr-90.

This project is complementary to Idaho National Laboratory's efforts to engineer a processing technology that will immobilize cesium and strontium isotopes using a fluidized bed steam reformer. The two major objectives of this project are to:

1) Synthesize candidate ceramics for Cs and Sr storage, including experiments to define process variables, feed compositions, and the product form
2) Characterize Cs/Sr-bearing ceramic products, including the critical behavior and attributes of candidate compounds, such as their Cs/Sr leach resistance, ceramic phase structures, and thermophysical properties

The chemical precursors to the reforming system are designed to produce ceramic storage from candidates for evaluation. The end result will provide a design basis for large-scale process definition. Because a small fraction of other fission products (e.g., yttrium, barium, and rubidium) tend to be extracted with the Cs/Sr in some separation schemes, the immobilization host must also accommodate minor levels of these isotopes.

Research Progress

Researchers established a lab-scale processing system, operating at nominal temperatures between 600°C and 800°C, to generate the Cs/Sr bearing ceramics. The system consists of a steam generator, tube furnace, sealed alumina tube inserted into the hot zone, atmosphere control system, liquid feed delivery tube, and post reaction gas scrubber/steam condenser. Candidate ceramic materials include stable aluminosilicates as well as aluminate, silicate, titanate, zirconate, and hafnate ceramics (e.g., Chabazite, Cs_2ZrO_3, Cs_2SiO_3, $SrAl_2O_4$, $SrTiO_3$, $SrZrO_3$, and $SrHfO_3$). Producing these ceramics requires precursors that can introduce aluminum, silicon, titanium, zirconium, or hafnium into the reaction chamber.

Figure 1 provides images from the initial screening work. This shows that stable powder products containing $CsAlSi_2O_4$ and $SrCO_3$ can be created from aqueous precursor solutions of $CsNO_3$ and $Sr(NO_3)_2$ by combining them with kaolin ($Al_2Si_2O_5(OH)_4$) and carbon precursors. Researchers determined that the original steam reforming design in this project was too vigorous for the planned experiments, as the majority of the early sample materials were ejected from the process vessel. They obtained the product materials shown in Figure 1 using a manual injection method with a syringe. Therefore, a new configuration is being designed based on the experience gained during the screening experiments.

In August 2006, the project relocated to Texas A&M University. As the system is being re-assembled, it is being modified to automate the liquid feed system used to inject Cs- and Sr-bearing solutions into the reaction chamber. The manual syringe is being replaced with a peristaltic pump to enable "hands free" operation and the cooling/condensation system is being replaced with a glass condenser to capture and recycle condensate back into the process vessel.

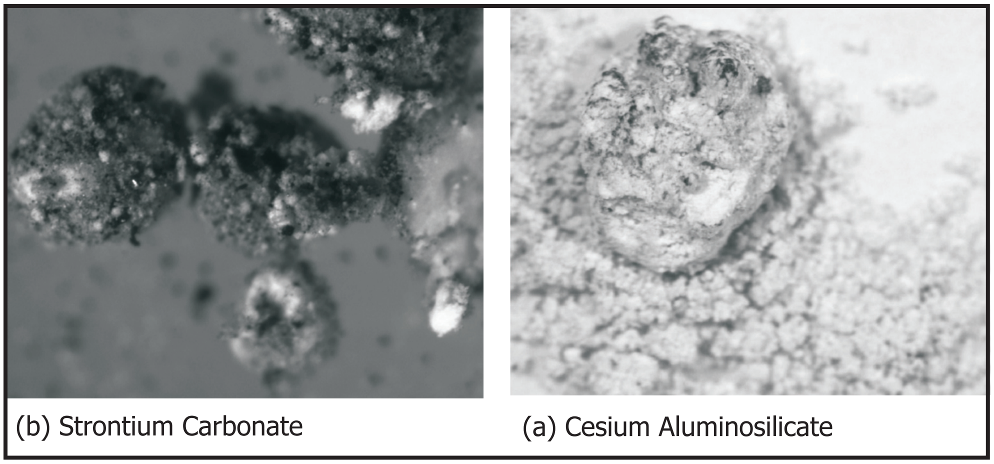


Figure 1. Images from the initial screening results showing powder products containing (a) cesium aluminosilicate ($CsAlSi_2O_4$) and (b) strontium carbonate ($SrCO_3$).

Planned Activities

After completing system modifications, researchers will continue to conduct fabrication experiments. The first experiment will combine cesium and strontium nitrates with kaolin to form mixed-oxide products containing both elements.

Following this, researchers will explore other mineral oxides. They will proceed with product testing and evaluation, as planned, using X-ray diffraction, electron microscopy, and leach testing. In addition, after reproducible ceramic forms are fabricated, researchers will evaluate the long-term radiation stability of the product forms using the ion beam accelerator laboratory at Texas A&M University.

NUCLEAR ENERGY RESEARCH INITIATIVE

Feasibility of Recycling Plutonium and Minor Actinides in Light Water Reactors Using Hydride Fuel

PI: Ehud Greenspan, University of California, Berkeley (UCB)

Collaborators: Massachusetts Institute of Technology (MIT), Argonne National Laboratory (ANL)

Project Number: 06-065

Project Start Date: March 2006

Project End Date: February 2008

Research Objectives

The objective of this project is to assess the feasibility of improving the plutonium and minor actinide recycling capabilities of pressurized water reactors (PWRs) by using hydride fuels instead of oxide. There are four general parts to this assessment:

1) Identifying promising hydride fuel assembly designs for recycling plutonium and minor actinides in PWRs
2) Performing a comprehensive systems analysis that will compare oxide fuel assemblies to the fuel cycle characteristics of plutonium (Pu) and minor actinide (MA) recycling in PWRs, using the promising hydride fuel assembly designs identified in Part 1
3) Conducting a safety analysis to assess the likelihood of licensing hydride fuel assembly designs
4) Assessing the compatibility of hydride fuel with cladding materials and water under typical PWR operating conditions

Research Progress

The first quarter was primarily devoted to establishing a database for performing the neutronic and thermal hydraulic analysis, for benchmarking computational tools, and for improving understanding of the physics of Pu-containing hydride fuel. The Westinghouse 4-loop Seabrook Power Station was chosen as the reference PWR power plant. Two oxide fuel assembly designs—CORAIL and CONFU—were adopted as references against which researchers will compare plutonium-loaded hydride fuel assemblies, with or without minor actinides.

The TRITON code sequence of the SCALE 5.0 code package was adopted for the neutronic analysis and benchmarked for the CORAIL fuel assembly against other deterministic and stochastic computational tools. Researchers found that the TRITON code sequence with the ENDF/B-V-based, 44 group cross section library is capable of simulating the neutronic and isotopic characteristics of CORAIL-type fuel assemblies with reasonable accuracy. However, there were significant discrepancies in the concentration of americium and curium isotopes at high burnups, primarily ^{242m}Am and ^{245}Cm. A thorough search for the reason revealed that the "branching ratio" for the ^{241}Am(n,γ) reaction to yield the isomer ^{242m}Am in the SCALE-5 library was too high. Researchers notified Oak Ridge National Laboratory (ORNL) developers and reduced the branching ratio from 16.2 to 11 percent, substantially reducing disagreement in the assembly-average ^{242m}Am concentration. With this modification, the TRITON sequence of SCALE 5.0 in use at UCB is adequate for comparing the neutronic characteristics of Pu-bearing hydride and mixed oxide (MOX)-fueled PWR fuel assemblies.

Researchers conducted a preliminary comparison between selected characteristics of a hydride fuel assembly against the CORAIL assembly. The hydride fuels design has an identical geometry and linear heat rate but is uniformly loaded with Pu in all the fuel rods. Preliminary results indicate that the hydride fuel assembly with the same cycle length as a CORAIL assembly offers the following advantages:

- A smaller infinite multiplication factor (k_∞) at beginning-of-life
- A smaller pin-wise power peaking factor
- A larger fractional transmutation of plutonium
- A smaller fissile-to-total ratio in the discharged plutonium, however, the hydride assembly generates a larger amount of minor actinides

The thermo-physical properties of thorium containing hydride fuel were compiled based on literature review and personal contacts with Japanese researchers.

A steady-state thermal-hydraulic analysis performed with the VIPRE code determined the maximum power attainable with the reference CORAIL and CONFU oxide fuel assemblies, against which hydride fuel assemblies will be compared. Researchers also evaluated a conventional uranium dioxide (UO_2) fuel assembly as a reference. Assuming that the required safety margin between operating and licensed power peaking factors is the same for all fuel types, researchers found that cores loaded with CONFU and CORAIL fuel assemblies can deliver only about 80 percent of the power of UO_2-fueled cores having the same maximum operating assembly peaking factor, geometry, and operating conditions. This is due to the more pronounced peak-to-average pin power distribution characterizing the CORAIL and CONFU heterogeneous fuel assemblies.

No substantial differences have been found between the performance of CONFU and CORAIL fuel assemblies. In spite of the larger pin peaking factor (i.e., 1.251 versus 1.152), the former yields a maximum power only 1 percent lower. This is mainly due to the suppressed power in the UO_2 pins next to the fertile-free fuel (FFF) pins and the presence of gadolinium (Gd). The significant non-uniformity in power distribution of adjacent rods tends to enhance subchannel mixing, thereby improving the margin to critical heat flux.

The researchers have negotiated with the Department of Energy for approval to transfer a TRIGA fuel element from the Davis campus of the University of California to the Berkeley campus. This will permit studying hydride fuel for compatibility with PWR coolant and Zircaloy clad. Also, ORNL has been contacted to provide thorium samples that will be hydrated for experiments on compatibility of thorium hydride fuel.

Planned Activities

Researchers will complete a comparison of the neutronic characteristics and performance of several types of hydride fuel assemblies against both the CORAIL and CONFU fuel assemblies. The hydride fuel to be examined will have different combinations of Zr-hydride and Th-hydride and different initial loadings of Pu and MA. They will also complete the steady-state thermal hydraulic analysis and initiate the transient thermal hydraulic analysis.

In the second project year, researchers will complete safety analyses, study the compatibility of U-$ZrH_{1.6}$ (TRIGA type) fuel with water and clad, and assess the systems implications of using hydride rather than oxide fuel for recycling Pu and MA.

NUCLEAR ENERGY RESEARCH INITIATIVE

Accelerator-Based Study of Irradiation Creep of Pyrolytic Carbon Used in TRISO Fuel Particles for the Very High-Temperature Reactor (VHTR)

PI: Lumin Wang and Gary S. Was, University of Michigan

Collaborators: Oak Ridge National Laboratory (ORNL), Idaho National Laboratory (INL)

Project Number: 06-113

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The primary objective of this project is to characterize the creep behavior of pyrolytic carbon (PyC), one of the structural materials in the tri-isotropic (TRISO)-coated fuel particles for use in the next generation of gas-cooled, very high-temperature reactors. When subjected to irradiation, creep of the pyrocarbon layers can cause radial cracking, leading to catastrophic particle failure. Therefore, a fundamental understanding of the creep behavior of PyC during irradiation is required to predict the overall fuel performance.

Researchers will conduct accelerator-based proton irradiation and *in-situ* measurements under stress at temperatures between 400°C and 1,200°C, using advanced analytical transmission electron microscopy (TEM) to study the PyC microstructure. They will correlate the experimentally determined creep coefficients with existing coefficients measured under neutron irradiation. They will also conduct initial experiments on the transport of select fission products, such as silver (Ag) and strontium (Sr), in PyC under irradiation and stress by implanting ions into the sample surface.

Research Progress

During this reporting period, researchers designed an accelerator-based irradiation creep testing system and have begun construction. The team designed a ceramic substrate heater and stage assembly and conducted the initial validity test of a laser speckle extensometer (LSE) on a pyrolytic graphite sample. Once installation of the system is complete, they will perform initial irradiation creep testing on commercial pyrolytic graphite.

System assembly. The primary objective of this project is to characterize the creep behavior of pyrolytic carbon under 3.2 MeV proton irradiation at a test temperature between 800°C and 1,200°C. Figure 1 presents a design for the complete irradiation creep test assembly that considers various parameters such as temperature, strain measurement, loading, and thermal insulation. The system assembly includes a thermal imager

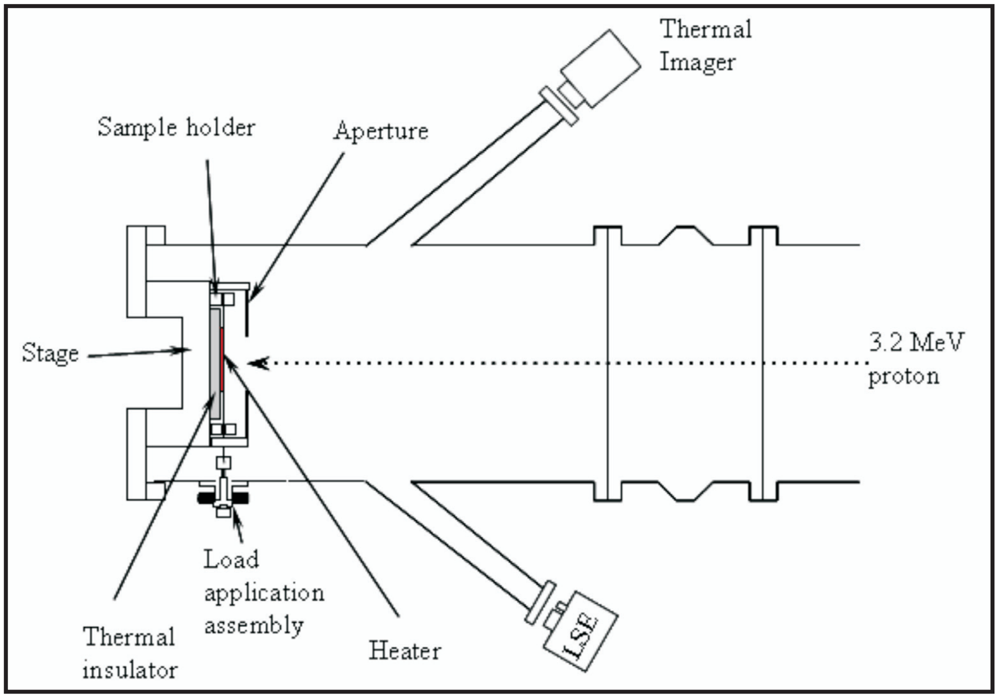


Figure 1. The test system assembly for *in-situ* creep measurement during proton ion irradiation.

for temperature monitoring, an LSE for non-contact displacement measurements at high-accuracy, a substrate heater and stage assembly for high-temperature application, an aperture system for fine control of the proton beam, and a constant stress loading system.

The thermal imaging software installed in the Michigan Ion Beam Laboratory, which has been successful for monitoring irradiation temperatures up to 500°C, can be extended to measure temperatures up to 1,200°C with the addition of a different data table.

Pyrolytic carbon samples will be secured by two ceramic sample holders (Figure 2) that serve to hold the samples in place and provide a thermal radiation barrier. Each sample holder is composed of two ceramic holding bars. The top bar tightly restrains the samples so they do not slip during the creep test, while the bottom holder lightly maintain the samples in contact with the heating surface to ensure uniform temperature distribution across the irradiated area.

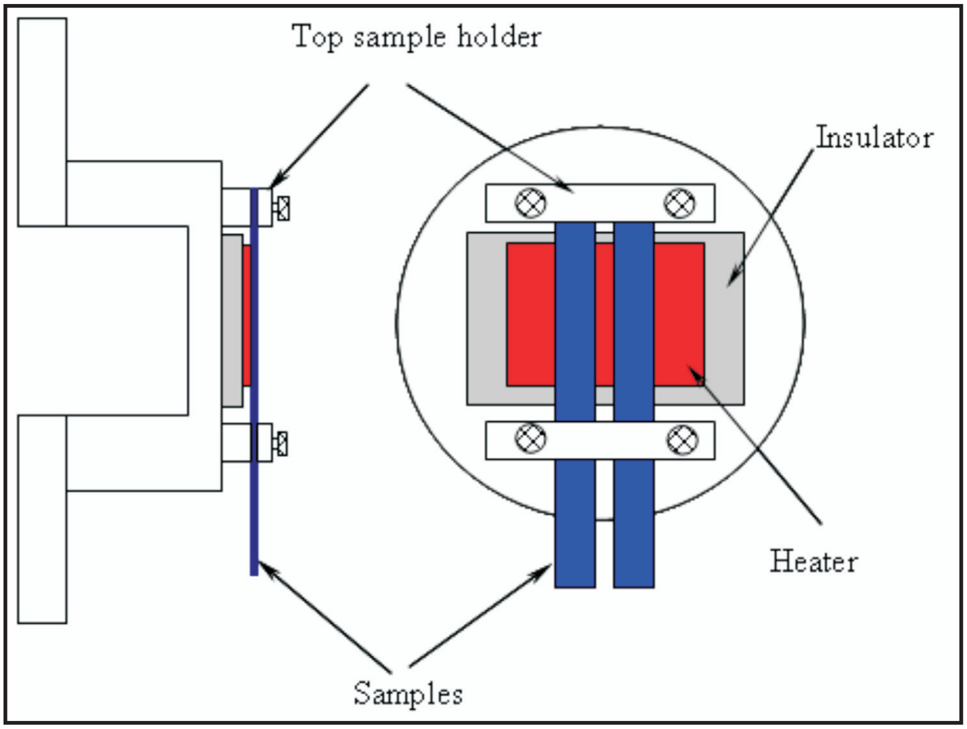


Figure 2. Sample holders.

Laser speckle extensometer. The LSE is designed to measure displacement with a resolution of approximately 0.1 µm. It is a non-contact device, which is well-suited for samples in a vacuum chamber. The basic LSE is comprised of an analog camera, a laser source, and operating software. A 532 nm YAG laser source with a dielectric filter will be used for high-temperature applications. The team has ordered a digital camera with four times better resolution.

The measuring principle of the LSE requires a quality speckle pattern, i.e., a granular pattern resulting from interaction of a coherent laser beam with an optically rough surface. To establish the quality of the speckle pattern on sample material, researchers sent out a small piece of pyrolytic graphite 3 × 10 × 0.2 mm for testing (Figure 3). The speckle pattern contrast, size, and count are all good for both the bright and dark area images. Resolution from the tested speckle pattern is better than 0.1 µm.

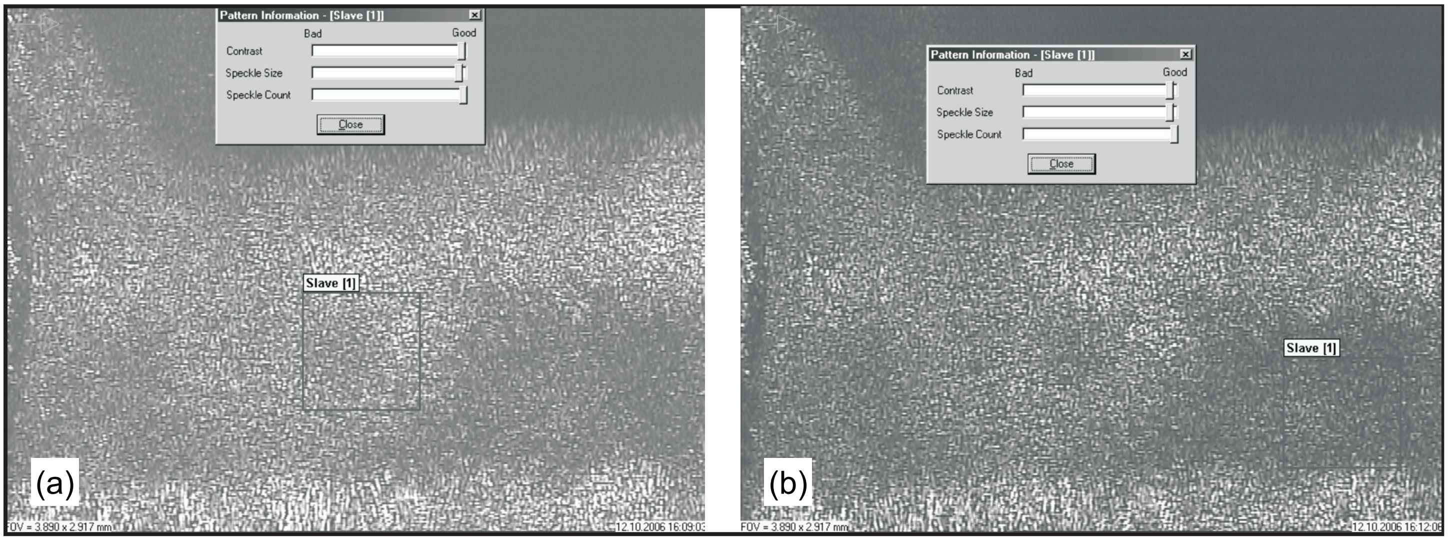


Figure 3. Laser speckle pattern on the pyrolytic graphite: (a) a bright area and (b) a dark area.

Planned Activities

By March 2007, the team expects to complete the development and construction of the test facility, including modification of the existing accelerator for the *in-situ* creep measurement during proton beam irradiation. Then they will perform the following activities:

- Conduct low-temperature irradiation (400°C and 600°C) on the reference PyC microstructure (unloaded) and perform data analyses
- Conduct low-temperature irradiation of PyC with *in-situ* creep measurement of the microstructure under stress and perform data analyses
- Conduct microstructural characterization of the PyC samples using TEM before and after irradiation to determine the main creep mechanism in PyC

Due to recent budget cuts, researchers may not receive expected PyC samples from national laboratory collaborators. Therefore, they have purchased some commercial pyrolytic graphite. Because the commercial pyrolytic graphite consists of large lamellar crystals, which is not representative of the microstructure to be used in the TRISO fuel, experimental data obtained from the commercial PyC may not be very useful for the VHTR project. The researchers are very concerned with this problem.

NUCLEAR ENERGY RESEARCH INITIATIVE

Development of Acetic Acid Removal Technology for the UREX+ Process

PI: R. M. Counce and J. S. Watson, University of Tennessee

Collaborators: Oak Ridge National Laboratory (ORNL)

Project Number: 06-116

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The purpose of this project is to identify and experimentally verify the best technology to separate or destroy acetic acid from the raffinate of the uranium extraction (UREX) segment of the UREX+ process. The UREX+ process is a series of solvent extraction steps designed to treat spent nuclear fuel by separating its various components for reuse and disposal. The leading technologies considered for eliminating acetic acid include adsorption, distillation, extraction, crystallization, and destruction. These alternatives are being evaluated using the available relevant literature. Flowsheets will be developed for selected technologies to provide a sound basis for further process evaluations.

Prior to the UREX segment of the process, acetohydroxamic acid is added as a complexant in the aqueous nitric acid solution used to dissolve the spent fuel. In the acid environment, some of the acetohydroxamic acid hydrolyzes to produce acetic acid and hydroxylamine. The acetic acid is assumed to leave the UREX segment of the process in the raffinate and must be separated or destroyed because it interferes with the downstream steps of the UREX+ process. Acetic acid is also an unwanted contaminant in any recovered and recycled nitric acid solutions.

Research Progress

The UREX+ raffinate stream was modeled as an aqueous mixture of 0.5 molar nitric acid and 0.05 molar acetic acid. Upon examining the component physical properties, researchers selected several technologies that provide separation of liquid species for further consideration. Solvent exchange, crystallization, distillation, and adsorption were investigated extensively during this period. Two other technologies (membrane separation and ion exchange) were eliminated early in the literature review. Membrane separation is considered undesirable because no membrane was found that is sufficiently selective at a single pass, and multi-stage membrane processes tend to be complex and costly. Ion exchange was also eliminated due to the stream characteristics. Ion exchange occurs primarily through the exchange of anions with the interior of a resin. For the UREX+ raffinate stream, no ion exchange resin was found with sufficient selectivity for acetate ions. The nitric acid depresses the dissociation of the acetic acid and reduces the separation/elimination of the acetic acid via ion exchange.

Researchers have completed the majority of the scheduled activities involving selection and screening of leading alternatives. This is in general agreement with the fraction of the project funds expended to date. The remaining tasks are to review and screen appropriate destruction technologies for acetic acid in aqueous nitric acid solutions and to provide the overall technology recommendations. Following is an explanation of research performed and being planned under each technology considered for eliminating acetic acid.

Solvent Extraction. The distribution coefficient for acetic acid between 0.5M nitric acid solutions and TBP-dodecane (or similar kerosene-like diluent) mixtures is of particular interest because these compounds are used as solvents during the UREX processing segment. The use of such solvents is not likely to affect the other steps in the UREX+ operations. The distribution coefficient is in a suitable range, so equipment size and liquid flow rates are likely to be reasonable. Some extraction of nitric acid as well as acetic acid is expected, but loss of a relatively small portion of the nitric acid is not likely to be objectionable. Some solvent is likely to be entrained and enter the rest of the system. Researchers would want to use the same diluent used in the UREX+ process—the only requirement on entrainment would be that it be sufficiently low so that the composition of the UREX+ solvent is not changed significantly or rapidly. Since TBP can extract a number of metals, including fission products and actinides, it is likely that some metals will be extracted and subsequently stripped from the solvent. Because the nitric acid concentration is significantly lower than that used in the main extraction step of the UREX+ process, the metals are not expected to be extracted strongly during the acetic acid removal. At the present time, the TBP-based solvent appears to be the most promising solvent extraction approach to acetic acid removal. Such a process may remove some metal ions, and the behavior of important fission products and actinides will need to be evaluated and controlled to prevent undesirable deposition of significant radioactivity.

The researchers would like to consider at least one other option that has not yet been studied: a "diluent-only case," that is, using the diluent throughout the fuel process system without an extractant. Although this option is somewhat improbable, it can be evaluated experimentally very quickly. If the same diluent can be used as the rest of the fuel processing system, there would be minimal risk of undesirable effects from entrainment of solvent (diluent) through the nitric acid product into other process steps. Also, the diluent would not be likely to extract any metal ions (fission products, actinides, etc.), so the acetic acid should be relatively free of radioactivity. The principal path for radioactivity to reach the recovered/removed acetic acid probably would be via entrainment.

At the expected nitric acid concentration of the stream, most of the acetic acid will not be ionized. While the resulting distribution coefficient to the diluent will not be as high as the ratio of the un-ionized acetic acid to the acetate ions, researchers hope to achieve a useful distribution of acetic acid to the organic phase. There is no limit to the value of the distribution coefficient that would be necessary for the diluent-only option to be viable, but researchers would like the distribution coefficient to the organic phase to be 0.1 or larger. Smaller distribution coefficients make operation of some liquid-liquid contactors difficult and require increasingly large solvent flow rates.

Even if extraction can be practical with diluent-only, it will also be necessary to strip the acetic acid. The preferential approach would be to strip with water alone since pH could be close to neutral, with hydrogen ion concentrations approaching values as low as 10^{-7} molar. However, a slightly alkaline strip could be used to improve the strip and/or concentrate the acetate.

Crystallization. Although the information on acetic acid–nitric acid mixtures is limited, it appears likely that effective separations are possible. However, three aspects of crystallization are likely to make it less desirable than other options. First, crystallization is usually more attractive for relatively concentrated acetic acid solutions. It is likely that crystallization would need a separate distillation step to concentrate the feed stream. Second, the crystallization of a mixed nitric acid-acetic acid species appears likely for aqueous solutions of mixed nitric and acetic acid. This would result in the loss of some nitric acid with the acetic acid, but that loss is likely to be acceptable. Finally, most crystallization operations involve some mechanical operations for crystal removal and washing, but alternate techniques for forming films of crystals that can be separated from the liquid with less mechanical effort could be explored.

Crystallization is a viable approach to acetic acid removal in this application, but it involves some uncertainties and less desirable features. It will continue to be considered but will receive more attention only if other approaches begin to look less desirable than expected.

Distillation. If the solution of interest is subjected to distillation, the overhead stream will be more concentrated in water than the original mixture while the residue stream will be less concentrated in water (and more concentrated in nitric acid). A concentration still for nitric acid usually results in a nearly pure water overhead stream and concentrated nitric acid stream in the residue stream. The maximum concentration from such an operation is the azeotropic concentration.

Results of a literature review indicate that acetic acid fed to a nitric acid concentrating still will likely remain with the concentrated nitric acid product. A multi-tower system would be necessary for removing the acetic acid.

Adsorption. It is generally accepted that the adsorption of weak electrolytes from aqueous solutions occurs through the association of the undissociated molecule with the surface. At conditions where the pH is lower than the pK of the ionizable solute, the equilibrium loading will be increased over that expected at conditions where the pH is higher than the pK. Acetic acid in the stream will be largely associated at expected pH due to the presence of nitric acid and the pK of acetic acid; nitric acid is a relatively strong acid while acetic acid is a relatively weak acid. Equilibrium capacity for acetic acid on various carbons and polymeric adsorbents is widely reported in the literature. Both carbon and polymeric adsorbents appear to have acceptable adsorption characteristics for further consideration.

The possibility of nitration reactions of nitric acid with polymeric adsorbents deserves careful investigation prior to selection of any adsorbent; however, the usual methods of adsorbent regeneration include stripping at a higher temperature (usually with steam), stripping with a reactive solution (such as an aqueous base), or leaching with an appropriate solvent (such as acetone, various acetates, and methanol). The non-functionalized adsorbents are more easily regenerated by solvents than activated carbon.

The major research accomplishments to date are presented in Table 1. The technologies investigated were solvent exchange, crystallization, distillation, adsorption, and destruction. Solvent extraction appears to be technically feasible and is a similar technology to that used elsewhere in the UREX+ system; regeneration of the solvent and removal of the acetic acid will add complexity to the process. Crystallization is a simple process but appears to require a preliminary concentration step to create conditions where the acetic acid will crystallize from solution; this technology would be needed to remove acetic acid from the recovered and concentrated nitric acid solution prior to its recycle. Distillation does not seem to offer any advantage for acetic acid removal unless coupled with crystallization or another unit operation. Adsorption is technically feasible with similar concerns for additional process complexity as those for solvent extraction.

Planned Activities

Researchers will make the final ranking of appropriate acetic acid removal/destruction technologies in the next fiscal year after the study of destruction technologies is complete. Development of flowsheets for leading technologies will also begin over the next fiscal year. In the final fiscal year, researchers will conduct testing to experimentally verify the design activities.

Technology	Pros	Cons
Solvent Extraction	• Similar to other UREX+ operations • Could use diluent and extractant already in UREX+ • Data exist on similar systems	• Probably should be restricted to solvents UREX+ • Strip step required • Possibly wash and/or solvent scrub step required
Crystallization	• Feasible • Could be used with distillation	• Requires concentration • Some mechanical operation likely
Distillation	• Feasible • Could be used with crystallization	• Removes water first (concentrates nitric acid) • Multiple towers required to remove acetic acid
Ion Exchange	• Uncertain feasibility	• No suitable adsorbent found
Destruction	• To be determined	• To be determined

Table 1. Technical progress.

NUCLEAR ENERGY RESEARCH INITIATIVE

Separation of Nuclear Fuel Surrogates from Silicon Carbide Inert Matrix

PI: Ronald Baney and James Tulenko, University of Florida

Collaborators: None

Project Number: 06-126

Project Start Date: March 2006

Project End Date: March 2008

Research Objectives

The objective of this work is to establish a protocol for dissolution of silicon carbide from ceria using technologies compatible with traditional fuel handling. Researchers will process samples using hot corrosion (molten salt) methods that will co-dissolve processed samples with metal silicides. They will study these melt processing techniques for ways of separating the matrix from urania and ceria. Ceria and other surrogate materials will be separated in a fashion comparable to methods reported in the literature. The resultant samples will be characterized for ease of separation, degree of safety (with regards to chemicals and reaction products), and cost.

Research Progress

A literature survey has identified the following available methods for the dissolution of silicon carbide (SiC):

- oxidation
- hydrothermal oxidation/corrosion
- dissolution reactions with metals and metallic alloys
- hot corrosion
- etching
- corrosion
- dissolution in molten oxides

After evaluating the various dissolution methods, researchers selected the hot corrosion method as the most viable, and procured the necessary equipment and materials.

Hot corrosion (i.e., molten salt) processing will be performed in a single-zone tube furnace connected to a gas delivery system. In this process, researchers place several alumina crucibles containing salt and SiC inside the furnace to melt the samples, removing them at different time intervals and cooling to room temperature for characterization. Air or a nitrogen-oxygen mixture (N_2-O_2) flow through the furnace's alumina work tube during melting, and laboratory air is used for cooling.

Researchers will first use SiC samples without ceria to establish a baseline reference and to determine the optimum processing parameters that provide the fastest dissolution rate. After completing this phase, they will evaluate SiC samples with different ceria content for dissolution reaction products and ease of separation of these products.

Although SiC is thermodynamically an unstable ceramic when reacting with oxygen, it is considered stable due to the slowness of the reaction at low temperatures. When oxygen is present in the environment, SiC reacts to form a thin, passivating dense silica (SiO_2) film according to the following reaction:

$$SiC(s) + 2O_2(g) \longrightarrow SiO_2(s) + CO_2(g) \qquad (1)$$

As the silica film develops through the "passive oxidation" process, it retards oxidation due to its low oxygen diffusivity. It is this film that provides SiC with its oxidation/corrosion resistance and chemical inertness.

The oxidation usually follows parabolic kinetics. Although SiC is used in applications that involve an oxidizing/corrosive environment, it is not well suited for combustion environments (e.g., gas turbines or coal-fired boilers). In such environments, the ceramic surface is quickly attacked by the alkali and alkali earth impurities that are present in the hot gases and condense on the cooler surface as carbonate and sulfate compounds.

The process of hot corrosion is complex, involving two different steps occurring simultaneously: 1) fluxing and dissolution of the silica layer to form silicide compounds and 2) oxidation of SiC to silica by oxidizing species present in the molten salts. Silicide compounds have a lower viscosity and higher oxygen diffusivity than silica, thus allowing the oxidation of the underlying SiC into silica and carbon dioxide (see equation 1). The process continues until the salt melt reaches a saturation point of the dissolves species, as in the case of a thin-layer coating, or until the SiC is consumed, as in the case of immersion in a melt bath. Additional reaction products that may be generated during the hot corrosion process, depending on the salts used, include nitrogen, carbon monoxide, carbon dioxide, and silicon monoxide.

Researchers performed a proof-of-concept experiment to illustrate the viability of dissolving SiC by alkali and alkali earth salt melts. A small piece of SiC from a military tank armor plate was exposed to molten sodium carbonate (Na_2CO_3, T_{mp}= 850°C) for four hours at 1,050°C in a laboratory air environment. The results indicated that a SiC dissolution reaction occurred, as shown in the before and after images in Figure 1 and indicated by the dimensional changes presented in Table 1.

	Before	After	Change
Base, mm	3	< 2.5	**> 0.5**
Height, mm	~ 5	< 4	**> 1**
Thickness, mm	1.1	0.6	**0.5**
Volume, mm	~ 8.3	< 3	**> 5.3**

Table 1. Dimensional change in SiC sample after exposure to sodium carbonate melt for 4 hours at 1,050°C.

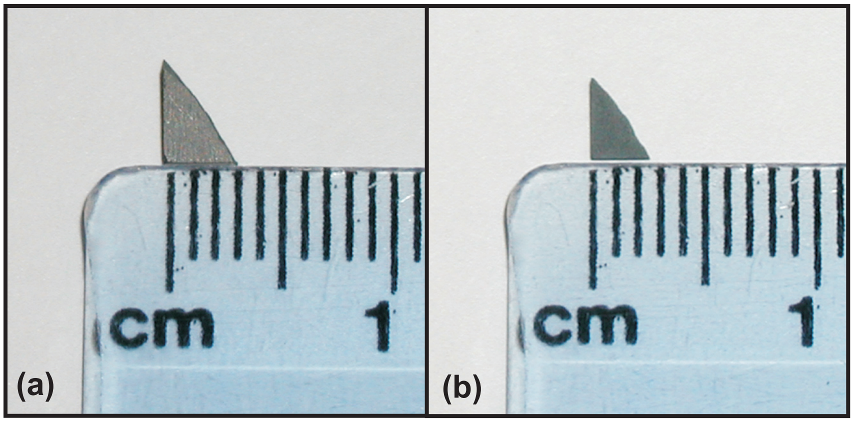


Figure 1. Images of a SiC samples before (a) and after (b) exposure to a sodium carbonate melt for 4 hours at 1,050°C in a laboratory air environment.

Another proof-of concept experiment entailed exposing a small piece of ceria to molten sodium carbonate, following the same experimental procedure as for the SiC sample. In this experiment, no reaction occurred between the ceria and the salt melt.

Planned Activities

The researchers plan to perform the following tasks over the next fiscal year:

- Fabricate SiC IMF pellets without ceria and SiC IMF pellets with two different ceria/SiC ratio compositions
- Perform hot corrosion of the SiC pellets without ceria to establish a baseline reference and determine optimum processing parameters
- Perform hot corrosion of the SiC pellets with ceria to determine dissolution rate
- Characterize the reaction products to determine what compounds are formed during the dissolution process using different characterization techniques, such as scanning electron microscopy (SEM) and X-ray diffraction (XRD)
- Evaluate the hot corrosion process for ease of separation of the reaction products and develop processes for separating these products
- Optimize the hot corrosion process for technology transfer from laboratory-scale to industrial-scale.

Enhancements to High-Temperature In-Pile Thermocouple Performance

PI: John Crepeau, University of Idaho

Collaborators: Idaho National Laboratory (INL)

Project Number: 06-134

Project Start Date: March 2006

Project End Date: March 2008

Research Objectives

There are insufficient data to characterize the performance of new reactor materials in high-temperature, radiation conditions. To evaluate candidate material performance, robust instrumentation is needed that can survive these harsh conditions. Traditional methods for measuring temperature in-pile either degrade at temperatures above 1,100°C or de-calibrate due to transmutation.

Several years ago, the INL launched an effort to develop temperature measurement methods suitable for long-duration, high-temperature in-pile testing. Initial results indicate that specialized alloy thermocouples fabricated from doped molybdenum/niobium-1% zirconium (Mo/Nb1%Zr) have the potential to provide the desired accuracy for long-duration tests. Although the performance of these thermocouples appears promising, there are several options that can potentially enhance their lifetime and reliability.

The major research objective of this project is to quantify the impact of candidate enhancements related to alloy materials, geometry, and fabrication techniques on thermocouple performance. Based on these evaluations, improved thermocouple designs will be fabricated and tested at high temperatures for long durations to quantify thermocouple accuracy, reliability, and lifetime. Ultimately, an optimized thermocouple design will be recommended for high-temperature in-pile testing.

Research Progress

During this reporting period, work continued on long-duration testing of specialized thermocouples, ductility evaluations of available non-commercial alloy wires, and development of fabrication steps for thermocouples of alternate geometries.

Researchers completed a long-duration test, which was initiated using other programmatic funding at INL's High Temperature Test Laboratory (HTTL), to evaluate the drift of specially developed thermocouples at 1,400°C. This test was conducted by placing thermocouples in a tube furnace held at 1,400°C that was purged with gettered high-purity argon. This test included six of the INL-developed doped molybdenum-niobium thermocouples: two using commercially available thermoelement wires Nb1%Zr and KW-Mo (molybdenum doped with potassium and tungsten), and four containing special Mo-low Nb alloys developed by Sylvania with commercially available Nb1%Zr. All of these thermocouples were fabricated with hafnia insulation and Nb1%Zr sheaths. The drift in the electromagnetic frequency (EMF) of representative thermocouples was minimal after more than 4,000 hours of testing.

Ductility evaluations were completed on candidate alloys by heating 0.0254 cm (0.01 in) diameter wires for 2-, 5-, and 12-hour intervals in gettered argon at temperatures of 1,400, 1,600, and 1,800°C. Ductility was evaluated by wrapping these heated wires around mandrels that were from 2 to 20 times the wire diameter. All candidate molybdenum materials remained ductile and the wires could be wrapped on the mandrels for several turns without breaking, even after heating for 12 hours at 1,400°C. In contrast, only the doped Mo wires remained ductile after heating at higher temperatures. After 5 hours at 1,800°C, both the Mo1.6Nb and Mo3Nb wires were too brittle for mandrel wrap tests. Tests were conducted only on molybdenum alloys because of delays in niobium alloy production.

For the alternate geometry evaluations, researchers prepared two thermocouples in each of three geometries—wire diameter of 0.005, 0.010, and 0.020 inches. However, one of the smaller diameter thermocouples failed during fabrication. The remaining five thermocouples were heat-treated for 20 hours at 1,700°C to stabilize grain growth. Data suggest that the smaller diameter thermocouple was more sensitive to oscillations of the tube furnace controller in maintaining the temperature at 1,700°C. Data also indicate that all three sizes of thermocouples stabilized within the first four hours of heat treatment. During the cool-down period, the remaining smaller thermocouple (with 0.005″ wires) experienced an open circuit failure. However, the larger diameter thermocouples and the two standard-sized thermocouples remained stable. Transient tests were performed to quantify thermocouple output. Changes in EMF were minimal (less than 1 percent) for the larger diameter thermocouple after two cycles. The results of this work will be presented at the *15th International Conference on Nuclear Engineering (ICONE)*.

Planned Activities

Efforts are underway to develop a fabrication process that will yield more robust, small diameter thermocouples. Then, the team will prepare additional samples for each thermocouple size in which the heat treatment duration will be limited to five hours, and evaluations will be completed to assess the effect of diameter on thermocouple performance.

NUCLEAR ENERGY RESEARCH INITIATIVE

Design and Development of Selective Extractants for An/Ln Separations

PI: Robert T. Paine, University of New Mexico (UNM)

Collaborators: Washington State University (WSU), Idaho National Laboratory (INL)

Project Number: 06-137

Project Start Date: April 2006

Project End Date: March 2009

Research Objectives

This project is designed to remove transuranic elements from spent nuclear fuel for storage or for reuse in transmutation processes. The proposed method will develop an efficient aqueous separation scheme for recovering americium (Am) and curium (Cm) from the acidic liquid remaining after UREX+2 processing to remove uranium (U), plutonium (Pu), neptunium (Np), cesium (Cs), and strontium (Sr). The method will also separate trivalent actinides from fission product lanthanide ions. The project focuses on the continued development and optimization of "NOPOPO ligands," which the researchers previously demonstrated are effective extractants under laboratory-scale conditions and show promise as a large-scale process add-on to UREX+2.

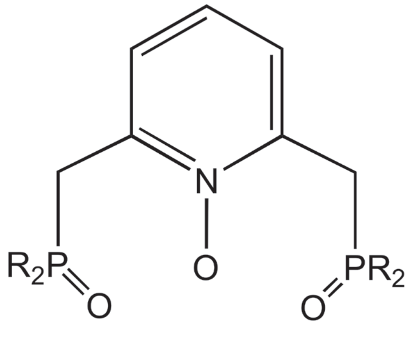
The primary objectives of this project include 1) the design, synthesis, and extraction performance characterization of 2,6-bis(phosphinomethyl)pyridine N,P,P´-trioxides (NOPOPO) as potential reagents for separating Am, Cm, and fission product lanthanides from other transuranics and fission products and 2) the development of a separations "platform" for the mutual separation of Am/Cm from the lanthanides. Preliminary analyses indicate that one member of the family of ligands, $(EtHx)_4$NOPOPO, offers improved separation of Am^{3+} ions from acidic aqueous solutions compared to the CMPOligand used in the transuranic extraction (TRUEX) process. The research is expected to produce a best-case extractant compound, which will undergo a complete round of synthesis optimization and performance characterization with a realistic raffinate stimulant representative of the uranium extraction (UREX+) process.

Specific project tasks include:

- Optimize the NOPOPO synthesis
- Conduct further extraction testing of $(EtHx)_4$NOPOPO
- Study extractant phase compatibility as well as hydrolysis and radiolytic stability
- Design and synthesize new NOPOPO derivatives with improved solubility, phase compatibility, and stability characteristics
- Conduct extractive testing of the new derivatives to determine their relative efficacy
- Conduct focused testing on the best-case extractant compound to optimize synthesis and characterize performance with realistic waste solutions
- Perform a cost analysis for the new process

Research Progress

Prior work performed by the research team has shown that modest quantities (2-10 g) of the new family of NOPOPO ligands, **1**, with a wide variety of aryl and alkyl R groups, could be prepared from three different synthesis protocols (Figure 1).



1

Figure 1. New family of NOPOPO ligands.

Subsequent work that focused on developing a hydrocarbon solvent soluble derivative suitable for actinide ion extractions showed that the derivative **3** with R = R´ = 2-ethyl hexyl (EtHx) could be obtained in 10 g batches with good overall yield. However, as initially described, the synthesis yields varied from batch to batch and the crude ligand often required extensive effort to obtain a suitably pure form. Therefore, the initial objective of the new program involved development of a reliable procedure for synthesis and purification of **3** with R = R´ = 2-EtHx. During the first six months of the project, researchers optimized the procedure summarized in Figure 1.

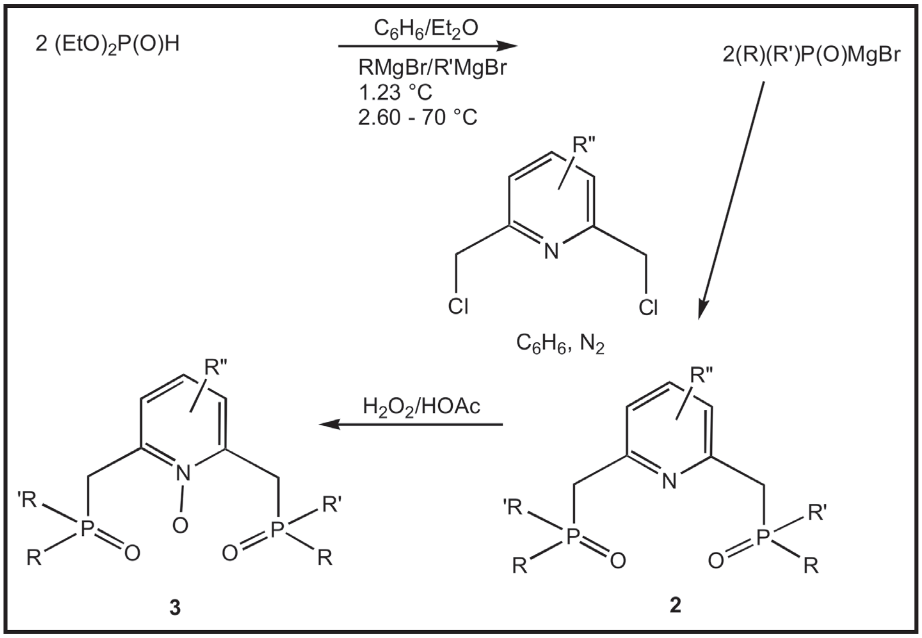


Figure 1. Scheme for synthesis and purification of 3 with R = R´ = 2-EtHx.

The synthesis has now been performed on a 20 g scale with yields of 80 percent or better. The team has identified the source of troublesome impurities and is working to eliminate the originating species. They have achieved success on small-scale batches (~ 2 g) so that only a single chromatographic column separation is required for purification.

During this initial project period, the researchers initiated hydrolytic stability studies. The ligand **3**, R = R´ = 2-EtHx, has been exposed to aqueous nitric acid (HNO_3) solutions of 0.5 – 4 molar (M) and potential reaction chemistry has been monitored by ^{31}P NMR. After two months of exposure at 23°C, no reactivity has been detected.

With the availability of larger amounts of **3**, it was possible to begin additional solvent extraction analyses. The group at WSU began a new series of lanthanide extractions, including cerium (Ce), europium (Eu), and ytterbium (Yb), from 0.1 M HNO_3 with **3**/dodecane mixtures using Inductively Coupled Plasma (ICP) analysis. The initial results show increasing distribution ratios going from light to heavy lanthanides. This is an interesting and unexpected result since the observed trend is opposite to that found with the popular neutral extractant CMPO. The fundamental explanation for this reversal is not known at this time, but continuing work may shed light on this interesting and potentially useful observation. The extractions were also examined as a function of metal nitrate, MNO_3, where M = lithium ion (Li^+), sodium ion (Na^+), or ammonium ion (NH_4^+), at a constant nitrate concentration (NO_3^-). The D values decrease by a factor of three across this series, which likely reflects anticipated water activity effects.

Planned Activities

UNM researchers will continue their effort to further scale-up the synthesis of **3** and optimize the purification procedure. They will also continue chemical stability testing of **3** in HNO_3 solutions. At WSU, the ICP analysis of the extraction performance of **3** (R = R´= 2-EtHx) toward a series of lanthanides will continue in order to verify the observations produced during the second quarter. INL will initiate a series of Am/Eu extractions at varied acid concentrations using **3** in dodecane, aimed at verifying results obtained earlier. Following the initial studies, the extractant will be subjected to gamma irradiation and then the extractions will be repeated. This set of experiments will provide on initial measure of radiation stability for the extractant in dodecane.

Next year, researchers expect to expand the scale-up of the synthesis of **3** (R = R´ = 2-EtHx) to 50 g. If successful, they will begin discussions with a commercial synthesis house regarding the scaling/cost issues surrounding this ligand. They will also initiate acid hydrolysis testing for **3** at higher temperatures (40–50°C) to determine long-term extractant stability toward HNO_3. It is expected that batches of at least two or three new NOPOPO derivatives will be prepared in order to examine electronic/steric modifications on extraction performance.

Further work on the extraction analyses will be largely determined by the results of the remaining studies. However, researchers expect to begin evaluating waste stimulant solutions.

NUCLEAR ENERGY RESEARCH INITIATIVE

Microwave Processing of Simulated Advanced Nuclear Fuel Pellets

PI: D. Clark and D. Folz, Virginia Polytechnic Institute and State University (VT)

Collaborators: University of Tennessee (UT)

Project Number: 06-141

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The objective of this project is to sinter simulated (non-radioactive) oxide and nitride inert matrix fuel (IMF) pellets using microwave energy. Researchers will characterize the sintered pellets with respect to density and grain morphology. The VT team will use microwave hybrid heating (multi-mode and single mode) to sinter the pellets, while the UT team will perform the same operations with direct microwave sintering.

The primary tasks of this work are to:

- Prepare green pellets
- Demonstrate direct microwave heating (DMH) to achieve sintering
- Demonstrate microwave hybrid heating (MHH) to achieve sintering
- Characterize pellets before and after microwave processing
- Evaluate microwave processes

Research Progress

During the past year, researchers fabricated over 150 oxide samples of partially stabilized zirconia (PSZ–3 mol% yttria) using uniaxial pressing at 45 ksi, followed by isostatic pressing at 30 ksi. They purchased a commercial microwave oven capable of reaching 2,100 watts at 2.45 GHz for multi-mode microwave hybrid heating and installed temperature measurement and data collection systems (Figure 1).

The team designed microwave-absorbing susceptor caskets, constructed from PSZ and aluminum oxide (Al_2O_3). Single and multiple sample loads are being used (Figure 2).

Figure 1. Commercial microwave oven (2.45 GHZ; 2,100 W maximum power) with shielded, grounded k-type thermocouple and refractory housing. A two-color optical pyrometer is used to monitor high temperatures.

Figure 2. Microwave hybrid heating caskets illustrating various sample loads and designs.

Based on geometric measurements and volumetric displacement, researchers have determined that volume shrinks by approximately 50 percent in the microwave environment at 33 minutes of total run time. Similar volume shrinkage is observed in the conventional ovens at 1,400–1,500°C after 2.5 hours. Thermal conductivity measurements of a conventionally sintered sample of PSZ and a microwave sintered sample of PSZ found the thermal conductivity of the microwave sintered sample to be about 9 percent greater. The team also assembled a single-mode microwave oven capable of continuously processing pellets/rods at high temperature and low power. As shown in Figure 3, they designed and implemented an instrument with customized software for controlling the thermal profile of the sample based on temperature measurements using optical pyrometers and control of the applied electromagnetic field in the sample.

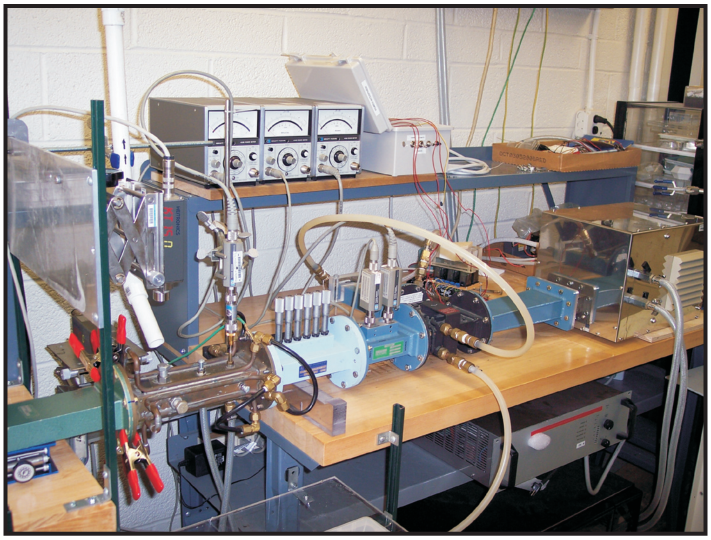


Figure 3. Single-mode microwave oven capable of delivering up to 1,400 W of microwave energy at 2.45 GHz.

Finally, they presented an invited talk on microwave processing of energy products at a National Academy of Engineering workshop in June.

Planned Activities

The team will initiate sintering experiments on 8 mol% yttria-stabilized zirconia and on dysprosia-stabilized zirconia in the second year. They anticipate testing nitride compositions, but emphasis will remain on oxides. They are moving toward processing under controlled atmospheres to manipulate the oxygen content in the pellets. During the next fiscal year, they plan to conduct a thorough characterization of structural and compositional uniformity, percent theoretical density (using pycnometry and Archimedes methods), and hardness as a function of position within the sample.

NUCLEAR ENERGY RESEARCH INITIATIVE

Radiation-Induced Segregation and Phase Stability in Candidate Alloys for the Advanced Burner Reactor

PI: Gary Was, University of Michigan

Collaborators: University of California-Berkeley, Los Alamos National Laboratory, Oak Ridge National Laboratory

Project Number: 07-015

Program Area: AFCR&D

Project Description

The objective of this project is to investigate the effect of irradiation on the segregation and phase stability in candidate alloys that may be used as structural materials for transmutation in the advanced burner reactor. This project will focus on ferritic-martensitic (F-M) alloys T91 and HT-9; an experimental oxide dispersion-strengthened (ODS) alloy; and an advanced austenitic alloy, D9, to investigate the electronic–magnetic–elastic interactions between chromium and radiation-induced defects. This project seeks to provide an understanding of radiation-induced segregation (RIS) and phase stability that can be used to develop predictive irradiation performance models.

Researchers will conduct experiments by proton and heavy ion irradiation over the dose range 3–100 dpa and the temperature range 350–550°C. Analysis of RIS, phase microstructure, dislocation microstructure, and hardening will be conducted on all conditions. Investigators will also develop *ab-initio* models of the electronic structure to investigate the configuration-dependent binding and migration energies of chromium (Cr) with vacancy and interstitial defects. This will enable development of atomistic-based kinetic Monte Carlo models to investigate the Cr diffusivity by interstitial and vacancy mechanisms.

Work Scope

The primary tasks are to:

1) Perform ion irradiation studies
   - Proton irradiation to 10 dpa at 350–550°C
   - Heavy ion irradiation to 100 dpa at 350–550°C
   - He implantation to 1 appm/dpa
2) Conduct analysis of irradiated alloys
   - Radiation-induced segregation
   - Phase and dislocation microstructure
   - Hardening
3) Develop modeling techniques
   - Atomic-scale Monte Carlo modeling of <100> loop formation mechanisms
   - *Ab-initio* calculations of vacancy – Cr atom and interstitial – Cr binding energies and configuration/composition-dependent vacancy jump activation energies in bcc Fe-Cr alloys
   - Kinetic Monte Carlo modeling of Cr RIS; compare with MIK rate theory model of Cr/Si RIS as a function of temperature and dose
   - Kinetic Monte Carlo and rate theory modeling of interstitial dislocation loop evolution as a function of temperature and dose
4) Compare model and experimental results

NUCLEAR ENERGY RESEARCH INITIATIVE

Chemistry of Transuranic Elements in Solvent Extraction Processes: Factors Controlling Redox Speciation of Plutonium and Neptunium in Extraction Separation Processes

PI: Alena Paulenova, Oregon State University

Project Number: 07-023

Collaborators: Argonne National Laboratory

Program Area: AFCR&D

Project Description

The objective of this project is to examine the factors controlling redox speciation of plutonium and neptunium in UREX+ extraction. The change in the actinide speciation will be described in terms of redox potentials, redox mechanism, kinetics, and thermodynamics of the process. Chemical kinetic and thermodynamic data will be used to facilitate the stable redox buffering conditions where the both Np and Pu are in the desired redox state.

Researchers will employ the radiochemical redox-speciation extractions schemes in parallel to the redox experiment. The distribution of the redox species will be studied using methods of visual and near-infrared spectroscopy, electrochemistry and spectro-electrochemistry. This work will result in creation of a database on redox stability and distribution of redox couples of plutonium and neptunium in the nitric acid/nitrate electrolyte and development of redox-buffering systems to stabilize the desired oxidation state of separated radionuclides. The effects of temperature and concentrations of acid and salt on the redox potential of actinide nitrate will be evaluated, considering a range of chemical matrix conditions. The database generated from the experimental work will be integrated into an existing actinide speciation code (AMUSE).

Work Scope

This project consists of the following three primary tasks:

- Estimate the redox speciation of transuranic elements neptunium (Np), plutonium (Pu), and uranium (U), as a distribution of metal oxidation states and a function of temperature and acid and salts concentrations
- Determine redox reactivity of Np, Pu, U, and technetium (Tc) with studied oxidation/reduction agents under different concentration and temperature conditions in both aqueous and organic matrices
- Estimate the redox buffer conditions, stabilizing desired oxidation state
- Model distribution ratios and develop database on redox buffering/separation factors
- Integration of the database into existing actinide speciation code (AMUSE)

NUCLEAR ENERGY RESEARCH INITIATIVE

New Fission Product Waste Forms: Development and Characterization

PI: Alexandra Navrotsky, University of California-Davis

Collaborators: Sandia National Laboratories; Eltron Research, Inc.; Brigham Young University

Project Number: 07-027

Program Area: AFCR&D

Project Description

This project will outline advanced methods for the chemical partitioning of spent nuclear fuel into cesium (Cs), strontium (Sr), and minor actinide constituents that can be stored for future disposition. Researchers will study new waste forms and disposal strategies specific to the steam reforming process for the production of the Cs/Sr storage form with respect to the incorporation of Sr and Cs, their decay products, and rare earth fission products. A broad characterization study of inorganic ceramic waste form phases and the thermochemistry of these phases will provide a comprehensive data set from which to select the appropriate waste form. Emphasis will be on perovskite phases as a major constituent of the final waste form. The goals of this project are to reduce the costs associated with guanidinium carbonate steam reforming waste process; to minimize the risk of contamination to the environment during waste processing; and to provide DOE with technical solutions to a variety of issues related to Cs, Sr, and minor actinide disposal.

The proposed work will provide information on the durability and stability of these waste forms so that their potential for viable storage or disposal scenarios can be evaluated. The technical objective of this work is to 1) fully characterize the phase relationships, structures, and thermodynamic and kinetic stabilities of crystalline metal oxide based waste forms (e.g., perovskites) and 2) establish a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry. Since Cs and Sr form new elements by radioactive decay over several hundred years, researchers will study the behavior and thermodynamics of these waste forms using non-radioactive analogues.

Work Scope

The team will focus on four research tasks that will provide the underpinning science necessary for establishing a steam reforming waste form, including:

- Phase identification and phase diagram determination
- Structure determination
- Thermochemical stability
- Structure-property relationships

Computations for Advanced Nuclear Fuels

PI: Sudarshan Loyalka, University of Missouri-Columbia

Collaborators: None

Project Number: 07-035

Program Area: AFCR&D

Project Description

To successfully implement an efficient and effective nuclear power strategy, it is essential to develop new fuels that can provide optimal performance over long periods of time. This research will develop advanced computational techniques to improve the understanding of fission gas distribution and heat transfer in solid fuel under normal and accident conditions.

In this project, researchers will develop atomistic-scale to continuum-scale models to replace the empirical models used in existing performance codes (such as FRAPCON for oxide fuels and PARFUME for TRISO fuels), which date back to the 1970s. The computational programs of fission product transport will apply to the pyrolytic carbon and silicon carbide coating of TRISO fuels as well. This will help provide estimates for the transport behavior of noble gases, iodine, tellurium, cesium, strontium, silver, palladium, and rare earth fission products in the layers of the TRISO-coated particle fuel under both normal and accident conditions—where measurements are either impractical or cost prohibitive. This work will also help reduce uncertainties and elucidate transport mechanisms.

Work Scope

This project will perform the following tasks:

- Construct a computer program for heat transfer in the solid fuel using the direct simulation Monte-Carlo technique
- Construct a computer program for fission gas distribution in the fuel using the direct simulation Monte Carlo technique
- Combine the two programs and conduct parametric studies to elucidate the role of geometry, materials, and irradiation on both the fission gas distribution and heat transfer
- Compare the computations against available experimental data

NUCLEAR ENERGY RESEARCH INITIATIVE

Experimental Development and Demonstration of Ultrasonic Measurement Diagnostics for Sodium Fast Reactor Themohydraulics

PI: Akira Tokuhiro, Kansas State University

Collaborators: None

Project Number: 07-037

Program Area: AFCR&D

Project Description

This research project will address some of the principal technology issues related to sodium-cooled fast reactors (SFR), primarily the development and demonstration of ultrasonic measurement diagnostics linked to effective thermal convective sensing under normal and off-normal conditions. Sodium is well-suited as a heat transfer medium for the SFR. However, because it is chemically reactive and optically opaque, it presents engineering accessibility constraints relative to operations and maintenance (O&M) and in-service inspection (ISI) technologies that are currently used for light water reactors. Thus, there are limited sensing options for conducting thermohydraulic measurements under normal conditions and off-normal events (maintenance, unanticipated events). Acoustic methods, primarily ultrasonics, are a key measurement technology with applications in non-destructive testing, component imaging, thermometry, and velocimetry.

This project will yield a better quantitative and qualitative understanding of the thermohydraulic condition of sodium under varied flow conditions. The scope of work will evaluate and demonstrate ultrasonic technologies and define instrumentation options for the SFR.

Work Scope

The researchers will demonstrate ultrasonic technology through the following activities:

- Design, construct, and operate a small, simple, university-based sodium flow loop with inventory of approximately 5–6 liters
- Develop and demonstrate ultrasonic velocimetry and thermometry, with a focus toward improved SFR O&M (i.e., using velocimetry and thermometry as diagnostic tools during normal and off-normal operations)
- Test a compact sodium-to-supercritical carbon dioxide (CO_2) heat exchanger and generate convective heat transfer data, correlations, and operational experience under normal and off-normal operations

NUCLEAR ENERGY RESEARCH INITIATIVE

Fundamental Processes of Coupled Radiation Damage and Mechanical Behavior in Nuclear Fuel Materials for High-Temperature Reactors

PI: Simon Phillpot and James Tulenko, University of Florida

Collaborators: Idaho National Laboratory, Los Alamos National Laboratory

Project Number: 07-046

Program Area: AFCR&D

Project Description

A longstanding issue for the nuclear industry is the degradation of the mechanical properties of nuclear fuels under irradiation, including both the fissionable material and cladding. Developing fuel systems with improved resistance to radiation damage will allow longer burnups, improved usage efficiency, increased time between refueling, and decreased waste. The objective of this project is to elucidate the relationship among the microstructure, radiation damage, and mechanical properties of nuclear fuel materials. This research will focus on developing an understanding of 1) the fundamental mechanisms of radiation damage in polycrystalline materials, 2) the effect this damage has on plastic deformation, and 3) the effect of mechanical deformation on radiation tolerance.

The researchers will examine hexagonal close-packed (HCP) titanium (Ti) and UO_2. The former is representative of HCP Ti alloys for fast reactors and zircaloy cladding in thermal reactors. To simulate radiation damage, they will apply state-of-the-art, large-scale, atomic-level simulation through a judicious combination of conventional molecular-dynamics (MD) and accelerated MD methods. They will elucidate mechanical behavior by applying large-scale MD simulations. This systematic program for simulating the effects of irradiation on the structural and mechanical properties of polycrystalline Ti and UO_2 will identify radiation damage mechanisms and provide insights into the expected behavior of nanocrystalline microstructures and nanocomposites. This work will ultimately help researchers design microstructures that are less susceptible to radiation damage and thermomechanical degradation.

Work Scope

This research will consist of the following four tasks:

- Determine effects of radiation damage in fine-grained polycrystalline Ti and UO_2
- Characterize the mechanical properties of unirradiated polycrystalline Ti and UO_2
- Elucidate the effect of radiation damage on mechanical properties of polycrystalline Ti and UO_2
- Determine the effect of plastic deformation on radiation resistance in polycrystalline Ti and UO_2

NUCLEAR ENERGY RESEARCH INITIATIVE

Economic, Repository, and Proliferation Impacts of Advanced Nuclear Fuel Cycles

PI: K.B. Cady, Cornell University

Collaborators: University of Texas at Austin

Project Number: 07-051

Program Area: AFCR&D

Project Description

Advanced nuclear fuel cycles that use plutonium or other minor actinides recovered from spent light water reactor (LWR) fuel can reduce the amount of material that would require geologic storage. This project will compare the use of fast reactor (FR) advanced nuclear fuel cycles with that of inert matrix fuel (IMF) in light water reactors as a means of reducing actinide inventory, focusing on their economics and proliferation resistance.

In addition to making use of the current LWR fleet, IMF can offer a four-fold increase in repository capacity when compared to direct disposal of an energy-equivalent quantity of spent LWR fuel, with over 98 percent destruction of plutonium-239. Research also suggests that leaving IMF pins in the reactor after their reactivity has been depleted (effectively making them actinide targets) could offer a significant increase in actinide destruction. Fast reactors can potentially increase repository capacity by more than an order of magnitude per kilowatt of electricity generated. However, FR spent fuel must be recycled many times in order to achieve this result, whereas the increase in repository capacity offered by IMF does not require reprocessing. Unlike previous studies which assumed that spent FR fuel be recycled continuously, this project will analyze the impact of IMF and FR transmutation strategies over a 100-year period, from 2030 to 2130.

Work Scope

This project will accomplish the following tasks:

1) Determine the material balances (including proliferation sensitive materials) for IMF and FR fuel cycles that operate over a finite time period
    - Use the burnup/criticality code, MCNPX/MONTEBURNS, and the fuel cycle analysis code REBUS-3 to determine the isotopic balances for representative transuranic vectors, typical LWR parameters, and FRs with different conversion ratios
2) Determine the radiological and heat load to a repository for each fuel cycle
    - Use ORIGIN 2.2 and the spent fuel composition for the respective IMF and FR cycles
3) Determine fuel cycle cost in \$/kWhr for each of the respective fuel cycles
    - Apply probabilistic discount model unit cost data published by the OECD/NEA
    - Investigate the effect of uncertainties in cost, discount rates, and time.

NUCLEAR ENERGY RESEARCH INITIATIVE

Analysis of Advanced Fuel Assemblies and Core Designs for the Current and Next Generations of LWRs

PI: Jean C. Ragusa, Texas Engineering Experiment Station

Collaborators: None

Project Number: 07-059

Program Area: AFCR&D

Project Description

This research will focus on developing light water reactor (LWR) fuel assemblies that can efficiently transmute plutonium and minimize the minor actinide inventories. The reprocessing of spent nuclear fuel can delay or avoid the need for a second geological repository in the U.S. Current light water reactor fuel assembly designs under investigation could reduce the plutonium inventory of reprocessed fuel. Nevertheless, these designs are not effective in stabilizing or reducing the inventory of minor actinides.

The project will study various fuel types, namely high burn-up advanced mixed oxides and inert matrix fuels, in various geometrical designs that are compliant with the core internals of current and future light water reactors. A total of 10 fuel pin designs and 13 fuel assembly designs will be analyzed and their neutronic/thermal hydraulic effects investigated. The best performing designs will be used in 3-D core depletion methodology to determine overall transmutation performance in various fuel cycle scenarios. Transmutation efficiency and safety parameters will be used to rank the various designs. Researchers will also assess the number of Generation IV reactors needed to close the fuel cycle.

Work Scope

This project will perform the following tasks:

- Develop and optimize fuel pin concepts
- Develop and optimize fuel assembly designs with improved transuranics transmutation capability
- Perform thermalhydraulic subchannel analysis
- Analyze the neutronic/thermal hydraulic effects
- Perform and optimize 3-D depletion cycles
- Evaluate diverse fuel cycle options
- Assess and rank designs for transmutation efficiency, safety, and radiotoxicity.

NUCLEAR ENERGY RESEARCH INITIATIVE

Powder Metallurgy of Uranium Alloy Fuels for TRU-Burning Fast Reactors

PI: Sean M. McDeavitt, Texas Engineering Experiment Station

Collaborators: None

Project Number: 07-060

Program Area: AFCR&D

Project Description

This project will develop a powder metallurgical fabrication technology to produce alloys of uranium (U), ziranium (Zr), and transuranics (TRU) using either hot extrusion or "alpha-phase" sintering at relatively low processing temperatures (500°C to 600°C). Researchers will quantify the fundamental aspects of both processing methods using surrogate metals to simulate the TRU elements. If successful, this process will produce novel solutions to some of the issues related to metallic fuels, such as fuel-cladding chemical interactions, fuel swelling, volatility losses during casting, and casting mold material losses.

Fast reactors will be evaluated to enable the transmutation of transuranic isotopes generated by nuclear energy systems. The motivation for this is that TRU isotopes have high radiotoxicity and relatively long half-lives, making them unattractive for disposal in a long-term geologic repository. Fast reactors provide an efficient means to utilize the energy content of the TRUs while destroying them. An enabling technology that requires research and development is the fabrication metallic fuel containing TRU isotopes using powder metallurgy methods.

Work Scope

There are two primary tasks associated with this project:

1) Hot working fabrication using mechanical alloying and extrusion
    - Design, fabricate, and assemble extrusion equipment
    - Develop extrusion database on depleted uranium (DU) metal
    - Develop extrusion database on U-10Zr alloys
    - Develop extrusion database on U-20xx-10Zr alloys
    - Evaluate and test tube sheath metals
2) Low-temperature sintering of uranium alloys
    - Design, fabricate, and assemble equipment
    - Develop sintering database on DU metal
    - Develop sintering database on U-10Zr alloys
    - Conduct liquid phase sintering on U-20xx-10Zr alloys
    - Develop sintering methods in tube sheath containers

NUCLEAR ENERGY RESEARCH INITIATIVE

Neutronic and Thermal-Hydraulic Coupling Techniques for Sodium-Cooled Fast Reactor Simulations

PI: Jean C. Ragusa, Texas Engineering Experiment Station

Collaborators: University of Chicago, Commissariat a l'Energie Atomique (CEA), Argonne National Laboratory

Project Number: 07-063

Program Area: AFCR&D

Project Description

The objective of this project is to develop and implement efficient neutronic–thermalhydraulic coupling algorithms for sodium-cooled fast reactors.

This project will involve prototyping the following two methodologies: 1) coupling paradigms using an operator-split technique that can preserve the accuracy order of each physics component and 2) coupling paradigms using Jacobian-free formulations with physics-based preconditioners. The researchers will address the different spatial and time scales found in sodium-cooled fast reactor applications and will apply their methodology to demonstrate inherent safety features of sodium fast reactors with metallic fuel, including their response to typical anticipated transients without scram will be modeled.

Work Scope

This project consists of the following primary work scope:

- Assess the inconsistencies in commonly used coupling strategies
- Analyze potential improvements to operator-split techniques
- Develop consistent nonlinear time integrators
- Apply the methodologies to demonstrate the inherent safety of metallic fuel sodium fast reactors
- Perform anticipated transients without scram analysis
- Assess the performance of the new technology

NUCLEAR ENERGY RESEARCH INITIATIVE

Fundamental Studies of Irradiation-Induced Defect Formation and Fission Product Dynamics in Oxide Fuels

PI: James Stubbins, University of Illinois

Project Number: 07-064

Collaborators: Los Alamos National Laboratory

Program Area: AFCR&D

Project Description

This project will address performance issues of oxide-type nuclear fuels in the proposed fast-spectrum advanced burner test reactor (ABTR). Studying radiation effects and fission product transport processes in oxide-type nuclear fuels will establish a fundamental understanding of fuel performance. Researchers will model irradiation effects in cerium and uranium oxide (CeO_{2+x}, UO_{2+x}, and $(CeU)O_{2+x}$) surrogate fuels, comparing their performance with mixed oxide (MOX) fuels. The irradiation effects will be induced by ion implantation over a range of energies and doses to simulate the effects of fission product damage. Transport and trapping of simulated fission products will also be examined. Researchers will use inert gas ions, such as krypton (Kr) and xenon (Xe), both for ion implantation experiments to cause irradiation damage, and for dynamic transport studies to understand trapping and defect mobility processes in these fuel forms. They will also examine ions that simulate fission products and can substitute for uranium or cerium atoms in the oxide structure.

The experimental studies will be complemented by modeling using molecular dynamics (MD) simulations of damage cascades in the oxide lattice and kinetic Monte Carlo (KMC) techniques to study defect dynamics. The MD approach is useful in understanding the early stages of damage during energetic displacement cascades under irradiation. KMC is useful for using the defect configuration energies from MD to examine defect and fission product transport mechanisms.

Work Scope

This project will perform the following principal tasks:

1) Assess damage in pure CeO_2 and UO_2
    - Perform irradiations of helium (He), Kr, Xe, molybdenum (Mo)
    - Conduct positron annihilation spectroscopy (PAS), transmission electron microscopy (TEM), and other analyses
    - Develop MD and KMC simulation models
2) Assess damage in complex oxides
    - Perform irradiations of He, Kr, Xe, Mo
    - Conduct PAS, TEM, and other analyses
    - Develop MD and KMC simulation models
3) Develop transport properties
    - Perform annealing studies
    - Conduct PAS, TEM, and other analyses
    - Develop KMC model

NUCLEAR ENERGY RESEARCH INITIATIVE

Identification and Analysis of Critical Gaps in Nuclear Fuel Cycle Codes Required by the SINEMA Program

PI: Adrian Miron, University of Cincinnati

Project Number: 07-071

Collaborators: Idaho National Laboratory, Idaho State University

Program Area: AFCR&D

Project Description

The focus of this project will be to 1) carry out a detailed review of the existing codes describing aspects of the nuclear fuel cycle and 2) identify the research and development (R&D) needs required to develop a comprehensive model of a global nuclear energy infrastructure and associated nuclear fuel cycles. Researchers will analyze the gaps in the nuclear fuel cycle computer codes that will be integrated into the Simulation Institute for Nuclear Enterprise Modeling and Analysis (SINEMA) pyramid architecture.

SINEMA is a simulation network that will model the global nuclear energy infrastructure, associated fuel cycles, and components. SINEMA will provide an integrated tool-box to support the global and domestic assessment, development, and deployment of nuclear energy systems at various levels of detail. The toolbox will contain multiple analysis codes aimed at different parts of the fuel cycle enterprise and cover a wide range of mechanistic models at multiple temporal and spatial scales.

The project's initial effort will be to evaluate existing models that describe various aspects of the nuclear fuel cycle. The review will include domestic and international top-level nuclear enterprise model codes down to micro-scale codes dealing with all aspects of the nuclear fuel cycle. The codes will be assessed through a systematic approach that will focus on input/output data, functional and design requirements, method of solution, strengths and weaknesses, computer language and platform, and capability to link with other codes.

Work Scope

This project will consist of the following three primary tasks:

1) Review nuclear fuel cycle codes
    - Develop appropriate questionnaires and typical letters to be submitted to code developers and their organizations
    - Conduct systematic and detailed review of nuclear fuel cycle codes
    - Develop relational database
2) Identify R&D needs and gaps in nuclear fuel cycle computer codes
3) Identify best code packages to be linked within the SINEMA framework

6.3 NUCLEAR HYDROGEN INITIATIVE

Eleven NERI research projects are currently being performed that closely relate to the goals of the Nuclear Hydrogen Initiative (NHI), three of which were awarded in FY 2005, six in FY 2006, and two new projects in FY 2007.

As discussed in Section 3, the ***Nuclear Hydrogen Initiative*** supports the President's vision for a future hydrogen economy by demonstrating economic, commercial-scale hydrogen production using nuclear energy. This initiative will develop technologies to produce hydrogen with heat and/or electricity from next generation nuclear energy systems at costs that are competitive with other transportation fuels.

In FY 2006, NHI research projects focused on developing an efficient flowsheet for the SI cycle, developing simulation tools, and conducting design/analysis of the SI cycle. Research in high-temperature electrolysis is enhancing electrolyzer performance, developing improved cell materials, and creating new seal designs. Reactor/hydrogen interface research is targeting development of molten salt technology, creation of new alloys and ceramics for the interfacing heat exchangers, and optimization of heat exchanger design and performance.

Planned NERI research efforts related to this initiative will focus on construction of integrated laboratory-scale system experiments in support of the three primary technologies:

- Hydrogen production with thermochemical cycles
- Hydrogen production with high-temperature electrolysis (HTE)
- Reactor plant–hydrogen production process interface

This section summarizes the NERI research being performed that supports the goals of the Nuclear Hydrogen Initiative.

Project Summaries and Abstracts

FY 2005 Project Summaries

FY 2006 Project Summaries

FY 2007 Project Abstracts

NUCLEAR ENERGY RESEARCH INITIATIVE

The Sulfur-Iodine Cycle: Process Analysis and Design Using Comprehensive Phase Equilibrium Measurements and Modeling

PI: Mark C. Thies, Clemson University

Collaborators: University of Virginia (UVa), Savannah River National Laboratory (SRNL)

Project Number: 05-006

Project Start Date: April 2005

Project End Date: March 2008

Research Objectives

Of the numerous thermochemical hydrogen cycles proposed for the centralized production of hydrogen from nuclear power, the Sulfur-Iodine (S-I) cycle has been identified as one of the most promising. However, because the S-I cycle involves complex, highly non-ideal phase behavior and reactions, many of the performance projections associated with this technology are based on uncertain and incomplete data. In order to successfully develop this technology for a future hydrogen economy, basic research on thermodynamic measurements and physical property models of the S-I cycle are needed.

This project will focus on three areas: 1) thermodynamic measurements, 2) physical property modeling, and 3) process modeling. Researchers will use initial properties and process modeling to select conditions for experimental measurement. Then, as measurements become available, they will refine property models for process modeling and use the results to identify additional experiments for minimizing remaining process uncertainties.

The results of this project will be transferred to the nuclear hydrogen community by process simulation of the S-I cycle, using reactive distillation to effect the decomposition of hydrogen-iodide (HI).

Research Progress

Researchers previously selected the HI decomposition section of the S-I cycle as a priority for experimental measurement and process modeling. They also chose to use the continuous-flow apparatus (CFA) technique to measure the complex phase behavior of mixtures of iodine (I_2), water, and HI at elevated temperatures and pressures. The I_2–water binary was selected for the first experimental measurements. Initially, they fabricated the tantalum (Ta) components and fittings required for the CFA. On the modeling side, they conducted test evaluations with Aspen Plus™ simulations of various sections of the S-I process to gain experience with the simulation environment. They also conducted thermodynamic analysis of the overall water-splitting process and initiated Sections II and III in the S-I cycle.

The CFA setup is shown in Figure 1. Many of the Ta components necessary for constructing the CFA have had to be fabricated in-house, including 125 high-pressure fittings and the inner chamber for the view cell. Note that Ta tubing and parts are used for those surfaces in contact with I_2-water solutions at elevated temperatures and pressures, Hastelloy C tubing is used for pure I_2 at temperatures below 150°C, and 316 stainless steel is used for pure water. A notable exception is the micrometering valves, which are still made of 316ss because alternative materials were unavailable.

Developing the capability to pump molten iodine into the CFA was a major focus of the team's efforts this year. After failed attempts with a syringe pump and a positive-displacement pump, researchers now use an indirect pumping method. As shown in Figure 1, compressed liquid water is delivered from a syringe pump into a reservoir heated to 130–140°C, where the water indirectly pumps the denser, molten I_2 to the impingement mixer. The interior of the I_2 reservoir is Teflon-coated to prevent corrosion and is periodically hydrostatically tested to twice its operating pressure. Small amounts of water will dissolve in the I_2, which is actually beneficial as a pre-mix before the impingement mixer.

Initial attempts to measure liquid–liquid equilibrium (LLE) for the I_2–water system at 200°C and 40 bar were partially successful. Molten iodine and water were

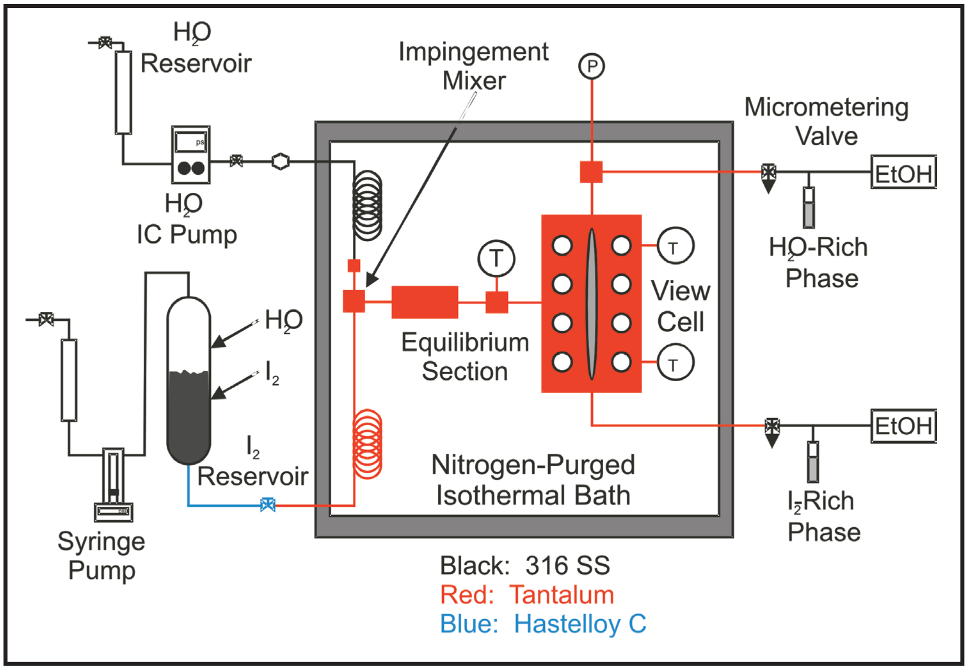


Figure 1. The continuous-flow apparatus.

delivered at constant flow rates from the I_2 reservoir and pump, respectively. An orange liquid, consisting of water saturated with iodine, was collected from the outlet of the top-phase micrometering (MM) valve. A dark purple liquid, consisting of iodine saturated with water, was collected from the bottom-phase MM valve. While the interior of the view cell was opaque under normal lighting, with an IR light detector researchers could observe the interface between the top, water-rich phase and the bottom, iodine-rich phase. After about 10 minutes of flow through the MM valves, researchers were no longer able to control the flow out the bottom MM valve. Inspection after shutdown revealed severe corrosion of the valve stem and seat. A number of alternative materials are being pursued, including wetted surfaces of Hastelloy C, Ta, and Teflon coating.

These I_2–water experiments also showed that pumping a homogenizing liquid directly into each collected phase immediately after reducing pressure is preferable to collecting a hot mixture of iodine gas and liquid water at 125–130°C. Anhydrous ethanol was selected because it is a good solvent for both iodine and water and is compatible with the team's analysis methods.

To confirm the ability of the CFA setup to generate quality phase-equilibrium data at elevated temperatures and pressures, the team is currently measuring LLE for the benzene–water binary system at temperatures of 200 to 250°C. This system has several features in common with the I_2–water system, such as LLE and an upper critical solution temperature at elevated temperatures and pressures. Data in the literature are available for comparison. Changes to the impingement mixing and equilibrium sections are in progress.

Researchers are also using the benzene-water system to evaluate the extent to which two-phase liquid flow in the lines exiting the isothermal bath can affect the measurement of phase compositions for systems exhibiting LLE. In particular, they ran a benzene-water mixture (77:23 weight-percent, respectively) through the CFA at 307°C and 2,800 psi—) conditions at which the mixture forms a single liquid phase. Samples collected from the top- and bottom-phase lines exiting the cell should have been identical. However, results indicate that a 65-90 g sample must be collected from each phase to "cancel out" the two-phase flow effects and obtain an accurate analysis of the cell contents (see Table 1). Similar "cumulative" methods will be used for I_2–water work.

Researchers continued Aspen Plus™ simulations of various sections of the S-I process to unravel the complexities of and gain experience with the simulation

Sample	Top Phase (Wt% Water)		Sample	Bottom Phase (Wt% Water)	
	Wt%	Error (±)		Wt%	Error (±)
F	23.80	0.43	A	24.17	0.44
G	25.36	0.46	B	24.24	0.44
H	23.18	0.42	C	24.24	0.44
I	25.09	0.45	D	23.25	0.42
J	18.90	0.34	E	20.92	0.38
L	24.47	0.44	K	25.94	0.47
N	22.93	0.41	M	20.49	0.37
Average	**23.39**	**1.54**	**Average**	**23.32**	**1.80**

Table 1. Consecutive 13-g samples of top and bottom phases illustrate impact of two-phase flow.

program and the thermodynamic modeling. These simulations were also useful in developing full consistency among the units and sections, as well as for exploring options for modifying the reactive distillation column in the HI decomposition section (Section III) of the S-I process.

A stand-alone, updated version of the software has been installed on a laptop, making flowsheet communication between SRNL and UVa compatible. The team worked to establish full consistency among the streams of the separate sections of the most recent General Atomics (GA) results and to develop a convergent Aspen Plus™ flowsheet for the Bunsen Section (Section I). Discussions are ongoing to resolve a consistency issue, as well as the uncertainties over the absorber unit's ability to remove unreacted SO_2 in Section I.

Examination of the operating conditions for the reactive distillation column has shown that increased operating pressure along with feed-stage relocation can yield better separation and significant reductions in the reboiler and condenser energy requirements. These results suggest that an equilibrium column could be significantly smaller than in current designs, which should enhance the attractiveness of the S-I process. This analysis also revealed the presence of multiple liquid phases in the reboiler simulations, and that efficiency is significantly improved over the single-liquid case. The results are more sensitive to the modeling than was previously thought. Based on these results, the modeling group has made specific recommendations to the experimental group regarding which ternary measurements for mixtures of I_2, water, and HI should be given the highest priority.

Researchers completed a tentative model-free analysis of the thermodynamics of water-splitting for the overall process and for the individual S-I sections, which included comparisons between fully reversible/no recycle, fully reversible/typical recycle, and real conditions. This analysis revealed that much of the inefficiency of the process is associated with recycling materials between sections rather than from inherent irreversibilities, with most of the effects appearing in Section III. However, some of the results were inconsistent, suggesting that some property values may be incorrect. Obtaining full consistency among all the cases has been inhibited by property mismatches at the intersections of flowsheet sections from different partners (involving temperature, pressure, composition, and rates). These discrepancies are being explored to determine whether current simulations have conditions that can be used for this analysis, or if standardized model conditions must be adopted until final reconciliation of the various sections is completed. Researchers have begun analyzing the overall process using the JAERI process described by Kasahara et al. and the results from the flowsheet.

Planned Activities

Researchers will use their CFA to measure LLE for the benzene–water binary system at temperatures of 200–250°C. They will test different impingement mixing and equilibrium section arrangements to confirm that the CFA design is ready for measuring quality data. Different delivery flow rates of water and benzene will be used to confirm that the system is not mass-transfer-limited. The volume of sample collected for each phase will also be varied to determine the optimal sample size for eliminating the effects of two-phase flow in the lines and for checking data reproducibility.

LLE experiments with the I_2–water system are expected to begin early in the year, as corrosion-resistant Hastelloy C and Teflon-coated micrometering valve parts are both now in-house. This will be followed by work on the ternary I_2-water-HI system. Researchers also plan to develop spectroscopic methods for determining the *in-situ* chemical species (e.g., iodine complex concentrations) present at elevated operating temperatures and pressures.

Researchers will complete all work on the current S-I thermodynamic model-free analysis, potentially extending this work to other identified S-I concepts. This analysis will also be accompanied by tests for property sensitivity within the various sections of the S-I process. They expect to reach complete consistency among the multiple S-I process sections, yielding a full, reliable process flowsheet that can significantly explore conditions that are sensitive to the property models. The team will improve the initially proposed properties and process models for the S-I cycle and use the updated models to 1) select experimental conditions for the ternary I_2-water-HI system and 2) identify additional experiments that are most critical for minimizing remaining process uncertainties.

Finally, researchers have been in contact with the Process Fluidics Group at the University of Sheffield to develop a follow-on proposal for international collaboration on a series of workshops designed to establish global standards, property models, and process simulations that will facilitate informed decision-making about energy efficiency, process reliability, equipment, and economics. Initial attempts for joint funding under I-NERI could not be completed because the UK partner does not have the necessary affiliation. Other sources are being pursued.

NUCLEAR ENERGY RESEARCH INITIATIVE

Silicon Carbide Ceramics for Compact Heat Exchangers

PIs: Dennis C. Nagle and Dajie Zhang, Johns Hopkins University

Collaborators: None

Project Number: 05-032

Project Start Date: April 2005

Project End Date: April 2008

Research Objectives

The objective of this project is to develop impervious, net-shaped, silicon carbide materials for the next generation of nuclear power plants, which will require high-temperature hydrogen-to-helium heat exchangers capable of prolonged operation at temperatures over 900°C. Current graphite block heat exchanger materials cannot operate unprotected in this environment because of hydrogen gasification reactions that consume the graphite. Silicon carbide (SiC) and other refractory carbides have very high thermal conductivities and are thermo-chemically stable at elevated temperatures; therefore, they are excellent candidate materials for use in high-temperature gas heat exchangers.

Traditional carbide processing techniques cannot produce silicon carbide with the complex geometries needed for nuclear energy heat exchanger designs. Researchers will establish an innovative way to fabricate fully dense and configurable silicon carbide monoliths from carbon substrates that can be easily machined into desired shapes. Technologies developed in this project will have a direct impact on new heat exchanger design and novel fabrication techniques for interconnections between metal and ceramic components in future nuclear reactors. The project consists of the following major tasks:

- Establish a liquid silicon infiltration method for fabricating configurable SiC monoliths from carbon substrates
- Eliminate residual porosity to achieve hermetic sealing in high-temperature atmospheres
- Characterize SiC microstructure, thermal/mechanical properties, and gas permeability
- Develop models to optimize channel configuration and geometry
- Manufacture a prototype heat exchanger, test, and compare experimental data to model predictions.

Research Progress

During the second year, researchers mapped the carbonization process of microcrystalline cellulose by studying the electrical and thermal properties of cellulose carbons. They further refined silicon carbide synthesis parameters and investigated operating conditions and performance requirements of high-temperature heat exchangers to provide a basis for their design.

Characteristics of carbon substrates, such as apparent density and micro-porosity, are important parameters that control the liquid silicon infiltration process for fabricating SiC monoliths. Understanding the compositional and structural evolution during carbonization is crucial for establishing optimum processing conditions to produce carbons that have the desired properties. By analyzing conductivity changes of microcrystalline cellulose carbons prepared at carbonization temperatures ranging from 250 to 1,000°C, researchers have discovered that microcrystalline cellulose carbons show four distinct AC electrical conductivity regimes.

As shown in Figure 1, each region reflects changes in the molecular structure of the microcrystalline cellulose and the carbon during the carbonization process.

- **Region I**. Dipole polarization is observed for the pure cellulose at 250°C, which slowly decreases as these polar groups are driven off up to 350°C.
- **Region II.** Upon reaching 400°C, AC conductivity exhibits a linear frequency dependence, dominated by the nucleation of carbon cluster-containing free electrons. AC conductivity continues to increase as heat treatment temperature rises to 500°C, due to

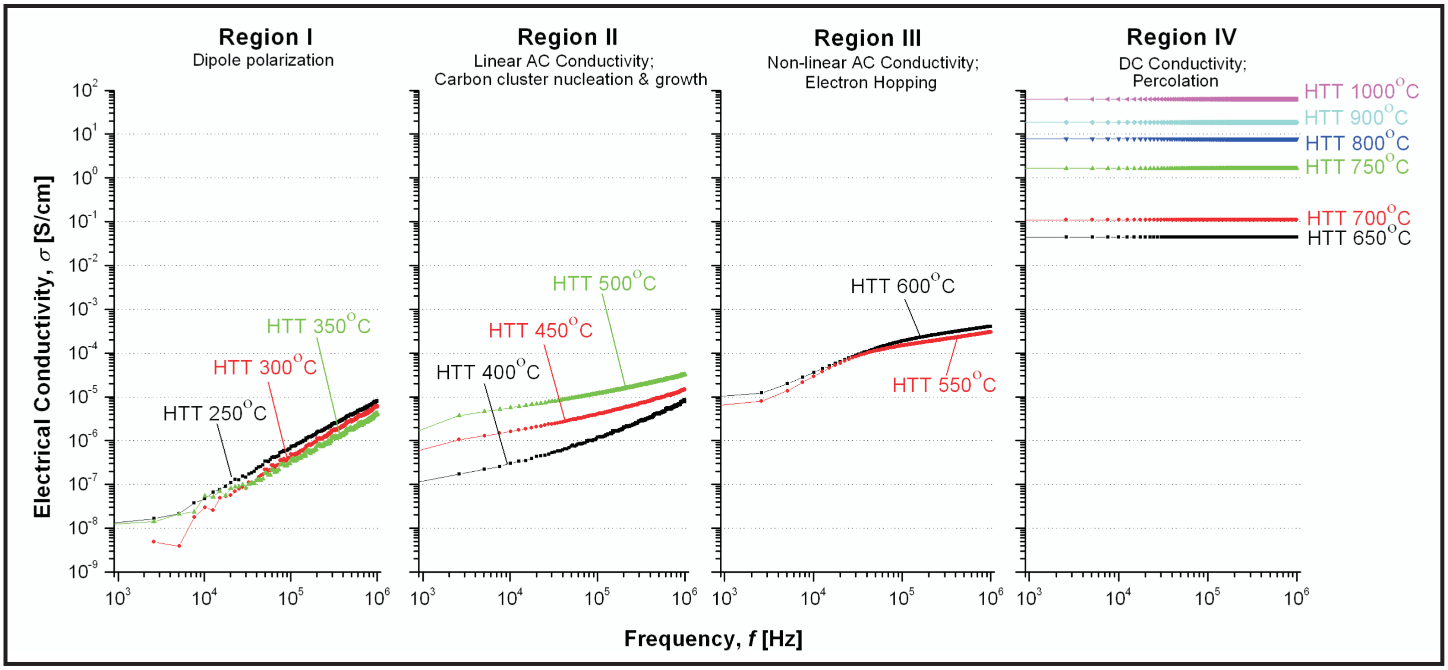


Figure 1. Electrical conductivity of microcrystalline carbons as a function of heat treatment temperature and frequency.

the carbon clusters growing in size and moving closer together while the structure shrinks.

- **Region III.** From 550 to 600°C, the carbon clusters become sufficiently close that AC conductivity exhibits a non-linear frequency dependence, indicating electron hopping between conducting carbon clusters.
- **Region IV.** Upon exceeding 600°C, conductivity transitions from AC to DC as the carbon clusters become percolated.

Researchers also measured thermal diffusivity, specific heat, and thermal conductivity for cellulose-derived carbons prepared at carbonization temperatures ranging from 250 to 1,000°C. Results show that thermal diffusivity increases as a function of increasing heat treatment temperature, suggesting that it is controlled by both carbon porosity and density.

Specific heat values indicated the coexistence of polar and non-polar phases in both partially carbonized materials obtained at lower heat treatment temperatures and fully carbonized materials formed at higher heat treatment temperatures. For partially carbonized materials, the polar phase consists of residual hydroxyl and carboxyl groups, whereas for fully carbonized materials the polar phase is believed to be composed of carbon clusters with delocalized sp^2 electrons. Such structural characteristics are supported by Fourier-transform infrared spectroscopy (FT-IR) characterizations. Finally, a linear relationship between testing temperature and thermal conductivity suggests phonon transport as the main mechanism for heat conduction. This is likely due to the absence or very low concentration of percolating electrons in these materials.

Many polycrystalline semiconductors, such as silicon (Si), germanium (Ge), strontium titanate ($SrTiO_3$), and zinc oxide (ZnO), exhibit highly nonlinear current-voltage (I-V) relations that are often referred to as the "varistor effect." This effect entails high resistivity at lower applied bias and lower resistivity at higher applied field, due to semiconductor grain boundary barrier breakdown arising from the electrical transport process. Electrical characteristics of grain boundaries (e.g., barrier potential and breakdown) often play an important role in determining the overall electrical behavior of the material.

Researchers successfully pinpointed the actual carbonization temperature at 605°C, where the electrical conductivity of cellulose carbons undergoes a transformation from semiconductor to conductor behavior. They have fabricated carbons with silicon-like, varistor-type nonlinear electrical conductivity, as shown in Figure 2. Researchers believe that the mechanism of such carbon electrical behavior is analogous to that of other varistor semiconductors which conduct carbon clusters at a "quasi-percolation" state and that percolation and electron transport are enhanced by higher applied bias. They are also preparing phenolic resin carbons for comparison to cellulose carbons.

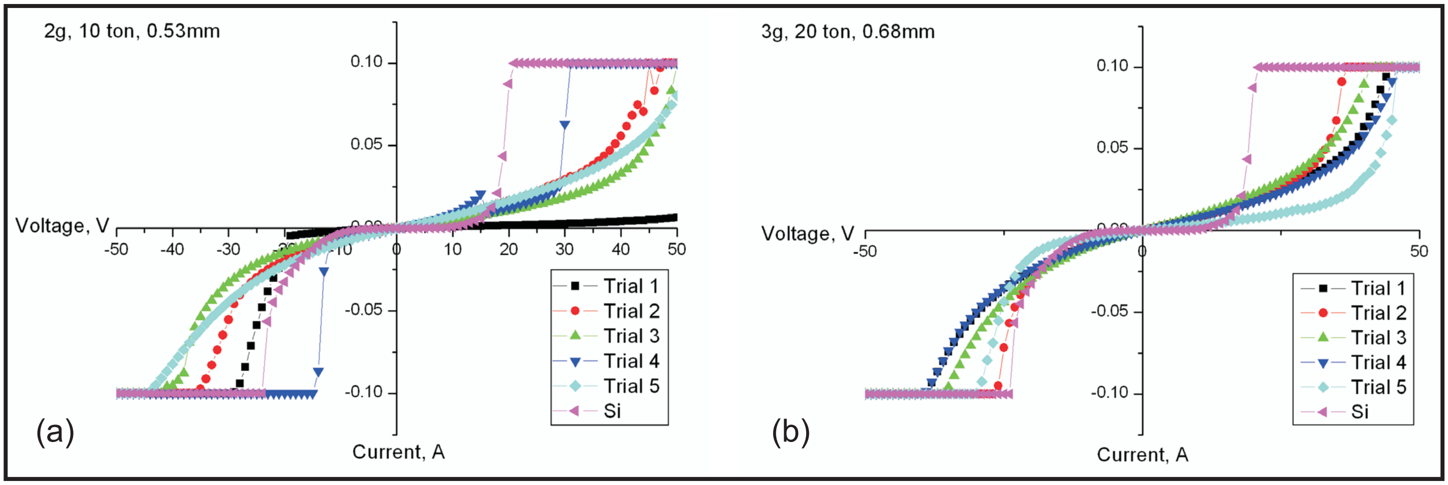


Figure 2. Varistor-type electrical conductivity of cellulose carbons prepared at 605°C with silicon reference: (a) 2 g cellulose precursor pressed at 10 tons (b) 3 g cellulose precursor pressed at 20 tons.

The previous annual report illustrated the process of forming SiC monoliths with liquid phase silicon (Si) infiltration of carbon pre-forms with engineered micro-porosities, using carbon substrates derived from a 6:4 mixture of cellulose and phenolic resin at 1,700°C. Researchers have made SiC disks with apparent density of up to 95 percent under such conditions. By examining differential thermal analysis data of the carbonization process and liquid silicon–solid carbon reactions, researchers can now precisely design parameters for carbonization and silicon infiltration. In order to improve temperature control, they have integrated the high-temperature reactor furnace with a temperature controller unit that allows accurate "hot zone" temperature readings and precise thermal programming.

Researchers have proposed three possible reaction mechanisms for the Si infiltration formation of SiC: 1) carbon dissolution and SiC nucleation and growth in molten Si, 2) absorption of molten silicon into solid carbon followed by carbide crystallization, and 3) carbon dissolution by molten Si and SiC nucleation and growth at the surface. Through literature review and studying reactions and their products under various conditions, researchers believe that the first mechanism, i.e., SiC formation from liquid silicon infiltration of carbon is most likely. This is illustrated in Figure 3.

Based on the operating conditions and performance requirements of high-temperature heat exchangers, researchers have defined a base model consisting of an amorphous carbon block with parallel, circular cross section flow channels to describe a simple heat exchanger design with helium as the working liquid (Figure 4a). The open circles represent the hot working fluid while the shaded circles represent cold fluid. The symmetric unit cell used for modeling is shown by the outlined triangle, represented as a three-dimensional segment in Figure 4b.

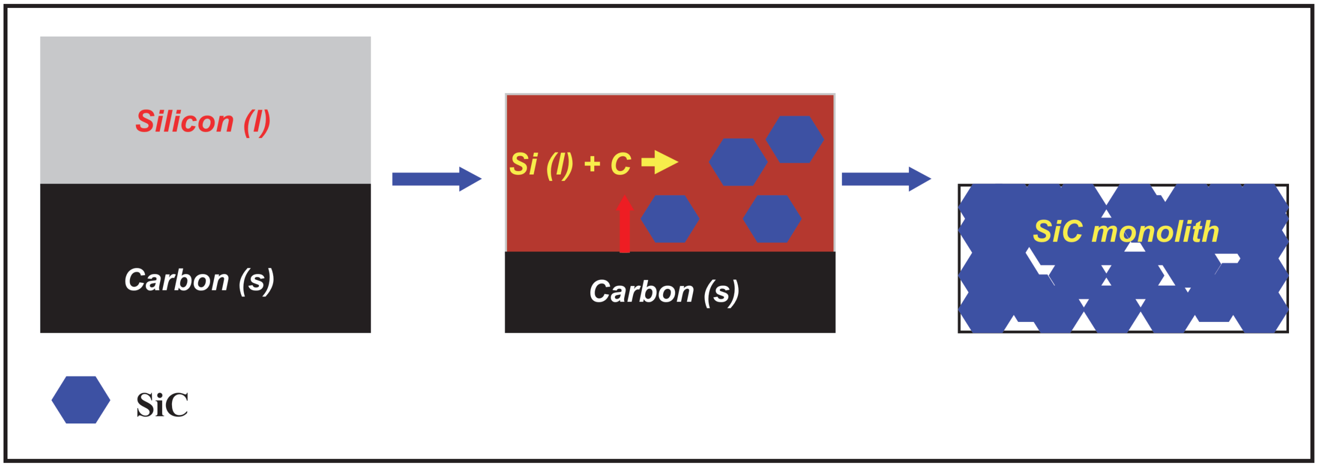


Figure 3. Reaction mechanism of SiC formation from liquid silicon infiltration of carbon.

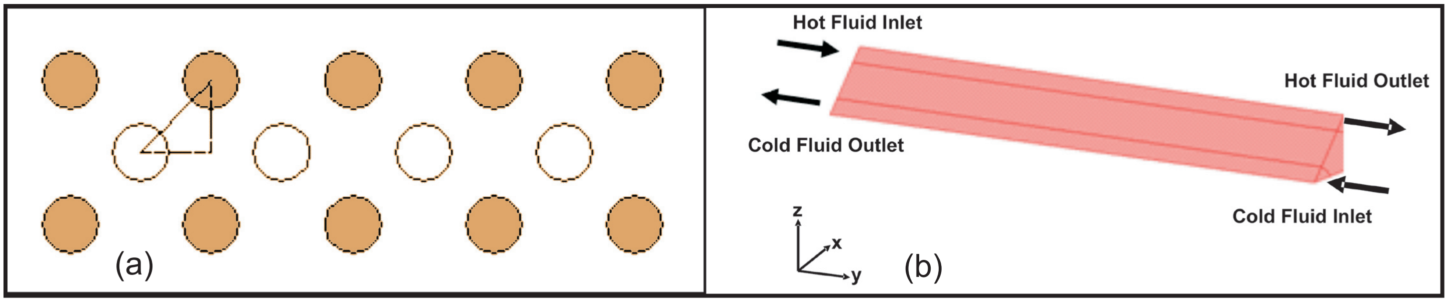


Figure 4. (a) Cross section of the heat exchanger matrix with circular flow channels; (b) representative model geometry based on symmetry (arrows indicating flow direction).

Planned Activities

Based on progress achieved during FY 2006, researchers are planning the following activities for further study:

- Further improve and refine liquid silicon infiltration techniques for SiC fabrication. A crystal growth furnace will be used to develop a dip-conversion process for Si infiltration, and the composition and microstructures of SiC will be studied in detail. Model experiments will be designed to reveal reaction mechanisms.
- Evaluate porosity reduction techniques including gas-solid phase carbon formation and glass sealing to achieve hermetic SiC monoliths.
- Examine mechanical properties and thermal conductivity of prepared silicon carbide at the operating temperatures of nuclear energy heat exchangers (900 to 1,000°C).
- Fabricate silicon carbide with larger dimensions and complex shapes/configurations (e.g., curves, micro-channels).
- Analyze the high-temperature heat exchange process and study silicon carbide heat exchanger design.

Molten Salt Heat Transport Loop: Materials Corrosion and Heat Transfer Phenomena

PI: Kumar Sridharan, University of Wisconsin

Collaborators: None

Project Number: 05-154

Project Start Date: April 2005

Projected End Date: April 2008

Research Objectives

The next generation nuclear power plant (NGNP) is likely to be a high-temperature reactor utilizing graphite moderation with TRISO (tri-isotropic coated) fuel particles in either a matrix or pebble bed configuration. The NGNP will be designed to produce electricity and process heat for hydrogen production.

Because the interface between the reactor and the hydrogen production system will involve long heat transfer paths at elevated temperatures, it will require a working fluid with superior heat transfer characteristics. The heat transport fluid should 1) be chemically compatible with the surrounding structural materials, 2) have superior fluid-mechanical and heat transfer properties, and 3) have acceptable safety characteristics under normal and abnormal conditions. Heat transport fluids such as high-pressure inert gas (helium or carbon dioxide) or molten fluoride salt are expected to satisfy these requirements. This project investigates the potential of molten salt as a possible transport fluid and also investigates the corrosion resistance of structural materials that would come into contact with the molten salt.

The objective of this project is to demonstrate that molten fluoride salt can be successfully implemented in a low-pressure intermediate heat exchange loop. The project focuses on utilizing molten salt as a process-heat transport fluid and on the corrosion compatibility of this medium with surrounding materials. The research objectives are to: 1) design, fabricate, and operate molten fluoride salt capsules in a flow loop under prototypic NGNP conditions using appropriate geometric scaling; 2) plan, design, and execute a series of corrosion compatibility experiments in the heat exchange loop in order to develop a database on the structural materials' behavior for a range of candidate materials that are being considered for the NGNP design; and 3) document the observed corrosion effects and heat transport performance as integral and separate-effects databases.

Research Progress

Researchers have developed an in-depth understanding of various issues pertaining to corrosion testing in a molten-salt environment, focusing particularly on safety and salt purity issues. They also developed a thermodynamic database of all relevant fluorides of cations in both the materials and the salts for predicting the corrosion of alloying constituents in molten fluoride salt environments.

The researchers procured 1) 18 kg of high-purity LiF-NaF-KF (FLiNaK) eutectic salt from Electrochemical Systems, Inc. (ECS), 2) 1 kg of non-hydrofluorinated FLiNaK from Idaho National Laboratory (INL), and 3) an atmosphere-controlled high-temperature furnace for conducting high-temperature corrosion tests up to 1,200°C. Corrosion tests were successfully initiated on a number of code-certified alloys and on nickel-electroplated Inconel 800H alloy at 850°C for 500 hours in both FLiNaK salts. The tests used a specialized containment design consisting of a graphite crucible encapsulated in 0.25 inch thick stainless steel shell and argon cover gas. Researchers performed post-corrosion testing weight loss and scanning electron microscopy (SEM) and SEM-Energy Dispersive Spectroscopy (EDS) analyses of the alloys. Additionally, they performed chemical analysis of the salts before and after corrosion tests using ICP-Mass Spectroscopy.

This project initiated studies to examine the strength of a high-temperature epoxy for joining graphite components because graphite, with its chemical inertness to molten salts, is likely to be a candidate structural material in molten salt systems (e.g., AHTR, intermediate heat exchangers). Studies were also initiated on heat transfer modeling in molten salts that will aid in the construction of the molten salt corrosion loop for heat and mass transfer experiments.

Corrosion Testing. Corrosion testing of candidate alloys is being performed in FLiNaK salt at 850°C for exposure durations of 500 hours. Crucibles made of POCO graphite (Grade AXZ-5Q1) purified to a total ash range of 5 ppm or less, particle size of .5 μm, and a pore size of .7 μm are being used as the primary containment for the molten salt and the alloy test samples. Three pre-weighed samples of a given alloy are being tested per crucible, with the samples fixtured to a vertical central graphite rod, as shown in Figure 1a. The graphite crucibles with the samples were then welded in stainless steel corrosion capsules, with small aligned holes in the graphite and stainless steel lids to introduce the molten FLiNaK salt, using the system shown in Figure 1b. The amount of salt introduced was monitored using a sensitive balance. The corrosion cell was then placed in the high-temperature furnace and samples tested at 850°C for 500 hours. After this exposure, the crucibles were inverted to drain molten salt away completely from the samples. The stainless steel and the graphite crucibles were then slowly cut open and the samples were detached from the vertical rod and cleaned to remove any residual salt prior to further analysis. Results of weight loss measurements due to corrosion-induced dissolution. (weight loss per unit area) are shown in Figure 2.

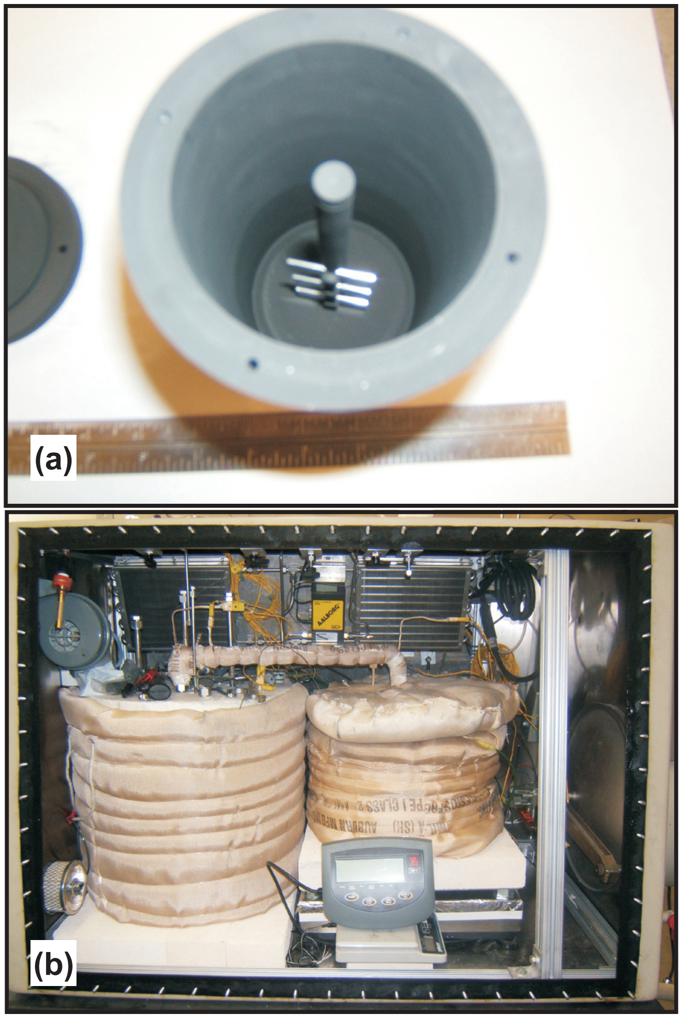


Figure 1. a) Graphite crucible with central graphite rod for fixturing the samples of a given alloy in triplicate and b) System for transferring molten salt into the graphite crucible.

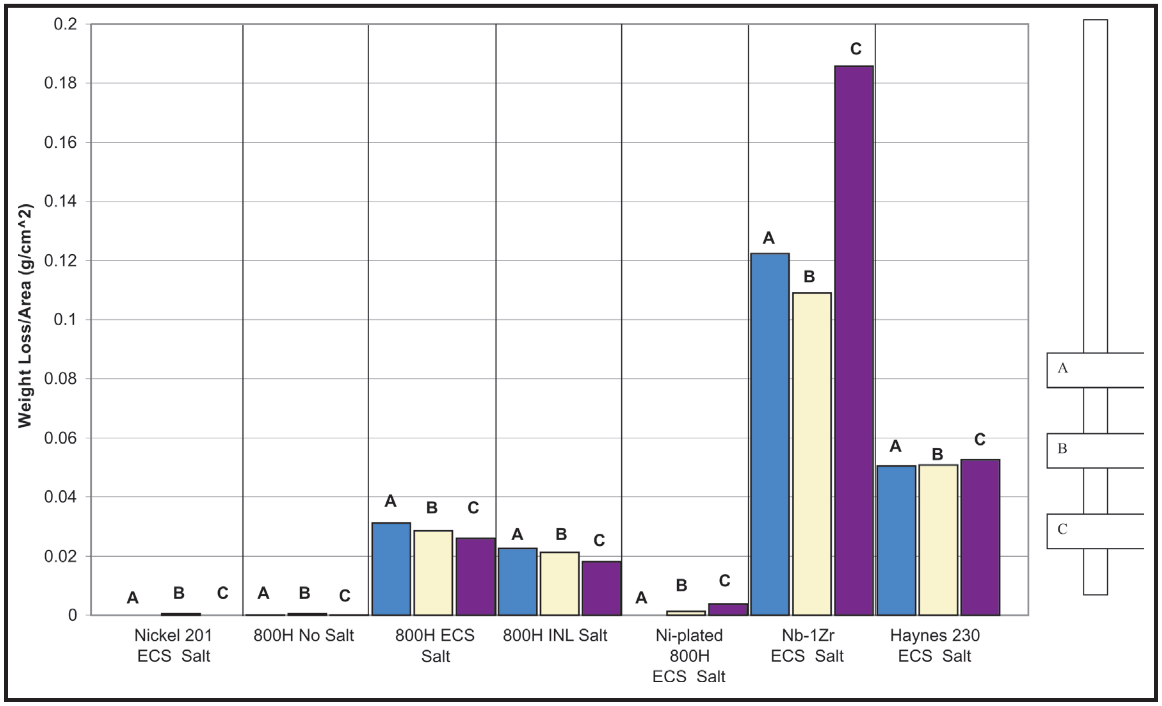


Figure 2. Weight loss due to corrosion for various alloys in molten FLiNaK at 850°C after 500 hours exposure, as a function of their position in the graphite crucible.

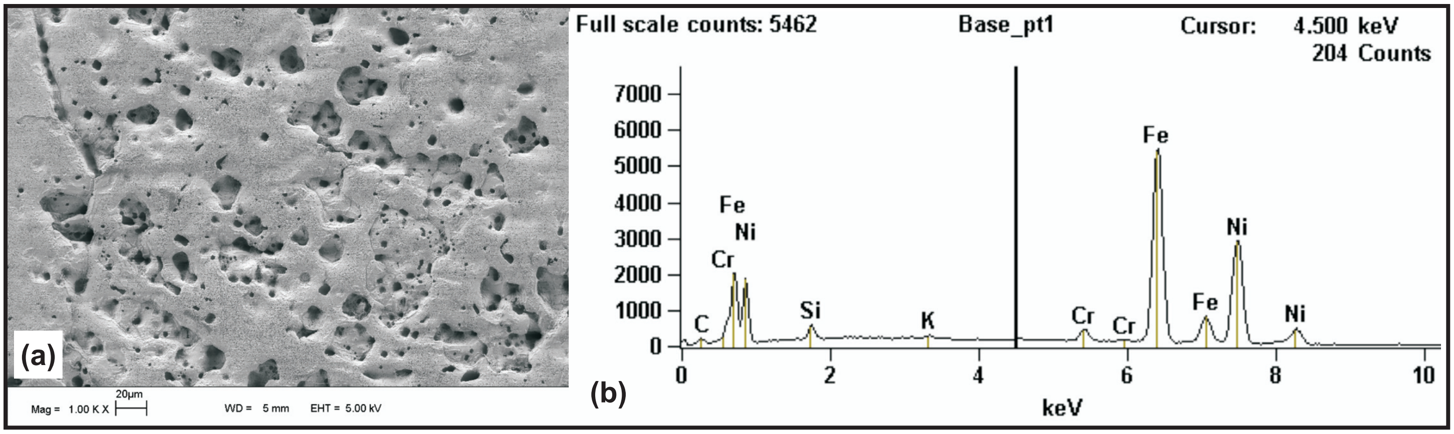


Figure 3. SEM-EDS analysis of alloy 800H after exposure to molten FLiNaK at 850°C, (a) pitting on the surface and (b) EDS analysis showing substantial depletion of Cr at the surface.

The Nb-1Zr alloy exhibited severe corrosion, particularly the sample closest to the base of the crucible, indicating that carbide formation may have played a role in the corrosion of this alloy. Although alloy Ni-201 exhibited the least weight loss, this alloy may be unsuitable as a structural material due to inadequate mechanical strength. Nickel electroplated 800H alloy exhibited outstanding corrosion resistance. Because electroplating is a relatively inexpensive commercial process, this approach may hold considerable promise for fabricating structural materials for molten salt systems. There was very little difference in the corrosion performance of alloy 800H in FLiNaK salts obtained from ECS and INL.

SEM-EDS analysis of the corrosion-tested samples is presently underway. Examination of alloy 800H after corrosion tests showed large pits at the grain boundaries and relatively smaller pits within the grains. A substantial depletion of chromium (Cr) was observed at the surface of this alloy indicating that Cr was preferentially leached into the molten salt during the corrosion tests. The results are shown in Figure 3.

Testing of High-Temperature Adhesive Strength of Epoxy. Graphite will be an important structural material in molten salt systems because of its relatively high chemical stability in molten fluoride salts and its outstanding high-temperature strength. An engineering issue in the use of graphite will be joining the graphite components by a technique that can provide adequate high-temperature adhesion strength and withstand chemical attack from molten salts. To address this issue, research is underway to evaluate the strength of a graphite epoxy, Resbond 931-1, in a high-temperature molten fluoride salt environment. This epoxy forms a 99.9 percent pure graphite bond. Small capsule tests are being conducted to evaluate its shear strength and chemical compatibility in FLiNaK environments up to 1,000°C. Figure 4 shows the graphite capsules used for testing the high-temperature shear strength of the epoxy; Table 1 lists test results. The quoted tensile strength of the epoxy is 2,500 psi and the tests showed that environment and temperature did not significantly effect the strength.

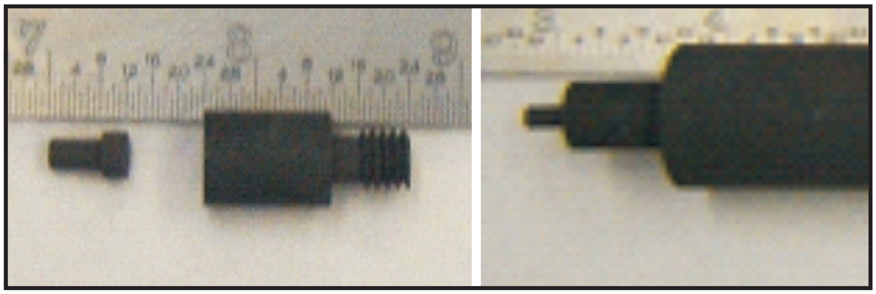


Figure 4. Photographs of the small graphite capsules used to measure the shear strength of epoxy in FLiNaK environments up to 1,000°C.

Capsule Environment	σ_{max} < 2,500 psi	σ_{max} > 2,500 psi
25°C Argon	1	3
1,000°C Argon	2	4
1,000°C FLiNaK	1	2

Table 1. Summary of the results of shear strength showing the number of ResBond epoxy samples that failed in the three environments tested.

Planned Activities

During the next year, researchers plan to:

- Test Hastelloy-X and Hastelloy-N alloys in molten FLiNaK at 850°C for 500 hours
- Perform detailed SEM-EDS analysis (both plan view and cross-sectional views) of all the samples in order the to gain a fundamental understanding of the corrosion processes in various alloys
- Perform X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis as needed to gain more fundamental insights into the corrosion performance of these alloys
- Control the redox potential of the molten FLiNaK salt by adding elements such as Zr
- Test selected alloys at 850°C after 500 hours in FLiNaK with a reducing environment

Ni-Si Alloys for the S-I Reactor-Hydrogen Production Process Interface

PI: Joseph W. Newkirk, University of Missouri-Rolla

Collaborators: Idaho National Laboratory (INL)

Project Number: 06-024

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

The goal of this project is to develop materials suitable for use in the sulfuric acid decomposition loop of the sulfur-iodine thermochemical cycle for nuclear hydrogen production. Materials must have both acceptable corrosion resistance and sufficient ductility for component fabrication and avoidance of catastrophic failure. Nickel-silicon (Ni-Si) intermetallics show promise for such critical applications as the sulfuric acid vaporizer, vapor superheater, and the decomposer. Past work indicates that adding minor alloying elements to Ni_3Si provides significant ductility at room temperature (7-10 percent elongation at failure), a unique property for normally brittle high-silicon materials. Ni_3Si can also be easily joined by traditional methods such as welding, and preliminary studies show that it has excellent corrosion resistance.

In this work, the team will further develop Ni_3Si to maximize its ductility and corrosion resistance, while reducing cost. Researchers will analyze the effects of adding elements such as niobium, boron, and iron. Microalloying may be used to improve resistance to corrosive impurities in the sulfuric acid processing stream, such as iodine. Finally, the team will study the extent to which iron can be substituted for nickel in Ni_3Si without adversely affecting ductility or corrosion resistance.

Researchers will document the mechanical properties of these new materials over a range of temperatures and strain rates. The results will improve material properties and microstructure. As a final test, corrosion-resistant materials will be subjected to flowing sulfuric acid (H_2SO_4) at temperatures and pressures comparable to the actual sulfuric acid processing loop (120-400°C at <10,000 psi) in order to measure corrosion rates. Various fabrication techniques will also be exercised by forming prototype plates, pipes, and forgings.

Research Progress

Researchers have begun characterizing the corrosion behavior of some baseline materials. Figure 1 shows a typical as-cast microstructure. A high-temperature peritectic reaction leads to the formation of three phases:

- ***Alpha phase*** is primarily nickel and has poor resistance to sulfuric acid.
- ***Beta phase*** is Ni_3Si and represents the desired structure.
- ***Gamma phase*** is another intermetallic compound (Ni_5Si_3) which is higher in silicon and has poor mechanical properties.

Niobium (Nb) or titanium (Ti) additions improve the mechanical performance of the material; one or the other is always present for that purpose. Earlier research has shown that titanium promotes corrosion of the alloy in sulfuric acid, while niobium has no deleterious effects.

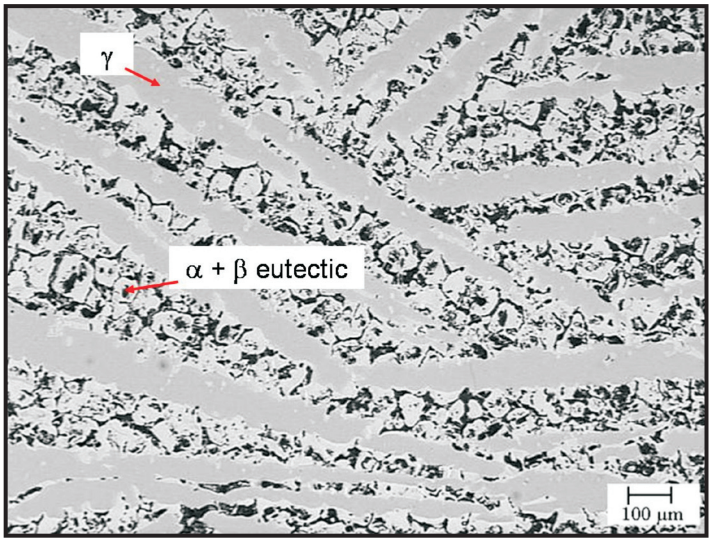


Figure 1. Typical as-cast microstructure.

As an initial part of this effort, the team has characterized the three alloys, given in Table 1. They have analyzed the surface chemistry of each alloy with auger electron spectroscopy (AES). In order to promote the formation of a passive film, which researchers believe is the mechanism for corrosion resistance, they exposed surfaces to nitric acid, a strong oxidizer. This created a relatively thick oxide film; however, identifying its structure is difficult because of the coarseness, as shown in Figure 1. To reduce this factor, the team will focus on thermally homogenized samples.

Alloy	Composition
A	$NiSi_{20}Nb_3B_{0.5}$
Mm#1	$NiSi_{20}Nb_3B_{0.5}$ + Mischmetal
J	$NiSi_{19}Nb_3Ti_1B_{0.5}$

Table 1. Composition of three alloys being characterized.

In order to fabricate this material into pipe and other shapes, researchers are studying its thermomechanical processing properties. Initial work centers on hot rolling to produce flat plates. They are sectioning samples of the material from the casting risers into different thicknesses for analysis. Repeated hot rolling and soaking are necessary to break up the cast structure and gain the expected increase in ductility. A rolling schedule has been established based on review of the available literature.

Researchers are investigating new alloy compositions to refine the corrosion behavior and to examine ways to reduce the nickel content. This work will be carried out in a vacuum induction furnace rebuilt with a new solid-state power supply.

Planned Activities

Efforts will continue to characterize the passivation reaction by exposing samples with homogenized microstructures to hot sulfuric acid. The early rolled material will be characterized as soon as it becomes available. Researchers will use scanning auger microscopy (SAM) to obtain information about the coverage of the various phases. They will also identify the effect of titanium on the corrosion behavior.

The team will carry out rolling experiments and measure mechanical properties. They will study new compositions cast with the induction furnace with respect to the formation of the beta phase and property optimization. New alloy composition will center on areas that have shown promise, such as molybdenum additions for improved corrosion resistance and iron for lower cost.

INL is building a hot corrosion test rig which the team will use to measure corrosion rates under conditions similar to those expected in the process.

NUCLEAR ENERGY RESEARCH INITIATIVE

Microstructure Sensitive Design and Processing in Solid Oxide Electrolyzer Cells

PI: Hamid Garmestani, Georgia Institute of Technology

Collaborators: Pacific Northwest National Laboratory

Project Number: 06-027

Project Start Date: March 2006

Project End Date: March 2009

Research Objectives

Solid oxide electrolyzer cells (SOEC), using heat and electricity from a high-temperature nuclear reactor, may be an efficient and cost-competitive means of splitting water to produce hydrogen. The objective of this project is to optimize the microstructure of solid oxide electrolyzer fuel cell materials. This will be accomplished by developing: 1) a multi-scale model for the treatment of transport properties of electrolyzer materials, and 2) methodologies based on spray pyrolysis techniques to construct large surface area porous-gradient fuel cell materials.

Researchers are developing processing techniques for synthesis of lanthanum-strontium-manganite (LSM) based cathode materials using spray pyrolysis. After optimizing the process parameters and precursor materials for the newly developed spray pyrolysis technique, they will examine its microstructure and transport properties. The team has developed a statistical mechanics-based model for transport properties of fuel cell materials. This model incorporates conductivity and elastic properties of porous microstructures. During the next two years, they will incorporate flow through porous media and other transport properties into the model and apply the resulting multi-scale model to optimize the SOEC microstructure.

Research Progress

During this fiscal year, the team concentrated on conducting a theoretical prediction of electrolyzer cell electrode properties and fabricating the electrodes using spray pyrolysis. As part of this task, they examined two different processing conditions and characterized the samples. The process parameters are currently being optimized.

Researchers have shown the potential of spray pyrolysis techniques to deposit large surface area porous LSMO ($La_{1-x}Sr_xMnO_3$) thin films over an yttria-stabilized zirconia (YSZ) electrolyte. They proposed a multi-scale model based on statistical continuum mechanics to predict the mechanical and electrical properties of heterogeneous porous media. This model is applied within the framework of microstructure sensitive design (MSD) to guide the design of the microstructure in porous LSM electrolyzer cell electrodes.

Synthesis of Large Surface Cathode Material Using Spray Pyrolysis. Researchers investigated spray pyrolysis as a method for depositing a porous LSM layer on pressed YSZ electrolyte substrate. The ideal goal is to manufacture a large surface area (>1 in^2) porous LSM cathode layer which has a gradient structure—fine near the electrolyte surface and a coarse outer layer forming massive columnar pores (Figure 1).

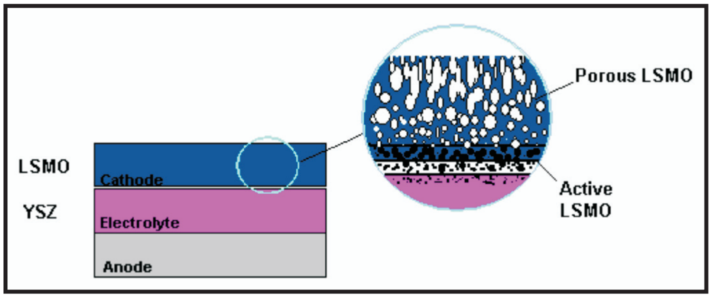


Figure 1. Schematic of ideal LSM cathode on YSZ substrate with columnar pores in outer layer.

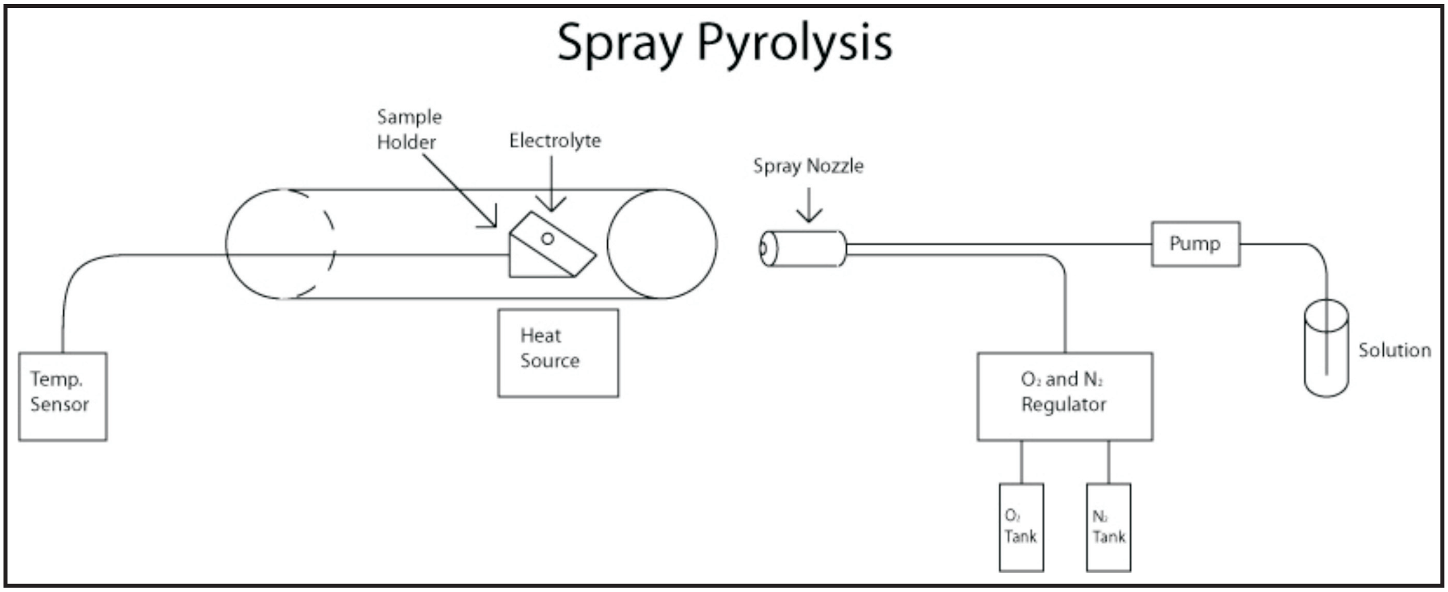


Figure 2. The fabrication of electrodes using spray pyrolysis.

For the synthesis procedure, researchers investigated the parameters to control pore size as a function of distance from the substrate. Figure 2 illustrates the fabrication of electrodes using spray pyrolysis. Researchers have prepared 17 samples from two different solutions: 1) water and 2) ethylene glycol dimethyl ether. The temperature was maintained in a specific interval that was changed for each sample.

To improve the microstructure, the team produced a series of samples and conducted scanning electron microscopy (SEM) and X-ray diffraction (XRD) examinations before and after the heat treatment followed by post annealing. The layer closer to the electrolyte surface is expected to be fine and the outer layer is expected to be course, as shown in Figure 3.

The main results are summarized below:

- When the nozzle speed and temperature are in the optimal range with respect to each other, an almost perfect chemical vapor deposition (CVD)–like layer can be obtained.
- Deposition temperature must be at least 520°C to obtain a suitable layer.
- Temperatures over 680°C produce no reasonable deposition due to gas-phase nucleation, which usually results in nano-powders; higher temperatures help decompose the precursors.
- Increasing speed leads to much thinner layers at lower temperatures, since there is insufficient activation energy and time to decompose the precursors. Therefore, the spray and vapors are transported by the carrier gases away from the YSZ.

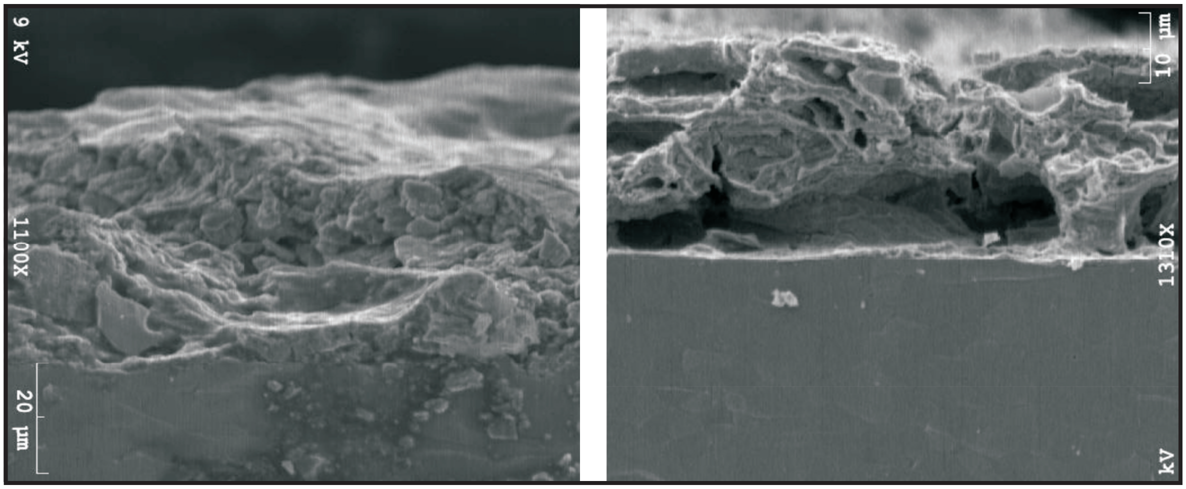


Figure 3. SEM micrograph and cross section of sample of porous LSM layer on YSZ electrolyte substrate produced from aqueous solution: (a) before heat treatment, (b) after heat treatment.

- Increasing the nozzle speed at high temperatures leads to a further decrease in the layer thickness since gas phase nucleation occurs. At the low end of the high-temperature range, the team found smaller particle formations that were embedded in the layer produced by the spray process, leading to a more porous structure.
- At the very high-temperature range, nano-particles are produced that will not deposit on the YSZ and may be carried away by the carrier gas.

Theoretical Modeling and Microstructure Design. A statistical mechanics model using probability density functions forms the framework to connect microstructure to transport properties. Using a Taylor series expansion taking into account only the first-order correction gives:

$$E(x) = E_0 + \int dx' G(x-x') * \tilde{\sigma}(E_0, h(x'))E_0 \qquad (1)$$

where E is electrical field, σ is conductivity, and G is the Green's function. The average field for state h can be determined from the above equation, and the correlation function $\langle \tilde{\sigma}(E_0, h(x')) \rangle_h$ described in terms of the conditional two-point probability density function:

$$\langle \tilde{\sigma}(E_0, h(x')) \rangle_h = \int f(r' \in h(r') | r \in h) \tilde{\sigma}(E_0, h(x')) dh(r') \qquad (2)$$

Figure 4 illustrates the cross-view microstructure of gradient LSM cathode deposited on YSZ electrolyte, showing the three sections: 1) electrolyte, 2) fine layer of LSM cathode, and 3) coarse layer of LSM. Predicted physical properties of these layers are shown in Figure 5.

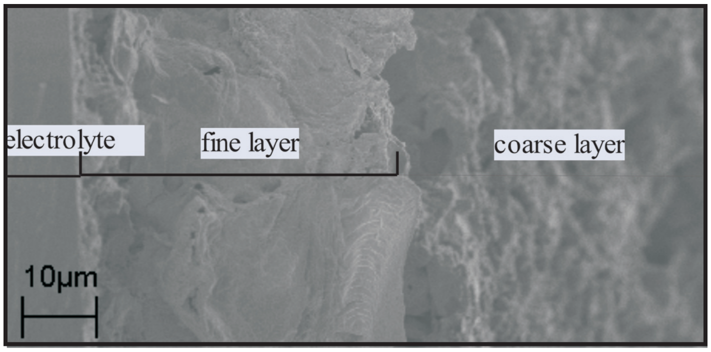


Figure 4. Cross section view micrograph of double-layered LSM deposited on YSZ electrolyte, showing the fine and coarse LSM layers.

Planned Activities

Researchers have proven that spray pyrolysis is a suitable route to make large surface area cathode material for SOEC. They have found that organic solvents need to be used for this process to prevent cracking of the YSZ and determined that both deposition temperature and spraying speed affect the porosity of the LSMO.

The next goal of this work is to determine the correct parameters and correct sequence to control a gradient layer formation with the current precursors. As the current metal-organic precursor and organic solvent systems are quite expensive, researchers are also interested in finding cheaper materials. Based on the previous results, they must optimize the conditions and sequence to obtain the best coatings.

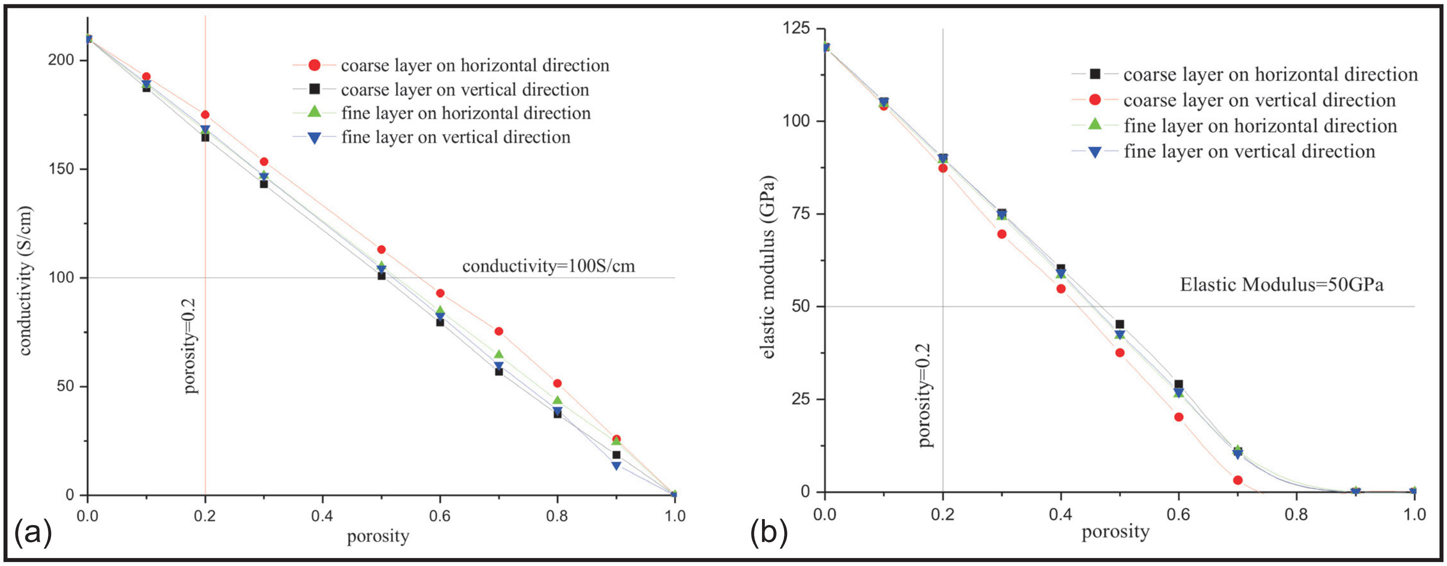


Figure 5. Prediction of normalized conductivity (a) and normalized elastic modulus (b) of two layers in the LSM cathode along two directions at different porosity using multi-scale model.

Once this is achieved, the team plans to build a more sophisticated computer controlled spray pyrolysis system. They have already developed a multi-scale model to link the porous microstructure of the cathode material to its transport properties and published results in several papers.

The team must still establish a framework to control the microstructure by adjusting the fabrication parameters. The specific tasks to be performed in the second year are as follows:

- Incorporate the flow through porous medium into the statistical model
- Develop a gradient statistical multi-scale model for the transport properties
- Develop a framework to control the microstructures based on process parameters
- Determine the correct process parameters to control and form a gradient layer
- Develop a computer-based spray pyrolysis system
- Find more cost-effective precursors for the LSMO cathode film.

NUCLEAR ENERGY RESEARCH INITIATIVE

Dynamic Simulation and Optimization of Nuclear Hydrogen Production Systems

PI: Paul Barton and Mujid Kazimi, Massachusetts Institute of Technology

Collaborators: None

Project Number: 06-041

Project Start Date: March 2006

Project End Date: February 2009

Research Objectives

This project is part of a research effort to design a hydrogen plant interfaced with a nuclear reactor—a promising alternative to fossil-fuel-generated hydrogen. The objective is to build models for dynamic simulation and optimization of hydrogen production options using nuclear energy. There is a natural interdependence between design and operational decisions for integrated nuclear hydrogen production systems. This interdependence requires a modeling and simulation environment that can capture the physical design descriptions and map these to steady state and dynamic predictions of the hypothesized system's behavior. Simulating these systems can provide invaluable information for the next step, whether this step is an experiment or design decision. The simulation environment must be adaptable, flexible, and expandable.

This project will develop a dynamic modeling, simulation, and optimization environment for nuclear hydrogen production systems. A hybrid discrete/continuous model will capture the continuous dynamics of the nuclear and hydrogen plants and their interface, as well as discrete events such as major upsets. This will allow researchers to study both plant operations and accident scenarios. Researchers can also use it to conduct parameter estimation studies to identify possible improvements in materials, mechanical design, and safety issues. The seamless connection between modeling and simulation can help establish optimal control schemes. These schemes can then be tested in the model.

Research Progress

This research project includes an analysis of the system interface operation and an overall process safety study. Three tasks were performed this year: 1) identifying key characteristics for subsystems as components in the overall model, 2) building the models for the different units, and 3) listing scenarios for study. Following is a description of the work performed under each task.

Identify key subsystem characteristics. High-temperature steam electrolysis (HTSE) and the sulfur iodine cycle (SI) appear to be the most promising technologies for nuclear hydrogen production at high temperatures and researchers will develop models to represent them.

The modular helium reactor (MHR) can provide the heat and electricity for these hydrogen production systems. Enough knowledge exists to build a dynamic model, and it has been studied coupled to a gas turbine (GT), which is fundamental for HTSE. This research project will study two specific configurations of a coupled nuclear reactor/hydrogen production system:

- High-temperature steam electrolysis (HTSE) with an MHR-GT
- Sulfur-Iodide (SI) cycle with an MHR

Researchers established two key parameters for modeling the heat transfer loop: 1) the number of loops to be used and 2) the heat transfer fluid. In the first stage, researchers will use one loop and then will extend the model to two loops. The heat transfer fluid selected is helium. Although helium requires very high pressures and has a low heat capacity, it is the only fluid that can provide safe and reliable operation.

Building the models. Each unit in the system is represented by modules containing differential-algebraic equations (DAEs). The system model is a set of equations containing all the modules and connections, and is written and solved using the Jacobian® dynamic simulation software. At this time, researchers are defining the dynamic models for the interface (compressors, pipes, heat exchangers) and for the HTSE plant (solid oxide electrolysis cell).

Deriving an adequate set of equations to represent the flow of helium in the pipes and heat exchangers has been the most challenging part of this task so far. The compressible Navier-Stokes equations describe the flow of helium in these situations, and at high Reynolds numbers they are a system of quasi-linear hyperbolic partial differential-algebraic equations. The numerical solution of these equations is not trivial—previous attempts to simulate systems involving a nuclear reactor have used numerical methods that introduce errors and produce unphysical numerical artifacts, such as oscillations. The research team is exploring specialized numerical methods for quasi-linear hyperbolic equations to produce an accurate representation of the scenarios studied.

Scenarios for overall process simulations. Researchers started defining the scenarios for the interface which couples the system and is the centerpoint for the interactions. They are defining start-up and shutdown procedures and are studying helium storage and loading. The main issue is how to coordinate the flow of helium into the loop. Researchers have been studying different configurations to represent this part of the system, employing hazard and operability (HAZOP) principles to determine the important events.

Planned Activities

During the next year, researchers will finish building the different models for each unit and the overall system model. They will validate modules using available experimental data and existing codes. They also expect to complete the selection, implementation, and parameter estimation of appropriate thermo-physical property models for the electrolyte solutions present in the SI process.

The list of scenarios will be completed, which will include accident scenarios for analysis. The system model will be used to study the different scenarios proposed.

Researchers will identify relevant process parameters and perform parameter estimation studies through dynamic optimization. The resulting dynamic problem will be large-scale and contain DAEs. The information gathered during these studies can be used for material selection and other design decisions.

Performance, efficiency, and other determined factors for hydrogen process alternatives will be compared. The performance of process alternatives will be predicted utilizing dynamic models. The different hydrogen production process alternatives for contrasting objectives will also be compared.

High-Performance Electrolyzers for Hybrid Thermochemical Cycles

PI: John W. Weidner, University of South Carolina (USC)

Collaborators: Sandia National Laboratory, Savannah River National Laboratory, Argonne National Laboratory

Project Number: 06-054

Program Start Date: March 2006

Program End Date: March 2009

Research Objectives

The objective of this project is to provide the scientific basis for developing high-performance electrolyzers for use in two candidate thermochemical cycles for producing hydrogen from nuclear power: 1) the hybrid sulfur process and 2) the modified calcium-bromine cycle. There are still a number of challenges in making these thermochemical cycles commercially viable, including 1) reducing the high cost of platinum and ruthenium catalysts, 2) minimizing SO_2 crossover (a serious lifetime-limiting phenomenon), and 3) finding suitable operating conditions for optimal electrolyzer performance and cycle efficiency. This work will build on the successful application of the proton exchange membrane (PEM) electrolyzer for producing hydrogen through the conversion of water and sulfur dioxide ($H_2O + SO_2 \rightarrow H_2SO_4 + H_2$) and the dissociation of hydrogen bromide ($HBr \rightarrow Br_2 + H_2$).

Researchers will explore methods for improving the utilization of platinum and ruthenium in the cathodes and anodes, along with replacing them with other materials (metal alloys, silicides, mixed metal oxides, or a combination). New membranes are being developed with low gas crossover and high conductivity, mechanical stability, and temperature resistance that enable operation at higher temperatures and pressures. The researchers will evaluate the most promising catalysts and membranes in the PEM electrolyzer over a range of conditions (i.e., 30-120°C, 1-10 atm, and 50-80 percent conversions) and will apply mathematical models to optimize cell and process performance.

Research Progress

During the initial phase of this work, researchers established the pertinent membrane and catalyst design parameters and operating conditions for future material development. They also conducted performance studies and modeling for the Hybrid Sulfur Process and the Modified Ca-Br-Cycle, which are described below.

Hybrid Sulfur Process. Researchers collected data on two different membrane electrode assemblies (MEAs) purchased from Lynntech and one made at USC (see Table 1). The catalyst loading was the same for both Lynntech MEAs (1.5 mg/cm^2 Pt-black) but the membrane materials were different (N115 and N212). Because N212 is 2.5 times thinner than N115, it transports water at a higher rate.

Supplier	Material	Catalyst Load	Relative Thickness
Lynntech	N212	1.5 mg/cm^2	0.4
Lynntech	N115	1.5 mg/cm^2	1
USC	N115	1.0 mg/cm^2	1

Table 1. MEA properties.

Figure 1 shows the current-voltage response of the PEM electrolyzer for the anodic oxidation of gas-phase SO_2 to H_2SO_4 and the cathodic reduction of protons to H_2. From the figure, researchers observed that both N115 MEAs performed the same, despite the different catalyst loading (1.5 vs. 1.0 mg/cm^2), furthering the hypothesis that catalyst loading is not an important factor in electrolyzer performance.

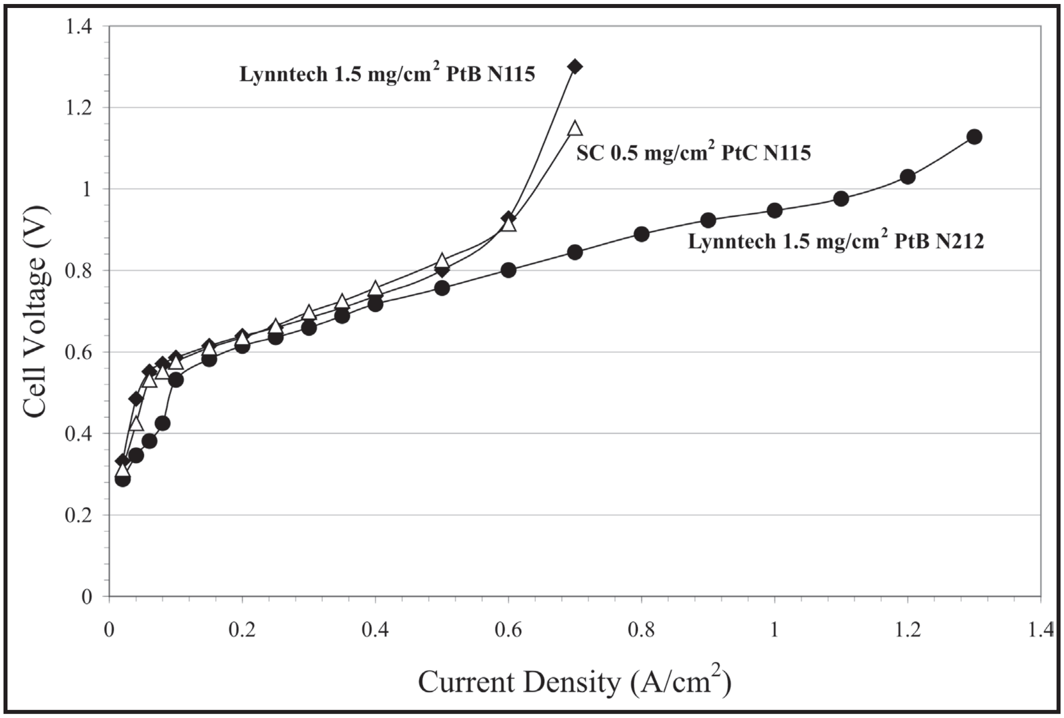


Figure 1. Current-voltage response of the PEM electrolyzers used in the Hybrid Sulfur Process at 1.0 atm and 80°C: with Lynntech MEAs, 1.5 mg/cm² Pt-Black on N115 (♦) and N212 (●); 0.50 mg/cm² Pt-carbon loading (Δ) shown for comparison.

There was significant improvement in performance with the N212 MEA. The electrolyzer does not experience the water transport limitations across this thinner membrane at current densities between 0.6 and 1.2 amps/cm². The N212 MEA was able to reach 1.22 amps/cm² at 1.05 volts, compared to 0.66 and 0.40 amps/cm² for the N115 and Westinghouse data (liquid phase), respectively.

Researchers also evaluated electrolyzer performance as a function of temperature. They observed a decrease in voltage with increasing temperature, which is consistent with the corresponding increase in membrane conductivity. Therefore, membrane properties dictate electrolyzer performance, not catalyst kinetics.

The other effect of the membrane on electrolyzer's performance is the concentration of sulfuric acid (H_2SO_4) produced. This is a key variable since it affects the overall operating efficiency of the Hybrid Sulfur Process. The more water sent to the high-temperature decomposition reactor, the more energy required for the process.

Researchers measured H_2SO_4 concentration as a function of current density for the N115 and N212 MEAs, operating the electrolyzer at 1 atm and 80°C. The acid concentration increased with increasing current since the amount of H_2SO_4 produced is proportional to current via Faraday's law. In addition, the acid was more concentrated for a thicker membrane because less water transported across the membrane.

At a fixed current, the thicker membrane is preferable because more concentrated acid is produced. For example, at 0.50 amps/cm², the acid leaving the N115 electrolyzer is 5.90 M, compared to 3.80 M for the N212 electrolyzer. However, the advantage of the thinner membrane is that it can be run at a higher current, which in turn results in higher acid concentrations. For example, at 0.40 and 0.60 amps/cm² for the N115 and N212 MEA, respectively, the concentration for both runs is approximately 5.0 M.

Modified Ca-Br Cycle. Researchers investigated the effects of 1) pressure, 2) temperature, 3) conversion percentage, and 4) membrane type and thickness. They ran the HBr electrolysis in the PEM electrolyzer at 80°C and 50 percent conversion at pressures ranging from 1.0 to 4.0 atm. Since the overall reaction produces the same number of moles in the gas phase as it consumes, it is expected that H_2 can be produced at any desired pressure without affecting the cell voltage, and, hence, process efficiency.

Researchers also ran the HBr electrolysis in the PEM electrolyzer at 1.0 atm and 50 percent conversion at temperatures of 60 to 85°C. At 60°C, the curve shifted upwards by approximately 100 mV at all current densities. A run at 100°C and 3.0 atm, which prevented boiling, resulted in a negligible effect on performance. As with pressure, percent conversion had no effect on cell voltage.

Finally, they also conducted tests at 80°C, 1.0 atm, and 50 percent for three different Nafion membranes: 112, 1035, and 115. The 1035 membrane has a higher proton density, which increases the conductivity. As expected, the 115 membrane performed the worst since it was thicker and less conductive. The other two membranes gave identical performance. The thinner membrane was offset by the higher low conductivity, which affected the water balance but not the voltage.

Planned Activities

These results revealed that the membrane is the key design parameter affecting electrolyzer performance. Membrane properties affect water transport, SO_2 crossover, and ohmic resistance, which can be modified by varying the thickness and equivalent weight of the Nafion membrane. However, these three phenomena cannot be independently modified via this approach. Therefore, the researchers are developing hydrocarbon-based membranes so that water transport, SO_2 crossover, and ohmic resistance can be optimized independently.

Catalyst loading and type do not affect electrolyzer performance. However, the choice of catalyst material greatly impacts cell cost. Therefore, researchers are developing low-cost, non-precious metal catalysts that are durable, yet do not adversely affect performance (i.e., current-voltage curve).

Finally, researchers are developing mathematical models to optimize design parameters (e.g., membrane and catalyst) and operating conditions (e.g., temperature, pressure, current). These models will also be integrated into process flow sheets in order to study overall process efficiency on electrolyzer performance.

Development of Efficient Flowsheet and Transient Modeling for Nuclear Heat Coupled Sulfur Iodine Cycle for Hydrogen Production

PI: Shripad T. Revankar, Purdue University

Collaborators: None

Project Number: 06-060

Project Start Date: April 2006

Project End Date: March 2009

Research Objectives

The main goal of this project is to develop a flowsheet for the closed-loop sulfur iodine (SI) cycle for nuclear hydrogen production. This flowsheet will use current advances in acid decomposition and product gas separation to achieve high thermal efficiency. It will result in the development of transient analysis methods for the SI cycle. Although the closed-loop SI cycle has recently been demonstrated on a bench scale, several challenges remain, such as maintaining stable operation, enhancing efficiency, obtaining thermodynamic data for the reactions, coupling to a high-temperature nuclear reactor, and determining transient behavior of the coupled system. This project will develop models to study transient performance of the closed-loop SI cycle. In addition, this research will explore several alternatives to SI cycles that have been proposed.

Specific objectives of the project are to:

- Perform benchmark flowsheet analysis of the baseline SI cycle
- Investigate membrane techniques for hydrogen-iodide (HI) and sulfuric acid (H_2SO_4) decomposition and separation processes
- Perform comparative flowsheet analyses of the modified cycles
- Develop component-wise SI cycle models for application to the transient analysis
- Perform preliminary analysis of transient behavior of the closed-loop SI cycle

Research Progress

The SI cycle consists of three chemical reactions expressed as the following equations:

Section I - Bunsen reaction:

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

Section II - Sulfuric acid decomposition:

$$H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$$

Section III - HI decomposition:

$$2HI \rightarrow H_2 + I_2$$

For the current work, the flowsheet that General Atomics (GA) previously developed for the SI cycle was considered as a baseline. During the first year, efforts focused on developing and benchmarking a simulation model for the GA SI cycle flowsheet. This analysis was carried out to establish the simulation capability and check the GA flowsheet model's repeatability.

The SI thermochemical cycle was simulated using the chemical process simulation code ASPEN PLUS version 12. The GA flowsheet was studied and ASPEN models for Sections I, II, and III were developed. A step-by-step simulation was performed starting from the single component simulation to the whole Section simulation. For the single component simulation, converged solutions were obtained comparable to GA's results. For the whole Section simulation, results of the converged solution for Section II were also comparable to GA's. Figure 1 shows that the present ASPEN results compare very well with GA's reported results for the SO_3 stream for Section II.

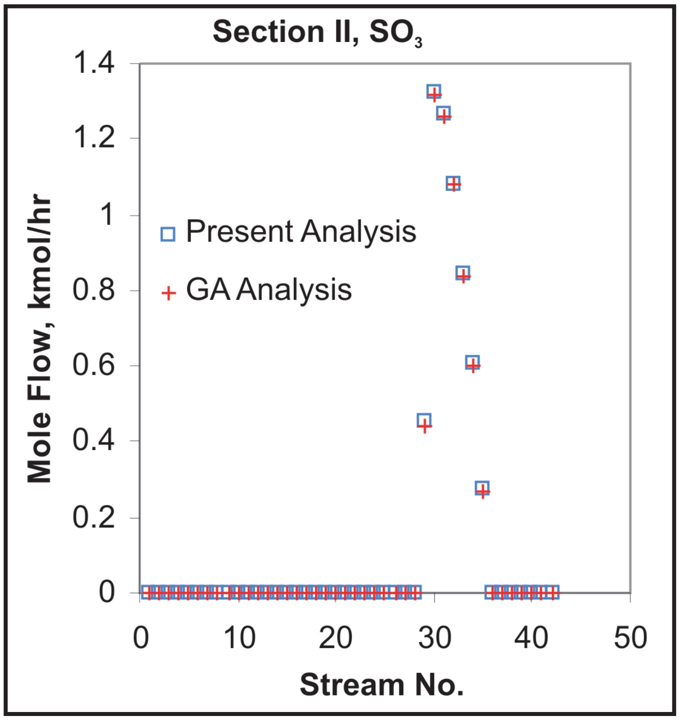


Figure 1. Comparison between GA and current ASPEN analysis.

In Section II, decomposition of the H_2SO_4 occurs in series of four decomposers. The effect of reaction temperature on the decomposition of H_2SO_4 was carried out by changing the decomposer temperature from 1,050 to 1,110 K. Figure 2 shows the mole flow rate of O_2 and SO_2 at the inlet stream to Section I for the Bunsen reaction. As reaction temperature decreases, the decomposition rate also decreased as expected. However, for the higher reaction temperature case (1,110 K), the decomposition rate decreased slightly, indicating that the current model is optimized for the design reaction temperature.

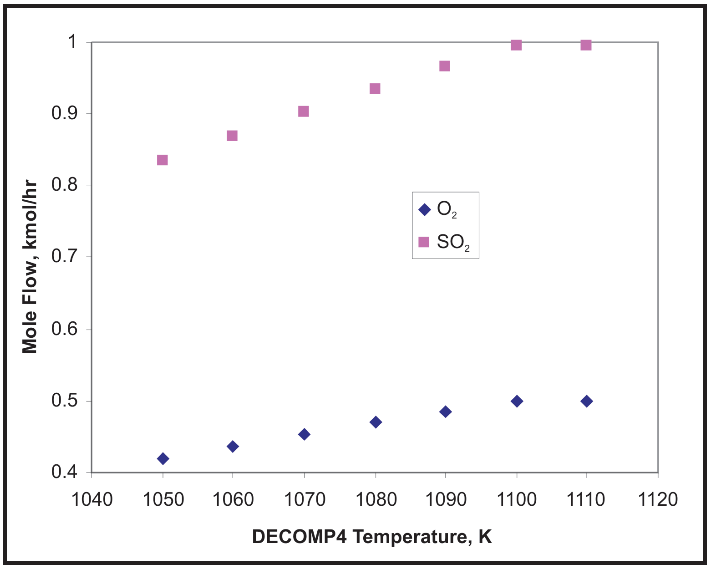


Figure 2. The effect of discomposure reaction temperature on the O_2/SO_2 mole flow generation.

Converged solutions for GA's flowsheet Sections I and III have not yet been obtained, although researchers have achieved convergence for each component. Researchers have tried various approaches, such as 1) changing process variables (P, T, flow rate), 2) applying different component analysis options (location of feed stage, boilup ratio, reflux ratio, heat duty, etc.), and 3) changing the equilibrium constants and chemical kinetics rate constants in trials. The three-phase separator in Section I and the reactive distillation column in Section III are the main components related to convergence, which are being further investigated.

Planned Activities

The remaining tasks for the first year are to 1) develop a modified SI Model based on the GA flowsheet and comparative study with the modified and baseline SI Cycle and 2) develop a membrane technique flowsheet for Section III and a simulation model for the membrane. The planned activities include modifying the three-phase separator in Section I and the reactive distillation column in Section III. These modifications will be made so that converged solutions can be obtained from the ASPEN simulation. A comparative study will then be made with the baseline SI cycle flowsheet. Researchers will conduct a literature search on the membrane separation techniques for implementing into Section III for HI decomposition. The flowsheet for Section III will be modified using membrane techniques and the simulation will be carried out.

NUCLEAR ENERGY RESEARCH INITIATIVE

Gradient Meshed and Toughened SOEC Composite Seal with Self-Healing Capabilities

PI: Kathy Lu, Virginia Polytechnic Institute and State University

Collaborators: Idaho National Laboratory

Project Number: 06-140

Project Start Date: June 2006

Project End Date: May 2009

Research Objectives

Hydrogen generation through high-temperature electrolysis, using nuclear heat from advanced gas-cooled or liquid-metal-cooled reactors, will play a significant role in the Nuclear Hydrogen Initiative. High-temperature steam electrolysis enhances the efficiency of hydrogen production by adding substantial external heat, which reduces electricity consumption. Very high-temperature advanced reactors can provide the necessary heat to enable high-efficiency hydrogen production without the use of carbon fuels.

However, the seals currently used in solid-oxide electrolyzer cells (SOEC) hinder this promising technology due to a mismatch in thermal expansion coefficients that causes seal cracking and gas leakage. The objective of this project is to match the SOEC seal expansion coefficient with other cell components by using a glass-filled, titanium-nickel-hafnium (TiNiHf) high-temperature shape memory alloy (SMA) mesh to create a transition gradient. This novel seal design will enable long-term SOEC operation by providing mechanisms for glass matrix toughening and crack self-healing.

Researchers will conduct experiments to approximately 500 hours duration and extrapolate the results to 40,000 hours or more in order to predict long-term cell performance. They will assess overall stability, performance, and cost of the seal using actual SOECs and analytical models.

Research Progress

This project will develop a novel composite seal by integrating 3-D printed shape memory alloy wires into a glass matrix. Using the unique structure of the SMA wire mesh, researchers will create a thermal expansion gradient across the seal thickness, provide self-healing of cracks by the alloy shape memory effect, and reduce thermal stresses by SMA phase transformation toughening. They are using TiNiHf as the SMA material and SLABS—an aluminosilicate-based compound ($SrO-La_2O_3-Al_2O_3-B_2O_3-SiO_2$)—for the glass matrix.

Researchers have synthesized TiNiHf and successfully achieved a shape memory effect. Differential scanning calorimetry and microscopy have shown that the alloy has shape memory phase changes between 180 and 250°C. After the alloy solidifies, a homogenization heat treatment is necessary in order to visualize the shape memory effect. Using scanning electron microscope (SEM), researchers found evidence of incipient melting during homogenization, which they believe is due to a slightly low nickel (Ni) concentration in the SMA alloy. Work is underway to increase the Ni content.

Researchers synthesized several batches of SLABS glass to make cylindrical dilatometry samples and milled them into powders. The dilatometry test shows the overall coefficient of thermal expansion (CTE) is $13.9 \times 10^{-6}/°C$. However, it changes significantly with temperature, as indicated in Table 1. These data pinpoint regions of different CTEs under the same SOEC thermal cycle within the same material.

Temperature Range	CTE
40-500°C	$7.02 \times 10^{-6}/°C$
500-700°C	$32.0 \times 10^{-6}/°C$
700-800°C	$21.4 \times 10^{-6}/°C$
Overall	$13.9 \times 10^{-6}/°C$

Table 1. Dilatometry test results of SLABS samples.

The most problematic region for the studied SLABS glass system is 40-500°C—the typical heating and cooling region. Researchers have demonstrated that the proposed SLABS glass has much higher CTE than the seal glasses currently used in SOEC research. This glass shows great potential for mitigating the thermal expansion mismatch issues that are hindering the long operational lifetime of SOECs.

The TiNiHf shape memory effect overlaps with this problematic low CTE region of the SLABS glass. This supports the assumption that gradient transition, phase transformation toughening, and SMA self-healing can be utilized to mitigate/eliminate the seal problem.

Planned Activities

Researchers plan to perform the following tasks over the next fiscal year:

- Continue to study TiNiHf high-temperature SMA and SrO-La_2O_3-Al_2O_3-B_2O_3-SiO_2 (SLABS) glass seal systems and tailor their compositions to produce complementary thermal behaviors during SOEC operation
- Use three-dimensional printing to build a TiNiHf mesh for the seal on the interconnect side and provide gradient thermal expansion coefficients from the interconnect to the electrolyte across the seal thickness to greatly reduce thermal stress
- Fill SLABS glass into the meshed TiNiHf structure, transitioning into pure glass on the electrolyte side, to make seals with transformation toughening and crack self-healing capabilities
- Conduct comprehensive seal testing to demonstrate smooth thermal expansion coefficient transition, cracking resistance, and crack self-healing capabilities of the new composite seal
- Conduct field testing using actual SOEC seal configurations and model the process to optimize cost and opportunities

Liquid Salts as Media for Process Heat Transfer from VHTRs: Forced Convective Channel Flow Thermal Hydraulics, Materials, and Coatings

PI: Kumar Sridharan, University of Wisconsin-Madison

Collaborators: None

Project Number: 07-030

Program Area: NHI

Project Description

This project investigates liquid salts as heat transfer fluids to utilize process heat from the very high-temperature reactor (VHTR) and other Generation IV reactors for hydrogen production. Favorable thermal properties (e.g., lower melting point, high boiling point, high heat capacity, chemical stability, and low pumping power requirements) allow for efficient transport of high-temperature thermal energy. Successful implementation of the liquid salt reactor/hydrogen production process interface will require an accurate assessment of the thermal hydraulics in small diameter channel, high-efficiency compact heat exchangers. In these small channels, under high flow velocity and high temperature conditions, both thermal hydraulics and materials will be key operational issues. In particular, information on corrosion/erosion resistance of materials and coatings for the construction of intermediate heat exchanger systems will be needed along with operational experience to determine the minimum channel sizes to avoid clogging and to optimize heat transfer.

Work Scope

1) Investigate materials and coatings corrosion performance in liquid salts:
    - Perform static corrosion tests of Alloy 800H, carbon-carbon composite, and Inconel 600 in liquid FLiNaK (LiF-NaF-KF) and liquid $MgCl_2$-KCl salts at 850°C for 500 hours
2) Fabricate a forced convection loop paired with a commercial liquid salt pumping system to achieve high velocity flows to study:
    - Thermal hydraulics in small channels to determine optimum heat transfer configuration while avoiding clogging due to corrosion products
    - Particle transport and deposition in liquid FLiNaK salt at 850°C for 1,000 hours
3) Evaluate materials and coating technologies for corrosion, erosion, and small channel clogging under prototypic velocity liquid salt flow conditions:
    - Optimized Ni electroplating and hard carbon coating/carbon-carbon composite
    - Electroplated Ni and hard carbon coating

Optimization of Heat Exchangers

PI: Ivan Catton, University of California-Los Angeles

Collaborators: None

Project Number: 07-057

Program Area: NHI

Project Description

The objective this research is to develop tools to design and optimize heat exchangers and compact heat exchangers (CHE) for intermediate loop heat transport systems found in the very high-temperature reactor (VHTR) and other Generation IV designs by addressing heat transfer surface augmentation and conjugate modeling.

This research will be performed in two parts. Researchers will search for augmented heat transfer surface morphologies using a combination of experiment and modeling. For a particular type of surface augmentation, they will conduct experiments to obtain closure of the model and then apply it to optimize the surface. A final experiment will confirm the findings of the model. These surfaces will become candidates for the next part of the research, where they will be integrated into a heat exchanger design. The objective is to develop and demonstrate a model that can be used to optimize heat exchangers. The model equations are available but have not been used for a two-fluid-stream heat exchanger, nor has closure been fully developed. Researchers will design and optimize a printed circuit heat exchanger (PCHE) for either a high-temperature Brayton cycle in support of the VHTR or for the reactor-hydrogen production process interface. The results of this research will be a validated computer program for the design of heat exchangers that maximize heat transfer and minimize pumping power.

Work Scope

The major technical objectives of the proposed research are to:

1) Develop a surface that increases surface heat removal effectiveness by a factor of four without a marked increase in pumping power
2) Develop a new type of mathematical model capable of predicting flow and heat transfer in 2-D and 3-D spatial structures at different scales
3) Design and carry out experiments to measure heat transfer augmentation and validate the heat exchanger and CHE models used for optimization
4) Design and test a printed circuit heat exchanger for a high-temperature inert gas cycle

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