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## Experimental investigation of steel corrosion in Lead Bismuth Eutectic (LBE): characterization, species identification, and chemical reactions

John Farley

*University of Nevada, Las Vegas, farley@mailaps.org*

Dale L. Perry

*Lawrence Berkeley National Laboratory*

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From: Ning Li, Ph.D.

AAA, Los Alamos National Laboratory

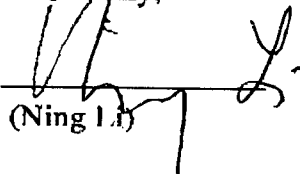
Date: April 30, 2001

To Whom It May Concern:

I believe that the work proposed by UNLV faculty Professor John Farley in **“Experimental investigation of steel corrosion in Lead Bismuth Eutectic (LBE): characterization, species identification, and chemical reactions”** is important and directly supports the DOE AAA Program.

I have worked with Professor Farley to identify the program needs and relevant R&D tasks, and to develop and substantiate the proposal. Understanding corrosion and corrosion control via active oxygen control in LBE systems through systematic experimental investigation and verification will greatly benefit the AAA Program in areas of spallation target and (possibly) nuclear coolant applications. This work also complements the corrosion testing planned for the LBE Materials Test Loop (MTL) in providing additional materials characterization.

Yours truly,



(Ning Li)

**Project Title: Experimental investigation of steel corrosion in Lead Bismuth Eutectic (LBE): characterization, species identification, and chemical reactions**

**Principal Investigator (PI):** John W. Farley (Project Director)

Dept of Physics, UNLV  
Mail Stop 4002  
4505 S. Maryland Parkway, Las Vegas NV 89154  
Phone (702) 895-3084      email: farley@nevada.edu

Dale L. Perry (co-PI)  
Mail Stop 70A-1150  
Lawrence Berkeley National Laboratory  
Berkeley CA 94720  
Phone: (510) 486-4819      email: dlperry@lbl.gov

**Collaborators (UNLV):**

Dan Koury (graduate student)  
Department of Physics, UNLV  
Mail Stop 4002  
4505 S. Maryland Parkway, Las Vegas NV 89154  
Phone (702) 895-1718      email: hilife@physics.unlv.edu

Brian Hosterman (graduate student)  
Department of Physics, UNLV  
Mail Stop 4002  
4505 S. Maryland Parkway, Las Vegas NV 89154  
to start fall 2001

**Collaborator (DOE):**

Ning Li  
LBE Project Leader  
Los Alamos National Laboratory  
Los Alamos NM 87545  
Phone (505) 665-6677      email: ningli@nanl.gov

**AAA Research Area: Transmuter**

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|-------|---------------|---------------|---------------|
| Total | \$150,165     | 158,689       | 161,930       |

**Abstract**

The goal of the present research is to achieve a basic understanding of corrosion of steels by Lead Bismuth Eutectic (LBE). Liquid LBE is under consideration in the transmuter as both a coolant and a target material. There have been studies of LBE, especially by the Russians, but a fundamental understanding and verification of its role in the corrosion of steels is still very

incomplete. Post-experiment testing and analysis will be performed on steel samples that have been in intimate contact with LBE. Chemical alterations and resulting chemical species will be measured at the steel surface. Techniques to be used include Electron Probe Microanalysis, Micro-Raman, x-ray photoelectron/Auger spectroscopy, and powder X-ray diffraction. In addition to these well-established laboratory-based instrumentation approaches at UNLV, we will use a state-of-the-art synchrotron-based spectroscopy and microscopy technique, the X-ray fluorescence microprobe at the Advanced Light Source, at Lawrence Berkeley National Laboratory. We will characterize spectroscopically both the LBE and the stainless steel before and after they interact to determine their composition, including minor components such as chromium and nickel. The proposed research moves toward establishing a rigorous experimental database of experimental measurements of LBE and its reactions with steels. Such a database can be used by DOE scientists and engineers in engineering efforts to control, avoid, and/or minimize the effect of corrosion of steels by LBE, under conditions appropriate to the transmuter.

## **Background and Rationale**

In proposed plans for accelerator transmutation of nuclear waste, intense beams (e.g., up to 45 mA) of medium-energy (e.g., 1000 MeV) protons strike a spallation target, producing neutrons, which sustain fission reactions in the nuclear waste, transmuting it to materials with no radioactivity or radio-isotopes with short half lives. This process places stringent requirements on the materials to be used in the construction of the facility: materials must be capable of withstanding very high neutron fluxes, elevated temperatures, and chemical corrosion. Material science questions may in fact be critical to the feasibility of the entire transmutation project. Materials must be found for a coolant that can conduct away the high heat (MW) load. Materials must also be found to serve as a spallation target, converting the incident proton beam to neutrons. Lead-Bismuth Eutectic (LBE) has been proposed for use in the transmuter, where it can serve two purposes: both as a coolant (removing heat from the nuclear waste) and as a spallation target (generating a neutron flux from the incident proton beam).

The LBE circulates within stainless steel piping and containers. An absolutely critical question is whether LBE can be engineered to be compatible with the stainless steel walls that contain it with sufficient lifetime. The deleterious process is the corrosion of stainless steel that has been in intimate contact with LBE. The 1999 *Roadmap for Developing Accelerator Transmutation of Waste (ATW) Technology* lists “Coolant Chemistry and Materials Compatibility” under the Target/Blanket R&D Activities.

The Russians have 40 years of experience with LBE coolant loops in their Alpha-class nuclear submarines, and they have performed laboratory studies of the reactions of LBE with US steels. Los Alamos scientists have reviewed these studies [He and Li, (2000)], in which several US steels [316 (tube), 316L (rod), T-410 (rod) HT-9 (tube), and D-9 (tube) and one Russian steel EP823 rod] were corrosion-tested. Los Alamos scientists are building and will operate a medium-scale LBE materials test loop (MTL).

There are still very important gaps in our understanding of the chemistry of corrosion in the LBE/steel system. For example: what are the chemical species created during the corrosion

process? What are the chemical reactions occurring? What is the morphology of the interface at both the macroscopic and microscopic scale? How do these reactions depend on temperature and the presence of trace elements? What is the heterogeneity of the corrosion process in a LBE system? What are the chemical species involved in the reaction as corrosion products? What about oxides of contaminant metal ions that may leach from the stainless steel during the course of the reaction of the LBE at the interface? Which metal ions are involved, and which chemical form do they exhibit? What is the oxidation state of each of the elements? What is the electronic structure of each of the elemental ions? What is the magnetic configuration of each of the appropriate ions? Is there any evidence for passivation at the interface of the reaction of the LBE with the steel substrate?

Answering these questions is necessary in order to understand the corrosion process, and hence to be able eventually to engineer the system in order to control or minimize the various corrosion processes in the LBE/steel system.

### **Research Objectives and Goals**

The research objectives are:

- To elucidate the mechanism(s) and kinetics of corrosion in LBE/steels, which have not been studied in detail.
- To determine the signature of the lead oxides, bismuth oxides and other chemical species in samples of steels that have been in intimate contact with LBE.
- To determine the forms of solid oxides from corrosion products and lead and bismuth.
- To measure the different responses of different kinds of steels to LBE.

The goals are:

- To understand the difference in corrosion behavior between different types of select candidate steels.
- To determine whether or not particular compositions of steels could be tailored to be especially corrosion-resistant, especially with regard to Si and Al.
- To provide an understanding of corrosion of steels by LBE that will allow the realistic formulation of strategies for passivating surfaces, minimizing corrosion, periodically flushing and cleaning of corrosion products, or lengthening service lifetime under realistic conditions.
- To advance the overall understanding of corrosion in LBE/steel systems.

### **Technical Impact**

Raman and infrared can differentiate among the different structural phases of elemental oxides present phases in the LBE/steel reaction systems, while, at the same time, giving a lateral mapping of the different species on the surface. X-ray photoelectron and Auger spectroscopy can give valuable information on the oxidation state, chemical state (including species), and the electronic and magnetic configuration of several of the metal ion species as a result of experimental parameters in their spectra. By using Auger transitions observed in the x-ray-generated x-ray photoelectron spectra, one can also derive valuable chemical information about

the products formed at the LBE/steel interface. Spectroscopic data such as these can be combined with microscopic data, along with x-ray diffraction data, which can be used to fingerprint structural forms of the elemental species formed in the reactions. The proposed work will make a major contribution to the understanding of the mechanism of corrosion in LBE/steel systems.

## **Research Approach**

Samples will be characterized using a number of experimental techniques:

(1) Electron Probe Microanalyzer (EPMA). In this test, a high voltage focused electron beam strikes a solid sample, causing fluorescence in the x-ray spectral region. The x-rays are characteristic of the kind of atom. This instrument is capable of measuring elements from boron ( $Z=5$ ) through uranium ( $Z=92$ ). This reveals the elemental analysis as a function of position. It does not reveal speciation; i.e., it does not provide information about the chemical species. This will be performed at UNLV by graduate students Dan Koury and Brian Hosterman under the supervision of John Farley and a UNLV staff scientist, Sarah Lundberg, whose formal title is "Microbeam Facility Analyst". This will show the presence of oxides and their spatial distribution, with a spatial resolution of about a micron. Tests will be run on steel samples and LBE samples, before and after exposure contact between steels and LBE. When analysis is complete, this will allow us to identify the elements present in the samples. After analysis, we can formulate hypotheses about the chemical reactions that give rise to such species.

(2) MicroRaman system. Raman data are taken from an extremely localized area on the surface of a sample. This Raman spectrum will be indicative of both the chemical species, and, in many cases, the structural polymorph, i.e., different structural phases of the same chemical compounds. This technique has a spatial resolution of a few microns along the surface. The measurements will be performed by graduate students Dan Koury and Brian Hosterman, under the supervision of John Farley and UNLV physics professor Ann Chopelas, in whose laboratory this instrument resides.

(3) X-ray diffraction. In this technique, a x-ray source (copper K-alpha, rotating anode) illuminates the sample, and an imaging plate collects the x-ray diffraction pattern. We can scrape a sample of powder from the surface, and perform x-ray diffraction on the powder. This reveals the crystal structure of the sample. This measurement will be performed by graduate students Dan Koury and Brian Hosterman, under the supervision of John Farley and UNLV physics professor Malcolm Nicol, in whose laboratory this instrument resides.

(4) XPS/Auger. In this technique, the sample is illuminated by x-rays, and the resulting photoelectrons are energy-analyzed. Some of the photoelectrons arise from Auger transitions within the sample. Such Auger transitions are characteristic of the element. This measurement will be performed by graduate students Dan Koury and Brian

Hosterman, under the supervision of John Farley and UNLV chemistry professor Allan Johnson, who is the UNLV contact person for this instrument.

(5) The four techniques mentioned so far employ laboratory instruments at UNLV. In addition, we plan to perform tests using synchrotron-based x-rays. Synchrotron radiation-based (SR) x-ray fluorescence (XRF) will be used, because it has been proved to be a sensitive analytical technique capable of providing direct quantitative information on chemical compositions. The x-ray fluorescence technique will give a detailed mapping (with a 1 micron resolution) of the heavy metal ions being studied. The sensitivity of the synchrotron x-ray fluorescence microprobe for many metals can approach the femtogram ( $10^{-15}$ ) level, one of the most sensitive of spectroscopic techniques that can be employed in conjunction with microscopic imaging. Synchrotron-based x-ray fluorescence microprobe techniques have been used by Dale Perry and co-workers Perry *et al*, *Appl. Spectrosc.*, 51, 1781(1997)] to map different metals such as calcium, nickel, and potassium, for example, in films of complex quaternary metal oxides. These measurements will be performed by graduate students Dan Koury and Brian Hosterman, who will travel to the ALS to perform the experiment, with Dale Perry supervising.

We wish to emphasize that these experimental techniques have already proven productive in the hands of Perry and co-workers. The proposed research uses the techniques of x-ray fluorescence (XRF) spectromicroscopy, x-ray photoelectron (XPS), and Auger electron spectroscopy (AES) to study the metal ions and their reaction chemistry. Perry and co-workers (*Inorg. Chim. Acta (Chemistry of the f-Block Elements)*, 127, 229(1987); *J. Mat. Sci. Lett.*, 5, 384(1986); *Inorg. Chim. Acta (Chemistry of the f-Block Elements)*, 127, 229(1987); *J. Appl. Phys.* 78, 5356(1995)) have used XPS to study several metal ion systems, along with combined XPS/AES (*Applications of Analytical Techniques to the Characterization of Materials*, D. L. Perry, Plenum Press, 1992), along with lead and oxides and associated compounds (*J. Vac. Sci. Technol. A*, 2, 771(1984)). Raman spectroscopy has been used by the same group to study the chemistry and bonding of a variety of metals, including uranium (*Spectrochimica Acta* 49A, 975(1993); 50A, 757 (1994)).

After taking the data, the analysis phase begins. Of course data alone, without the necessary analysis or interpretation, cannot yield scientific understanding. Typically the analysis and interpretation phase takes much longer than the actual data taking. The analysis and interpretation are intended to yield a consistent picture of the chemical species present and their spatial heterogeneity, the chemical reactions occurring in the LBE/steel system, and the dependence of the chemical reactions upon composition, temperature, and time. When the analysis and interpretation is complete, we will write up the results for presentation at scientific meetings, incorporation in student theses, and publication in the peer-reviewed scientific literature. Dale Perry, an expert in the field, will be of great help to the graduate students in the analysis portion of the work.

## **Expected Technical Results**

The various types of data will yield the elemental composition of the samples and the spatial distribution of elements, both before and after corrosion.

The working hypothesis of the proposed research is that the oxygen in lead and bismuth is important in the corrosion processes in bismuth-lead eutectics and their interaction with steels and other system components. Metal oxides may be formed as a result of leaching of the contaminant parent metal from the steel matrix as coolant contaminant.

Accordingly, we expect to learn the chemical species present and their spatial heterogeneity, the chemical reactions occurring in the LBE/steel system, and the dependence of the chemical reactions upon composition, temperature, and time.

## **Capabilities at the University, Los Alamos, and Lawrence Berkeley Lab (Advanced Light Source)**

- Electron Probe Microanalysis facility. UNLV. Geosciences. Sarah Lundberg, staff scientist and contact person
- MicroRaman system. UNLV. Laboratory of Physics Prof. Ann Chopelas.
- X-Ray diffraction system. UNLV. Laboratory of Physics Prof. Malcolm Nicol.
- XPS/Auger. UNLV. Housed at DRI; UNLV Chemistry Prof. Allen Johnson, contact person
- X-ray fluorescence microprobe. ALS Beamline 10.3.1. Dale Perry, contact person.
- A wide variety of standalone equipment, Lawrence Berkeley National Laboratory. Dale Perry, contact person.
- Lead-Bismuth Eutectic (LBE)/steel Materials Test Loop (MTL), at Los Alamos. Ning Li, contact person.



## **Project Timeline for the first year (2001-2002)**

### Timeline narrative

This proposal describes a research program that will take three years to complete. The timeline describes the expected technical results, milestones, and deliverables for the **first year only**. At the end of the first year, a separate proposal will be submitted for the second and third year. Its scientific and technical content will depend on the results of the measurement and analysis made during the first year. The budget is included for the second and third year to give an indication of the expected budgets for years 2 and 3.

The two graduate students will become familiar with LBE, its scientific literature, and the major pieces of scientific instrumentation.

### Expected technical results for the first year

Documentation of the chemical forms and states of elements in various candidate steels of interest; understanding of the exact composition of the steels.

Understanding of the different lead oxide phases in precipitation.

Understanding of the different bismuth oxide phases in precipitation.

Preliminary determination of the metal oxide phases formed in LBE/steel reactions.

### Milestones for first year (June 1, 2001- May 30, 2002)

- Familiarization with the major pieces of equipment at UNLV by graduate student Dan Koury (September 2001). The second graduate student, Brian Hosterman, will start at UNLV in September 2001.
- Familiarization with the scientific literature of LBE by both graduate students (December 2001).
- Take preliminary measurements of LBE and appropriate steels and products formed in the reaction between LBE and steels (March 2002).
- Study of the different phases produced, depending on the results from the previous point (May 30, 2002).

### Deliverables for the first year

- **Collaboration with DOE project:** Monthly communication with phone or email with Dr. Ning Li, National Project collaborator to update on progress, discuss problems, and allow for re-focusing if necessary to address shifts in direction by the National Project.
- **Progress Reports:** Brief reports indicating progress will be provided every quarter (to support DOE AAA quarterly meetings).
- **Bi-Annual Reports:** written reports detailing experiments performed, data collected and results to date.
- **Final Report:** Written report detailing experiments performed, data collected, results, and conclusions to be submitted at the end of the project.
- **First Manuscript submitted** to peer-reviewed scientific journal May 30, 2002 for publication.
- **Data** to be incorporated into student theses.

## References

Xiaoyi He and Ning Li, "Review of Russian's reports on results of corrosion tests on 316, 316L, T-410, HT-9, and D-9 steels", manuscript in preparation (2000).

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