5-31-2002

Modeling Corrosion in Oxygen Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrodynamics-Phase Two

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Project Title:

Modeling Corrosion in Oxygen Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrodynamics-Phase Two

May 31, 2002

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AAA Research Area: **Transmuter**

Requested Funds: $109,011 (Year Two)

Abstract

The proposed work will combine chemical kinetics and hydrodynamics in target and test-loop lead-bismuth eutectic (LBE) systems to model system corrosion effects. This approach will result in a predicative tool that can be validated with corrosion test data, used to systematically design tests and interpret the results, and provide guidance for optimization in LBE system designs. The task includes two subtasks. The first subtask IS to try to develop the necessary predictive tools to be able to predict the levels of oxygen and corrosion products close to the boundary layer through the use of Computational Fluid Dynamics (CFD) modeling. The second subtask is to predict the kinetics in the corrosion process between the LBE and structural materials by incorporating pertinent information from the first subtask. In many cases a component fails because of the combined effect of mechanical or hydraulic factors and corrosion. Such cases are of three types: stress corrosion, corrosion fatigue, and liquid-velocity effects (corrosion erosion and cavitations). The compatibility issues arising from the interaction of liquid metals, corrosion/dissolution, with structural materials at temperatures of interest are important while lead alloy as a coolant for a fast breeder type nuclear reactor is used. In the second year of the second subtask will focus on the kinetics of the dissolution/deposition process as a function of temperatures, flow velocities, dissolved metal concentrations and the oxygen potentials of the

system, the kinetics of film formations in the presence of oxygen, and the kinetics of transports of metal through the oxidized surface film. Both mass transfer controlled and the diffusion coefficient of dissolved species will be parametrically studied for the corrosion process.

Work Proposed for Academic Year (short sample also of work so far during this funding year) 2002-2003

The first subtask of phase II is similar to that of Phase I but more expanded where a series of parametric runs will be performed over a realistic range of values of the average eutectic flow velocity, average mean bulk eutectic flow inlet temperatures and average inlet oxygen concentrations in the three predefined geometries already used in phase I study. These are namely a straight flow section, an elbow bend and a tee section. The thermal-hydraulics study involves using a CFD code (2-D simulation) such as STAR-CD to obtain averaged values of streamwise velocity, temperature, oxygen and corrosion product concentrations at a location deemed close to the walls of the LBE loop at more than one axial location. The oxygen and corrosion products inside the test loop will be simulated to participate in chemical reactions with the eutectic fluid as it diffuses towards the walls. Details of the geometry of these loops will be obtained from scientists at LANL. These values will act as a set of starting boundary conditions to the second task.

The major concern with using of Pb-Bi is its compatibility with the containment structure. Liquid metal corrosion can proceed via various processes: dissolution, formation of intermetallic compounds at the interface, penetration of liquid metal along grain boundaries, which depend on experimental factors such as: temperature, thermal gradients, solid and liquid compositions, velocity of the liquid metal. [Balbaud-Celerier and Barbier, 2001] Sannier, Flament, and Terlain have shown that the corrosion rate of martensitic steels, at 475^{0}C (hot leg temperature) and for a temperature gradient of 60^{0}C (cold leg temperature is 415^{0}C, increases from 21 to 93 µm per year when the alloy of lead-lithium velocity increases from 0.019 to 0.18 meter per second. In 1999, Pointevin, Bergerson, Deffain, Enderlehave, Lenain, and Raballand have also shown that the velocity of liquid lead-bismuth could reach values up from 3 to 5 meters per second in the spallation module. Balbaud, Barbier, and Konys have developed an experiment device which consists in a rotating cylinder operating under controlled hydrodynamic conditions in order to evaluate the Pb-Bi velocity effect on the corrosion of steels.

Scientists have noticed that the concentration of oxygen dissolved in the liquid alloy could control the corrosion rate of steels exposed to Pb or Pb-Bi. At high oxygen concentration, an oxide layer could be formed on the steel surface (lead oxides are less stable than iron oxide), which protects it from corrosion. At low oxygen concentration, there is no oxidation and corrosion occurs by dissolution of the steel components in the liquid metal. [Balbaud-Celerier and Barbier, 2001] The surface of oxide layer in contact with the bulk flow of liquid metal may also be eroded under a high fluid velocity. Then the metal of surface will no longer be under protection because a porous oxide layer will be formed.

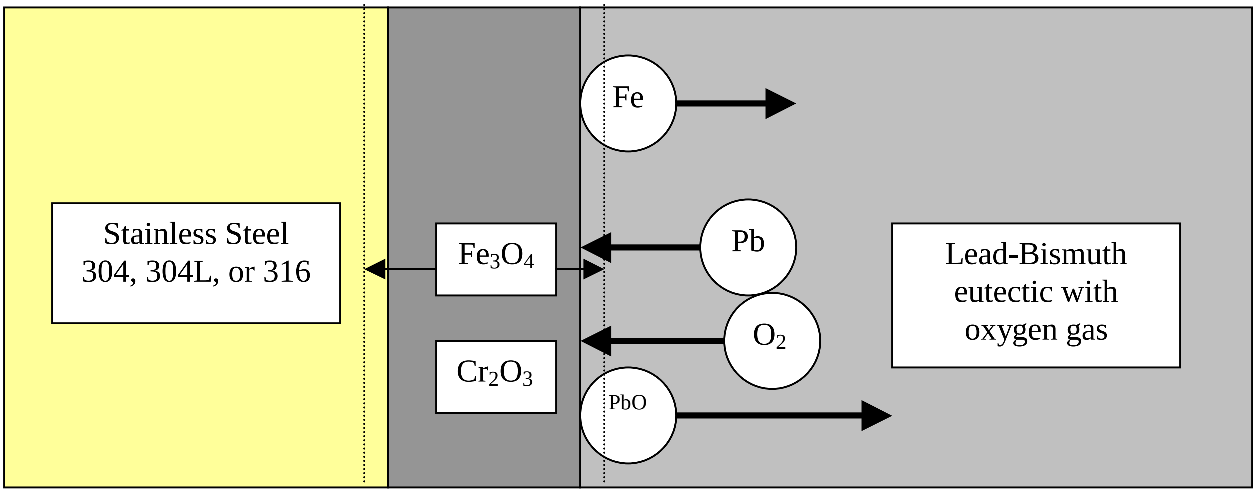


Figure 1. Schematics of corrosion processes between the metal surface and the liquid metal

Balbaud-Celerier and Barbier have indicated that the different mechanisms of combined action of flow and corrosion lead to basically four types of flow-induced corrosion: mass transported-controlled corrosion, phase transport-controlled corrosion, erosion-corrosion and cavitation-corrosion. The main interactions between a flowing fluid and a solid surface are dependent on momentum transport and mass and heat transfer such as convective diffusion-controlled and kinetics-controlled._A justification of the need of this parametric approaches is the fact that some of the kinetics and mass transfer coefficients are not well-known and defined yet. Also previous published studies indicate the importance of the thermal-hydraulics on the corrosion and core flow reactions. (i.e.. Ballinger and Lim report 2000) Oxygen is added into LBE to form iron oxide on the stainless steel pipe surface. The reaction is very fast at first stage. Later O_2 will diffuse into the oxide layer and make the layer expand in both directions. In this way, the dissolution of many metal elements in steel can be greatly decreased. From present research status, researches on LBE corrosion problem with high O_2 concentration have not yielded any validated data yet. But there are some models been published for low O_2 concentration.

Chemical kinetics may be described as the study of chemical systems whose composition changes with time. These changes may take place in the gas, liquid, or solid phase of a substance. A reaction occurring in a single phase is usually referred to as a homogeneous reaction, while a reaction which takes place at an interface between two phases is known as a heterogeneous reaction. An example of the latter is the reaction of a gas adsorbed on the surface of a solid.

The chemical change that takes place in any reaction may be represented by a stoichiometric equation such as

$$aA + bB \rightarrow cC + dD$$

where a and b denote the number of moles of reactants A and B that react to yield c and d moles of products C and D. For example, the formation of lead oxide from iron oxide and lead may be written as the balanced, irreversible chemical reaction. After quick formation of oxide film on the surface, the dissolution of metal elements is down to a negligible level. The concentration of iron in bulk flow is decided by following reaction:

$$\frac{1}{4}Fe_3O_4 + Pb = \frac{3}{4}Fe + PbO$$

It is of great significance to track the concentration of iron, so that we can prevent the clogging in loop. By focusing on this, we are able to provide valuable data for loop design.

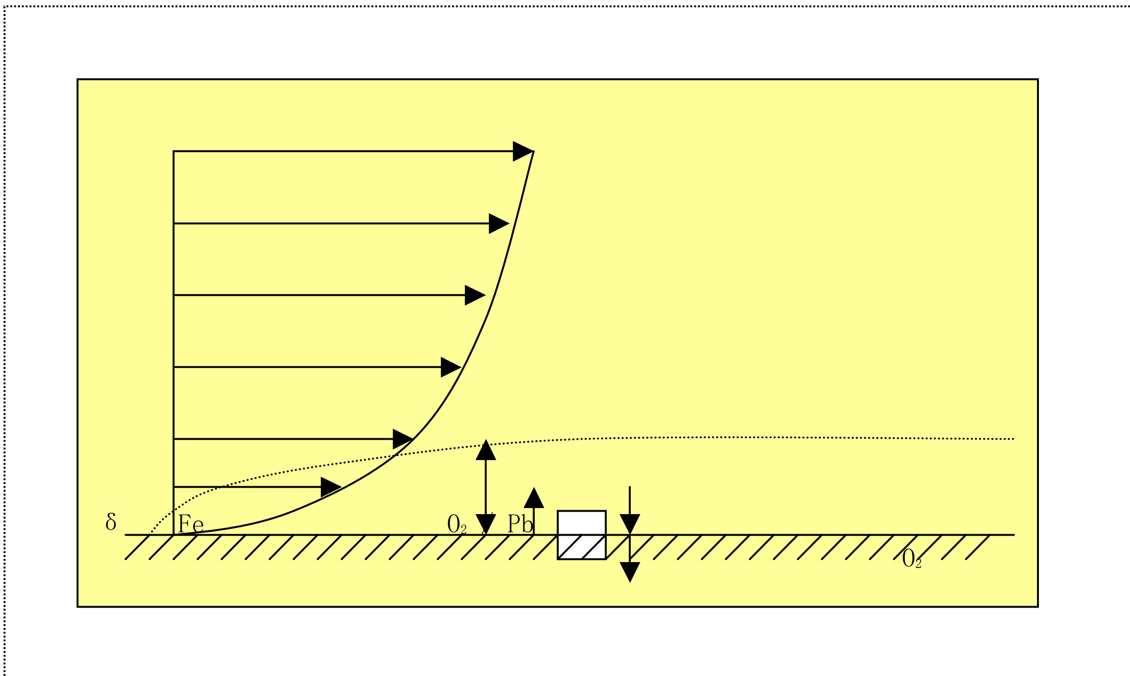


Figure 2. The diffusion process of species through the hydrodynamics boundary layer

The change in composition of the reaction mixture with time is the rate of reaction, R. The rate of consumption of reactants A and B and the rate of formation of products C and D can be written as

$$R = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[d]}{dt}$$

In virtually all chemical reactions that have been studied experimentally, the reaction rate depends on the concentration of one or more of the reactants. In general, the rate may be expressed as a function of these concentrations,

$$R = f\left([A],[B]\right)$$

In some cases the reaction rate also depends on the concentration of one or more intermediate species, e.g. in enzymatic reactions. In other cases the rate expression may involve the concentration of some species which do not appear in the stoichiometric equation; such species are known as catalysts. The most frequently encountered functional dependence given by above equation is the rate's being proportional to a product of algebraic power of the individual concentrations, i.e.,

$$R \propto [A]^m [B]^n$$

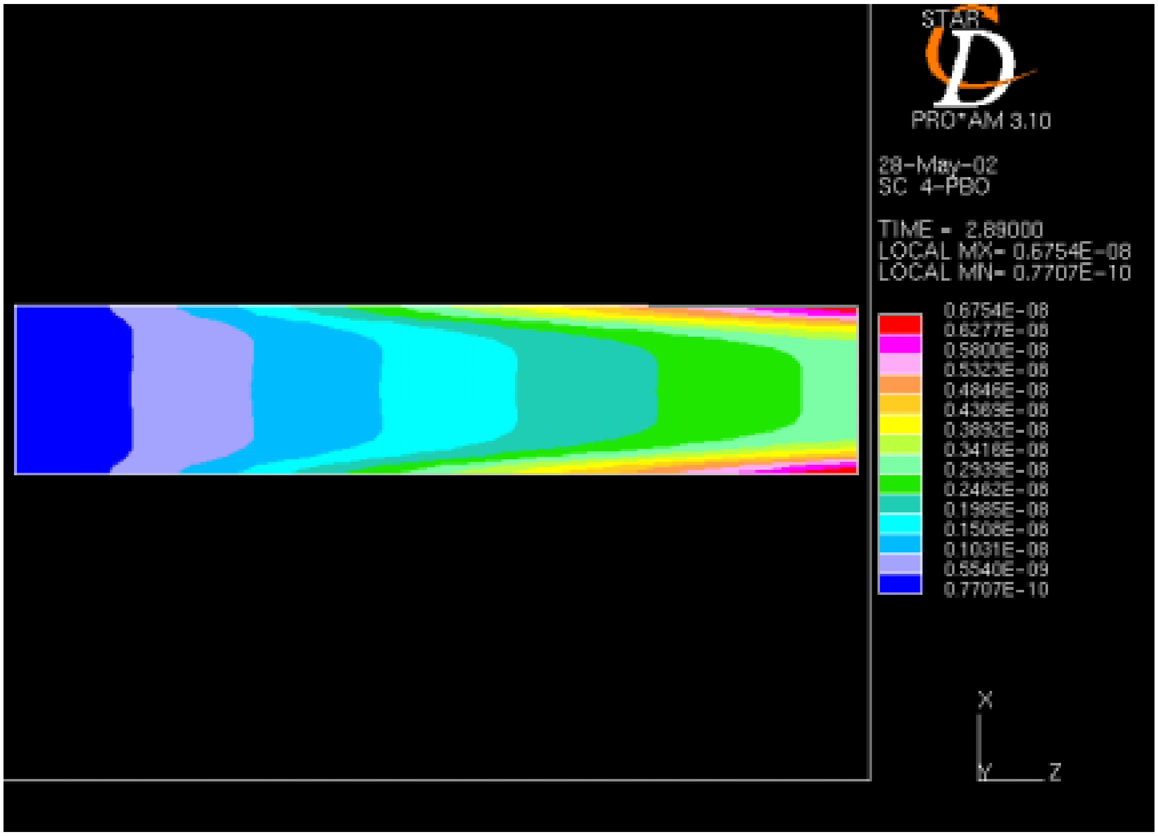
The exponent m and n may be integer, fractional, or negative. This proportionality can be converted to an equation by inserting a proportionality constant k, thus;

$$R = k[A]^m [B]^n$$

This equation is called a rate equation or rate expression. The exponent m is the order of the reaction with respect to reactant A, and n is the order with respect to reactant B. The proportionality constant k is called the rate coefficient. The overall order of the reaction is simply p=m+n. Since the mechanisms of reactions are not well defined, the reaction rates will also be studied parametrically.

As a sample of the analysis done so far on the core reaction chemistry a sample of the PbO concentration is shown in figure 3 with a listing of the boundary conditions imposed on the results of this STAR-CD run. The figure shows the low concentrations of the PbO at the inlet and their eventual increase as the flow progresses from left to right. Some profiles of this concentration are seen transversely across the pipe and these are suspected to be due to the effects on the velocity profiles in the transverse direction as well where higher mixing rates would be expected near the core region as opposed to the wall region. Work is proceeding with finalizing runs to obtain information about surface corrosion chemistry on the pipe's inside surface.

The second subtask and the more important objective of this project is to use the information supplied by the first subtask as the boundary conditions for the kinetic modeling of the corrosion process at the internal walls of the test loop. The outcome between wall conditions and the core will be obtained from the use of a subroutine attached to the STAR_CD code. The subroutine is named CHEMKIN and is supposed to do the surface corrosion analysis on the inner metal surface of the loop piping. Hence the steady state corrosion/precipitation in an oxygen-controlled LBE system will be investigated through the help of this code on both the thermal-hydraulic and chemical kinetics. The information is expected to help predict the likely locations for corrosion and precipitation along the axial length of parts of the test loop. Also an



Initial Concentration of Oxygen ------- 5.E-08
Initial Concentration of Lead ----------- 0.999999
Initial Velocity ------------------------------- 1.9m/s
Initial temperature of the fluid --------- 900K

Figure 3. Typical Results of PbO Concentrations in the Core Region of Flow As Predicted by STAR-CD

attempt will be made to model one sample insert into one of the above predefined and studied geometries proposed above.

1. Background and Rationale

Lead bismuth eutectic (LBE) has been determined from previous experimental studies by the Russian and the European scientific communities to be a potential material that can be used as a spallation target and coolant for AAA-proposed applications.

Properly controlling the oxygen content in LBE can drastically reduce the LBE corrosion of structural steels. However, existing knowledge of material corrosion performance was obtained from point-wise testing with very limited density. The transport of oxygen and corrosion products, and their interaction and variation of corrosion/precipitation along the flow are not well understood. This has been illustrated by the work of Xiaoyi and Li and was recently presented at seminars and meetings at UNLV by Dr. Ning Li of Los Alamos National Laboratory.

An experimental study monitored corrosion history of specimens in one test loop over several thousand hours and showed that corrosion would occur at higher temperatures, i.e. 550 C, but precipitation occurs around 460 C, which is at the intermediate temperature level. This confirms that the temperature distribution in an LBE system is important for understanding system corrosion performance.

The proposed research is divided into three phases. Each phase will be carried out over a one-year period.

- Phase I will simulate the application and validity of a commercially available thermal-hydraulics/ surface corrosion code to predict the corrosions effects on the tube walls for a number of loop conditions.
- Phase II will simulate numerically and using a parametric approach the effects of several parameters such as mean bulk eutectic axial velocities, mean bulk eutectic temperatures, mean inlet oxygen concentrations on the corrosion effects on the loop inner walls . An attempt will also be made to study corrosion (numerically) on a predetermined metal testing sample placed inside the loop.
- Phase III will involve the experimental testing of placing these components inside the loop and obtaining experimental data on corrosion effects for comparison with results of Phase II.

2. Research Objectives

The following are the three research objectives for Year Two of this project:

1. Predict the distributions of LBE streamwise velocity, temperature and oxygen and corrosion product concentrations in the test loop in the interior of the LBE flow for several partial loop sections using the parametric study approach for several of the parameters mentioned above i.e. inlet flow velocity, inlet bulk temperatures and inlet average oxygen concentrations.
2. Attempt a surface corrosion simulation for a sample placed inside one of these partial loop sections.
3. Attempt to compare some of the simulation results with any experimental data that maybe available in the literature. So far not much experimental data was found in the open literature to compare with in regards to these simulation results. Experimentally determining these corrosion rates are beyond the means available to this project but perhaps other AAA might be interested in taking the task on as it is important data.

The simulation in the bulk region of the test loop can use STAR-CD in a basic 2-D mode along the axial direction and the radial direction. The results of values of oxygen and corrosion concentrations, axial velocity and temperature will be obtained at a location close to the wall.

Appropriate models for the flow regime will be incorporated for this bulk flow such as two-equation models for turbulent flow when the need arises.

STAR-CD will accept thermophysical properties that are functions of temperature to be used as inputs into the conservation equations.

The second objective requires that we will look more closely at the reaction rates close to the wall where structural metals react with oxygen. Since the reaction kinetics of oxygen and substrate in the LBE loop is not well understood, a parametric study of chemical kinetics is needed to understand the corrosion process in the LBE loop design.

This parametric study will be coupled with CFD from the first subtask. The velocity of the LBE in the loop along with the temperature, oxygen, and corrosion product concentrations will be predicted close to the substrate to support the calculation of corrosion and precipitation rates in the entire system.

An attempt to compare a set of results of the second subtask with existing experimental data to ascertain the validity of the model and will look to see how improvements and tweaking can be made to both models of subtasks 1 and 2.

All of the above work will be performed with close communication with LANL scientists to ensure that the objectives of the research are appropriately focused on AAA Project needs.

Technical Impact

Corrosion effects on U.S. steels: The AAA Project requires a more thorough understanding of the effect and rates of corrosion inside LBE systems. Direct testing, although absolutely essential, can be relatively expensive, time consuming and inadequate to predict system corrosion performance beyond test conditions.

Results of previous experimental studies: Several U.S. steels [316 (tube), 316L (rod), T-410 (rod), HT-9 (tube), and D-9 (tube)] in an oxygen controlled LBE flow loop have been tested at the Institute of Physics and Power Engineering (IPPE) in Obninsk, Russia. These tests were contracted by LANL. In the tests, the Russia steel EP823 (rod) was also included for comparison. These samples were inserted in IPPE's CU-1M non-isothermal loop for time intervals of 1000, 2000 and 3000 hours at two temperatures of 460 C and 550 C. The oxygen level in LBE is controlled at 30-50 ppb by weight. The velocity in the test section is around 1.9 m/s, typical of coolant flow in LBE-cooled reactor cores. Local metal corrosion, typically on T410 and 316L have been observed in these tests. The proposed research will should help explain these observations.

Long term effects: There also exists an initial oxidization stage lasting about 2000 hours in which the formation of oxide films are observed at both corrosion and precipitation sites. The corrosion rate beyond this initial stage is quite different from that in the initial stage. Corrosion occurs at a site at 550 C, but precipitation appears to occur at a site at 460 C. This implies the results from a site at 460 C cannot be used to predict performance of materials at the same temperature but in a different location in a system.

Asymptotic corrosion rates prediction: Using CFD with chemical kinetics can assist the experimental design to get reliable data for the asymptotic corrosion rate and the thickness of the oxide films that is non-uniform along the flow direction. In addition, a predictive capability needs to be established in the U.S. through the use of CFD codes coupled with knowledge about the reaction chemistry and kinetics of these potential corrosion rates so that if new components need to be investigated as far as their behavior when exposed to LBE and oxygen one can use the code with reasonable confidence after its proper validation.

Primary Hurdles: One of the technical hurdles to overcome is to develop an efficient numerical model that has the right chemistry reaction rates for use in different components of a typical LBE flow loop.

Research Approach for Phase II

The proposed project has been broken into five tasks for the Phase II (second year of funding). Two graduate students will be involved in this effort (Kanthi Dasika and Chao Wu).

1. Literature search: A detailed literature search and documentation will be made in the open literature and especially the European and Russian (English language publication) literature to find more completely what has been done in this research topic. Dr. Li has indicated that this area of modeling is still in its infancy and hence the interest in the proposed research.
2. Nodal models already prepared from Phase I study will be used to perform the parametric study to investigate the effect of several parameters on the corrosion simulated rates. This part of the study points out the importance of the thermal-hydraulic conditions close to the wall on the corrosion dynamics on that wall surface. This fact is highlighted by a recent report written by Ballinger and Lim (2000) emphasizing the first effect on the second one. These parameters are:
   a-average inlet eutectic axial bulk velocity would determine the velocity profiles close to the wall.
   b-average eutectic inlet temperature will determine average simulated temperature values and to a certain if heat flux conditions are known the temperature profiles close to the wall.
   c-average cross-sectional inlet oxygen weight percent of oxygen to eutectic which determines the overall core oxygen values and also how much oxygen is available for surface reactions after any potential reactions with the core materials is exhausted.
3. Testing and shakedown of developed models with their related corrosion models will be used to run some limiting cases of the parameters to make sure reasonable thermal-hydraulic/corrosion kinetic values of the variables are obtained. This step includes the injection of the appropriate reaction rates in the bulk region of the loop/system for reactions between the LBE and oxygen.
4. Presentation of the results of the simulation in item 3 and for all the other intermediate parametric values chosen so that as complete a picture as possible is obtained of the variation of corrosion kinetics as a function of these parameters.

5. Reporting requirements: weekly updates may be reported to the Intercollegiate Programs Coordinator, monthly updates will be provided to the UNLV AAA Program Director, quarterly progress reports will be delivered to the UNLV AAA Program office and LANL researchers overseeing the project. A final report will also be published as well as papers in conferences and journals at the end of the project.

Research Approach for Phase III

Experimental effort: The LANL Materials Test Loop (MTL) offers an excellent platform to perform testing for validation and improvement of the model. There is also a possibility that a LBE test loop will be built at UNLV. This would offer an opportunity to validate some of the simulation results performed in Phase I and Phase II by performing the necessary long-term corrosion experiments for these objects.

Capabilities at UNLV and LANL

UNLV has a 2000 ORIGIN parallel processor with several other mainframes for the purpose of this computational task. The university is consistently trying to increase the number of processors available on this machine to speed up the processing time needed for large-scale problems.

Prof. Samir Moujaes is an Associate Professor of Mechanical Engineering at the University of Nevada, Las Vegas and will serve as Principal Investigator for this project. Prof. Moujaes has worked for five years on computational aspects of cooling of canisters for the Yucca Mountain Project for DOE. Two emplacement configurations of high level waste containers were investigated and the temperature profiles and air velocity profiles under natural convection conditions were calculated. Other computational work involved developing two- and three-dimensional models for the description of heat transfer processes in residential gabled attics under the influence of the three modes of heat transfer. Currently a model is also being developed to describe the interaction of this heat transfer on the heat pickup of the supply air through a typical attic placed supply duct. Other experimental work has involved two-phase flow hydrodynamics and the determination of profiles of localized values of void fraction and dispersed phase axial velocity through the use of locally developed dual-tipped fiber optics probes. Prof. Moujaes has also been involved with R&D on the testing for three-phase hydrodynamics and heat transfer of slurry derived from coal for a Solvent Refined Coal (SRC-I) process. He has published several papers in ASME, ASHRAE, and the Journal of Energy Engineering and is a reviewer for these organizations. He is an Associate Editor for the JEE and has also organized and chaired sessions in some of their conferences.

Prof. Yi-Tung Chen is Research Associate Professor of the Department of Mechanical Engineering and Interim Director of the NCACM at the University of Nevada, Las Vegas. He received his B.S. degree in Chemical Engineering in 1983, and his M.S. and Ph.D. degrees in Mechanical Engineering in 1988 and 1991, respectively, from the University of Utah. He has a minor degree in Nuclear Engineering. Prof. Chen is an expert in experimental and computational aspects of momentum, heat, and mass transfer. His research interests include chemical kinetics modeling, high level radioactive waste repository design, atmospheric sciences, magnetohydrodynamics modeling, ground water transport, energy conservation, and biomedical engineering. He also has a strong background in organic chemistry, biochemistry, polymer chemistry, and physical chemistry. His research experience includes being PI and co-PI on projects involving the study of flow and heat transfer and species transport in unsaturated porous media funded by DOE, the burning of rocket motors under the Joint Demilitarization Technology (JDT) program funded by DoD, and atmospheric modeling funded by the NOAA Cooperative Institute for Atmospheric Sciences and Terrestrial Applications. He is also co-PI on an EPA project dealing with environmental monitoring for public access and a groundwater modeling project funded by DOE.

Dr. Ning Li, staff scientist from LANL will be the AAA Project collaborator of this project as he is one of the original participants and designers of the model target geometry that was devised and tested at IPPE. Hence, he has an interest in exploring what some of the CFD results show and how they compare with experiments for predictive purposes. Dr. Li does not require funding from UNLV to participate in this project.

Project Timetable and Deliverables

Two meetings are scheduled for the second year of the project. The first to discuss preliminary results of code simulations and the second towards the end of Year One to present final results and obtain feedback from collaborators.

Time Schedule and Major Milestones

	Qtr 1			Qtr 2			Qtr3			Qtr 4		
Tasks	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug
1. Literature search	■											
2. Development of model	■	■	■	■	■	■	■					
3. Testing and shakedown for items 2&4								■	■			
4. Development of chemical kinetics model at wall	■	■	■	■	■	■	■					
5. Running and presentation of results for item 2								■	■	■	■	■
6. Running and presentation of results for item 4								■	■	■	■	■
7. Reporting Requirements												
Travel for LANL for meetings												
TRIP EXPLANATION												
Trip 1	To discuss with LANL scientists progress so far on modeling effort											
Trip 2	To discuss and obtain feedback from LANL on preliminary final results											

(Work is assumed to begin September 1, 2002).

Los Alamos NATIONAL LABORATORY Advanced Accelerator Applications Addressing the Nation's Nuclear Needs PROGRAM

From: Ning Li, Ph.D.
AAA, Los Alamos National Laboratory

Date: July 12, 2001

To Whom It May Concern:

Corrosion and materials compatibility in LBE systems present one of the critical challenges in the R&D areas of AAA, especially for deploying high-powered LBE spallation targets. Testing experience exists in Russia for specially developed alloys, but it is sorely lacking for US materials. Limited preliminary testing showed promise of some candidate steels. In any case, test results cannot be applied to systems with conditions different from the test loops used without better understanding of the influence of flow and temperature distributions on corrosion in LBE systems. This is demonstrated in the modeling effort we undertook at LANL ("A Kinetic Model for Corrosion and Precipitation in Non-isothermal LBE Flow Loop", Journal of Nuclear Materials (2001)).

I have had several technical discussions with Drs. Moujaes and Chen on modeling the system corrosion performance in oxygen-controlled LBE systems, and interacted with them throughout the preparation of the proposal. I think some very unique and valuable results will emerge from this work, and will help the AAA Program establish international leadership in this particular area. I strongly support the proposal "Modeling Corrosion in Oxygen Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrodynamics" by Drs. Moujaes and Chen.

Yours truly,

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(Ning Li)