ARGONNE NATIONAL LABORATORY ANNUAL REPORT OF LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM ACTIVITIES FOR FY 1994

Strategic Planning Group
Office of The Director
February 15, 1995

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Argonne National Laboratory
Annual Report of Laboratory Directed Research and Development Program Activities for FY 1994

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Materials Science and Technology

Computational Science and Technology

Biological Sciences

*CCST projects

INTRODUCTION

Program Overview

The purposes of Argonne's Laboratory Directed Research and Development (LDRD) Program are to encourage the development of novel concepts, enhance the Laboratory's R&D capabilities, and further the development of its strategic initiatives. Projects are selected from proposals for creative and innovative R&D studies which are not yet eligible for timely support through normal programmatic channels. Among the aims of the projects supported by the Program are establishment of engineering proof-of-principle; assessment of design feasibility for prospective facilities; development of an instrumental prototype, method, or system; or discovery in fundamental science.

Several of these projects are closely associated with major strategic thrusts of the Laboratory as described in Argonne's Five Year Institutional Plan, although the scientific implications of the achieved results extend well beyond Laboratory plans and objectives. The projects supported by the Program are distributed across the major programmatic areas at Argonne as indicated in the Laboratory's LDRD Plan for FY 1994. The following table displays the area of principal emphasis (indicated by an "X") as well as additional area(s) (indicated by an "O") to which a contribution was made by each FY 1994 project.

A brief description of Argonne's LDRD management process and a table of funding profiles for each project active in FY 1994 then follow. The FY 1994 DOE approved funding cap was $15 million or about 3.5% of Argonne's estimated FY 1994 operating budget. Actual expenditures amounted to $11.865 million. Individual reports summarizing the purpose, approach, results and accomplishments of projects funded under Argonne's LDRD Program for FY 1994 comprise the bulk of this report.

Finally, Appendix A summarizes funding and topics of new projects begun to date in FY 1995.

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Proposal Number	Advanced Accelerator and Detector Technology	X-Ray Techniques for Research in the Biological and Physical Sciences	Nuclear Technology	Materials Science and Technology	Computational Science and Technology	Biological Sciences	Environmental Science	Environmental Control and Waste Management Technology	Novel Concepts in Other Areas
94-001N	X			O					
92-022R2	X								
94-057N	X								
93-151R1	X			O					
94-144N	X			O					
92-162R2	X	O							
94-191N	X			O					
94-192N	X	O							
92-182R2	X								
93-002R1	O	X							
93-003R1		X							
93-004R1		X							O
93-007R1		X		O					
94-142N		X							
93-150R1		X		O					
93-152R1		X							
93-041R1		X	O						
94-193N		X							
94-002N			X		O				
94-015N			X	O					O
93-047R1			X						
93-043R1			X						
93-040R1			X	O					O
92-047R2			X		O				
94-046N			X						
94-112N			X	O					
94-114N			X					O	
94-186N			X					O	
94-187N			X	O					

1994 AREAS OF TECHNICAL IMPACT

Proposal Number	Advanced Accelerator and Detector Technology	X-Ray Techniques for Research in the Biological and Physical Sciences	Nuclear Technology	Materials Science and Technology	Compu-tational Science and Technology	Biological Sciences	Environ-mental Science	Environ-mental Control and Waste Manage-ment Technology	Novel Concepts in Other Areas
94-032N				X					
94-053N				X					
94-055N				X					
92-023R2				X					
94-058N		O		X					
94-059N		O		X					
94-060N		O		X					
94-103N				X	O				
94-165N				X				O	
94-169N				X					
94-179N				X				O	
94-182N				X				O	
94-133N				X					
94-047N			O		X				
94-054N					X				
94-190N					X				
94-194N					X	O			
93-097R1						X			
92-180R2						X			
93-090R1					O	X			
92-160R2						X	O	O	
92-108R1						X			
93-156R1					O		X		
94-106N					O		X	O	
91-034R1					O		X		
94-154N							X		
94-157N					O		X		
94-033N								X	
93-094R1								X	

1994 AREAS OF TECHNICAL IMPACT

Proposal Number	Advanced Accelerator and Detector Technology	X-Ray Techniques for Research in the Biological and Physical Sciences	Nuclear Technology	Materials Science and Technology	Compu-tational Science and Technology	Biological Sciences	Environ-mental Science	Environ-mental Control and Waste Manage-ment Technology	Novel Concepts in Other Areas
94-102N				O			O	X	
94-115N			O					X	
94-117N			O					X	
94-118N			O	O				X	
94-167N								X	
94-003N			O						X
94-056N									X
93-006R1		O							X
93-091R1		O		O				O	X
94-168N					O				X

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LDRD Management Process

Research and development activities at Argonne are organized under four associate laboratory directors who oversee the research conducted in 23 programmatic divisions. At the top of the organization is the laboratory director. He is assisted by the chief operations officer (who manages the Laboratory's physical plant and support functions), the chief financial officer, and the deputy to the laboratory director (who heads the Strategic Planning Office). This group of eight sit as the Strategic Planning Board and make final recommendations concerning laboratory directed R&D.

Responsibility for all final decisions concerning Argonne's LDRD program resides with the laboratory director. Certain responsibilities regarding funding, oversight, proposal evaluation, and project direction are delegated. The laboratory director also delegates selection of a fraction of LDRD projects to individual associate laboratory directors and retains the prerogative to make his own selections as well. Beginning in FY 1995, and as described in the FY 1995 LDRD Plan, another fraction is reserved for support of the Director's Individual Investigator LDRD Program, which uses a peer review committee to evaluate relatively small, short-term, single investigator proposals. The remainder of projects is selected by the Strategic Planning Board, which is also charged with recommending the proportion to be delegated to other LDRD components. In FY 1994 the Board retained selection prerogative for projects totaling 98% of the LDRD budget. In FY 1995 the corresponding figure is about 85%. The laboratory director coordinates plans for the various components of the program. For FY 1994, the laboratory director authorized a special emphasis on proposals that integrate basic and applied research and instituted a screening panel, the Coordination Council for Science and Technology (CCST), to solicit and present proposals to the Strategic Planning Board. An addendum to Argonne's FY 1994 LDRD Plan describes this fully. Proposals of all types are reviewed by the Strategic Planning Office for adherence to DOE guidelines and laboratory administrative procedures. They are then reported to the laboratory director, who must approve them in terms of content and aggregate budget. At the end of the fiscal year, accomplishments of all LDRD projects are reported to the laboratory director and DOE. As examples, calls for proposals and proposal guidance issued in 1994 are attached as exhibits A through H. The charge to the CCST is attached as exhibit I. The charge to the Director's Review Committee for the Individual Investigator Program is attached as exhibit J.

Coordination, oversight, and administration of the Laboratory's LDRD program is the responsibility of the deputy to the laboratory director. He is assisted by the associate director of the Strategic Planning Group, who has direct responsibility for the day-to-day administration of the LDRD program and for coordination of LDRD reports and plans. Responsibility for the actual conduct of all laboratory directed R&D resides individually with the associate laboratory directors and their line managers. Flow charts attached here as Figures 1 through 4 schematically describe the administrative processes for the various components of the Program.

The LDRD program is funded lab-wide through the Laboratory's indirect budget which derives from a uniform levy against all program operating budgets. The bulk of the initially planned LDRD budget is committed near the beginning of the fiscal year after most proposals have been evaluated (during September and early October). The laboratory director and the Strategic Planning Board maintain the option to fund new starts during the year either by increasing the

total LDRD budget plan (within the DOE approved cap) or by redirection of previously authorized funds. Although many projects propose two or three year durations, funding levels and project selection are determined annually, based on technical progress and the Laboratory's strategic goals and resources.

Figure 1

Argonne's LDRD Administrative Process:
Centralized Program

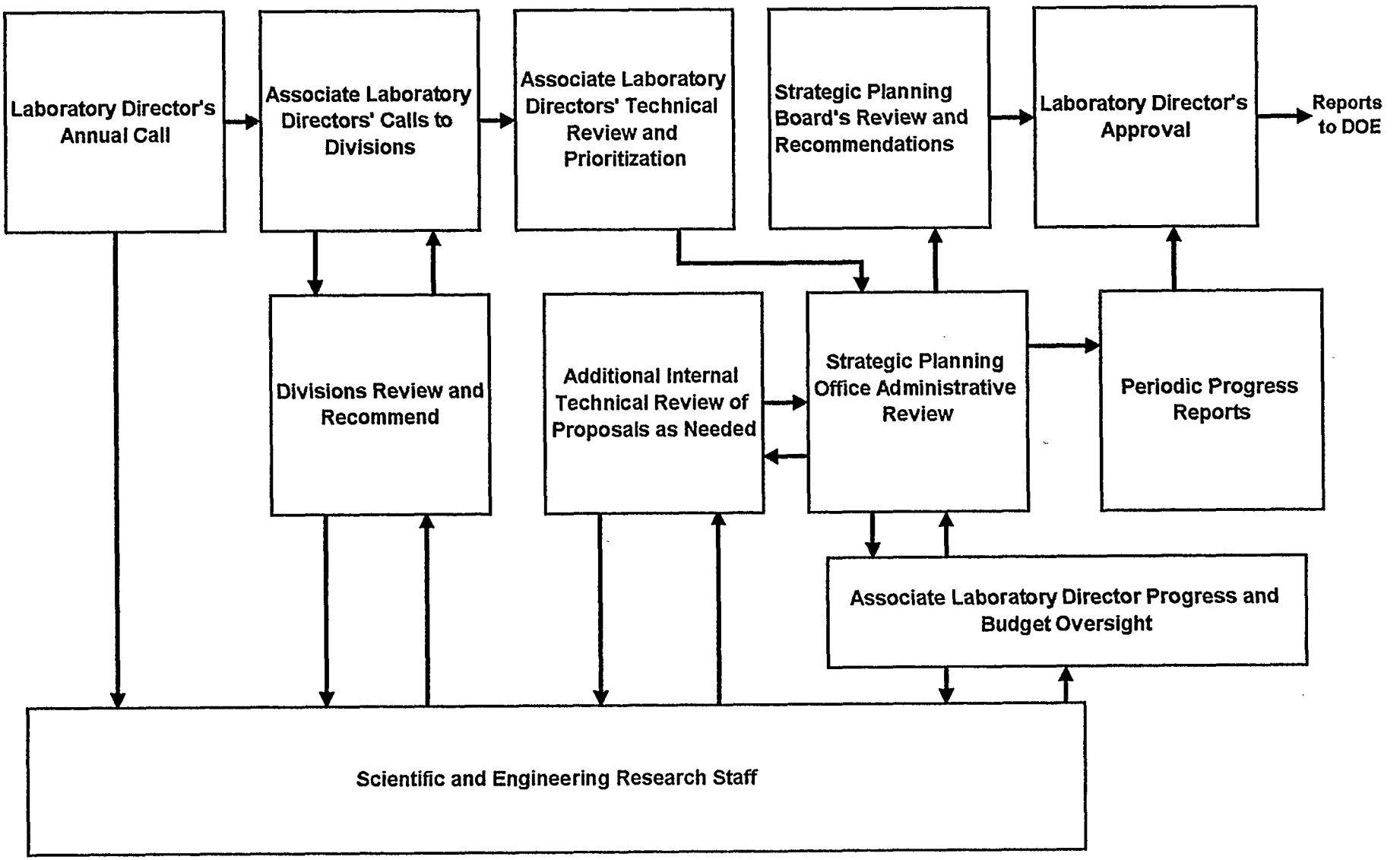


Figure 2

Argonne's LDRD Administrative Process:
Coordinating Council for Science and Technology (CCST)

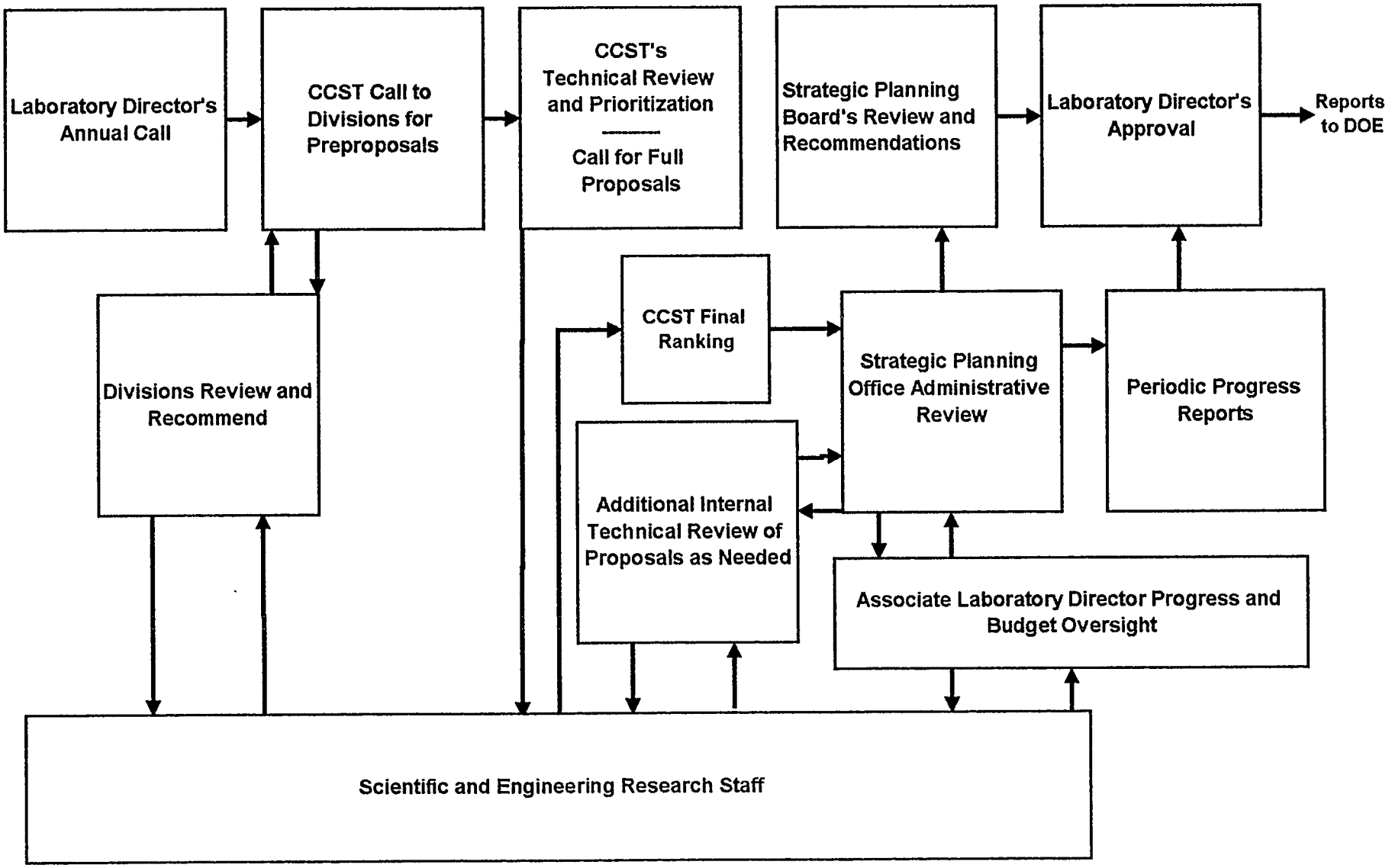


Figure 3

Argonne's LDRD Administrative Process:
Decentralized Program

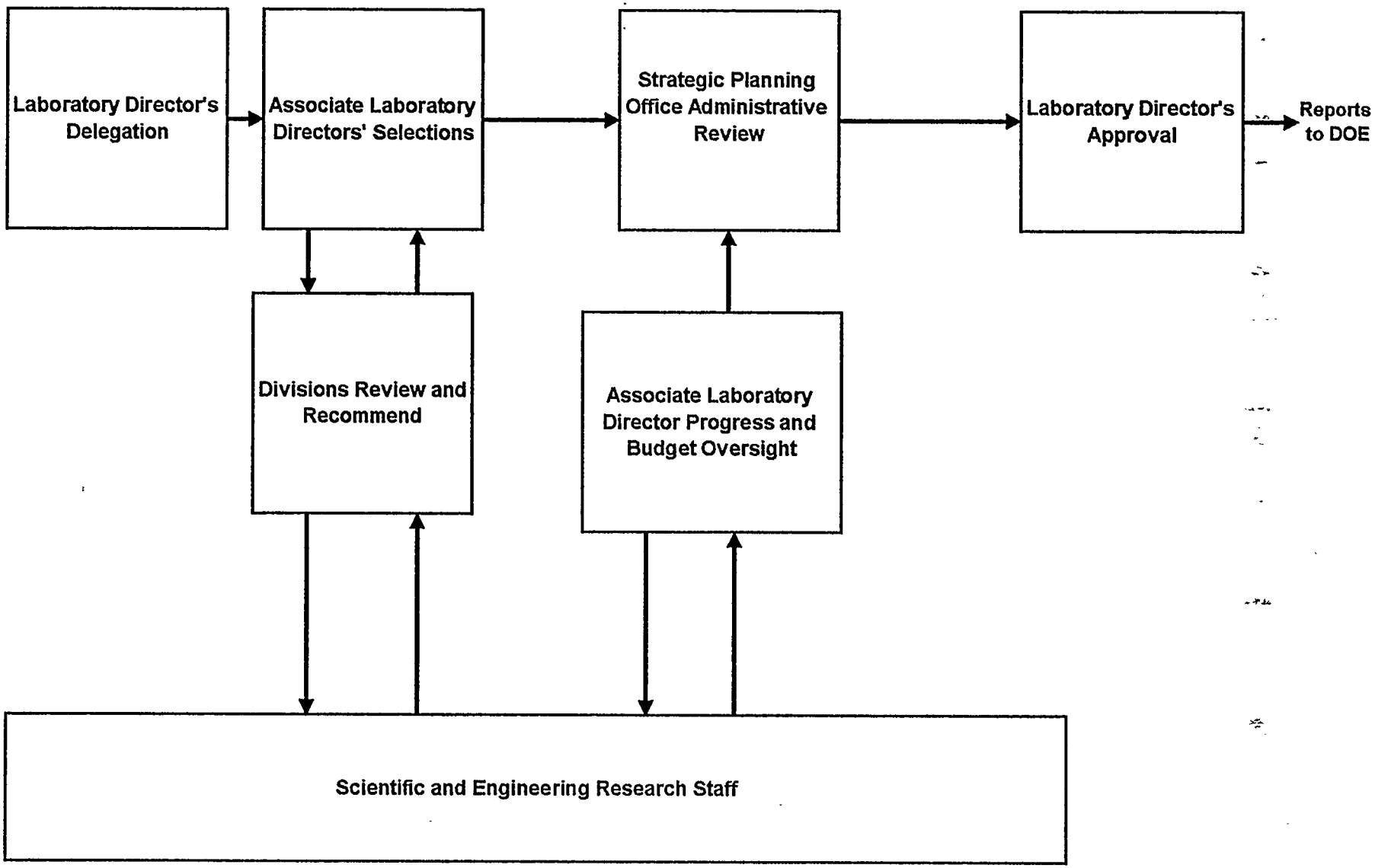
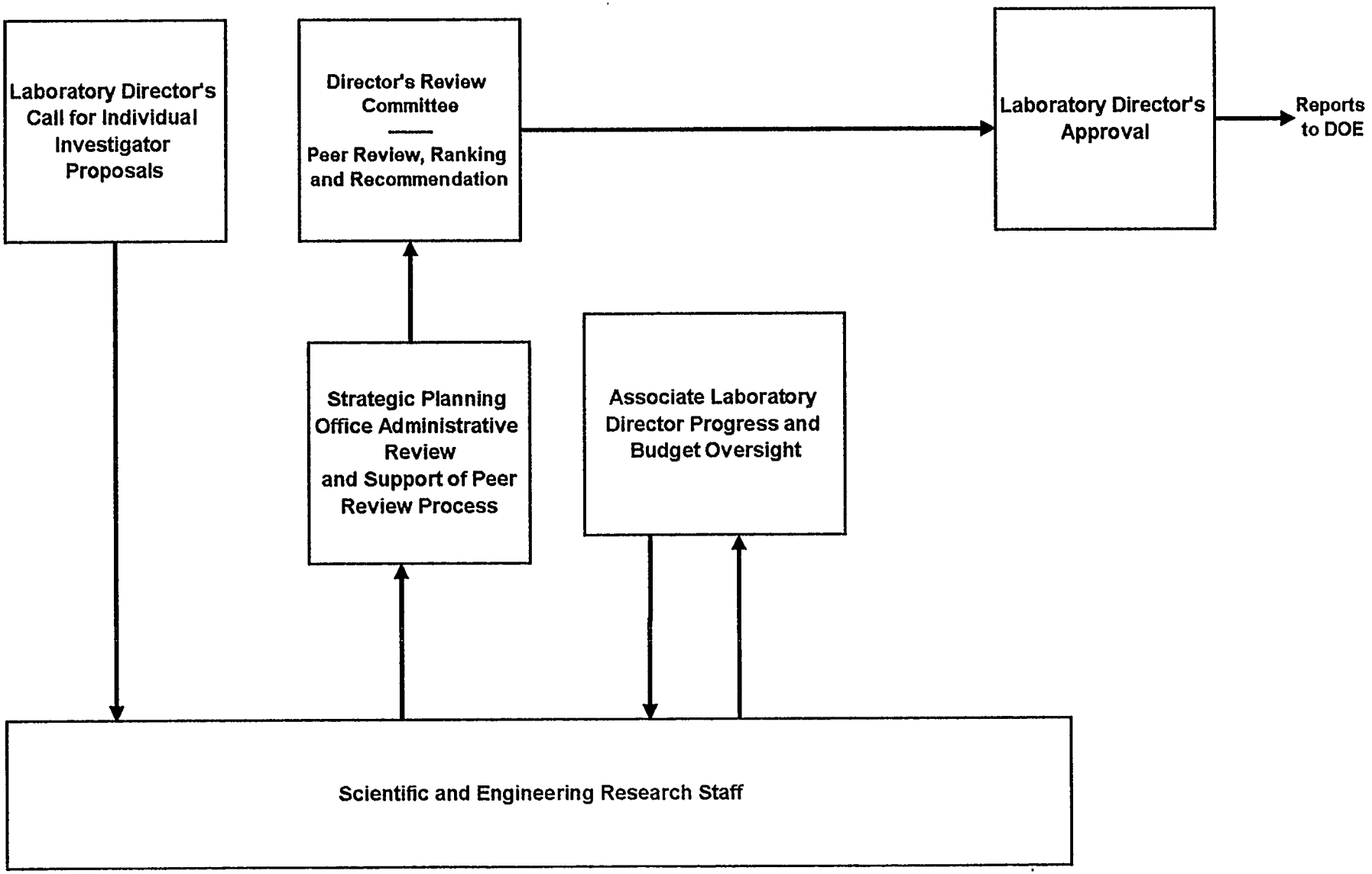


Figure 4

Argonne's LDRD Administrative Process:
Individual Investigator Program



ARGONNE NATIONAL LABORATORY

Exhibit A

INTRA-LABORATORY MEMO

DATE: May 3, 1994

TO: Argonne Technical Staff

FROM: A. Schriesheim

SUBJECT: **FY 1995 LDRD Proposals**

Proposals to the Laboratory Directed Research and Development (LDRD) Program are now being solicited for fiscal year 1995. I encourage you to propose novel and innovative ideas in your field of expertise that might qualify for LDRD support. The LDRD program is small compared to major Laboratory programs. However, just as past LDRD projects were the basis for some of our large programs today, I expect several projects you propose for next year will be building blocks for Argonne programs of the future. LDRD both enhances our research capabilities and tests exciting new concepts as it advances the Laboratory's overall strategic plan. Our vitality as a leading R&D resource for the nation can be assured through programs such as LDRD.

Current guidelines for LDRD proposals are being distributed to Associate Laboratory Directors. They will be available from division offices through which proposals should be submitted. Argonne's Coordinating Council for Science and Technology will soon issue a supplementary call and guidance specifically for proposals linking applied and basic research. I expect we will see an impressive set of innovative proposals for FY 1995.

AS/ENK:jr

c: J. Asbury
H. Drucker
F. Fradin
E. Kaufmann
D. Moncton
J. O'Kelley
R. Teunis
C. Till

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ARGONNE NATIONAL LABORATORY

Exhibit B

INTRA-LABORATORY MEMO

DATE: May 3, 1994

TO: H. Drucker
F. Fradin
D. Moncton
R. Teunis
C. Till

FROM: A. Schriesheim

SUBJECT: Call for FY 1995 Laboratory Directed Research and Development Proposals

Guidelines for the submission of project proposals for consideration for support under the Laboratory Directed Research and Development Program are attached. Please transmit this call for proposals to staff in your area. With your divisions and staff, you should assure that each proposal received is technically reviewed and is screened for conformance with DOE and Laboratory guidelines and acceptance criteria. Proposals which do not meet LDRD criteria will be returned.

DOE 5000.4(a), the relevant Order defining LDRD procedures and content, is attached for your reference. Section 9 of the Order is most pertinent for responding to this call.

A sample proposal format is also attached and must be followed to facilitate record keeping and reporting requirements. In addition, a one-page evaluation form must be completed for each proposal.

We estimate that the FY 1995 funding level for the LDRD Program will total $12 million, unless future budget developments suggest a change at a later date. All proposals submitted, a memo stating your recommended priorities, and a list of technical staff who aided in the technical review process should be submitted to Elton Kaufmann, Strategic Planning Office, no later than July 1, 1994. I plan to complete the review and allocation process with the Strategic Planning Board during September. Once our FY 1995 Laboratory budget is better defined, I will notify you of the amounts set aside for our decentralized (ALD discretionary) LDRD program.

You may expect a subsidiary call for proposals through our Coordinating Council for Science and Technology (CCST) which adds special criteria to the general ones in the attached. Please **do not submit duplicate proposals** both through the CCST and directly to the Strategic Planning Office.

AS/ENK:jr
Attachments

c: J. Asbury
J. Day
M. Hennebry
R. Huebner
E. Kaufmann
L. LeSage
J. O'Kelley
E. VanBerkum

ARGONNE
NATIONAL
LABORATORY

Exhibit C

INTRA-LABORATORY MEMO

May 31, 1994

TO: Division Directors
Department Heads
Program Managers

FROM: H. Drucker HD — ALD, EEST
F. Fradin FF/mw — ALD, PR

SUBJECT: Call for Science and Technology LDRD Preproposals

We assume that the Coordination Council for Science and Technology (CCST) will be involved again in reviewing LDRD requests for projects bringing together basic and applied scientists in pursuit of technologies that might be of interest to DOE and, eventually to DOE's new industrial partners. As was the case last year, we will be using the criteria developed by CCST and, of course ,the standard LDRD criteria. As was the case last year, we ask for preproposals one page in length per the format attached. SINCE WE RECEIVE MANY PROPOSALS, LET US WARN YOU THAT PREPROPOSALS LONGER THAN ONE PAGE SELDOM GET READ. This point, we trust, is clear.

Please provide proposals to Dr. Drucker by June 30 for review by CCST. CCST will help, when appropriate, in identifying potential collaborators. Preliminary decisions on proposals will be made in early July, and full proposals will be due by July 31.

Given the excellence of last year's proposals, we believe that this program has the strong support of all concerned. Please give this appropriate distribution such that we can repeat last year's success.

HD/FF:njv
Attachments: 3

ARGONNE NATIONAL LABORATORY

Exhibit D

INTRA-LABORATORY MEMO

DATE: June 16, 1994

TO: Argonne Technical Staff

FROM: Alan Schriesheim, Laboratory Director

SUBJECT: Addendum to LDRD Call for Proposals for FY 1995: Individual Investigator Awards

Argonne's Laboratory Directed Research and Development Program, beginning with Fiscal Year 1995, will reserve a portion of available funds for support of relatively small individual-investigator projects. These projects will normally not exceed $75K in total cost and normally be funded for a single year. Successful proposals will be selected through a Laboratory-wide competition. A Director's Review Committee will evaluate and rank submissions and report its recommendations directly to me. Criteria against which proposals will be judged and guidelines on format, submission procedures and deadlines are provided in an attachment to this Call. Our traditional LDRD Program will continue according to the guidelines and schedule announced in early May. Investigators who have already responded to the previous Call and are interested in seeking an individual investigator award should familiarize themselves with the attached guidelines and discuss their options with their division management. I expect this new component of our LDRD Program will contribute significantly to Argonne's ability to remain at the leading edge of those science and engineering fields required to fulfill our future missions.

AS:jr
Attachment

c: Strategic Planning Board
E. Kaufmann

Exhibit E
(7/1/92)

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT FUND

GUIDELINES AND PROCEDURES

PURPOSE

The ANL Laboratory Directed Research and Development Fund (LDRD) is established to support and encourage new ideas and novel approaches to scientific and technical problems. It is expected that efforts supported by the LDRD program will lead to new funded programs and new directions for the Laboratory, while taking maximum advantage of the talents and creativity of Argonne staff.

PROCEDURES

1. LDRD projects to be funded will be selected on a competitive basis from all proposals submitted by Argonne staff.

2. Each proposal will identify the principal investigator(s), state the purpose of the project, define the project's scope, and provide a brief summary of the planned project. The proposal should specify the amount of funding required and, if the project is expected to extend over more than one year, the funding needed until completion. Projects may not be extended beyond three years unless exceptional circumstances obtain.

3. A new proposal must explicitly state that no prior LDRD funding was devoted to any aspect of the work. If part or all of the project received prior-year LDRD funding, proposals must specify amounts by fiscal year and trace any changes in project title which have occurred. Any initiation or termination of subtasks within a project during or between fiscal years must be reported and explained.

4. The Strategic Planning Board will review the proposals submitted, obtain any additional information considered necessary, and submit its recommendations for funding to the Laboratory Director.

5. Budgets will be established for each of the approved projects, and appropriate accounts will be opened to collect charges.

6. Proposals may be submitted to the Strategic Planning Board at any time. However, a majority of the funds will be committed at the beginning of the fiscal year. A limited amount (up to 20%) may be reserved to allow the laboratory to support new projects or to respond to opportunities. In addition, funding allocations may be changed during the year by the Strategic Planning Board in response to new needs or opportunities.

7. The resources to be made available for the LDRD program will be established by the Laboratory Director, within the DOE approved maximum, prior to the beginning of the fiscal year.

8. A written report will be prepared by the principal investigator(s) for each year of each funded project. The report should summarize the technical results obtained by the study in sufficient detail and at a level of presentation so that a non-specialist can appreciate the content and accomplishments. The report should also identify opportunities for new funding resulting from the study. The report should be submitted within one month after the completion of the project or within one month after the end of the fiscal year, whichever comes first. Explicit guidelines on content and format of the report will be distributed before fiscal-year end.

PROGRAM SELECTION GUIDELINES

1. The LDRD program will be administered according to the guidelines established by DOE for the use of LDRD Funds (See Attachment A: Guidelines excerpted from DOE Order 5000.4, 2/28/91).

2. LDRD projects should emphasize scientific and technical excellence and be at the forefront of science and technology.

3. LDRD projects should offer the promise to enhance the Laboratory's capabilities and be relevant to the long-term Strategic View of the Laboratory. (See Section III of the FY 1992 - FY 1997 Institutional Plan.)

4. LDRD projects should involve adequate effort and resources to insure proposed ideas are thoroughly tested. However, LDRD projects will generally not exceed 1.5 FTE of effort plus M&S (total $200K in any one year and, if a multi-year project, should not exceed $500K in total). Separately identifiable tasks that can stand alone as LDRD projects should not be combined into larger, single PI, projects.

5. LDRD projects may not be used to substitute for or supplement funds from DOE or other sponsors. LDRD projects may not be used to prepare conceptual design reports, or to fund construction line-item projects, facility maintenance, or capital expenditures of a general purpose nature.

Exhibit F
(Rev. '95)

LDRD PROGRAM PROPOSAL FORM

(On cover page to be attached to each proposal submitted to Strategic Planning Office)

PROJECT TITLE:

PRINCIPAL INVESTIGATOR(S):

ANL DIVISION(S):

ALD OFFICE:

PRIOR LDRD FUNDING:
CURRENT REQUEST:
FUTURE LDRD FUNDING:

PURPOSE: (One paragraph statement of the nature and purpose of the project.)

♦ ♦ ♦ ♦ ♦ ♦ ♦

Body of proposal must incorporate all, but no more than, the following elements:

PROJECT TITLE:
(Repeated from cover page)

PURPOSE:
(One paragraph statement of the nature and purpose of the project).
(Repeated from cover page)

WORK SCOPE:
(Delineation **by reference only** of the principal types of activities to be carried out. Details should be deferred to the BRIEF PROJECT SUMMARY paragraph below. Taken together with the PURPOSE paragraph, this should give enough detail so that a non-specialist will fully understand intent and scope.)

BACKGROUND:
(Description of technical/scientific opportunity or need in the context of the state of the field and prior work, if any, at ANL and elsewhere.)

BRIEF PROJECT SUMMARY:
(More complete description of scientific/technical activities referenced in the WORK SCOPE including anticipated approach, tools, milestones, collaborations, etc. Preparation of reports, proposals, presentations and organizational aspects of collaborations may NOT be principal activities.)

JUSTIFICATION:
(Estimation of likely scientific/technical benefits and potential for follow-on research support.)

BUDGET AND EFFORT:
(Budget & effort plan broken down as effort (in $ and FTE), M&S, low value procurement, and subcontracts. No expenditure for capital equipment is provided for under LDRD).

ESTIMATE OF COMPARATIVE CONTRIBUTION TO LDRD PROGRAM OBJECTIVES:

Development of a novel R&D idea	____%
Development of a new lab capability	____%
Advancement of Laboratory R&D strategy	____%
TOTAL:	100%

Exhibit G

LDRD PROGRAM
PROPOSAL EVALUATION FORM

Project Title: _____

P.I./Division: _____

		Yes	No	Unknown
(1)	Will this funding be used to initiate a new project which is beyond the exploratory phase?	___	___	___
(2)	Will this funding be used to substitute for or increase funding for tasks normally funded by DOE or other users of the Laboratory?	___	___	___
(3)	Will this allocation create an implicit commitment of multiyear funding by initiating projects which will require significant funding in future years to reach a useful stage of completion?	___	___	___
(4)	Will this allocation be used to fund construction design (conceptual design, Title I, or more advanced design): or	___	___	___
(5)	Fund construction line-item projects, in whole or in part; or	___	___	___
(6)	Fund facility maintenance; or	___	___	___
(7)	Fund capital expenditures of a general purpose nature?	___	___	___

Reviewer's Evaluation/Judgment of proposal: (Circle) **(Must be completed or proposal will be returned)**

Scientific/Technical Merit:	Outstanding	Good	Adequate	Marginal	Poor
Relatedness to Lab Strategy:	Outstanding	Good	Adequate	Marginal	Poor
Innovative Appeal/Exploratory Nature:	Outstanding	Good	Adequate	Marginal	Poor
Expected Contribution to Science/Engineering Advance:	Outstanding	Good	Adequate	Marginal	Poor
Prospects for Future Support:	Outstanding	Good	Adequate	Marginal	Poor

Other Comments: _____

_____

_____

_____

DIRECTOR'S INDIVIDUAL INVESTIGATOR LDRD PROGRAM

Proposal Submission Guidelines

A. Selection Criteria:

Proposals will be ranked according to two principal criteria.

1. Inherent scientific and technical merit: Is the proposed project technically sound and at the forefront of its technical area in comparison to work underway elsewhere?

2. Leverage for new avenues of R&D: If successful, is the project likely to lead to an expanded effort funded from other sources (including Argonne's traditional LDRD program)?

B. Format:

1. Proposal format must strictly adhere to the same format required of proposals to the traditional LDRD Program (obtainable from division and associate laboratory director offices), but be no longer than ten pages including the cover page. The top line of the cover page should indicate "**FOR SUBMISSION TO THE DIRECTOR'S INDIVIDUAL INVESTIGATOR LDRD PROGRAM.**" Signature lines at bottom of the cover page for all cognizant division directors and associate laboratory directors should be added.

2. The lead investigator may append a curriculum vitae no longer than two pages to the proposal.

C. Requirements and Restrictions:

1. Proposals not consistent with requirements of DOE Order 5000.4a (copies available from ALD offices or directly from the LDRD manager in the Office of the Director) will be returned without review.

2. The laboratory director would like to fund as many projects in the individual investigator category as possible. Therefore, except under extenuating circumstances, projects are limited to a duration of one year and a total cost of $75,000.

3. Proposed projects may not be supplements to or continuations of current or past funded LDRD projects.

4. Only one lead principal investigator may submit each proposal. Collaborating investigators may be named. Substantial portions of the budget should not be directed to outside consultants or subcontracts, however involvement of post-doctoral researchers is encouraged. The lead investigator and principal collaborators may not be a current member of the Director's Review Committee.

5. The division director(s) and associate laboratory director(s) in whose area(s) the work will be performed must sign the cover page attesting to the availability of the lead investigator and collaborators as well as the facilities needed by the project, if it is funded.

D. Content:

1. The proposal must be self-contained and provide sufficient information relevant to the two above selection criteria to enable review by the Director's Review Committee. The introductory "purpose" paragraph should be written in a way accessible to a technical nonspecialist.

2. Most small projects must rely on use of existing Laboratory facilities and other resources in order to reach a useful stage of completion. The proposal must specify what and where these resources are.

E. Submission:

An original and four copies of the completed proposal (with necessary signatures on the cover page) should be submitted to the LDRD manager in the Office of the Director no later than close of business July 31, 1994.

F. Reviews and Reports:

1. Proposals will be reviewed by the Director's Review Committee (DRC) composed of Laboratory scientists and engineers appointed by the laboratory director and drawn from the broad spectrum of Argonne divisions. In addition to evaluation of the written proposal, Committee review procedures may include:

   - Interviews of the principal investigators by selected members of the DRC;
   - Presentations to the DRC by principal investigators and collaborators;
   - Reviews by experts not on the DRC or by reviewers external to Argonne, at the discretion of the DRC chairperson.

2. The full list of proposals will be forwarded to the laboratory director with the ranking provided by the DRC.

3. All review discussion and documentation will be held in strict confidence by the DRC and the LDRD manager's office. The list of projects approved by the laboratory director will be published.

4. The annual report requirement for the Individual Investigator LDRD Program is the same as that for the traditional LDRD Program. Reports from both components will be collected into a single program report for transmission to DOE. The DRC may request brief midyear progress reports or presentations at its discretion.

5. Any proposed change in scope or change in availability of resources must be reported to the chairman of the DRC and the LDRD manager immediately when it occurs.

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Coordination Council for Science and Technology

CHARGE

To identify and develop opportunities for integrating the Laboratory's basic research capabilities in support of the technology missions and programs of the Laboratory and the Department of Energy; to promote the establishment of joint basic and technology development programs in support of this goal; to monitor the progress of such programs; and to advise Laboratory management concerning policies for the effective integration of basic research and technology development programs.

The Council will be co-chaired by the Associate Laboratory Directors for Physical Research and for Energy, Environmental and Biological Research. Other standing members will include the following directors of programmatic divisions: Materials Science, Chemistry, Mathematics and Computing Sciences, Environmental Research, Energy Systems, Environmental Assessment and Information Systems, (APS) Experimental Facilities, Chemical Technology, Engineering Physics, and Materials and Components Technology. A rotating membership of senior scientists and engineers will also be appointed by the Laboratory Director.

To support the goals and activities of the Council, the Laboratory Director will set aside, each fiscal year, a portion of funds for Laboratory Directed R&D (LDRD) Program for allocation to joint basic-applied projects. The Council shall recommend annually projects for consideration by the Strategic Planning Board and the Laboratory Director for LDRD funding.

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LDRD DIRECTOR'S REVIEW COMMITTEE

(Established by the Laboratory Director 6/94)

Purpose: LDRD DIRECTOR'S REVIEW COMMITTEE conducts a peer review of proposals submitted to the Laboratory Director for LDRD funding under the Director's Individual Investigator LDRD Program. It applies criteria as described in submission guidelines for the Program and ranks submissions against them. The mechanics of the peer review process are determined each year by the Committee to conform to the number and distribution of proposals and the distribution of technical expertise on the Committee. The Committee's goal is to provide a rank ordered list of proposals to the Laboratory Director for final approval and determination of the Program's funding level each year. The Committee members adhere to guidelines governing confidentiality of deliberations and avoidance of conflict of interest. The Chairperson of the Committee may authorize consulting with nonmembers where special technical expertise is needed for the peer review. The Committee also assumes responsibility for monitoring the progress of projects it has recommended in order to identify changes in scope of work or changes in the availability of resources required by the projects.

Members:

John P. Ackerman, Jr., Vice Chairman
Samuel D. Bader
Edmond L. Berger, Chairman
Maryka H. Bhattacharyya
Samit K. Bhattacharyya
Richard R. Cirillo
David J. Hill
Julie D. Jastrow
Elton N. Kaufmann, Executive Director
Tuncer M. Kuzay
Ewing L. Lusk
Frederick E. Mills
John Noonan
John R. Norris, Jr.
Harry P. Planchon, Jr.
Douglas L. Porter
William W. Schertz
John P. Schiffer
Robert K. Smither
Richard A. Valentin
David P. Weber
Randall E. Winans

The Committee initially comprises twenty members. All members are appointed by the Laboratory Director after consultation with line managers and current and former Committee members. The total number of members may be adjusted in response to the number of proposals received. No member will hold a management position of division director level or above. Each technical directorate of the Laboratory shall be represented by no less than four members or one-fifth of the total number of members, which ever is greater. To the extent possible, while adhering to the previous criterion, no division shall have more than one member at any time. Normally members' terms are three years except for the case of inaugural members whose terms are distributed from one to three years to allow staggering of the appointments and replacement of about one-third of the members annually. The Laboratory Director appoints a chair and vice chair in the inaugural year and thereafter a vice chair annually. The vice chair becomes the chair in the following year. The Laboratory's LDRD Manager serves as executive director for the Committee and the Manager's office supports the Committee's administrative needs.

Meetings: As required.

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

DIRECTOR'S REVIEW COMMITTEE

Guidelines and Responsibilities

Proposal Receipt, Peer Review, and Ranking:

Proposals to the Individual Investigator component of the LDRD Program will be received in the Office of the Director by the LDRD manager where they will be logged in and screened for compliance with DOE and Laboratory requirements and for adherence to the attached Proposal Submission Guidelines. Screened proposals will be forwarded to the Chairperson of the Director's Review Committee who will, with the advice of the Committee, oversee a distribution and review procedure taking into account proposal topics and Committee-member areas of expertise.

The process will insure that all Committee members become sufficiently familiar with all proposals to knowledgeably rank them according to the criteria specified in the Proposal Submission Guidelines. Review procedures should include an opportunity for lead investigators to present and explain their proposal to, at a minimum, a subgroup of the Committee. As many meetings of the full Committee as are necessary to adequately discuss all submissions should be convened. Committee meetings will normally be closed, but may be open when investigators are delivering oral presentations at the Committee's request. Proposals that do not present a sufficiently clear and/or detailed picture of the proposed work may either be rejected without further consideration or returned for augmentation, depending on the Committee's judgment of its potential.

The products of the review procedure will be a rank ordered list of proposals provided to the laboratory director by September 30 and a short paragraph critiquing each proposal which will be returned to the lead investigator of each submitted proposal (whether funded or not). The laboratory director, with advice from the Strategic Planning Board, determines the size of the Individual Investigator component of the Program. Feedback to investigators of rejected (low ranked) proposals should be specific and helpful so chances for future awards are enhanced.

It is the purpose of the Individual Investigator component of LDRD to provide an avenue for funding of modest projects that are highly deserving but would likely not have been funded through the traditional LDRD mechanism. The same proposal may therefore not be submitted to both components of the LDRD Program in the same year. However, if the Committee determines that the character of the proposal is such that it more properly should have been considered in the traditional component of the Program, it may be so redirected.

In exceptional cases, e.g., when the natural pace of a project demands it, the Committee may recommend spreading an award over two years, subject to adequate progress.

The Committee may determine that some projects will require monitoring after funds are awarded. Particularly high risk projects may have crucial midyear milestones, or a project's prosecution may depend on the availability of special equipment which could be delayed or withdrawn. Also, the LDRD manager may have advised the Committee of an investigator initiated change in work scope. The Committee may request midyear progress reports and/or interviews and may recommend early termination of a project as warranted. Unspent funds would, at the discretion of the laboratory director, be available for midyear starts of other Individual Investigator projects.

The final reports of all funded projects will be made available to the Committee for comments. Any such comments will be made a part of the project's record.

Committee Operations and Member Roles and Responsibilities:

The laboratory director will appoint a chairperson and vice chairperson who will chair meetings of the Committee and make Committee assignments to accomplish the review process. The chairperson may enlist nonmembers of the Committee (inside or external to Argonne) when particular expertise is not available among the members. The chairperson's term as chair will be one year and he/she will be succeeded by the vice chairperson. Initial member appointments will be for terms of one, two, or three years and subsequent appointments for three years in order to stagger terms.

The LDRD manager will function as executive director for the Committee, provide information on DOE and Laboratory guidelines, serve as liaison to the Office of the Director, and arrange for clerical and secretarial support as required.

All scientific and engineering staff below division director grade and not excluded by conflict-of-interest considerations (see below) are eligible for appointment to the Committee by the laboratory director. It is anticipated that the majority of members will have substantial experience in their technical fields and be familiar with the peer review process. Membership of the Committee will be chosen to reflect the diversity of, and to represent proportionately, all major research organizations and interests of the Laboratory. The laboratory director will accept nominations for Committee membership from expiring members and from associate laboratory directors. The Committee shall initially comprise approximately twenty (20) members. The number may be adjusted based on numbers of proposals received and experience with the time requirements of the review process.

Conflict of Interest:

Neither lead investigators nor principal collaborators on proposals to this component of the LDRD Program may accept appointment to the Committee. However, members may be investigators on projects funded through the traditional LDRD process. Members in line or program management positions must abstain from ranking of proposals originating in their areas. Any other special relationship of a member to a particular proposal should be disclosed to the Committee chairperson.

Confidentiality:

Committee members must agree to maintain strict confidentiality concerning the status of any proposal during review and concerning the written or verbal content of Committee deliberations, during or after the review process, whether these occur during official Committee activities or during informal interactions among Committee members or with proposing investigators. Committee meeting minutes will not document discussions of the merits of proposals, only preserving a record of decisions taken by the whole Committee. Any nonmember reviewers who help the Committee must agree to the same confidentiality requirements to which members are bound.

1994 Annual Report
Argonne National Laboratory
Laboratory Directed Research and Development Program

FIVE YEAR FUNDING SUMMARY
IN $K
(for projects active in FY 1994)

Proposal No.	1992	1993	1994	1995*	1996*	TOTAL
94-001N	-0-	-0-	141.2	200.0	-0-	341.20
92-022R2	180.4	704.3	586.5	-0-	-0-	1,471.20
94-057N	-0-	-0-	187.2	300.0	300.0	787.20
93-151R1	-0-	187.3	207.3	215.0	-0-	609.60
94-144N	-0-	-0-	69.4	85.0	90.0	244.40
92-162R2	238.8	176.0	147.4	-0-	-0-	562.20
94-191N	-0-	-0-	84.0	100.0	180.0	364.00
94-192N	-0-	-0-	57.5	-0-	-0-	57.50
92-182R2	‡	‡	213.9	-0-	-0-	213.90
93-002R1	-0-	250.9	248.6	-0-	-0-	499.50
93-003R1	-0-	225.9	202.0	-0-	-0-	427.90
93-004R1	-0-	312.0	353.1	290.0	-0-	955.10
93-007R1	-0-	58.3	98.8	90.0	-0-	247.10
94-142N	-0-	-0-	198.8	150.0	100.0	448.80
93-150R1	-0-	145.3	81.5	150.0	-0-	376.80
93-152R1	-0-	183.1	150.7	150.0	-0-	483.80
93-041R1	-0-	137.9	223.6	350.0	-0-	711.50
94-193N	-0-	-0-	84.5	160.0	180.0	424.50
94-002N	-0-	-0-	111.6	-0-	-0-	111.60
94-015N	-0-	-0-	111.3	100.0	85.0	296.30
93-047R1	-0-	207.5	190.2	-0-	-0-	397.70
93-043R1	-0-	248.2	225.2	225.0	-0-	698.40
93-040R1	-0-	216.2	124.4	140.0	-0-	480.60
92-047R2	164.6	125.9	170.0	-0-	-0-	460.50

Proposal No.	1992	1993	1994	1995*	1996*	TOTAL
94-046N	-0-	-0-	89.7	200.0	-0-	289.70
94-112N	-0-	-0-	212.2	-0-	-0-	212.20
94-114N	-0-	-0-	314.7	150.0	350.0	814.70
94-186N	-0-	-0-	371.8	300.0	480.0	1,151.80
94-187N	-0-	-0-	226.0	200.0	200.0	626.00
94-032N	-0-	-0-	160.8	140.0	141.0	441.80
94-053N	-0-	-0-	205.8	-0-	-0-	205.80
94-055N	-0-	-0-	155.1	25.0	-0-	180.10
92-023R2	153.1	239.2	175.2	50.0	-0-	617.50
94-058N	-0-	-0-	209.5	140.0	-0-	349.50
94-059N	-0-	-0-	88.9	-0-	-0-	88.90
94-060N	-0-	-0-	56.3	60.0	-0-	116.30
94-103N	-0-	-0-	218.4	130.0	-0-	348.40
94-165N	-0-	-0-	176.9	140.0	200.0	516.90
94-169N	-0-	-0-	162.4	140.0	200.0	502.40
94-179N	-0-	-0-	140.2	140.0	200.0	480.20
94-182N	-0-	-0-	144.4	140.0	190.0	474.40
94-133N	-0-	-0-	181.3	-0-	-0-	181.30
94-047N	-0-	-0-	179.8	200.0	250.0	629.80
94-054N	-0-	-0-	160.6	160.0	-0-	320.60
94-190N	-0-	-0-	158.9	150.0	150.0	458.90
94-194N	-0-	-0-	125.1	-0-	-0-	125.10
93-097R1	-0-	18.0	14.4	-0-	-0-	32.40
92-180R2**	47.5	337.7	296.0	105.0	-0-	786.20
93-090R1	-0-	284.8	270.8	165.0	-0-	720.60
92-160R2	329.5	302.6	239.7	-0-	-0-	871.80
92-108R1	242.1	-0-	290.4	190.0	-0-	722.50
93-156R1	-0-	189.8	143.7	-0-	-0-	333.50
94-106N	-0-	-0-	106.6	-0-	-0-	106.60

Proposal No.	1992	1993	1994	1995*	1996*	TOTAL
91-034R1	9.9†	-0-	105.7	115.0	-0-	230.60
94-154N	-0-	-0-	184.2	-0-	-0-	184.20
94-157N	-0-	-0-	144.9	-0-	-0-	144.90
94-033N	-0-	-0-	87.2	-0-	-0-	87.20
93-094R1	-0-	88.9	201.0	140.0	-0-	429.90
94-102N	-0-	-0-	178.0	-0-	-0-	178.00
94-115N	-0-	-0-	191.0	-0-	-0-	191.00
94-117N	-0-	-0-	225.1	-0-	-0-	225.10
94-118N	-0-	-0-	175.8	-0-	-0-	175.80
94-167N	-0-	-0-	133.6	140.0	-0-	273.60
94-003N	-0-	-0-	128.4	118.0	-0-	246.40
94-056N	-0-	-0-	158.5	-0-	-0-	158.50
93-006R1	-0-	122.1	192.5	-0-	-0-	314.60
93-091R1	-0-	93.3	91.8	-0-	-0-	185.10
94-168N	-0-	-0-	123.1	140.0	175.0	438.10
	1,365.90	4,855.20	11,865.10	6,283.00	3,471.00	27,840.20

*1995 and 1996 figures represent estimates and not actual expenditures.
**Fourth quarter start
†FY 1991 cost
‡Subtasked under other project in FY92 & FY93.

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94-001N -- AMORPHOUS SILICON SENSORS: A NEW DETECTOR TECHNOLOGY

Associate Laboratory Director Area: Operations

Principal Investigators: I. Naday and S. Ross, Electronics and Computing Technologies

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$141.2K
FY 1995	$200.0K
FY 1996	$ -0-

Purpose: The purpose of this project is to develop an entirely new generation of comparatively low-cost, high-resolution, large-area, imaging detectors based upon the amorphous silicon array technology currently being developed by Xerox Corporation. We believe that detectors based upon this new technology, providing unprecedented large detection areas, capable of operating in high-intensity X-ray applications, providing high-spatial resolution--at a relatively low cost compared to currently used technologies, will find many new important uses in a broad range of photon imaging applications. In particular, development of such detectors can meet a critical need of structural biology and materials crystallographic researchers at third generation light sources such as the Advanced Photon Source (APS). More specific, the first application and demonstration of such a development is being directed to meeting the needs of the Structural Biology Center at APS.

Approach: The Xerox Corporation is currently developing a new generation technology for plain paper copiers based upon the use of amorphous silicon detector arrays. The requirements for copiers closely parallel those for imaging applications in basic research, i.e., large area (Xerox is currently using 24 x 19 cm arrays), high-spatial resolution (127 micron pixels), and relatively low cost compared to currently used systems. With the incorporation of suitable phosphors, these amorphous silicon arrays can be used for a broad range of X-ray and ultraviolet imaging applications. Because of the importance of such an emerging technology, engineers in the Electronics and Computing Technologies (ECT) division and researchers at Xerox Corporation are committed to demonstrate the applicability of these new arrays to a broad spectrum of research applications. Xerox provides ECT with the amorphous silicon array technology and materials, ECT provides the electronics and applications expertise, and together various applications are to be demonstrated.

In order to assess the application of such a technology in photon imaging, a number of critical parameters must be evaluated. We must evaluate the inherent noise level, dark background, detectivity, differential quantum efficiency, spatial and temporal resolution, repeatability and image latency performance of these detectors as their electronic control signals, temperature, coating phosphor and readout timing are varied. To accomplish these studies, low-noise readout electronics, environmental controls (low temperature operation), digital clocking circuitry, and computer data interfaces must be developed. These are being developed and tested using the extensive electro-optics, computing and fabrication facilities in ECT as well as the rotating anode

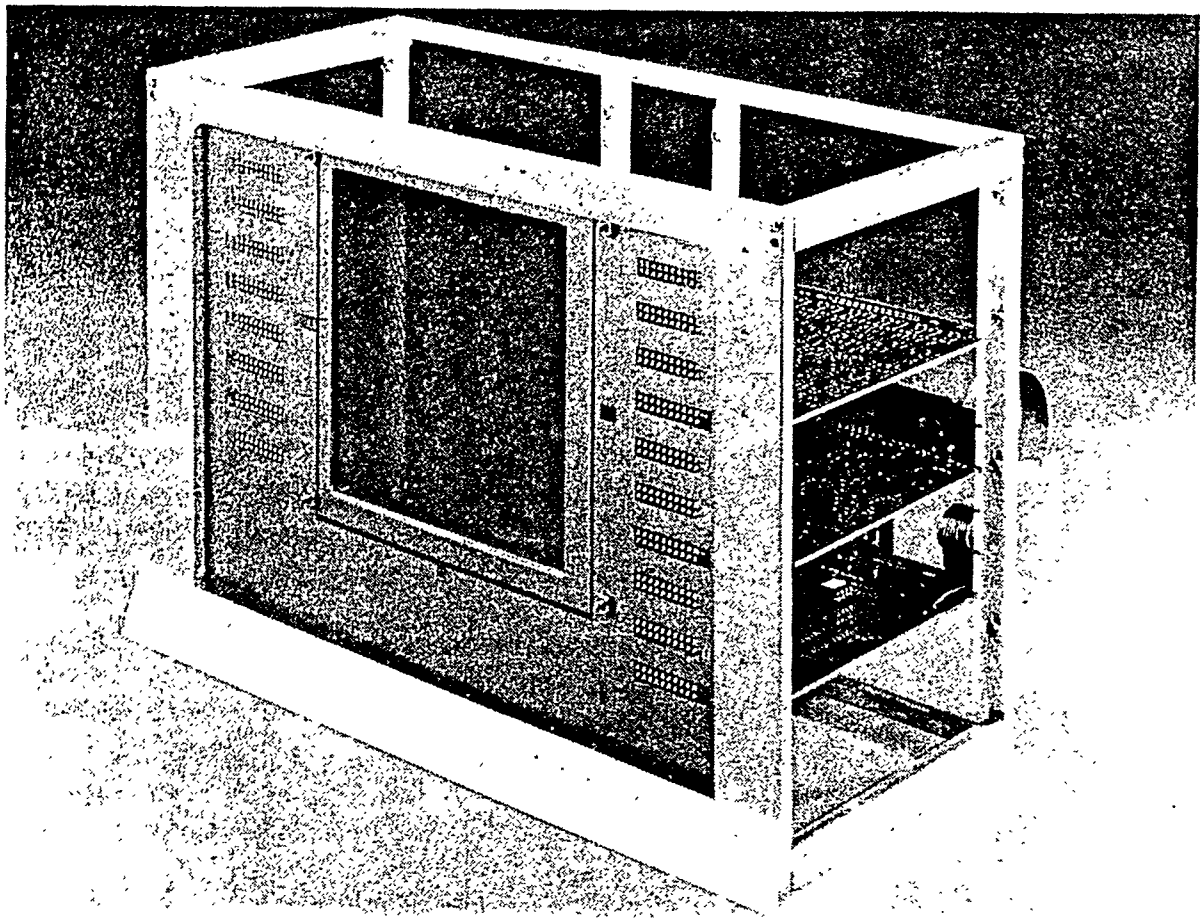
X-ray facility and the National Synchrotron Light Source (NSLS, Brookhaven National Laboratory) X8C-beam line operated by the ANL Structural Biology Center.

Technical Progress and Results: This work began in FY 1994. We designed, fabricated and performed initial tests on electronic circuitry to drive the 11 cm x 14 cm amorphous silicon prototype "small" amorphous silicon sensor array supplied by Xerox. A novel method was developed to interface the glass substrate of the amorphous silicon detector to standard printed circuit boards. We tested a bank of 256 amplifier chains to read out the low-level analog voltages from the array, voltages which reflect the detected electro-optical signal. Custom digital control circuitry was developed and implemented which provides a flexible method of testing the arrays in various modes of operation. We interfaced the readout electronics with standard VME based electronics to pass the digital image data on to a computer for analysis. A frame was manufactured to hold the array and its support electronics and to allow eventual control of its temperature. The attached photograph shows the prototype system at its current state of development.

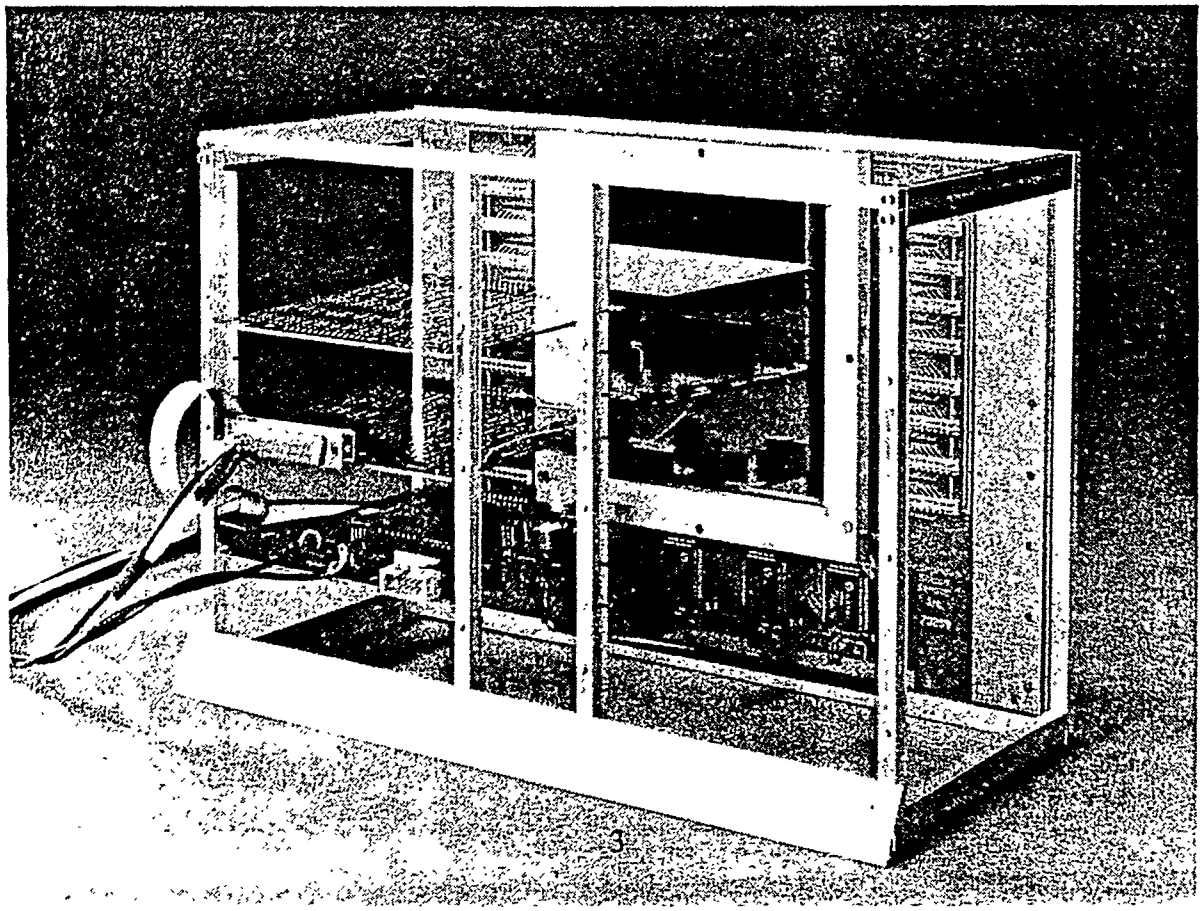
Two computer models were developed for the performance of the array. The first is a spreadsheet system model necessary to select overall parameters of the detector. It predicts the performance of the amorphous silicon arrays as X-ray detectors at protein crystallography synchrotron and rotating anode X-ray sources. Our modelling results give us high confidence that this technology will be very useful in large angle X-ray scattering environments, by yielding adequate signal to noise performance. We performed this modelling both for the actual current array under test and the future "large" 28 cm amorphous silicon array. We also wrote a PSPICE computer model to specially predict and aid in the development of the low noise readout electronics. This model aids the understanding of the various photo-optical signals, noise and spurious electronic signals.

Continued LDRD support has been requested for FY1995. The electronics described above will be fully integrated with the 11 cm Xerox array, and the array will be fully characterized, with an emphasis on how it will perform as a detector at both a synchrotron x-ray beamline and on a rotating anode x-ray source. We expect to measure the noise and background signal of the array as a function of temperature and readout timing, measure the image lag as a function of temperature and to measure the interaction of the array with the phosphor coating.

Specific Accomplishments: We completed the design and construction of the test detector prototype. The ECT detector development project was peer reviewed by the CMB University of Chicago Review Committee as part of the Structural Biology Program Review. Following is an excerpt from the Committee's report referring to the amorphous silicon array development: "Looking further into the future, the development of amorphous silicon detectors could have a very big impact on the crystallography field. Exploration of such new concepts, as well as continuing to improve and refine the more established approaches, is a vitally important component of the project." A proposal was submitted to the National Institute of Health for a multi-year commitment to develop this detector into a fully operational synchrotron and rotating anode x-ray detector. Results of this work were presented at the Workshop on Detectors for Third-Generation Synchrotron Sources, Feb. 14-15, 1994.



Front View



Rear View

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92-022R2 -- FEASIBILITY STUDY FOR THE INTENSE PULSED NEUTRON SOURCE UPGRADE

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigator: Y. Cho

Funding Profile:

FY 1992	$180.4K
FY 1993	$704.3K
FY 1994	$586.5K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: ANL has been a pioneer in development and utilization of accelerator based pulsed neutron sources since the 1970's. The purpose of this LDRD was to update recent development from around the world, and to develop an up-to-date design to assess the scope of upgrading the IPNS to a 1-MW beam power utilizing the existing infrastructure of the former ZGS complex. Construction of such facility at a future date could be one of the major initiatives for the Laboratory. Fiscal Year 1994 funds supported studies of various possible accelerator configurations and comparisons between them, identifying the most important R&D topics pertinent to all spallation source accelerator configurations, carrying out some of these R&D topics, and estimating costs of such an accelerator facility and rehabilitating of existing buildings to house the facility. Instrumentation and target station studies were also carried out in conjunction with the accelerator studies.

Background: Recently, the neutron scattering science community has aired the need for high power pulsed sources in the beam power range of 1 to 5 MW. European scientists have proposed a 5 MW source, the European Spallation Source (ESS), and the Kohn Subcommittee of the DOE Basic Energy Science Advisory Committee has recommended consideration of a 1 MW source in the United States. In response to these calls for the facilities, scientists and engineers from several laboratories in this country, as well as, from Germany, UK, Italy, Switzerland, Netherlands, Sweden, Denmark and Austria have been working on possible configuration of accelerators to facilitate such high powered sources. A project called *Austron*, which was designed by personnel from CERN for an Austrian consortium of universities and research institutions, is under funding consideration by the governments of Austria, Czech Republic, Hungary and Slovak. The European Union has just funded for a feasibility study of the 5 MW ESS. The fund distributed to various institutions from the EC totals about US $2.5M. In addition, the participating institutions are to contribute equal amounts to the effort. In the United States, ANL and LANL have been studying 1 MW source design each using their existing infrastructure, while BNL has been working on a 5 MW green field source.

Approach: The ANL concept consists of a low energy (400 MeV) linac, a fast cycling synchrotron, and two neutron generating target stations. These technical facilities are to be housed in the ZGS area. The work performed in FY94 included:

1) optimization of synchrotron geometry to fit into the existing tunnel
2) optimization of injection and extraction geometry

3) optimization of injection and capture processes
4) optimization of radio-frequency voltage programming
5) determination of synchrotron magnets apertures
6) optimization of magnet performance
7) optimization power supplies to minimize the power consumption

The work performed in this year also included continued investigation of "beam loss" during injection, acceleration, and extraction processes. The beam loss is defined to be any protons lost from the controlled processes of injection, capture, extraction, and transport. Lost particles from these processes would result in an undesirable effect of producing residual radioactivity in accelerator components, and if the uncontrolled losses are severe, personnel access to the hardware and hands-on maintenance of this hardware would become extremely difficult. This continued study resulted in specification of linac performance parameters. The new parameters not only alleviate the beam losses but also make the construction of the linac easier because the new parameters are less demanding.

Personnel involved in the past year's work are: R. Kustom, A. Rauchas, E. Lessner, F. Mills, D. McGhee, K. Thompson, R. Nielsen, W. McDowell, D. Horan, K. Harkay, M. Fathizadeh, G. Norek, K. Symon, and Y. Cho.

Technical Progress and Results: The result of the last year's work shows that a 1 MW pulsed source based on a rapid cycling synchrotron technology utilizing existing infrastructure at the former ZGS complex is feasible. A four-side synchrotron of some 190 m circumference can be housed in the ZGS Ring Building to provide a proton beam of 2 GeV in energy and 0.5 mA in average current. A 400 MeV proton linac could be housed in a new building designed for a high intensity proton linac.

Accelerator hardware, such as magnets, power supplies, rf cavities, rf power sources, vacuum chamber system, were investigated and refined during the past year, and it was concluded that all hardware performance requirements, as defined by the physics requirements, are attainable, and refinements obtained in this year's study were incorporated in the study.

The physics study emphasis was to continue to simulate and to understand the injection, capture, and acceleration processes. The main goal is to understand and to eliminate the beam loss mechanisms from the injection, capture and acceleration processes, and at the same time the beam being accelerated should meet the stability criteria on both longitudinal and transverse phase spaces.

This study found that handling of the beam during the injection and acceleration processes would be easier if the injected beam has a large energy spread and larger transverse emittances. This is in contrast to the ESS requirement of having very small energy spread and small emittances. The ANL results were reported at the General Meetings of ESS, and the ESS personnel adopted the ANL ideas.

Specific Accomplishments: The results of this year's work were presented at the First General Meeting of European Spallation Source ESS (Jülich, Germany, February 1994) EPAC-94 European Accelerator Conference (London, UK, July 1994), and the Second General Meeting of European Spallation Source (Ancona, Italy, October 1994).

A 400 MeV proton linac feasibility study is completed and documented. The linac design uses R&D results from the SSC linac work, and the linac could be available through an industrial firm.

Feasibility of using the existing infrastructure to house and to operate the proposed facility is documented by Plant Facilities and Services Division.

An overall feasibility study report will be submitted to peer review.

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94-057N -- DEVELOPMENT OF BASIC CONCEPTS AND COMPONENTS FOR THE ACCELERATION OF RADIOACTIVE BEAMS

Associate Laboratory Director Area: Physical Research

Principal Investigators: J. A. Nolen, I. Ahmad, B. B. Back, C. N. Davids, W. F. Henning, R. C. Pardo, K. E. Rehm, J. P. Schiffer, and K. W. Shepard, Physics Division

Funding Profile:

FY 1992 $ -0-
FY 1993 $ -0-
FY 1994 $187.2K
FY 1995 $300.0K
FY 1996 $300.0K

Purpose: There is currently considerable enthusiasm within the international nuclear physics community for the research that could be done with a general purpose facility capable of producing and accelerating intense beams of radioactive isotopes. The goal of this project was to develop some of the critical technical concepts necessary to support a proposal for such a radioactive beam facility at Argonne exploiting ATLAS as the post-accelerator. The objectives of this first year's work were to evaluate various driver accelerator choices through nuclear physics simulations of production cross sections, initiate feasibility studies of targetry options such as the use of liquid uranium, evaluate options for a very high resolution mass separator for nuclear isobars, and identify via simulations the critical parameters of the very low velocity and low charge-to-mass ratio preaccelerator.

Approach: A "white paper" for a major radioactive beam facility has been written by the North American Committee for an Isospin Laboratory, but detailed proposals for such a facility must be generated by specific laboratories. To be considered as the site for a U.S. Isospin Laboratory Argonne must develop at least a conceptual proposal in time for consideration by NSAC for the next Long Range Plan, which is scheduled to begin in early 1995. Because of ATLAS, Argonne is in a strong position to obtain funding for such a facility, which is expected to be a $100-200 million project. However, a credible proposal must be supported by technical feasibility studies like those being carried out under this LDRD project.

A complete radioactive beam facility consists of several major components: a "driver" accelerator with high power beams (about 100 kW) to make radioactive isotopes via spallation reactions, the target complex in which the isotopes are produced and initially ionized, the pre-accelerator and isobar separator section, the main accelerator for the radioactive beams, and the experimental facilities for research with the beams. The last two items are well covered at Argonne by the existing ATLAS facility. Hence, the present efforts are concentrated on computer simulation studies and hardware tests to develop and refine concepts for the following: (1) a cost effective driver accelerator to create a wide variety of radionuclides far from the stable isotopes, (2) new targets such as liquid uranium for use at very high beam power, (3) a high-acceptance mass separator with resolution of about 30,000 to separate individual isotopes of a given isobar, (4) a preaccelerator for very low velocity and low charge-to-mass ratio heavy ions,

and (5) efficient methods for stripping and/or charge state enhancement of such ions. A parallel effort has involved some test runs at ATLAS to demonstrate a possible application of radioactive beams for wear analysis, and to establish credibility in the field of radioactive beams by actually accelerating a radioactive ion for a nuclear physics experiment.

The methods employed during FY 1994 were primarily computer simulations to quantitatively evaluate the options for the various components of the proposed facility. Existing apparatus in the Reactor Engineering Division permitted experimental evaluation of some containment materials for liquid uranium. Also, existing apparatus at ATLAS was used to carry out two different demonstration experiments using the radioactive isotope ^{18}F. Further experiments, to get yield data on specific, interesting radionuclides, have been approved by the respective Program Advisory Committees at ATLAS at ANL and the National Superconductor Cyclotron Laboratory at Michigan State University; these experiments are scheduled for November and December, 1994.

In addition to the Physics Division permanent staff listed as PIs above, several visitors, temporary staff, students, and staff from other divisions contributed to this LDRD project during FY 1994. These included: Cheng-Lie Jiang, a visiting scholar; J.-W. Kim, a new post doc; Michael Paul, a visiting scholar; Jerry Nichols and others from his group in Medical Physics at the University of Wisconsin at Madison; Jeff Binder and Jim Sienicki of Reactor Engineering; Norbert Schmidt, Maricio Portillio, and Michael Bruns, students; and Jeffrey Dooling, temporary staff appointee.

Technical Progress and Results: The investigations supported by this LDRD project have led to the block diagram of a radioactive beam facility based on the use of ATLAS as the post accelerator. This is shown in the first figure. Two major Monte Carlo-based computer codes have been obtained and made operational in Physics; these are LAHET and ISAPACE, which predict yields of radionuclides for various input beam species and energies and specified target geometries. Global predictions made using LAHET for one choice of beam and target are shown in the second figure. Such results are essential in justifying our choice of driver linac.

Initial tests of materials for containing liquid uranium as a production target material for high power beams have been carried out by the Reactor Engineering group. These results are very promising, and the tests will be continued in FY 1995. An especially promising crucible, nitrided Tribocor, has been identified and a manufacturer located. Also, an innovative approach to reducing the release time of radionuclides from liquid targets by rapid circulation of the liquid has been proposed by the Reactor Engineering group.

Preliminary calculations of a very high resolution mass separator, with the design goal of 1 part in 30,000 resolution, have been carried out. There are no existing devices with this resolution and the required acceptance. A preliminary design for a Japanese facility exists and is being used as a basis for comparison with new designs. This work is still in progress.

Progress has been made in the two critical areas of the pre-accelerator concept. The first critical area involves a radio frequency quadrupole (RFQ) to accelerate very low velocity heavy ions with q/m values of 1/132 or lower. Such an RFQ to operate in the continuous wave mode has never been designed. Software to begin this design has been written as is currently being

verified prior to initial design work in early FY 1995. The second critical area involves a superconducting linac stage operating in the same velocity range as the present positive-ion injector (PII), but with a much lower q/m, 2/132 or less. Simulations have been carried out for this linac, and these indicate the need for the development of a high gradient superconducting quadrupole for transverse focussing of such ions. Magnetic and conceptual mechanical designs for such a quadrupole have been worked out, so that the next important step is to actually build a test unit during FY 1995.

A new concept for increasing the charge state of a DC beam of low velocity heavy ions, an Electron Beam Charge State Amplifier (EBQA), has been developed under this LDRD project. The concept is still very speculative, but could represent an important breakthrough for the radioactive beam preaccelerator. Extensive simulations have been carried out, but proof of the concept will probably require significant hardware tests.

Specific Accomplishments: Perhaps the most significant quantifiable accomplishment of our work-to-date on the radioactive beam initiative is the pre-proposal document prepared and submitted by the Physics Division to the Nuclear Physics Division of DOE/ER at their request. There have been several other workshop contributions and drafts of papers based on aspects of the work discussed above: There are drafts of papers prepared for publication on the results of using radioactive beams for wear analysis, as well as, on the simulations of the EBQA concept. There were five different contributions at two separate workshops sponsored by the North American Isospin Laboratory Committee. These contributions were on preaccelerator concepts and issues related to targetry and yields of radionuclides from various driver accelerator beams.

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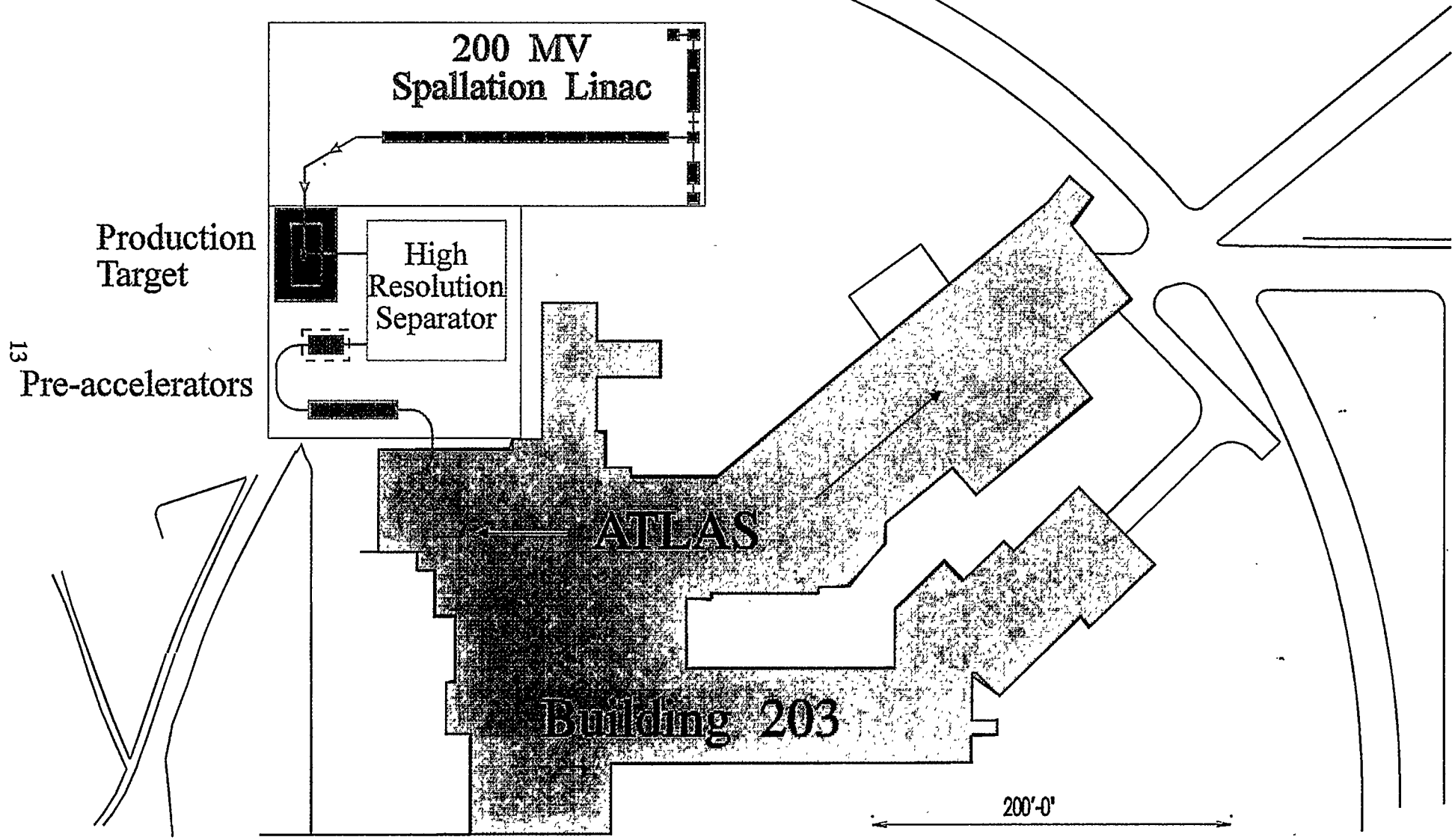
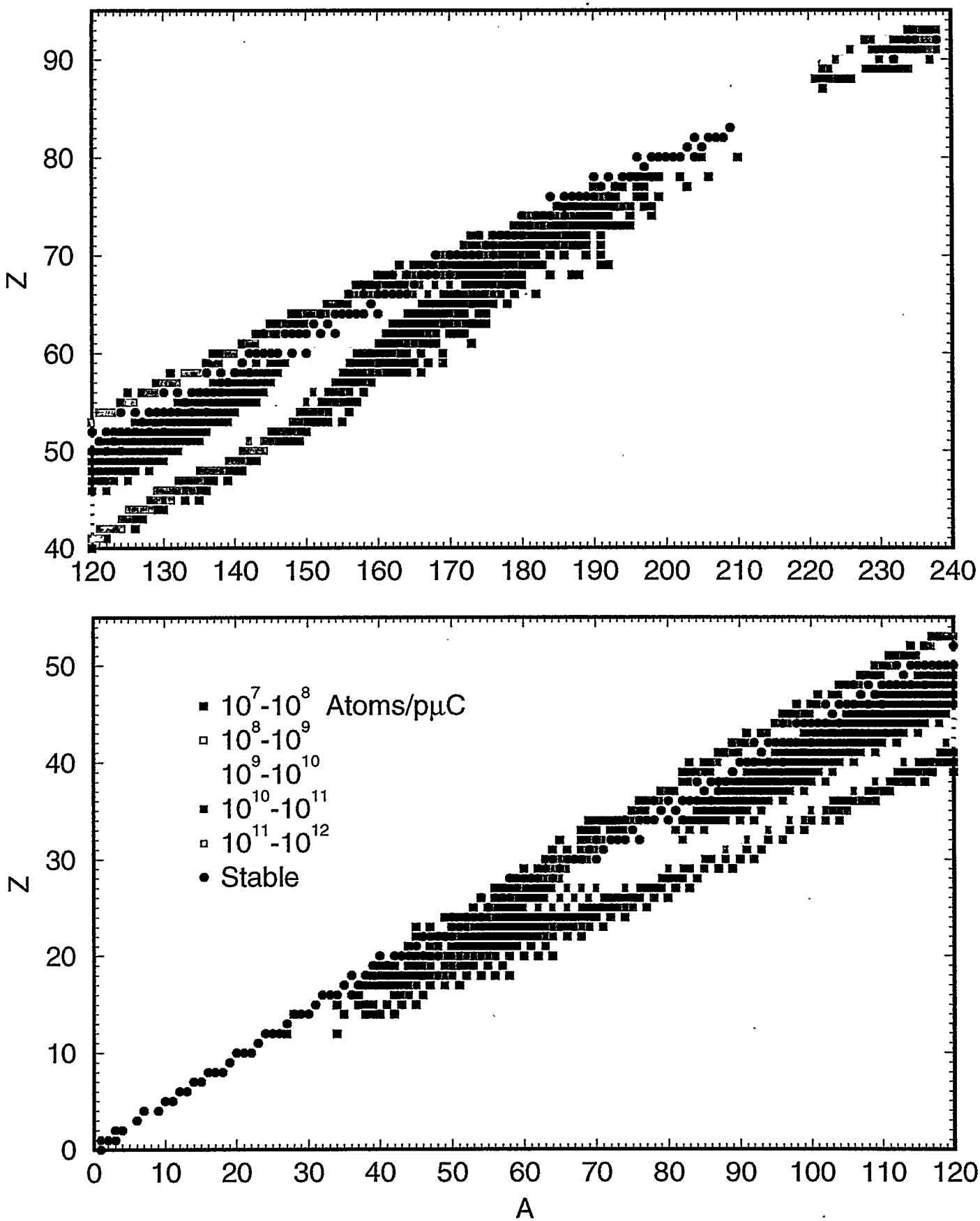
Argonne National Laboratory
Exotic Beam Facility
Conceptual Layout



Radioisotope production rates

100 MeV neutrons on thick ^{238}U target



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93-151R1 -- MILLIMETER WAVE LINAC AND UNDULATOR DEVELOPMENT USING MICROFABRICATION TECHNIQUES

Associate Laboratory Director Area: Advanced Photon Source

Principle Investigator: R. L. Kustom, Accelerator Systems Division

Funding Profile:

FY 1992 $ -0-
FY 1993 $187.3K
FY 1994 $207.3K
FY 1995 $215.0K
FY 1996 $ -0-

Purpose: The purpose of this project is to investigate the feasibility of building microfabricated rf cavities for mm-wave linacs and/or undulators using high-aspect-ratio micromachining techniques. This fabrication technique is a newly developing technology which could lead to fascinating applications of interest to the scientific and industrial communities. The goal is to demonstrate proof-of-principle feasibility of building mm-wave rf structures for linacs, undulators, and free-electron lasers (FELs) within three years and secure DOE funding for a more extensive R&D program and to attract private industry participation.

Approach: High-aspect-ratio micromachining techniques have evolved to where microcomponents can be manufactured out of copper, silver, nickel, and nickel alloys with features as small as a few microns with dimensional tolerances as good as 25 Å and machining depths of a few mm with very little runout, thus the term high-aspect-ratio. Quite intricate structures such as submillimeter gears, motors, and actuators can be fabricated. Electric fields as high as 50 to 100 MV/m and magnetic fields as high as 0.5 to 1.0 tesla can be achieved in these small components. The possibility of making 3-dimensional structures is rapidly approaching reality. These possibilities provided the stimulus for investigating mm-wave structures for compact electron linear accelerators and undulators that could be used for vacuum ultraviolet (vuv) and X-ray synchrotron radiation sources.

The elements of this technology that are being addressed by this project include development of mm-wave rf structures through computer studies, oversized models for rf testing to verify computer studies, and construction and excitation of actual small scale test sections; development and testing of masks for fabrication of structures; development of 3-D fabrication, assembly, and alignment techniques; studies of beam dynamics; and, study of related technology such as cooling, vacuum, and rf sources for excitation. The work on three-dimensional fabrication and alignment techniques is being done at the University of Illinois - Chicago under subcontract with Professor Alan Feinerman and some of the work on rf structures is being done at the Technical University of Berlin under subcontract with Prof. Heino Henke.

Technical Progress and Results: During FY 1993, we performed computer calculations on a number of candidate rf structures to determine which might achieve the best rf performance consistent with the construction technique required by the high-aspect-ratio micromachining process. A muffin-tin structure with a $2\pi/3$ radian phase advance per cell at 120 GHz gave a suitable accelerating field for a reasonable excitation power. These structures can be

manufactured in 7 cm lengths which are compatible with present 10 cm disk semiconductor technology. A 10 X (12 GHz) model was built with seven complete cells and input and output coupling cells for matching the rf. Tests on this oversized structure demonstrated the validity of computer calculations. An alternate structure, a side-coupled cavity arrangement, was successfully tested at the Technical University of Berlin.

X-ray masks were made at the University of Illinois - Chicago. These masks included sample structures that have special alignment grooves for testing accuracy of alignment techniques. The masks also included sample quadrupole sections and possible magnetic mm-wavelength undulators. Techniques for testing the alignment included capacitive measurements on special sub-millimeter sized parallel plate capacitors. These capacitors were also put onto the masks.

A computer program was written for studying the beam dynamics in the rectangular geometry required for these structures. The beam dynamics equations need to account for the nonsymmetrical fields generated in the rectangular structure. These equations are quite different from those for the normal circular structures conventionally used. The program was successfully operated and used with actual fields of the muffin-tin structure.

Computer analysis of the thermal load and heating was performed on the $2\pi/3$ muffin-tin structure using the ANSYS code. The preliminary results indicate that the structure can be adequately cooled. The largest temperature rise can be kept to below 40°C when the accelerating field is 10 MV/m.

This fiscal year (1994), we micromachined our first $2\pi/3$ linac structure. The high degree of precision that is possible was apparent in this structure. The rf cavity features that were machined on the die were easily within ± 2 microns and the overall features of the surface were dominated by the surface irregularities of the substrate which was not diamond turned. Twenty diamond turned substrates that have a ± 1 micron surface finish have been delivered for future cavity construction. This should improve the overall quality in the next units to be built. Much of this work was done by Professor Alan Feinerman and one of his students, Ted Willke, from the University of Illinois at Chicago. They prepared the optical and x-ray masks and performed the alignment and tolerance measurements on the cavity features.

Quite a few rf and system analysis studies were performed. These studies focussed on types of rf structures, different linac assemblies and operating scenarios. The most likely options for operating parameters appear to be either, (1) operate at short pulse, 400 to 2000 Hz repetition rate with a 1%, or less, duty factor, (2) operate with a superconducting cavity at CW, or (3) operate with a long pulse normal conducting structure with a 10-15% duty factor.

A new constant gradient (CG) rf structure has been developed. The physical features are compatible with the deep x-ray lithography machining technique. The new CG structure generates a constant accelerating field and constant power distribution along the axial length, unlike the constant impedance structure. The new CG structure also has a vastly improved heat removal capability over the rectangular cell design with which we had originally started the study.

Specific Accomplishments:

1. "120 Ghz mm-Wave Planar Accelerating Structure Linac System for Production of Short Wavelength Synchrotron Radiation," A. Nassiri, et. al., Linear Collider Workshop 1993 (LC'93), SLAC, October 1993.
2. "Initial Beam Simulation for the mm-Wave Accelerating Structure," A. Nassiri, Internal Note, October 1993.
3. "Investigation of Planar mm-Wave RF Structures Focussing and Bunching," S. Vaganian, H. Henke, TET-NOTE 93/015, November 1993.
4. "50 MeV mm-Wave Electron Linear Accelerator System for Production of Tunable Short Wavelength Synchrotron Radiation," A. Nassiri, et. al., International Electron Device Meeting, Washington, DC, December 5-8, 1993.
5. "Beam and Structure Misalignment Errors," A. Nassiri, Internal Note, February 10, 1994.
6. "Alternating Phase Focusing (APF) in mm-Wave Linear Accelerators," F. Mills and A. Nassiri, Internal Note, February 28, 1994.
7. "Misalignment Errors and Their Effects on the Electron Beam in mm-Wave Linac," A. Nassiri, Internal Note, February 1994.
8. "Tunable RF Undulator Using a Rectangular Waveguide," P. Matthews, Internal Note, April 1994.
9. "A mm-Wave RF Structure for Relativistic Electron Acceleration," H. Henke, et al., Internal Note, May 10, 1994.
10. "Electromagnetic Field Measurements on a mm-Wave Linear Accelerator," P. Matthews, et. al., EPAC'94, London, Great Britain, June 1994.
11. "Parallel Reflector Waveguide as Microwave Undulator," Y. Kang, R. Kustom, A. Nassiri, and P. Matthews, EPAC'94, London, Great Britain, June 1994.
12. "RF Measurements of a 12 Ghz Scale Model of a Planar Structure," Y. Kang, P. Matthews, A Nassiri, and R. Kustom, EPAC'94, London, Great Britain, June 1994.
13. "Investigation on the mm-Wave Linear Accelerator Project," P. Matthews, Internal Note, July 7, 1994.
14. "Micro-Structures," R. Kustom, et. al., International Linear Accelerator Conference, KEK, Japan, August 1994.
15. "Effects of Quantum Excitation and Residual Gas Scattering on the Beam Lifetime in the mm-Wave Undulator for the APS Storage Ring," A. Nassiri, Internal Note, September 1994.

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94-144N -- SHORT WAVELENGTH PULSED MAGNETIC UNDULATOR DEVELOPMENT USING MICROFABRICATION TECHNIQUES

Associate Laboratory Director Area: Advanced Photon Source

Principle Investigator: F. E. Mills, Accelerator Systems Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$ 69.4K
FY 1995	$ 85.0K
FY 1996	$ 90.0K

Purpose: The purpose of this project is to investigate the feasibility of building microfabricated pulsed magnetic undulators for mm-wave linacs and/or free electron lasers (FELs) using high-aspect-ratio micromachining techniques, to determine the parameter field over which these devices could operate and be of interest to the scientific community, and to develop a proof-of-principle design.

Approach: High-aspect-ratio micromachining techniques have evolved to where microcomponents can be manufactured out of copper, silver, nickel, and nickel alloys with features as small as a few microns with dimensional tolerances as good as 25 Å and machining depths of a few mm with very little runout, thus the term high-aspect-ratio. Quite intricate structures such as submillimeter gears, motors, and actuators can be fabricated. Electric fields as high as 50 to 100 MV/m and magnetic fields as high as 0.5 to 1.0 tesla can be achieved in these small components. The possibility of making 3-dimensional structures is rapidly approaching reality. These possibilities provided the stimulus for investigating micro-undulator structures for compact electron linear accelerators that could be used for vacuum ultraviolet (vuv) and X-ray synchrotron radiation sources.

The elements of this technology that are being addressed by this project include development of mm-size pulsed magnetic structures through computer studies, oversized and actual size models for magnetic field measurements and testing to verify computer studies, and construction and excitation of actual small scale test sections; development and testing of masks for fabrication of structures; development of 3-D fabrication, assembly, and alignment techniques; studies of beam dynamics; and, study of related technology such as cooling, vacuum, and pulsed power sources for excitation. The work on three-dimensional fabrication and alignment techniques is being done at the University of Illinois-Chicago under subcontract with Professor Alan Feinerman.

Technical Progress and Results: During FY 1994, we performed computer calculations on a number of candidate undulator structures to determine and understand magnetic field properties which might achieve the best performance consistent with the construction technique required by the high-aspect-ratio micromachining process.

Electromagnetic field computations were performed to establish a desirable field pattern for the undulator. This was solved by using counter-flowing currents in the top and bottom of the

undulator, shifted by one pole. The problem of current flowing across the pole instead of through the conductor was partially solved by making the conductor width 0.2 mm and the pole width 0.3 mm, rather than vice versa.

Other problems with current flow could not be completely resolved immediately because the 3-D eddy current software appeared to have some problems enforcing current conservation. This problem is being discussed with the vendor and they will provide a version which will allow us to complete this analysis. All the simulations done so far suggest that an undulator with the proper field and current is feasible.

Two model undulators were designed and fabricated in the initial stage of this project. These devices were fabricated according to the numerical 2-D and 3-D magnetic field simulations. The first one is a 10x scale model with an undulator period of 1 cm fabricated from a steel piece using precision electric discharge machining (EDM). This model is now being prepared for the initial magnetic tests. A second actual model with 1 mm undulator period was fabricated at the University of Illinois/Chicago by Professor Alan Feinerman which is also being prepared for magnetic measurements. To be able to measure the undulator fields in small gap, two methods have been developed. In the first case, a pickup coil will be fabricated using the printed circuit technology which will provide enough sensitivity for small field measurements. For very small gap size, conventional field probe measurement techniques are not sufficient in determining the undulator field profile. A new method is being developed and implemented which employs magneto-optical techniques using a single detector crystal to measure the change of a given polarization state of a laser beam to induce information on the magnetic field value and distribution inside the undulator.

A computer program was written for studying the beam dynamics in a 3-D undulator field. An analytical analysis separating the effect on beam motion with and without parts governing the radiation aspect of the beam motion through undulators was performed. An approximate solution for the beam motion through the undulators was obtained. The effect of errors on the beam motion was analytically solved. A program using MATHEMATICA was developed to simulate the full motion through such undulators. At present, the radiative aspects in the undulators are being studied.

This fiscal year (1994), we extensively performed magnetic field computer simulations to characterize the performance of both the actual (1mm period) and the 10x scale model (1 cm period). The initial numerical simulations have provided us with the necessary information about the physics of these short period devices to conclude that proper field and current distribution is feasible. Two test models have been fabricated and in the process of being measured. A magneto-optical field measurement system is being put together which uses a laser system along with a crystal to measure the field inside the undulator. Professor Alan Feinerman, from the University of Illinois/Chicago has fabricated the first 1 mm-period undulator using conventional machining technique.

Specific Accomplishments:

1. "mm-size Micro-Undulator for Production of Short Wavelength Synchrotron Radiation", A. Nassiri, F.E. Mills, and L. Turner, 6th Workshop on Advanced Accelerator Concepts, Lake Geneva, Wisc., June 1994.

2. "A Summary of the Micro-Undulator Design for the Advanced Photon Source (APS) Electron Linac", A. Nassiri, F.E. Mills, internal note, February 1994.

3. "ELEKTRA Computations of a 1-mm Period Undulator Driven by Electric or Magnetic Scaler Potential," L. Turner, F. E. Mills, A. Nassiri, Vector Field Users Group Meeting, Framingham, Mass., October 14, 1994.

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92-162R2 -- INVESTIGATION OF NOVEL DETECTORS FOR ULTRA-FAST TIME-RESOLVED STUDIES

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigators: B. Rodricks and D. Mills, Experimental Facilities Division

Funding Profile:

FY 1992	$238.8K
FY 1993	$176.0K
FY 1994	$147.4K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: To continue on the development of programmable readout electronics and state-of-the-art real-time high-resolution display necessary for the readout of Pixel Array Detectors (PADs).

Approach: Over the past twenty years, synchrotron radiation has been used extensively as a source of X-rays in the fields of physics, chemistry, biology, medicine, and others,[1] first in a parasitic mode at high energy physics facilities like at the Stanford Synchrotron Radiation Laboratory (SSRL) and the Cornell High Energy Synchrotron Source (CHESS), and then at dedicated facilities like the National Synchrotron Light Source (NSLS). At present, four ultra-high brilliance insertion-device-based third generation synchrotron sources, namely the Advanced Photon Source (APS), the Advanced Light Source (ALS), the European Synchrotron Radiation Facility (ESRF), and the Super Photon Ring (SPring-8) are in their construction phase. During this period of time, photon brilliance has increased many orders of magnitude[2] allowing the advance of established techniques and opening up new avenues of research. Unfortunately, during this remarkable pace of growth in beam brilliance, the research and development of detectors have not kept pace. A large percentage of forefront X-ray science is still done with scintillation detectors. In experiments where two-dimensional detectors are required, X-ray sensitive photographic film or imaging plates have been used. Charge coupled devices (CCDs) are being increasingly utilized where positional information is required.[3] (There are numerous situations where positional information is necessary such as angiography, protein crystallography, X-ray holography, various transmission imaging studies, and time-resolved studies.) The advantages of charge couple devices (CCDs) over film or imaging plates are their high spatial resolution and low noise. The disadvantages are their limited dynamic range and a serial readout that is inherently slow.

No currently available area detectors have framing rates greater that 100 Hz. Pixel array detectors (PADs) have the potential to have framing rates approaching a megahertz and, hence, provide a marked improvement in high-speed area detector performance. There are two main aspects to the development of a practical PAD system. First, the pixel array chips must be fabricated. The chip fabrication part of the project is a joint collaboration with Prof. Sol Gruner and Prof. Peter Eisenberger of Princeton University. The second aspect is the development of a sophisticated flexible electronic readout system that allows us to first characterize the device and then control it in normal operation. The devices being fabricated are experimental devices,

thus, the readout requirements will vary from device to device. Hence, to read-out the device and to optimize performance, we are developing a software programmable system.

The second aspect of the readout system is data storage. Because the device is being designed for very high speed experiments, we need a high speed data storage system that can store data at a sustained speed without any computer overhead. For the readout electronics, we decided on a modular system based on the industrial standard VXI mainframe where modules from different high technology companies follow the same protocol and can be controlled from a single controller.

Technical Progress and Results: This project is split up into three phases:

i) The development of a PAD (funding for which is not a part of this project).

ii) The development of a PAD readout system.

iii) The development of a fast data acquisition system.

This report deals with the development of the data storage system. FY 1992 was when we investigated the feasibility of a novel hybrid pixel array detector. This resulted in a white paper from Sarnoff Research Center which described a design for a high-speed PAD.

When one deals with experimental devices with CCD architecture (PADs), a very versatile readout electronics system is required. The potential amplitudes, phase relationships between clocking waveforms and clock speeds of these devices are not precisely known in advance and hence, one has to be in a position to change these during optimization and characterization of the device.

To enable us to have all parameters under software control, we settled on the VXI architecture. Being state of the art, the VXI system required extensive startup software and interaction with many commercial vendors to have some of their modules modified to our specifications. FY 1993 LDRD was used to develop such a system. The high-speed readout of a PAD requires that the data be stored at a comparable speed. To satisfy this requirement we need to look at novel techniques to data storage, for which, we are in consultation with high technology companies and other research laboratories to assist us in the design of a high-speed data acquisition system. Our requirements for such a system were: (1) it must be modular for expansion purposes; (2) to have a high throughput data storage system that can store data at either an internal or external clock rate; (3) required a 32 bit word to be stored at 10 MHz or greater per channel; (4) to have a data storage capacity of 256 Mbytes or greater per channel; (5) to be programmable to allow for histogramming, averaging or continuous storage or raw data.

Specific Accomplishments: Since the FY 1994 LDRD is the final year of the project, we would like to summarize the accomplishments achieved over the past three years. FY 1992 LDRD was utilized investigating the feasibility of a Pixel Array Device. After consulting with relevant scientists and engineers from industry and national research laboratories, changes were incorporated into the initial design of the device. The most important of these changes, which have been detailed in the Sarnoff White Paper, are as follows:

1. Device yields will be higher if active structures, such as an amplifier per pixel, are avoided.

2. A MOS CCD-like buried-channel well structure would be able to meet the noise, dynamic range, and timing requirements with higher yields than active structures.

3. A high-Z radiation blocking layer/interconnect structure would have to be microfabricated to separate the radiation sensing pixels from the MOS electronics. This would likely be one of the most challenging parts of the project and will certainly require a microfabrication capability.

4. Yields and the eventual shift to full-size devices would be facilitated by subdividing both radiation sensing and MOS structures, i.e., both sides of the radiation blocking layer would be tiled with smaller chips.

5. A correlated double sampling (CDS) amplifier has been designed and characterized by Sarnoff for military CCD applications. The use of CDS amps allows all eight PAD frames (which may be acquired in < 10 microsec) to be read out within 50 msec, enabling data dumping at video rates. At this data rate, readout is analog-to-digital converter (ADC) and storage electronics limited.

We decided on a plan of action whereby the project was divided into three phases.

Phase I.	Development of 256 x 256 test PADs.
	Off-chip electronic conceptual design.
Phase II.	Scale up to full size PADs.
	Assembly of off-chip electronics and software.
Phase III.	PAD production and beamline integration.

Over the past year, the designed has evolved still further. Rather than go with the MOS type buried CCD architecture for the storage device, we are going with conventional capacitors for data storage from each pixel. Although the design is more complicated, it is based on standard computer chips and techniques which conventional foundries are more familiar with. As of today, we have gone through two iterations at the foundry on the design of the storage subsystem of the PAD. The second iteration has resulted in a chip that has 8 storage capacitors per pixel. The chip has been tested and found to work correctly. All 8 capacitors can be injected with charge and can be readout sequentially or randomly.

FY 1993 LDRD was utilized designing a flexible readout system for devices with CCD like architecture. A VXI-based readout system has been developed. It consist of a series of arbitrary waveform generators controlled by a high speed controller in a VXI mainframe. The system is controlled by a 486 PC. The system can readout CCD type structures with a clock speed of 50 MHz. The peak-to-peak voltage output is 30 V- far more than will be needed for the PAD readout. The voltages can be changed is steps of 50 mV with a maximum offset of 15 volts. The readout system can generate any type of waveform with phase relationship between modules having a time resolution of 25 ns- far more than will be needed for the readout of a PAD. The system is controlled by buttons generated on a color terminal connected to a PC. The software allows for real-time images to be displayed and manipulated. The system was tested using a high-speed 8 channel CCD as our test device.

In conjunction with the detector development group from the ESRF, a system with the requirements for the high speed storage as described in the Technical Progress and Results section of this document, has been designed. A module is presently in fabrication. This module based on the VXI architecture has 256 Mbytes of dynamic RAM memory on it. It can store data at 10 MHz using either an external or internal clock. It uses standard SIMM memory chips that are used in most computer systems. Currently each SIMM can store 16 Mbytes of information with module being able to accommodate 16 such chips.

Over the last three years of the project, we have fabricated a test PAD storage subsystem that works according to the design, designed a flexible readout system that is used for the readout of the PAD and designed a high speed data storage subsystem in collaboration with the detector group at ESRF and Professor Sol Gruner of Princeton University. All the fundamental parts for the realization of a working Pixel Array Device are under control. During the next two years we plan on fabricating a prototype PAD device that will be tested at the Advanced Photon Source subject to available non-LDRD funds.

References:

[1]For an overview, see series *Handbook on Synchrotron Radiation* (North-Holland, Amsterdam, 1983 and 1987).

[2]See "7 GeV Advanced Photon Source: Conceptual Design Report," Argonne National Laboratory Report No. ANL-87-15, April 1987.

[3]B. Rodricks, C. Brizard, *Nucl. Instrum. Methods* A311, 613-619 (1992).

94-191N -- IN-SITU SURFACE MONITORING SYSTEM FOR SYNCHROTRON OPTICS IN HIGH HEAT LOAD ENVIRONMENT

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigators: George Srajer amd Dennis Mills, Experimental Facilities Division

Funding Profile:

FY 1992 $ -0-
FY 1993 $ -0-
FY 1994 $ 84.0K
FY 1995 $100.0K
FY 1996 $180.0K

Purpose: The project objective is the development of an opto-mechanical system for direct, real-time monitoring of thermally induced surface distortions of synchrotron radiation optical elements, particularly mirrors, subjected to high heat fluxes.

Approach: The shape or "figure" of X-ray mirrors for third-generation synchrotron sources, such as the Advanced Photon Source (APS) is critical for the delivery of the full X-ray brilliance to the experimental stations. However, the price for high brilliance is the unprecedented high power of the synchrotron beam. The combination of high total power and power density imposes demanding requirements on beamline components since their surfaces will be susceptible to heat induced distortions. For example, the APS undulator A will produce a total power of 1.5 kW and a power density of 140 W/mm^2, which is significantly more than the Cornell High Energy Synchrotron Source F-2 wiggler (1.0 kW and 10 W/mm^2), and the National Synchrotron Light Source X25 focused wiggler (0.04 kW and 120 W/mm^2).

Deviations from the desired shape (slope errors) less than an arc second can severely degrade the performance of mirrors for the APS. X-ray mirrors are routinely measured off-line (that is not in the beamline) in specialized laboratories for both surface roughness and figure (under ambient thermal conditions), but *in-situ* diagnostic, such as being proposed in this project, is much rarer. Our goal is to explore various approaches to *in-situ*, real-time monitoring of high-heat-load mirrors and to fabricate a prototype system (or systems) that might be suited to such measurements.

The monitoring system is essentially a metrology unit that is used to determine a change in surface profile of an X-ray optical component under a thermally loaded condition. At present, we believe that the best approach for this system is an optical sensor (Hartmann-type[1]) that utilizes optical leverage to measure slope differentials at various places along the optic surface.

The proposed monitoring system (figure 1) consists of four subcomponents:

(a) Laser-diode reference source with collimating optics
(b) Beam distribution/collection unit
(c) Telescope optics and CCD array
(d) Image-processing computer and software

The laser diode and collimating optics supplies a beam to a series of beam splitters in the beam distribution/collection unit which then directs the split beam to multiple places on the particular optic (mirror or monochromator) surface. Reflected beams are then collected by other beam splitters in the beam distribution unit and guided through a telescope to form multiple images on a CCD array. The image processing computer performs calculations on the multiple images and convert data to slope difference values. The initial step is to use independent transmit and receive beam splitters. Subsequently, we may evaluate the possibility of using a single beam path in connection with polarizing beam splitters and wave plates.

Our design goals are to:

(a) Develop a multi-channel version of the Hartmann-type sensors
(b) Achieve very high angular resolution of the order of 1 μrad (or .2 arcsec)
(c) Incorporate the monitoring system into a vibration-free support
(d) Develop software for data collection and analysis
(e) Construct a compact, portable and rather inexpensive system

Cyndy Bresloff was the main collaborator who helped in purchasing and evaluating optical components for the *in-situ* monitoring system.

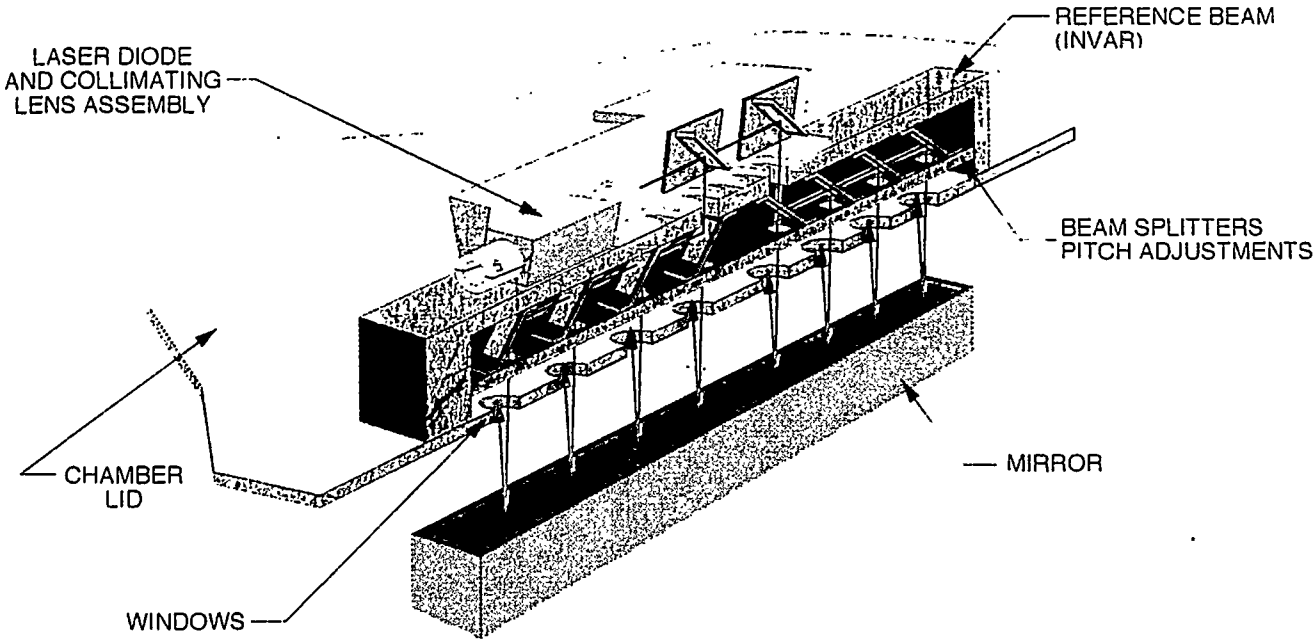
Technical Progress and Results: A design study of the *in-situ* monitoring system was completed. Based on this study, a decision was made to build an eight-element test sensor. A collimating optic was designed and a vibration-free optical table was purchased. Transmittance calculations through the beam-splitter network, which is a part of the beam distribution/collection unit, were done. Depending on the signal/noise ratio, design guidelines were established for the wave front sensor, which is the heart of the detection optic.

Currently, the APS is waiting for the delivery of a high-heat load mirror that will focus synchrotron radiation from a beamline at the Cornell High Energy Synchrotron Source (CHESS). The focused beam in the experimental station will have both total power (900 W) and power density (250 W/mm^2) comparable to the APS's Undulator A. This will enable various beamline components (monochromators, mirrors, beam stops, beryllium and diamond windows, etc.) that are being designed for the APS to be tested in the high-heat-load environment. This mirror will be a perfect candidate for the test of the monitoring system. In collaboration with personnel at CHESS and the Photon Sciences Inc., the ultra-high vacuum chamber for the mirror has been designed and manufactured in such a way that a proposed monitoring system (figure 1) can be placed on top of the chamber. The modification involved replacing a conventional lid with a lid that allows optical access, i.e., it contains a series of quartz viewports. The lid has been fabricated as well. Although this part is not directly related to the project, it is crucial for later *in-situ* testing of the monitoring system.

Specific Accomplishments: The preliminary design for the monitoring system has been completed, a series of calculations were done and a purchase of miscellaneous hardware components has begun.

Reference:

1. J.C. Fontanella, *J. Optics* (Paris) **2,** 99 (1991).


REFERENCE BEAM
(INVAR)
LASER DIODE
AND COLLIMATING
LENS ASSEMBLY
BEAM SPLITTERS
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CHAMBER
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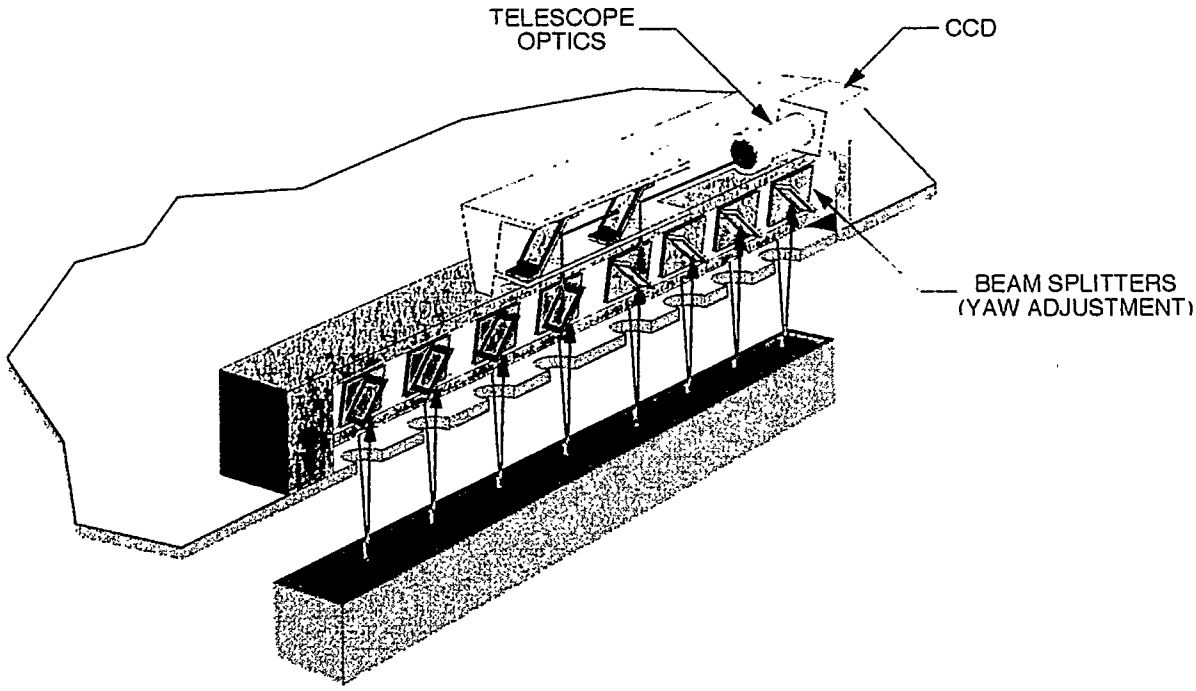
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94-192N -- DEVELOPMENT OF FOCUSING OPTICS AND DETECTORS FOR INELASTIC SCATTERING HAVING A RESOLUTION OF 0.2 eV

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigators: A. Macrander and V. I. Kushnir, Experimental Facilities Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$ 57.5K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The project objective was to obtain i) a spherically focusing analyzer made from single crystal Ge and ii) a sagittally focusing stage for the second crystal of the high heat load inclined crystal monochromator that has been developed at the APS. (Obtaining detectors was stated as a goal in the original LDRD proposal but became a matter of straightforward procurement from a supplier.) The implications of success are twofold. First, an enhanced scientific capability that will make possible a wider range of inelastic X-ray scattering studies will result , and second, valuable expertise in the construction of focusing crystal optics will be obtained. The successful sagittal focusing of an inclined crystal monochromator also has implications for future high heat load monochromator designs.

Approach: A committed effort to build an inelastic X-ray scattering (IXS) instrument having a resolution of about 10 milli-eV has been on-going as part of the SRI CAT (Synchrotron Radiation Instrumentation Collaborative Access Team) of the APS. This resolution is desirable for the study of phonons in condensed matter. However, a coarsened resolution of 0.2 eV is also desirable especially for the study of electronic excitations, and this goal was deemed possible with only minor reconfigurations of the spectrometer. Key additional optical components were needed to accomplish this goal, and this project was directed towards obtaining a Ge analyzer and a sagittal focusing second crystal stage. Previously, researchers in the field of IXS had attempted to make such an analyzer but failed because the Ge wafers cracked. Sagittally focusing an inclined crystal monochromator has never been attempted before.

For the Ge analyzer two possible approaches were open to us: 1) to dynamically bend a wafer, or 2) to glue and press a wafer into a precisely ground spherical form. The first approach had been successful with silicon crystals up to a diameter of 1 inch at the National Synchrotron Light Source (NSLS), but failed when workers at NSLS attempted to scale up to larger diameters. We decided to take the second approach.

For the sagittal focusing the possibility of collaborating with UNI CAT (University-National Laboratory-Industry Collaborative Access Team) members was open to us. UNI CAT was also interested in obtaining a sagittal focusing inclined crystal. One of us (V. Kushnir) has particular expertise in the design of sagittal focusing crystals and, in particular, is co-inventor of the recent successful innovation that avoids the use of stiffening ribs. Upon discussion with UNI-CAT members, it was agreed that they would work primarily on the design of the bender. The

complete design would then be available to the SRI-CAT. We would work under LDRD on the design and construction of the crystals themselves for both CATs. This separation was adhered to during the course of this work. In the end, there was a considerable flow of ideas and comments back and forth between the two CATs since the bender and crystal need to work together as a unit.

Technical Progress and Results: i) Ge Analyzer - After a series of progressively more successful attempts, an analyzer with a useful diameter of 74 mm was constructed. This analyzer is shown in figure 1. Tests on analyzers have been performed in-house using conventional X-ray generators as well as at Cornell High Energy Synchrotron Source (CHESS) and at NSLS. The most successful procedure we have found to construct an analyzer is: 1) first prepare a two-component epoxy mixture by pumping the air out of the mixture in a bell jar, 2) spread the epoxy over a concave form and then place the wafer over the epoxy in as dust free an environment as possible, then 3) press the wafer into the form while the epoxy is exuded. The epoxy we have used had a viscosity of 100 cps, and the curing was done at room temperature.

The Ge wafer was sliced from a 90-mm-diameter, (111) oriented boule for which we measured a value of 0.068 milliradians FWHM for the Ge(333)xGe(333) double-crystal ($\pm$) rocking curve using CuKα radiation. Since the theoretical double crystal rocking curve FWHM is 0.032 milliradians, a value of 0.042 millirad is deduced by quadrature subtraction for the mosaic broadening for each crystal (assumed to be identical). The ratio of the intensity diffracted by the second crystal to that incident on it in this same double-crystal arrangement was 65%.

Slope errors for the analyzer were obtained by measuring the change in Bragg angle for the Ge(111) reflection as the analyzer was translated across the beam. For the best analyzer to date, analyzer #6 , a value of 0.29 millirad for the RMS slope error (compared to a perfect sphere) over 34 mm translation along a radius was measured. We also measured an RMS value of 0.28 mrad over 33 mm translation in the opposite direction (i.e., along one diameter). Given an analyzer position such that the angular acceptance of the analyzer is comparable to these slope errors, we estimate from these measurements that the analyzer should have a useful diameter of $\sim$67 mm.

We have also characterized analyzers using synchrotron radiation. We tested analyzer #6 at NSLS using 7.603 keV radiation at a Bragg angle of 87°. The dynamical Darwin width is 0.21 millirad at this Bragg angle. The analyzer was arranged to diffract the beam coming from the monochromator with the incident beam traversing the sample position but with no sample present. A two-theta scan around the sample position was made from which the useful diameter of the analyzer was obtained. The FWHM of the scanned profile was 74 mm. The complete profile drops to zero very rapidly outside this diameter. We note that the measured result is close to the expected value as gauged from slope error measurements.

During undulator experiments at CHESS we measured the IXS resolution function. The resolution function is a convolution of the monochromator spectral reflectivity function with that for the analyzer. The beam from the undulator source had a vertical divergence of only 0.035 millirad FWHM. The monochromator optics were designed to match this divergence and have a spectral FWHM of 0.15 eV. We measured a value of 0.30 $\pm$ 0.07 eV for the elastic peak from a powdered C_{60} sample for a Ge(444) analyzer set to Bragg diffract at 89.2°. Projecting

these results to the APS where we expect to have only 0.025 millirad vertical divergence, we expect to be able to reach the desired resolution of 0.2 eV.

Actual IXS measurements have been made with analyzer #6, and clear spectra with excellent statistical accuracy have been obtained on single crystals of silicon carbide. An example spectrum revealing the presence of a plasmon is shown in figure 2.

ii) Sagittal Focusing - After iterating on the design of the bender with UNI-CAT a U shaped crystal design was decided upon. The central (bottom) part of the "U" is a relatively thin (0.6-1 mm) membrane, and the two "legs" of the "U" have much larger thickness (5-10 mm), which allows to consider them as infinitely stiff and therefore to achieve uniform loading of the thin part of the crystal. The design of the crystal developed for SRI CAT is such that the aspect ratio is large enough to avoid anticlastic bending of the central part of the crystal without stiffening ribs.

After discussions with us, UNI-CAT has chosen a crystal design with stiffening ribs on the thin (bent) part of the crystal. The design is shown in figure 3. The crystal for the SRI-CAT is slightly smaller than that shown in figure 3, and has no ribs. This division was made so that both types of crystals, i.e., both with and without ribs could be tried.

The sagittal focusing crystals are intended to be used as the second crystals of the double-crystal high heat load monochromator in the so-called inclined diffraction geometry. A value of 80° was chosen for the inclination angle for SRI CAT purposes, and 70.5° for UNI-CAT. Due to a high sensitivity of the inclined diffraction geometry to misalignments of the crystals we produced both second (U-shaped, bent) and first (plane) crystals with the same orientation from the same boule, and keep an absolute accuracy of orientation about 0.1°.

A bender and piezoelectric stages have been procured for future tests. A procedure to construct the crystals in the crystal fabrication facility at the APS was chosen and, recently, crystals have been cut from [110] oriented silicon boules.

At this time we feel that the major objectives of the LDRD proposal have been met with one year's worth of effort, and that the SRI CAT is now in a position to do successful IXS with a coarsened resolution of 0.2 eV with the optics already in hand. In other words we are of the opinion that enough has been accomplished in both the analyzer and sagittal focusing activities that further LDRD funding would not be appropriate.

Specific Accomplishments: A Ge analyzer for IXS with a large active area (74 mm) has been constructed for the first time. A report of this accomplishment was made at the International SRI meeting in August 1994 and is in press at the *Review of Scientific Instruments*.

A sagittal focusing bender design and designs for two types of crystals were finished. These now await testing.

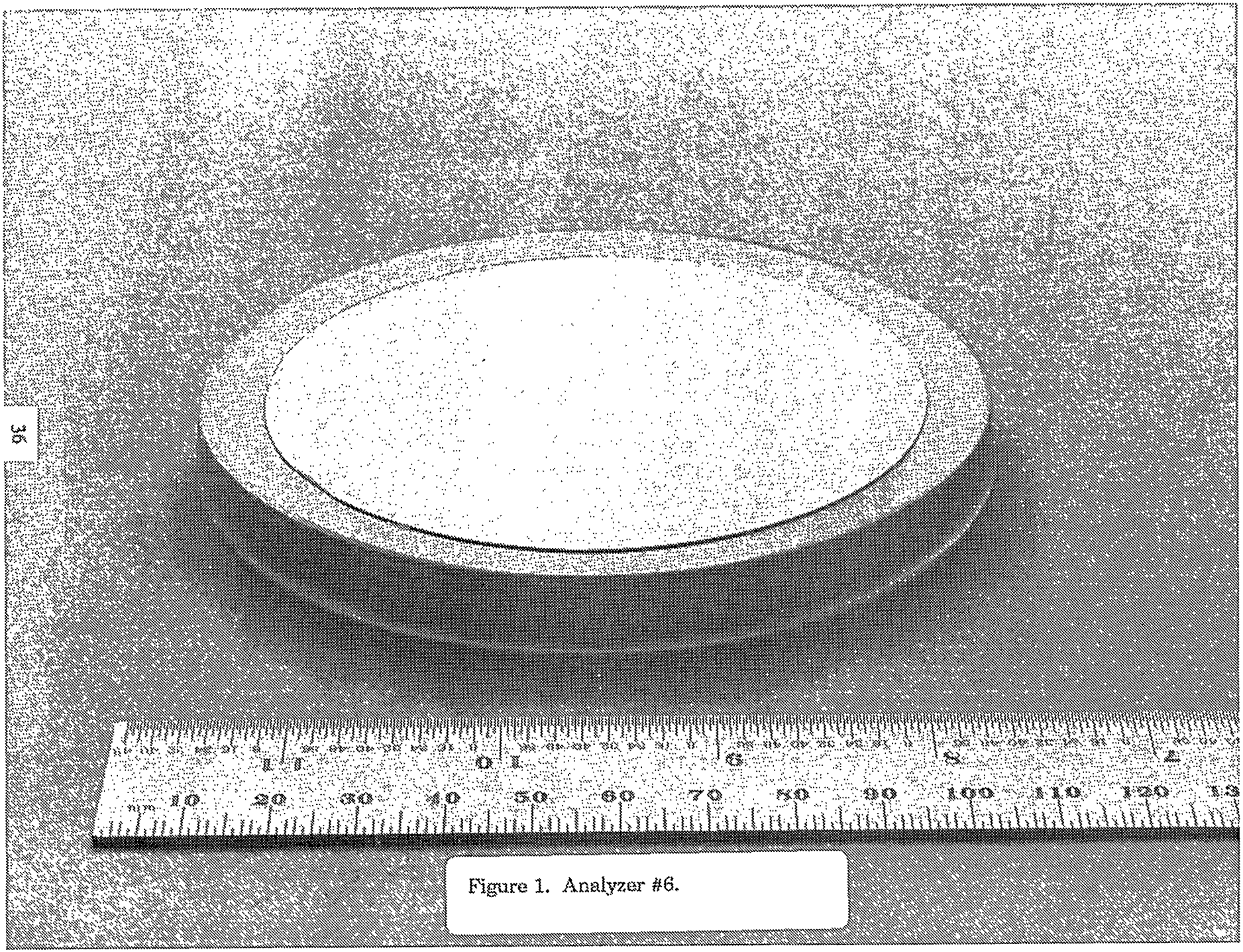

Figure 1. Analyzer #6.

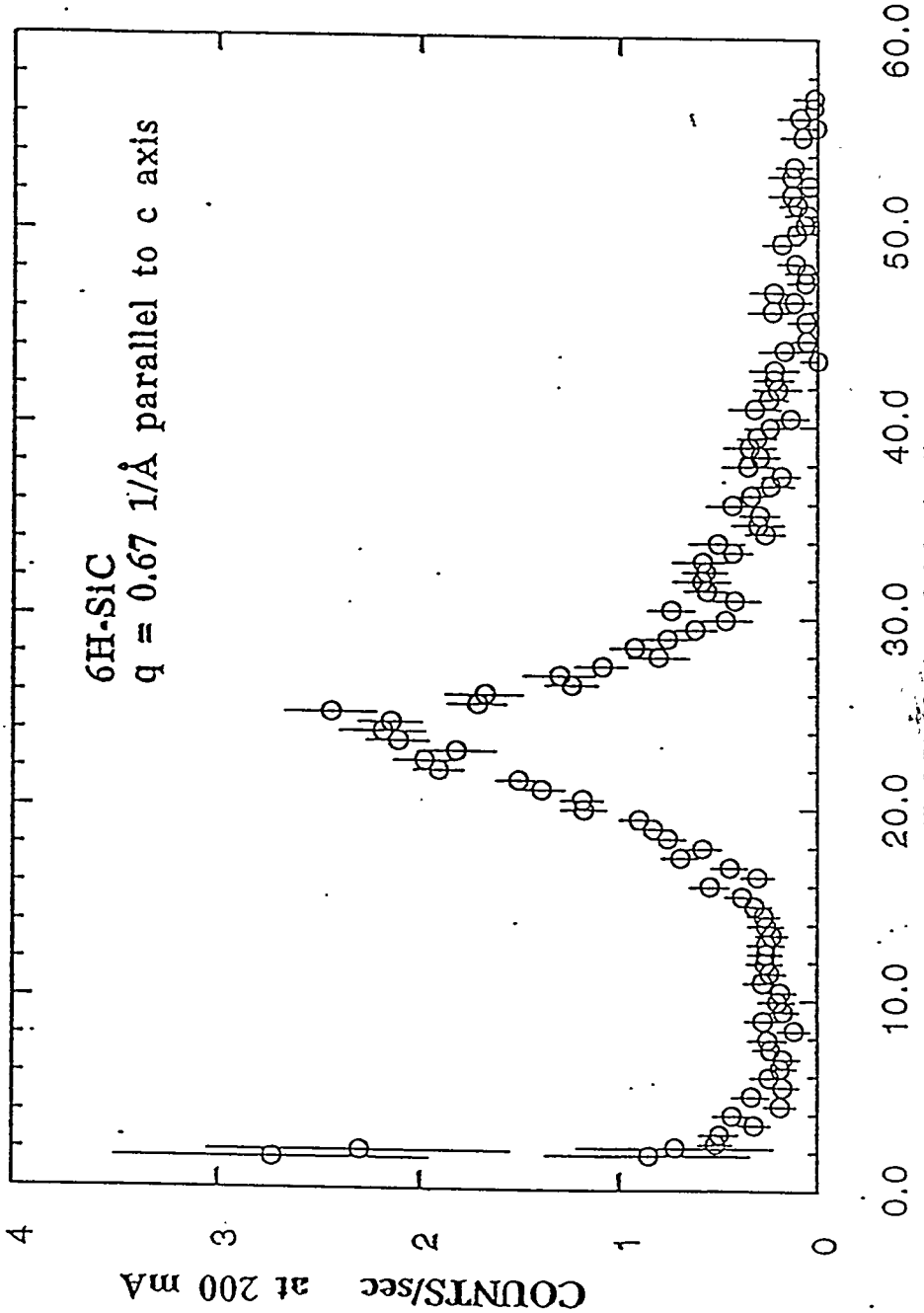

Figure 2. IXS data for single crystal 6H-SiC showing a plasmon peak.

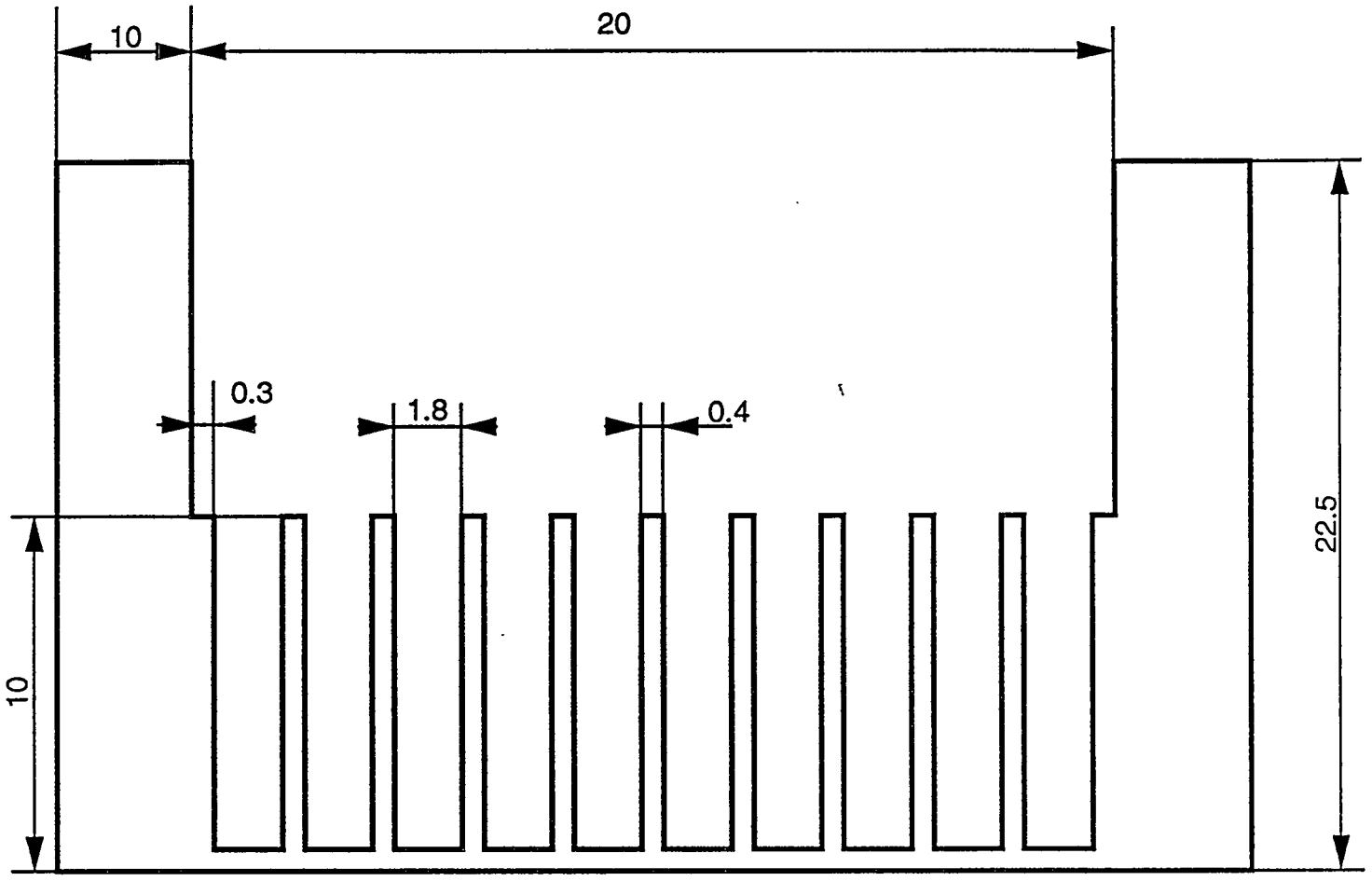

Figure 3. Ribbed sagittal focusing crystal intended for UNI-CAT

92-182R2 -- FEASIBILITY STUDY FOR THE TARGET STATIONS FOR THE INTENSE PULSED NEUTRON SOURCE UPGRADE

Associate Laboratory Director's Office: Physical Research

Principal Investigators: J. M. Carpenter and B. S. Brown, Intense Pulsed Neutron Source

Funding Profile:

FY 1992	$ [1]
FY 1993	$ [1]
FY 1994	$213.9K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: Complete the feasibility study and cost estimate for the neutron target and moderator systems for an IPNS upgrade.

Approach: Pulsed neutron sources, led by the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory and ISIS, the spallation neutron source at Rutherford, have already made outstanding contributions to condensed matter research. The complementary capabilities of pulsed neutron sources in relation to reactor sources have been convincingly demonstrated. Indeed, in many areas, pulsed sources are even now superior to reactor sources. The main point to make in comparing the different types of sources is that reactor sources cannot be easily scaled up to any significant degree. The Advanced Neutron Source (ANS) is designed [at a total project cost (TPC) of $2.7B] to increase the neutron flux by only a factor of five over ILL (Institute Laue-Langevin), the world's premier research reactor at Grenoble, which is over 20 years old. In contrast, the Europeans are proposing a pulsed source, the European Spallation Source (ESS), that will be an increase of a factor of 30 over ISIS for about $1B. The large difference in extra capability versus cost reflects the fact that reactors are a mature technology while the developing technology of accelerator based neutron sources promises efficient, effective, safe and non-proliferating extensions of neutron research capabilities.

The Argonne plan for an IPNS upgrade that was presented to the Basic Energy Sciences Advisory Committee (BESAC) Panel on Neutron Sources (chaired by W. Kohn) will be a significant gain (x6) over ISIS, making it the most powerful spallation source in the world. Advanced concepts (5 MW beam power) can be tested on the upgrade. Argonne has many points favoring building an advanced source here, such as a strong history of neutron scattering, the very successful operation of IPNS, long and successful experience with accelerators, the APS favorable record for design and construction, and a significant savings by building the new source at Argonne by using existing components, buildings, and infrastructures.

Technical Progress and Results: The LDRD project in FY1992 to study the PNRF concept was abruptly redirected in early July when the Director of ER at DOE, W. Happer, established a panel reporting to BESAC to study future neutron sources. A preliminary design of the IPNS

[1]Subtask of another project in FY 1992 and FY 1993.

upgrade was presented to the Panel in September 1992. In January 1993, the panel made as one of their principal recommendations "the development of competitive proposals for the cost-effective design and construction of a 1-MW pulsed spallation source (PSS)." In response to this recommendation, the feasibility study for the IPNS upgrade continued through FY 1994.

As part of this effort, workshops were held jointly with Los Alamos on "Accelerators for Advanced Spallation Neutron Sources" at Santa Fe in February 1993 and at Argonne in May 1993 to discuss "Scientific Opportunities at Future Spallation Neutron Sources."

Activities pursued during FY1994 were the reiteration of the design of the target stations and the elaboration in greater detail of conventional facilities related to the target stations. The comments of the Target Station Review Committee which met in July 1993 significantly guided the reiteration. We have considerably improved on the originally reviewed concepts and in the course of the work found it necessary to change the reference design target material. We prepared detailed information required for the conventional facilities estimates that were made under the aegis of the Accelerator Design portion of this study. We prepared new materials to expand and alter the existing feasibility study report according to the newly completed work.

One of the major changes the review group suggested was to provide for quicker, easier servicing of the target-moderator-reflector module. The new design has a split target as originally, but in a single unit that facilitates removal. The arrangements for access to the moderators have been greatly simplified, no longer requiring that the reflector be disassembled to remove any moderator.

We completed a study of available information on the irradiation and corrosion behavior of heavy refractory metals as target material. Upon completion of the Loss-of-Coolant Accident (LOCA) analysis for the original design basis tantalum target, we found that temperatures would be higher than desirable because of the levels of post irradiation decay heat. Tungsten is superior to tantalum in this respect. Reports of Russian work were found that show that corrosion of tungsten in the water cooled radiation environment can be suppressed by plasma coating with titanium, enabling tungsten to be used without concern for the corrosion of the bare metal. Consequently we have redone the design on the basis of tungsten alloy target material.

Design of cooling system components and arrangements was completed. These details enabled completion of the estimates for conventional facilities, including several needed minor new structures. Detailed specifications were completed for electrical, water, compressed air, heating, ventilation and air conditioning, etc. services to the experimental facilities, which enabled conventional facilities estimates to be completed. We introduced the concept of raised flooring in the experiment halls to facilitate conventional services and signal cable access to the neutron scattering research instruments.

Specific Accomplishments: Chapter 3 of the IPNS Upgrade Feasibility Study, Target Stations for a 1-MW Pulsed Spallation Neutron Source, was printed in May 1993. This was formally reviewed in July 1994, and studies in FY 1994 have led to considerable revisions of this report.

A workshop on "Technology and Science at a High-Power Spallation Source" was held at Argonne in May 1993. The proceedings of the workshop were published in February 1994.

"Refinements on Material Selection for a Target for the 1 MW Neutron Spallation Source," J. L. Routbort, May 1994.

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93-002R1 -- DESIGN OF NEW DEVICES FOR PRODUCTION OF ELLIPTICALLY POLARIZED X-RAYS FOR THE BASIC ENERGY SCIENCES SYNCHROTRON RADIATION CENTER

Associate Laboratory Director Area: Physical Research

Principal Investigators: M. Bedzyk, M. Ramanathan, and P. A. Montano, Materials Science Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$250.9K
FY 1994	$248.6K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: To design optical components for the use of elliptically polarized synchrotron radiation at the BESSRC beam lines.

Approach: To design and develop new optical components for the elliptical multipole wiggler beam line at Basic Energy Sciences Synchrotron Radiation Center at the APS. To continue with the design in collaboration with the APS staff of the EMPW device with the desired characteristics for the scientific program of BESSRC beam line at APS. The optical components will be preliminarily tested at our beam lines at NSLS. The construction of the Basic Energy Sciences Synchrotron Radiation Center will facilitate the access by ANL researchers and general users science and will make important contributions to materials sciences, chemical sciences and atomic physics. The study of the magnetic structures of novel materials will become a reality with the advent of easily tunable polarized radiation from wiggler sources. Magnetic scattering experiments require a high photon flux and defined polarization. The APS is an ideal source of X-ray radiation for such studies. Present generation facilities do not have the brilliance needed to tackle some of the most important problems in magnetic scattering using X-rays such as, for example, determination of the magnetic structure of thin films.

Technical Progress and Results: We have modified in collaboration with the APS staff the requirements for the design of the insertion device to produce circularly polarized X-ray at the BESSRC beamline. The central piece in the production of circularly polarized high energy X-rays at this facility is the insertion device. We propose to use an elliptical multipole wiggler for such purposes. The EMW vertical magnetic field is produced by the 20 periods of the hybrid magnetic structure with the period length of 15 cm. In the current design a peak field value of 1 T for the vertical component is achieved that corresponds to a vertical K_y of 14. (K is the Kincaid deflection parameter and K_x and K_y are its horizontal and vertical components.) The peak field value for the horizontal component is 0.076 T and the K-value is equal 1.06. The EMW has an internal ends compensation system in order to control a first and second fields integrals with the required accuracy. The EMW electromagnet poles are fabricated from laminated iron in order to operate with a switching frequency up to 10 Hz. The hybrid magnetic structure and the electromagnet are mounted on the support frame with the drive system that permits to change the gap of the hybrid structure. The vertical K in this case will change from 14 to smaller values and when it will reach the value equal of 1 the EMW will operate as a

helical undulator. Field computations were carried out with the nonlinear 3-D magnetostatic code TOSCA. For the geometry shown, $K_y = 12$ for the hybrid magnet and $K_x = 1.06$ for the electromagnet. K_y can be increased by placing magnet and pole materials more efficiently in the available space. K_x is limited by the large gap (71 mm) and the silicon steel of the electromagnet yoke and pole, which saturates at a relatively low flux density. Refining the design of the yoke and pole should allow a higher value of K_x. Figure 1 shows a schematic design of one quarter period of the insertion device. Figure 2 shows the magnetic field profile for a quarter period of the insertion device.

The total length of the straight section where the EMW will be located is 5.59 m and the device is 3 m in length. The vertical aperture of the vacuum chamber is 1.94 m, enough to place inside the vacuum chamber (VC) two non-evaporative getter (NEG) strips of 15 mm width each. These NEG strips are spot welded to the side walls of the vacuum chamber and can provide enough pumping speed to maintain the necessary pressure inside the vacuum chamber (1^*10^{-9} torr). To activate the NEG strips we are going to bake the whole EMW VC with the NEG strips inside to a temperature up to 450°C. Two long bellows sections will accommodate the thermal expansion of the EMW VC and make available smooth temperature transition to other parts of the vacuum system whose temperature during the baking procedure should not be higher then 180°C. Inside the multifunctional box made of stainless steel there is a cooled copper transition section from the storage ring elliptical aperture to the rectangular aperture of the EMW VC. It has two pumps (30 l/sec ion pump and a 220 l/sec lamped NEG pump) and two ports for rough pumping and for the ion gauge and RGA heads. On the downstream side of the EMW VC there is a second transition piece from the EMW VC to storage ring VC. The remaining part of the straight section is occupied by a short section of the standard storage ring vacuum chamber.

Figures 3 and 4 show the results of the calculations for the brightness and degree of circular polarization (P_c). The brightness and P_c were evaluated as a function of photon energy using the Stokes parameters. We used a vertical angular divergence value, $s_{y'}$, of 9 mrad. The calculations shown in figures 3 and 4 were performed for a vertical observation angle equal to zero (on axis). One can observe the high degree of polarization that is attained at high energies as well as with the high brightness of the source. The circular polarization can be changed from right to left by switching the electromagnets polarity, it can be done as fast as 10 Hz. By focusing the beam high brilliance can be achieved which is very favorable for surface scattering experiments.

The EMW beamline will consist of three experimental stations. The beamline optics will deliver monochromatic radiation with tunable energy, bandpass, and polarization. The three stations will operate in tandem with only one station receiving X-rays at any one time. The three stations have three distinguishing functions; namely Compton Scattering, Magnetic Scattering and Spectroscopy, and a white light hutch (i.e., for Laue measurements). The optics going from downstream to upstream will consist of a cooled vertically focusing mirror, a double crystal monochromator and a steering mirror. The monochromator system will be designed in such a fashion that the degree of circular polarization will not be perturbed by the optical components. We plan to use this monochromator in the range between 10 to 40 keV. For high energy scattering experiments (60 keV or more) the mirrors and double crystal monochromator will be moved vertically to allow the x-radiation to impinge on a Si (111) crystal water cooled

double focusing monochromator. When the beamline is operating at high energies a set of filters will be introduced before the monochromator to absorb the majority of the photons below 40 keV. At lower energies the EMW device will operate with lower K_y values to reduce thermal loads on the optics. The mirrors and monochromators will be water cooled.

Our objective is to obtain high photon flux with energies above 20 keV and well characterized polarization. For Compton scattering the detectors should have high efficiency for high energy X-rays. We are planning to use an array of solid state detectors. The sample will be mounted in a magnetic field (an electromagnet for rapid magnetic field reversal). Electron detection in coincidence with the scattered X-ray can also be used in thin film samples. Such experiments can reveal more details of the energy -momentum space in a small volume than conventional Compton scattering. The realization of such experiments is strongly dependent on the photon flux at the high energy end of the wiggler's radiation.

Specific Accomplishments: A paper was presented at the International Conference on "Synchrotron Radiation Instrumentation," Stony Brook, L.I., N.Y. (July 1994).

A paper, "Elliptical Multipole Wiggler Facility at The Advanced Photon Source," by P.A. Montano[1], G.S. Knapp[1], G. Jennings[1], E. Gluskin[2], E. Trakhtenberg[2], I.B. Vasserman[2], P.M. Ivanov[2], D. Frachon[2], E.R. Moog[2], L.R. Turner[2], G.K. Shenoy[2], M.J. Bedzyk[1], M. Ramanathan[1], M.A. Beno[1], and P.L. Cowan[3] will appear in the *Review of Scientific Instruments*.

[1] Materials Science Division, Argonne National Laboratory, Argonne, Ill. 60439.
[2] Experimental Facilities Division, APS, Argonne National Laboratory, Argonne, Ill. 60439.
[3] Physics Division, Argonne National Laboratory, Argonne, Ill. 60439.

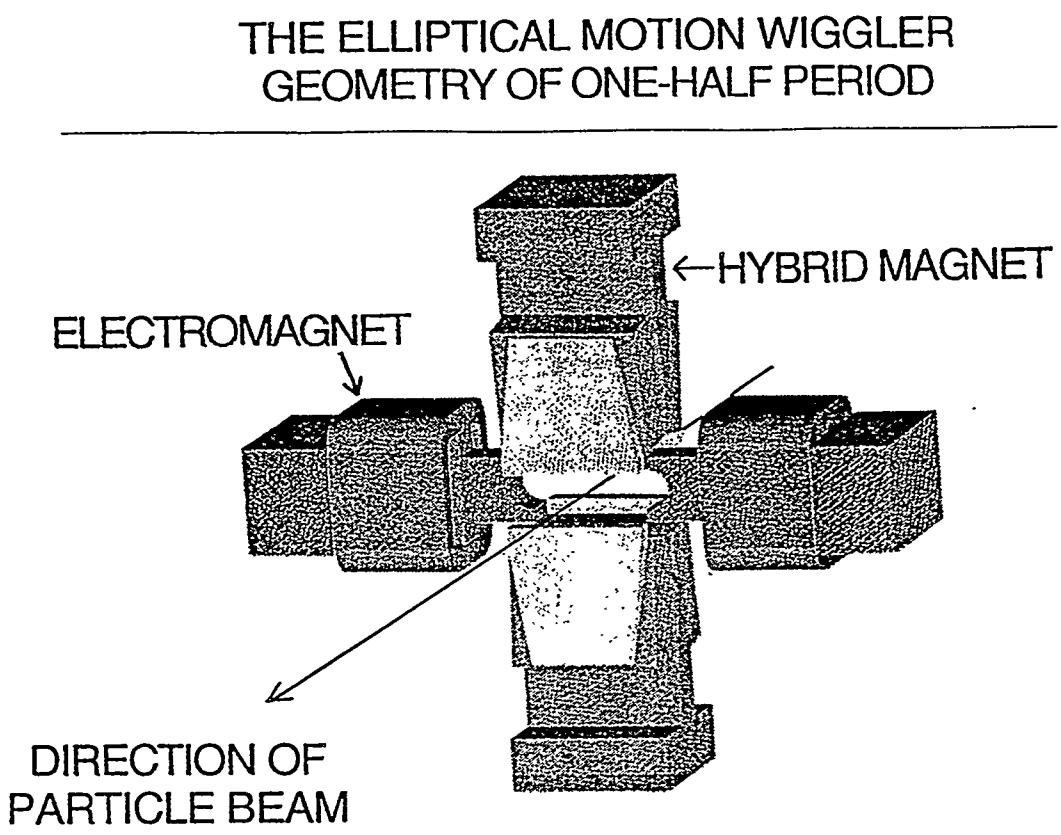

Figure 1. Schematic design of one quarter period of the insertion device.

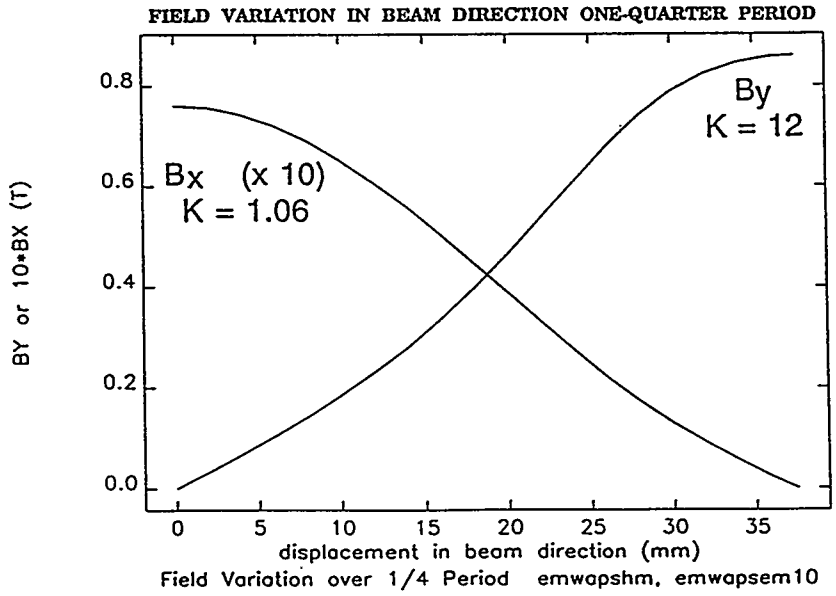

Figure 2. Magnetic field profile for a quarter period of the insertion device.

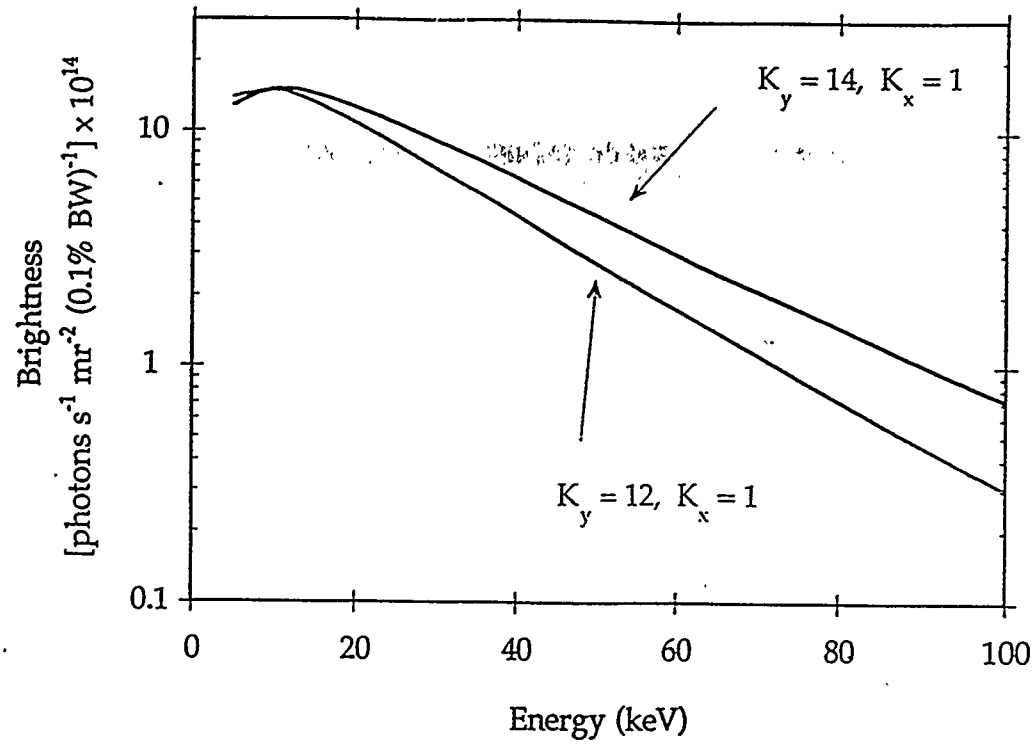

Figure 3. Brightness vs photon energy for K_y=12 and 14, K_x=1.

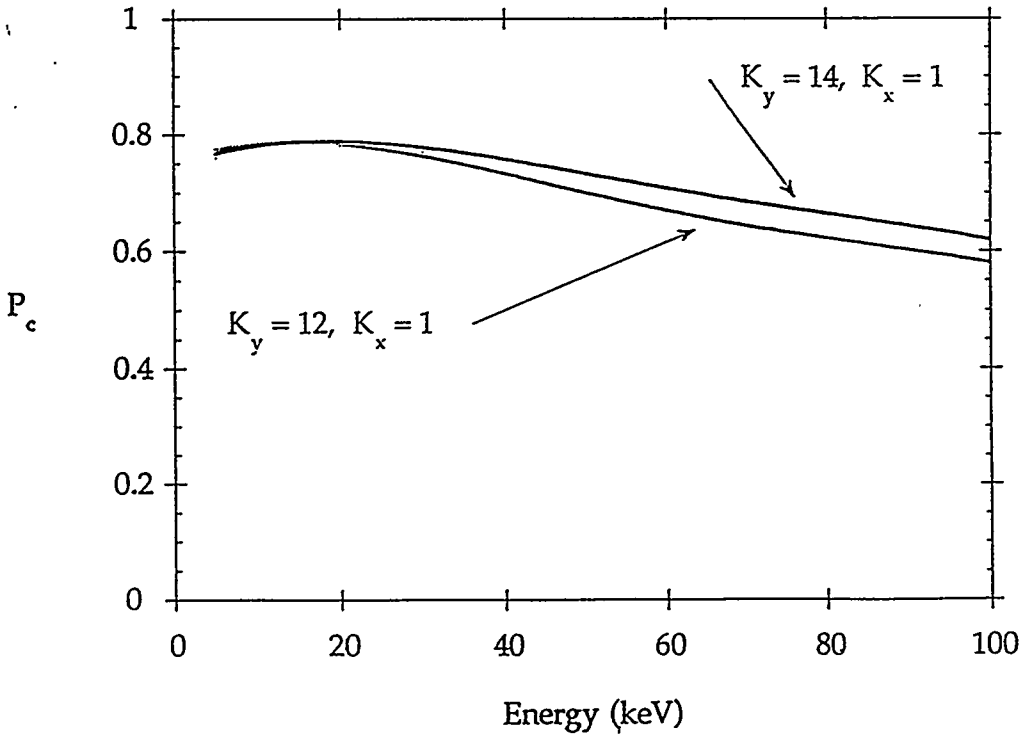

Figure 4. Degree of circular polarization (Pc) vs photon energy for K_y=12 and 14, K_x=1.

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93-003R1 -- DEVELOPMENT OF SMALL ANGLE SCATTERING AND ANOMALOUS SMALL ANGLE SCATTERING TECHNIQUES

Associate Laboratory Director Area: Physical Research

Principal Investigators: G. S. Knapp, M. A. Beno, and M. Ramanathan, Materials Science Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$225.9K
FY 1994	$202.0K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The principal objective of this project was development of new techniques for small angle X-ray scattering, (SAXS) and anomalous small angle X-ray scattering (ASAXS). An APS undulator is an ideal source for SAXS measurements in that it is very well collimated and very intense. In order to use this high brilliance X-ray source, the continued development of new instrumentation using a new focusing optic system has been carried out.

Approach: Small angle X-ray scattering (SAXS) is a powerful technique for studying structural features with length scales falling in the 10 to 10000 Ångstroms, providing information on the size and morphology of the particles in a matrix, particle size distribution in the case of polydispersed systems, and dimensionality of fractal objects and surfaces (mass and surface fractals). Anomalous small angle scattering (ASAXS) gives more detailed information since the contribution of a particular type of atom to the scattering can be changed thereby allowing one to derive much more information about the distribution of those atoms in the material. These methods have been widely used for the characterization of microstructure in various branches of science and technology, including condensed matter physics, biophysics, polymer science, metallurgy and ceramics.

SAXS is a weak effect compared to, for example, Bragg diffraction from crystals and thus requires a highly collimated intense beam. The ASAXS technique which involves measuring differences between SAXS patterns imposes very stringent limitations on scattering intensity, noise and background. The properties of synchrotron radiation from an undulator source are well matched to the experimental requirements of the SAXS and ASAXS techniques since this type of insertion device produces a very small, highly collimated beam. The Basic Energy Sciences Synchrotron Radiation Center (BESSRC) will develop a SAXS facility at APS to carry out structural studies on materials of interest to the Chemistry and Material Science Divisions.

The optical systems used for anomalous synchrotron small angle scattering studies have in general involved the collection of spectra one point at a time. Those instruments which utilize an area detector provide high data rates but are not suitable for measurements near absorption edges since the sample induced backgrounds would exceed the small angle scattering signal. To rapidly collect high resolution SAXS and ASAXS data at a APS undulator beamline, the development of new crystal optics is necessary.

Technical Progress and Results: We have developed a new class of focusing crystal optics which allow the collection of SAXS or ASAXS patterns with a 1-dimensional or 2-dimensional detectors. Theoretically, these techniques should provide data collection rates many times faster than the traditional point by point data collection methods but retain the excellent energy resolution and low backgrounds provided by these slower methods. Testing of these new SAXS techniques has been done on the focused beamline, X6B, at NSLS. These tests have allowed us to collect data for standard samples with high spatial and energy resolution in times comparable with the best SAXS beamlines at NSLS. This method (see figure 1) uses a focusing diffracted beam monochromator and a linear position sensitive detector. Using this method, fluorescence, slit scattering and scatter from windows and air in the vicinity of the sample can almost be eliminated. This new method allows a range of angles to be measured at the same time thereby increasing the count rate by a large factor. We have also begun testing this new method for ASAXS measurements of Steel samples using NSLS beamline X6B. This work done in collaboration with D. Alexander (ANL-MSD) and P. Jemian (UNI-CAT) showed that this method can be used to collect high quality ASAXS data rapidly in both the large and small momentum transfer regions. At the same time, fluorescence, slit scattering and scatter from windows and air in the vicinity of the sample were almost eliminated. This new method allows a range of angles to be measured at the same time thereby increasing the count rate by a large factor for ASAXS also.

The results for a standard sample using this technique are shown in figure 2. The total data collection time for the SAXS pattern of the collagen fiber was only a few minutes using this technique. The most prominent peaks in the pattern are the sixth, ninth and eleventh order diffraction peaks from the 650 Å fibers of the muscle protein.

Some of the improvements to the instrument which must still be tested are the use of a larger sample to detector distance for increased angular resolution. This may also serve to further reduce the instrument background, although both the angular resolution and background from this run were excellent. The use of a 2-dimensional detector should also help to provide more detailed information in a shorter time.

Specific Accomplishments: The SAXS method employing a curved focusing perfect crystal analyzer and linear position sensitive detector has been shown to provide small angle scattering data of equal or better quality than conventional methods with data collection times a fraction of those required for point by point methods. The use of this technique for ASAXS measurements has also been demonstrated.

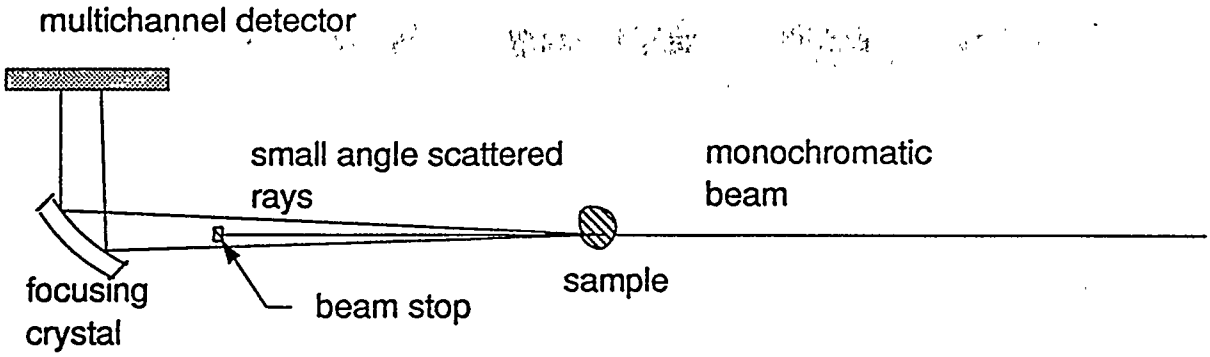

Figure 1. Schematic drawing of a crystal geometry for small angle scattering employing a bent focusing perfect crystal analyzer and a multichannel detector. This optic has been shown to possess high spatial and energy resolution and to suppress sample induced backgrounds.

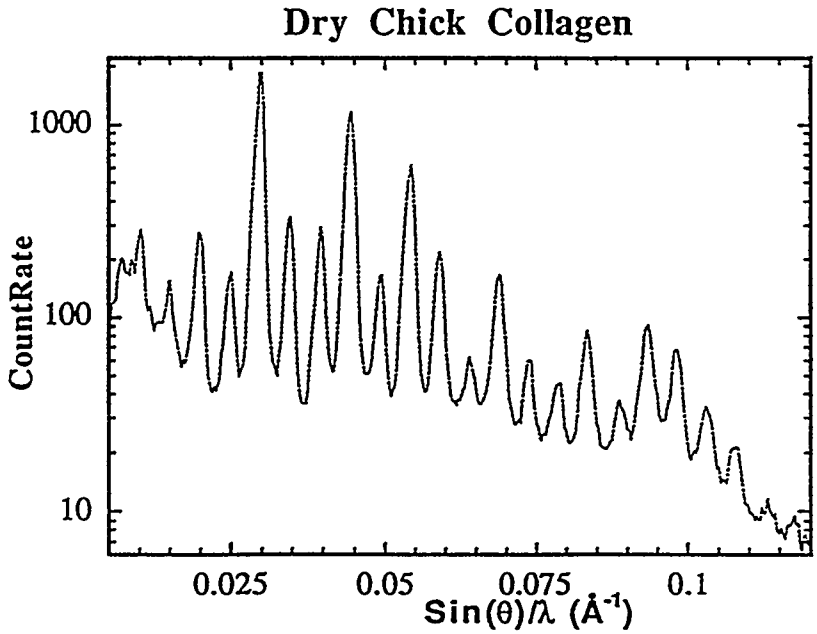

Figure 2. Small angle scattering from dry chick collagen. The pattern shows the excellent spatial resolution and low background achievable with this technique.

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93-004R1 -- ABSORPTION, FLUORESCENCE AND COINCIDENCE EXPERIMENTS USING SYNCHROTRON RADIATION

Associate Laboratory Director Area: Physical Research

Principal Investigators: P. L. Cowan (Deceased, 8/16/94) and D. S. Gemmell, Physics

Funding Profile:

FY 1992	$ -0-
FY 1993	$312.0K
FY 1994	$353.1K
FY 1995	$290.0K
FY 1996	$ -0-

Purpose: Investigate problems in atomic, molecular and optical (AMO) physics using synchrotron radiation.

Approach: There are two principal components in our effort to establish a program in AMO physics with synchrotron radiation: 1) performance of experiments at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, and 2) preparations to conduct a research program at the Advanced Photon Source (APS) at Argonne.

1) Work at the NSLS (H.G. Berry, P.L. Cowan, D.S. Gemmell, J. Suleiman, and T. LeBrun). We shared with staff from NIST the responsibility for operation of the X24A beamline at the NSLS. We provided half the support for the beamline technical support person (B. Karlin) and we performed measurements at the beamline with objectives that included developing expertise and research goals for a program at the APS. Our work received important theoretical guidance in this period from the presence in the Physics Division of M. Ya. Amusia as an Argonne Fellow.

2) Preparations for the APS (H.G. Berry, P.L. Cowan, D.S. Gemmell, E.P. Kanter, T. LeBrun, and L. Young). The APS is expected to commence operations for research early in 1996. The Basic Energy Sciences Synchrotron Research Center (BESSRC) is likewise expected to start its research programs at that time. As members of the BESSRC CAT (Collaborative Access Team), we began preparing, together with scientists from the University of Western Michigan and the University of Tennessee, to initiate a series of atomic physics experiments that will exploit the unique capabilities of the APS, especially its high brilliance for photon energies extending from about 3 keV to more than 50 keV.

Technical Progress and Results:

1. At the NSLS: Several measurements (including some in collaboration with NIST) were completed at the X24A beamline over the past year, including:

   - X-Ray Absorption Spectroscopy in Argon - We studied multiple excitation of the KM and KL systems in argon. The experiment used a low-pressure absorption chamber. The signals were obtained from a PIN diode located after the chamber, normalized to an

initial ion-chamber signal. Relativistic Hartree-Fock calculations (the GRASP II code) enabled us to identify most of the structures. Several of these identifications did not agree with earlier assignments from previous lower-resolution experiments. Our excellent signal-to-noise ratio allowed us to pinpoint very weak features in the spectra. This work was part of the Ph.D. thesis of J. Suleiman. We extended the measurements using the pressure-variation technique to determine precise values of the absolute attenuation cross section for X-rays around the argon K edge. We reached our goal of obtaining the 1% accuracy necessary to distinguish between several different calculations. Previous measurements were accurate to about 5%.

- Alkali Photoabsorption Spectra - Initial experiments used a heat pipe to study the K-edge absorption spectrum in atomic potassium vapor. To examine very weak features, we constructed an improved heat pipe with absorption-lengths stable over time periods of up to a week. We studied the photoabsorption spectra of potassium at a few hundred volts above the K-edge in the photon energy range 3600 to 3650 eV. Using the GRASP II multiconfigurational Dirac-Fock code, we made preliminary identifications of most of the peaks observed at the K and KM edges. We were able to produce a theoretical spectrum for the K edge which agreed very well with the measurements by including an experimental width and calculated oscillator strengths, plus an arctangent function to account for the ionization threshold. Initial absorption measurements were also made near the K edge in rubidium. We made a systematic comparison of these alkali spectra with those of the corresponding closed-shell rare gases obtained previously at X24A and elsewhere. We found a significant enhancement of the 4p (in potassium) and the 5p (in rubidium) resonances as compared to the argon and krypton spectra.

- Photoabsorption in Helium from 2 to 14 keV - We measured the total attenuation cross section of helium with 1 - 2% accuracy for photons in the energy range from 2 to 14 keV using the X24A, X23B and X23A2 beamlines. At these energies, the photoionization and coherent (Rayleigh) scattering cross sections decrease rapidly, so that Compton scattering dominates at the higher energies. We were able to verify this and to demonstrate the importance and relevance to recent measurements of the ratio of double-to-single photoionization of helium. The measured absorption cross sections are close to recently calculated values. We held a two-day workshop at Argonne in October 1993 on these topics. The proceedings were published as an ANL Report.

- Argon and Potassium Ion Time-of-Flight Spectra near the K Edge - We studied the photoion production from argon and potassium around their respective K edges. The argon emerged from a nozzle which for the potassium measurements was replaced by a heated oven jet. Ions with charge states ranging from 2 to 8 were detected by a channel-plate detector at the end of a time-of-flight apparatus and their relative intensities measured as a function of energy from 100 eV below the K edge to above the KM resonances. Charge-state production rates in this region are smooth and slowly varying. Although the 4p resonance typically has a width of less than 1 eV in photoabsorption studies, the ion charge states +4, +5 and +6, especially, have broader distributions of up to 10 eV. This extended variation below threshold is probably due to interferences in the photoionization from doubly-excited states of the neutral atom.

- X-Ray Resonant Raman Spectroscopy - X-ray resonant Raman scattering has great promise as a high-resolution x-ray probe of the electronic structure of matter. Unlike other spectroscopies, the technique avoids the loss of energy resolution through inner-shell-hole-lifetime broadening. In addition, measurements of polarization and angular anisotropic effects are helpful in studies of symmetries of electronic states of atoms and molecules.We began studies of the L edge of xenon, where the lifetime broadening is a major feature of spectra previously observed. The many fluorescence channels enabled us to examine several possible polarization effects.

- Auger Resonant Raman Spectroscopy - We extended the resonant Raman techniques to electron spectroscopy to study the KLL Auger spectrum in argon. The Raman spectrum showed excitation to the 4p, 5p and higher Rydberg resonances, while other Auger lines had negligible intensity. Their wider spacing in the ion spectrum yielded much better resolution in the spectra, so that the higher Rydberg states could be partially resolved.

- Coincidence Studies of Inner-shell Vacancy Cascades - We began developing coincidence techniques that are expected to help understand the complex decay paths of inner-shell-vacancy states decaying via Auger and fluorescence processes. Thus, for example, we have studied specific pathways that follow the excitation of a 1s electron in argon by using a cylindrical-mirror analyzer to detect electrons in coincidence with photons measured with a Si(Li) detector.

2. Preparations for the APS: The first APS atomic physics experiments will be conducted on the BESSRC undulator beamline and we have thus concentrated over the past year on various aspects of that beamline and its associated experimental areas. During FY 1994 our group has undertaken responsibilities in such areas as hutch design, evaluation of undulator performance, sagittal focussing in the cryogenically cooled crystal monochrometer, user policy, interfacing and instrumentation, etc. We have produced detailed design drawings for the three experimental hutches in preparation for a preliminary design review. In FY 1995 progress will continue on design and construction of high-performance X-ray mirrors, crystal monochromators and timing shutters. These devices have to maintain their alignment under the high radiated power loads expected at the APS. In FY 1994 we developed plans for an atomic physics research program at the APS. Initial experiments will probably utilize existing apparatus developed for work at the NSLS. We are, however, planning to move rapidly to more sophisticated measurements involving, for example, ion-beam targets, simultaneous laser excitation, and the spectroscopy of emitted electrons and X-rays. Thus our plans for FY 1995 include a design study for a small accelerator (and possibly a small ion-storage ring) inside the atomic physics hutch to be used in conjunction with a fast high-powered synchronous laser, and various electron and photon spectrometers. We hosted an international workshop on "Atomic Physics at High-Brilliance Synchrotron Sources" at Argonne in April, 1994. The proceedings are in press.

Specific Accomplishments:

"Resonant X-ray Raman scattering from atoms and molecules," P.L. Cowan, in *Resonant Anomalous X-ray Scattering, Theory and Applications*, G. Materlik et al (eds), Elsevier Science B.V., p449 (1994).

"Cascade effects on the Ar LMM Auger spectrum," J.W. Cooper, S.H. Southworth, M.A. MacDonald, and T. LeBrun, *Phys. Rev.* A50, 405 (1994).

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Proceedings of the Workshop on "Atomic Physics at High-Brilliance Synchrotron Sources," April 23-24, 1994. In press.

"On the mechanism of the smooth increase of the mean ion charge in argon photoionization near the K-edge," M. Ya. Amusia, *Phys. Lett.*, A183, 201 (1993).

"High-energy behavior of the double photoionization of helium from 2 to 12 keV," J.C. Levin, I.A. Sellin, B.M. Johnson, D.W. Lindle, R.D. Miller, N. Berrah, Y. Azuma, H.G. Berry and D.H. Lee, *Phys. Rev.*, A47, 698 (1993).

"Lattice position of Si in GaAs determined by X-ray standing wave measurements," A. Shih, P.L. Cowan, S. Southworth, L. Fotiadis, C. Hor, B. Karlin, F. Moore, E. Dubisz, and H. Dietrich, *J. Appl. Phys.*, 73, 8161 (1993).

"Comparison of double and single ionization in He by photons and by charged projectiles," I.A. Sellin, J.C. Levin, R.D. Miller, N. Keller, Y. Azuma, H.G. Berry, N. Berrah-Mansour, and D.W. Lindle, SPring-8 Workshop on "Atomic Physics at High Brilliance Synchrotron Radiation Facilities", Japan Castle Research Center, Himeji, Japan, March 23-24, 1992 (Proceedings published 1993).

"Ion charge-state production and photoionization near the K-edge in argon and potassium," H.G. Berry, Y. Azuma, P.L. Cowan, D.S. Gemmell, T. LeBrun and M. Ya. Amusia, Proceedings of the 7th International Conference on the Physics of Highly Charged Ions, Vienna, Austria, September 19-23, 1994. In press.

93-007R1 -- DEVELOPMENT AND CHARACTERIZATION OF TRANSITION METAL CLUSTER BEAMS FOR X-RAY ABSORPTION STUDIES

Associate Laboratory Director Area: Physical Research

Principal Investigators: S. J. Riley and M. B. Knickelbein, Chemistry Division

Funding Profile:

FY 1991	$ -0-
FY 1992	$ -0-
FY 1993	$ 58.3K
FY 1994	$ 98.8K
FY 1995	$ 90.0K

Purpose: A method for producing a high flux, nearly continuous molecular beam of transition metal clusters is needed in order to perform in-flight X-ray studies of these transient species at APS. Currently available methods of gas phase metal cluster generation employ high peak power, low-repetition rate (<100 pps) pulsed lasers for the metal vaporization process. This project investigates the use of a special high-repetition rate laser for vaporization of transition metals as a means of quasi-continuous production of a high-density metal cluster beam.

Approach: There is slowly emerging an understanding of the relationships between metal cluster structure and chemical reactivity. Such understanding is vital to the eventual design of more efficient and selective heterogeneous catalysts. What little we now know has been derived from chemical probes of cluster structure, but these are inadequate to provide detailed information as to metal-metal coordination and the location of adsorbate binding sites. Calculations have shown that if stable, high-flux cluster beams can be produced, X-ray absorption studies at APS will be able to provide such information.

The scope of this project is to develop and refine a method of producing a stable, quasi-continuous molecular beam of metal clusters, adapting existing cluster source technology for use with a high average power, high repetition rate pulsed copper vapor laser, and to characterize the number density and size distribution of the clusters so produced.

A high repetition rate (6 kHz) copper vapor laser will be used in conjunction with a cooled, continuous-flow cluster source in order to investigate production of continuous metal cluster beam.s Various transition metals will be investigated in order to gauge the generality of the method. Detection and mass analysis of the neutral cluster distribution will be accomplished via laser ionization time-of-flight mass spectrometry, a capability already in place.

Technical Progress and Results: The project centers around a Plasma Kinetics copper vapor laser that is on loan from another group. In the first year an existing laboratory was modified to accommodate this laser, and the laser was prepared for operation. In last year's Annual Report we noted that the cluster source and molecular beam/mass spectrometer apparatus are already in operation, so we felt that investigations could begin as soon as the laser was made operational. This turned out to be more of a problem than we anticipated. Considerable effort and time were spent before we could get the laser to work reliably, but we were finally able to

do so. Metal target vaporization tests demonstrated the production of an aluminum atom beam, but the laser's fluence (photons/cm^2) was too low to produce sufficient atom density for cluster formation. We have procured unstable resonator optics for the laser which should greatly increase its beam quality and allow focussing to higher fluences. We have every expectation that cluster studies can begin very soon.

Specific Accomplishments: N/A

94-142N -- INELASTIC X-RAY SCATTERING STUDIES USING HIGH AND ULTRA HIGH ENERGY RESOLUTION

Associate Laboratory Director Area: Physical Research

Principal Investigator: P. A. Montano, Materials Science Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$198.8K
FY 1995	$150.0K
FY 1996	$100.0K

Purpose: We propose to design a new experiment for X-ray inelastic scattering using synchrotron radiation at the NSLS. This experiment will serve as a prototype for our research program at the Advanced Photon Source (APS).

Approach: The construction of the Basic Energy Sciences Synchrotron Radiation Center will facilitate access by ANL researchers and general users to new fields of condensed matter science. The use of X-ray inelastic scattering to study collective excitations in condensed matter opens new frontiers of research. This technique will play a prominent role with the arrival of the APS. The use of X-rays promises to displace other commonly available techniques in the study of collective excitations in solids.

Inelastic X-ray scattering is an important tool to study a large number of physical properties in condensed matter systems. The arrival of synchrotron radiation sources has provided enough photons to evaluate the feasibility of inelastic scattering experiments.[1,2] The high brilliance of the APS undulator will make it an optimal source of photons for inelastic scattering experiments. One advantage of X-ray vs neutron inelastic scattering is the possibility of studying collective excitations in small samples (~ 1 mm^2). Inelastic X-ray scattering can be used to determine electron momentum distributions, to obtain information on collective and single excitations of electrons, to measure the lattice dynamics of solids (ultrahigh energy resolution), and Raman scattering[3]. For the band width of 0.1 to 1 eV (high energy resolution), we can study unbound (band forming) electrons including conduction electrons. The high energy resolution of 0.1 to 1 eV is also important for studies of collective excitations (plasmons). There are other techniques that provide information on collective excitations, such as electron energy loss. In these techniques multiple scattering effects at high momentum transfers tend to make interpretation of the measurements very complicated. Therefore, none of these techniques are expected to be as accessible to theoretical modeling and provide as clean data as X-rays inelastic scattering. We plan to use this experimental technique to study collective electronic excitations from solids. High photon energy studies of inelastic X-ray scattering are also of interest in that the validity of the used physical approximation is dependent upon the momentum transfer and, hence, scattering angle. We plan to build a new apparatus to be used for X-ray inelastic scattering experiments. To carry out detailed studies of the collective excitations in high temperature materials like 6H-SiC.

Technical Progress and Results: Study of dynamic structure factors of condensed matter systems, $S(\vec{Q},\omega)$, has been limited to inelastic neutron scattering experiments. One clear advantage that inelastic X-ray scattering measurements have over the neutron inelastic scattering measurements is the fact that energy transfer and momentum transfer are nearly independent quantities. Therefore the energy transfer of X-rays can be measured at a fixed momentum transfer. This degree of freedom opens up new regions in the $(\vec{Q},\omega)$ phase space diagram that was not accessible by any other means. We propose to use this experimental technique to study small single crystals, excitations from the surface in a total reflection geometry, etc. Inelastic X-ray scattering has also important advantages for studies of atomic and inner-shell physics. High-resolution studies have the interesting feature that narrow energy band-pass translates into longer photon-atom interaction times. High photon energy studies of inelastic X-ray scattering are also of interest in that the validity of the impulse approximation is dependent upon momentum transfer and, hence, scattering angle. The study of scattering in the intermediate momentum-transfer regime involves significant contributions from transition moments higher than the dipole.

We study the collective electronic excitations in materials of technological importance with relative low Z value. This is necessary in order to have access to a large number of scatterers in the sample. The present synchrotron radiation sources do not allow to obtain high fluxes at high X-ray energies. This situation will be radically changed once the APS becomes operational. We decided to use silicon carbide samples for our measurements. We use three different single crystal samples of 6H-SiC. The samples were fully characterized using in house X-ray diffraction. The quality of the single crystals and rocking curves was determined prior to the inelastic scattering measurements. The inelastic scattering measurements were performed at beamline X-21 at the NSLS. This is a wiggler beamline dedicated to this type of experiments. We joined forces with A. Macrander from the APS to carry out these measurements. We measured the inelastic scattering in hexagonal 6H-SiC with the scattering vector along the (0001) direction. The measurements were very successful and are the first of its kind in carbidic materials. We clearly observe the plasmon peaks as well as the new excitations that appear as a function of the scattering momentum (see figure). We clearly observe the breakdown of the random phase approximation at high q- values. The plasmon peak around 23 eV shows a small dispersion. The new peaks that appear at high q- values are tentatively associated with effects near the Brillouin zone boundary, there is also evidence of an interband transition around 10 eV. A full theoretical calculation of $S(\vec{Q},\omega) \alpha$ Im $(1/\epsilon)$ is in progress. These calculations will help in explaining the inelastic scattering at low and intermediate q values. We expect at least one publication on this research, since it is the first study of inelastic scattering in such materials.

We propose to continue with the study the electronic collective excitations in silicon and titanium carbides. We plan to investigate the role the Brillouin Zone boundaries in the X-ray inelastic scattering process. We plan to measure the dispersion of the plasmons over a wide range of q, and test the limits of the random phase approximation to describe the collective excitations. We want to measure the dynamic structure factor of electrons in the solid, off-diagonal elements of the inverse dielectric matrix, and electronic resonant or non resonant Raman scattering. We will limit our research to technologically important materials like SiC and TiC, they also fulfill the required constraint of having low Z values.

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2. E. Burkel, B. Dorner and J. Peisl, *Europhysics Letters* (1987).

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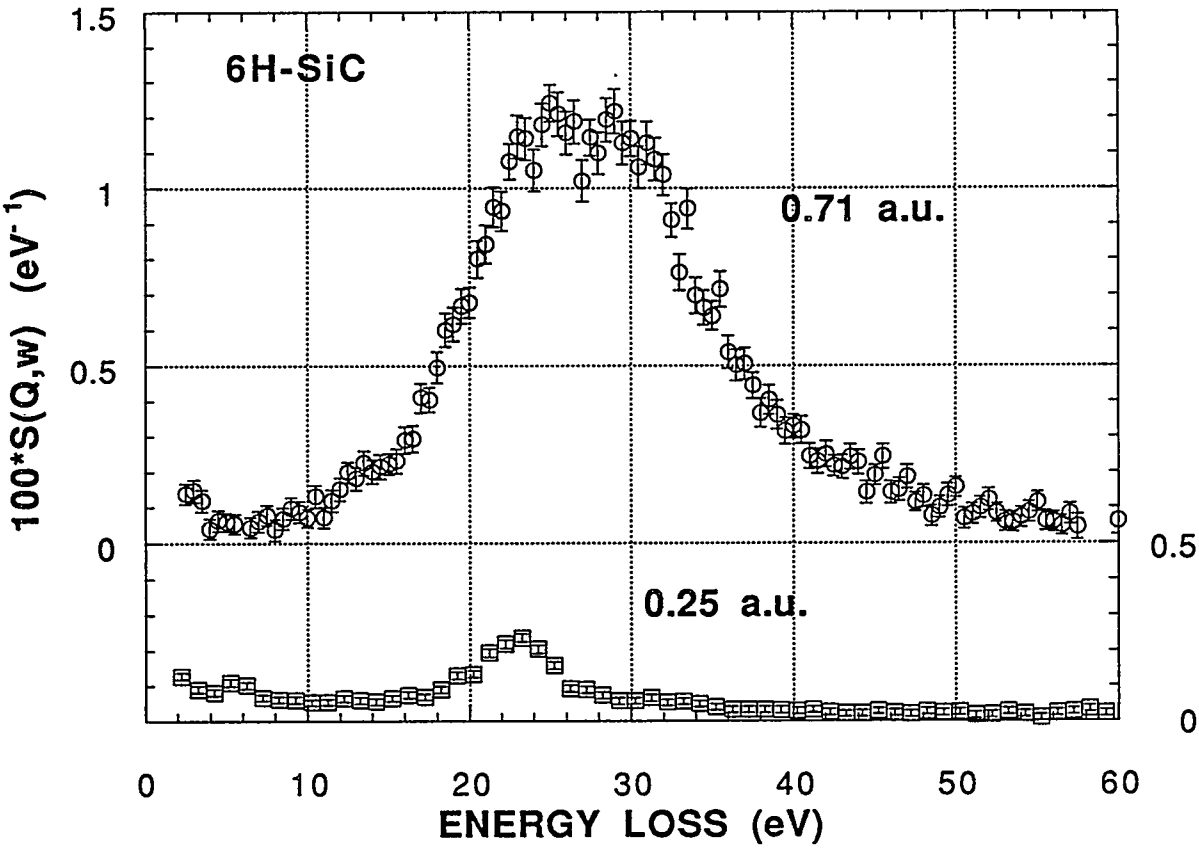
6H-SiC
0.71 a.u.
0.25 a.u.
100*S(Q,w) (eV-1)
ENERGY LOSS (eV)
1.5
1
0.5
0
0.5
0
0
10
20
30
40
50
60

93-150R1 -- NOVEL APPLICATIONS OF UNDULATOR RADIATION: HOLOGRAPHY, INTENSITY INTERFEROMETRY, AND SPECKLE

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigators: Ian McNulty, Barry Lai, Wenbing Yun, and Efim Gluskin, Experimental Facilities Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$145.3K
FY 1994	$ 81.5K
FY 1995	$150.0K
FY 1996	$ -0-

Purpose: The main thrust of the program is to develop novel applications that exploit the unprecedented brilliance of the 0.1 to 1-nm wavelength X-ray beams that will be produced by undulator sources at third-generation synchrotron facilities currently under construction worldwide (e.g., APS, ESRF, SPring8). The three applications determined to be of particular significance and with high long-term potential are holography, interferometry, and speckle methods. These techniques offer substantial advantages over conventional, non-brilliance-dependent X-ray techniques currently in use, and are likely to impact substantially on the future direction of applications of high brilliance X-ray beams.

Approach: Three techniques were selected in our study because of their high potential. X-ray holography is promising for imaging microstructures in three dimensions with spatial resolution substantially better than its optical analog. In addition, it can provide volumetric information with very little sample damage. X-ray intensity interferometry can be a very useful coherence and source diagnostic technique. It is immune to the phase-fluctuation problem often encountered in amplitude interferometry. X-ray speckle can be very useful for characterizing surface inhomogeneities or fluctuations on submicron length scales. To take full advantage of these novel applications of undulator radiation, it is essential to study their feasibility, develop the necessary X-ray optics, and conduct proof-of-principle experiments. Three postdoctoral fellows at APS, Lisheng Yang, Zhonghou Cai, and Zhongde Xu; Kegang Huang of the ANL Materials Science Division; and Yiping Feng, who recently joined our scientific staff, contributed substantially to this program.

Technical Progress and Results: This R&D program has made significant experimental and theoretical achievements in FY 1994 in these three areas.

1. X-ray holography - We made considerable progress with high resolution 3D X-ray holography in FY 1994. The major achievements include a scalable soft X-ray holography experiment with 2D and 3D test objects, a scanning microtomography experiment using a 3D test object and soft X-rays, development of new higher efficiency hard X-ray phase zone plates, and development of a hard X-ray holographic/scanning microscope. Potential applications of 3D X-ray holography we have identified that have significant technological and industrial significance include high resolution imaging of bacteria such as *clostridium sp.* which are used for bioremediation of heavy metal wastes, location of interconnect micro-defects in

microelectronic circuits, and optimization of shape-specific zeolites for environmental contaminant adsorption.[1]

Following an earlier demonstration of 3D X-ray Fourier transform holography with a one-dimensional object, we repeated the experiment with more complex well-characterized 2D and 3D specimens at the X1A beamline at the National Synchrotron Light Source (NSLS).[2] In collaboration with Dr. James Trebes and Dr. Waleed Haddad of Lawrence Livermore National Laboratory, and Dr. Erik Anderson of Lawrence Berkeley Laboratory, we created a 3D test object consisting of two planes of microfabricated gold patterns on silicon nitride membranes. The patterns in the test object are surrounded by an opaque field, acting as an order-sorting aperture to minimize the background due to unwanted zone plate diffraction orders. The pattern thickness was chosen to enable sufficient photon statistics to be recorded even when two features overlap in projection. The 3D test object was used in a scanning soft X-ray microtomography experiment in which we tested a miniature precision sample rotation stage and new 3D reconstruction codes. We found the most useful reconstruction algorithm for limited tomographic data sets is an algebraic reconstruction technique (ART) code. Using ART, we reconstructed a volumetric data set describing the test object in 3D from which views from arbitrary view angles could be rendered. The volumetric data set was reconstructed from nine projections of the test object recorded over a -55° to +50° range of incidence angles. These results clearly indicate that a depth as well as transverse resolution of better than 100 nm was achieved.[3]

We also developed high resolution X-ray focusing optics with improved efficiency in FY 1994. The design and performance of our existing hard X-ray phase zone plates was enhanced, and we developed a new high efficiency zone plate design based on a three-step approximation to an ideal parabolic zone profile. These zone plates are well suited to forming the precision spherical reference wave needed for Fourier transform X-ray holography. This novel approach promises to deliver the highest efficiency X-ray zone plate lenses yet fabricated. Diffraction-limited performance of these optics was demonstrated with 8 keV X-rays using the X6 beamline at the NSLS.

Progress toward realization of hard X-ray holographic tomography included initial design of a precision holographic/scanning microscope consisting of a multiaxis scanning specimen stage and zone plate stage, and development of a CCD camera using both direct front-surface illumination and phosphor downconversion for detection of 0.5 - 12 KeV X-rays.

2. Intensity Interferometry - Our main goal for FY 1994 was the completion and demonstration of the intensity interferometer using partially coherent 0.3-0.5 keV undulator radiation. This intensity interferometer is designed for current-mode operation using a high-brightness source of soft X-rays.[4] It consists of an array of fixed pairs of slits followed by a wedge-shaped reflective beamsplitter, two fast microchannel-plate detectors, and a 1-GHz electronic correlator consisting of dual low-noise broadband amplifiers, a fast mixer, and a low-drift digital integrator circuit. Measurements of the detector and correlator system indicate the time resolution is better than 1 ns. The interferometer is designed to yield a coherence measurement of an undulator beam in several minutes. After the initial checkout and testing phases, we completed the final assembly of the instrument and aligned it first optically using a HeNe laser, then with soft X-rays. The X13A undulator beamline at the National Synchrotron Light Source[5,6] was completed

on schedule in early FY 1994, providing an ideal opportunity to test the interferometer with a high-brightness second-generation undulator source. The long-term stability of the X-ray beam at X13A was characterized and steps were taken to improve the beam stability in order that long-term correlation measurements are not affected. Spectral analysis and central intensity measurements were conducted at X13A, indicating that the soft X-ray undulator source and spherical grating monochromator exceeded our performance expectations for providing the necessary coherent flux in order to complete the proposed scope of the project. Preliminary results obtained with the interferometer are promising: background noise and drift are satisfactory, and initial data may show evidence of photon correlations.

In FY 1994 we also began development of new models to describe the spatial coherence of high brightness X-ray beams. Concurrent with rapidly growing interest in the coherence properties of synchrotron radiation from high brightness X-ray undulators and free-electron lasers,[7] the need to model as well as characterize these properties for coherence-dependent applications has become paramount.

3. X-ray Speckle - We chose copolymer samples of polystyrene and polymethylmethacrylate as model systems for studying X-ray speckle. Upon annealing, micron-size islands and holes are formed on the surface of these copolymers, whose size and distribution depend on the annealing time and temperature. During the initial experiments in FY 1994, we succeeded in obtaining high contrast speckle patterns when X-rays were scattered coherently from the surface.[8] The coherence of the X-ray beam was verified by measuring the Airy diffraction pattern from the collimating pinhole. The grazing incidence geometry employed renders the technique applicable to a large class of materials, such as low-Z samples, liquids, disordered materials. The next step was to study the time-evolution of the speckle pattern *in situ* during the annealing process. A special sample cell was designed and constructed for that purpose. With this sample cell, we obtained a sequence of speckle patterns versus sample temperature when an initially smooth copolymer sample was annealed in vacuum. The speckle patterns clearly indicated a 2-stage roughening process of the surface. These patterns provide information about the domain distributions from the nearest-neighbor distances (1-2 mm) up to length scale >100 mm, which is difficult to study *in situ* during annealing by other methods, such as optical microscope or atomic force microscope. This very likely was the first time-resolved result demonstrated with X-ray speckle. It indicates that time correlation on the millisecond scale can be studied with the third-generation sources. In FY 1995 we will continue in-depth studies of the copolymer surface morphology, demonstrate intensity fluctuation spectroscopy with this sample system, and develop fast algorithms for reducing the speckle patterns.

Specific Accomplishments:

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3. W.S. Haddad, I. McNulty, J.E. Trebes, E.H. Anderson and R.A. Levesque and L. Yang, "Ultra High Resolution X-Ray Tomography," *Science*, in press.

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7. I. McNulty, *X-ray Intensity Interferometry with a Short-Pulse FEL*, Technical Report SLAC-437, 249 (SSRL, Stanford University 1994).

8. Z. Cai, B. Lai, W. Yun, I. McNulty, K. Huang, and T. Russell, "Observation of X-Ray Speckle by Coherent Scattering at Grazing Incidence," *Phys. Rev. Lett.* **73**, 82 (1994).

93-152R1 -- DEVELOPMENT OF INTERFEROMETER-BASED FOURIER TRANSFORM X-RAY TECHNIQUES

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigators: W. Yun, Z. Cai, E. Gluskin, and B. Lai, Experimental Facilities Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$183.1K
FY 1994	$150.7K
FY 1995	$150.0K
FY 1996	$ -0-

Purpose: The project objective was to develop interferometer-based Fourier transform techniques in the X-ray region and to explore their applications to spectroscopy and the imaging of surfaces and interfaces. The realization of these techniques will extend our spectroscopic capabilities into the X-ray region and will significantly improve detection sensitivity of small optical-refractive-index changes in media, with the potential to image surfaces and interfaces. Successful demonstration of the X-ray Fourier transform techniques will offer many unique capabilities for real-time imaging of surfaces and interfaces and for real-time spectroscopy, which are of major interest in the application of third-generation synchrotron sources currently under construction.

Approach: The ability to study both the amplitude and the phase distributions of a signal wave offers many unique capabilities beyond simple detection of signal wave intensity. This ability can be realized by either detecting the interference of a signal wave with a mutually coherent wave or detecting the interference of several wavefronts from a signal wave through wavefront division. Techniques based on these interferometric properties have been well utilized in spectroscopy and imaging in the electromagnetic spectrum from IR to UV light.

Although some novel techniques and applications that make use of the interference in the X-ray region have been long recognized, application of these interferometric techniques has been limited to a few special areas. These limitations result mainly from the difficulty of setting up an optical system to continuously scan the relative phase difference between the two interfering beams. The scope of this project was to develop two types of Fourier transform X-ray interferometers. The first type is an amplitude-division interferometer that consists of a phase shifter and a long path length Laue-Laue-Laue (LLL) crystal interferometer with skew symmetry (figure 1). The second type is a wavefront-division interferometer (figure 2) in which a continuous scan of the optical-path difference can be obtained by employing one-dimensional translation. For both interferometers, the relative phase differences can be easily determined, and, thus, practical applications are possible.

The project methodology involved the use of an existing synchrotron radiation source and the third-generation source in APS to investigate the characteristics, such as resolving power, throughput, and sensitivity, of the wavefront-division and amplitude-division X-ray interferometers from generated interference patterns. Novel applications to Fourier transform

spectroscopy and to Fourier transform imaging of surfaces and interfaces will be also investigated. Scientific collaborators were Dr. I. McNulty and Mr. D. Legnini of the Experimental Facilities Division at ANL, and Dr. P. Siddons of Brookhaven National Laboratory.

Technical Progress and Results: The effort in the first year (FY 1993) of this project was concentrated on the preliminary design and detailed assessment of different X-ray interferometers and the development and procurement of necessary optics and instrumentation. For the amplitude-division interferometer, we designed a unit combining a LLL crystal interferometer with a pair of beryllium phase shifters. Be phase shifters were designed and purchased, and a single crystal (Si 220) LLL interferometer for 8-keV X-rays was fabricated. In order to have the split beams recombined well, the beam splitter, reflection crystals, and analyzer were made in an integrated unit from a piece of single crystal (figure 1). For the wavefront-division interferometer, we preliminarily designed a novel configuration with two mirrors that reflect X-rays at grazing incidence for wavefront splitting and recombining and a four-mirror unit that generates optical-path differences. A preliminary analysis on the throughput, energy bandwidth, and energy resolution, as well as the feasibility of this interferometer, was conducted.

During FY 1994, we characterized the Be phase shifters in more detail. A continuous phase change of 2000p and, thus, a resolving power of 2000 for 8-keV X-rays is possible with this phase shifter. We completed an experimental characterization on the LLL interferometer and found that the transmission of the X-rays from the interferometer was slightly less than expected. Therefore, the LLL crystal interferometer was modified accordingly. The construction of the amplitude-division interferometer has been completed. A new experimental characterization of the LLL interferometer and the demonstration of the amplitude-division X-ray interferometer are expected to be carried out in FY 1995.

For the wavefront-division X-ray interferometer, we made a more detailed analysis of the manufacturing tolerance for beam splitters and reflecting mirrors, based on the accomplishments in FY 1993. Using the representation of the Fourier transform of the interferences between two wavefronts and the limited spectral distortion arising from deviations of the optical paths of rays within the source aperture, it was found that the surface roughness and flatness of the beam splitters and the mirrors were highly restricted (less than 2 Å in surface roughness (rms), and less than 0.5 μrad in surface slope error), yet, could be achieved with existing manufacturing technology. In order to assure the spectrum region and the resolution of the interferometric spectrometer, we have designed flexure-based rotation and translation devices for positioning mirrors and translating the four-mirror unit in accuracies required by our analysis. Mirrors, stages, and motion control system have been procured. Also, a linear hard X-ray phase zone plate, which combines two spatially coherent beams with known relative phase delays to generate an interferogram, has been fabricated. The zone plate was tested at the NSLS, and an efficiency of 30% and a focal size better than 0.7 μm at the first order were found, suggesting that it is a suitable device for beam recombining.

In addition to the amplitude-division and wavefront-division X-ray interfero-meters, we have made an effort toward developing a high-resolution, high-speed X-ray imaging system with which an interferometer without moving parts would be possible. In the imaging system, a scintillation crystal ($CdWO_4$) was used to convert an X-ray image into a visible light image, and

a high-speed lens system was used to transfer the visible light image into a CCD detector with adjustable magnification. Because of the high spatial resolution (2μm) of the imaging system, it is possible to record a hard X-ray interferogram at the point where two coherent X-ray beams meet. This capability may permit us to develop real-time Fourier transform techniques and other novel capabilities.

The thrust for FY 1995 is to repeat the experiment, performed by Profs. Appel and Bonse, using the amplitude-division interferometer. The interference spectrum in our system and its resolving power should be easily processed to obtain the spectral distribution of the copper K_{a1} and K_{a2} doublet. For the wavefront-division interferometer, we will first fabricate and characterize the flexure stages for mirror angular positioning (in a step of 0.5 μrad) and translation (in a step of 20 Å). These flexure stages will be made of low-expansion alloys, such as invar, in order to have thermal stability. Next, we will complete the construction, characterization, and demonstration of the wavefront-division interferometer. We also plan to demonstrate a hard X-ray interferometer without moving parts, in which a spatially coherent hard X-ray beam is reflected by two flat mirrors arranged with a small mutual angular offset. Because of the off-set angle, there will be a continuous phase shift between the two beams across the encountered area. As a result, an interferogram is formed, and it can be recorded using the high-resolution, high-speed X-ray imaging system we developed in FY 1994.

Specific Accomplishments:

1. E. N. Kaufmann, W. Yun, "Third Generation Synchrotron Radiation Source Applied to Materials Science", International Conference on Advanced Materials, Tokyo, Japan.

2. W. Yun, "Development of Interferometer-based Fourier Transform X-ray Techniques", internal presentation in XFD, ANL.

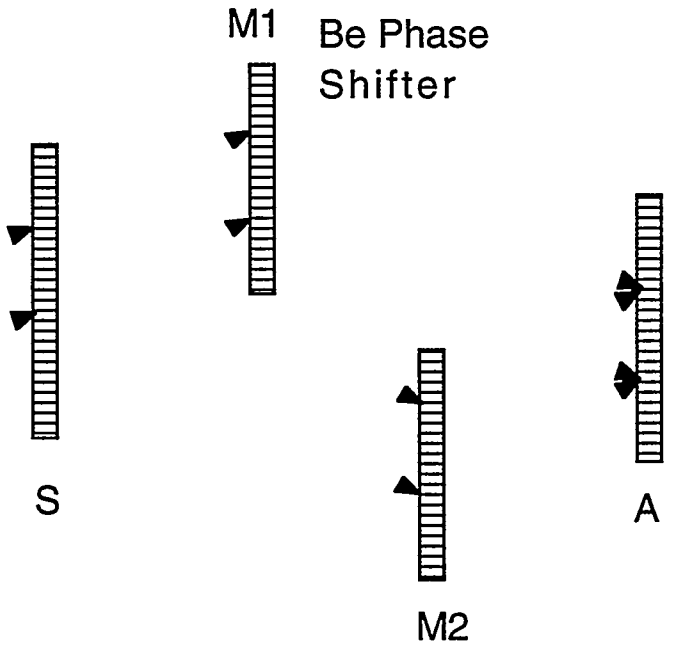

Fig. 1. Schematic of the amplitude-division Fourier transform interferometer to be developed. This interferometer consists of a skew symmetry LLL interferometer and a phase shifter. The LLL interferometer consists of a beam splitter S, two transmission mirrors/crystals M1 and M2, and an analyzer A. The relative phase difference between the two interfering beams split by S is obtained by adjusting the thickness of the phase shifter. Real-time Fourier transform spectroscopy or Fourier transform imaging of surfaces and interfaces may be obtained by using a single wedge rotated 90 degrees from that shown above. A position sensitive detector is required to record the intensity distribution behind the analyzer crystal A.

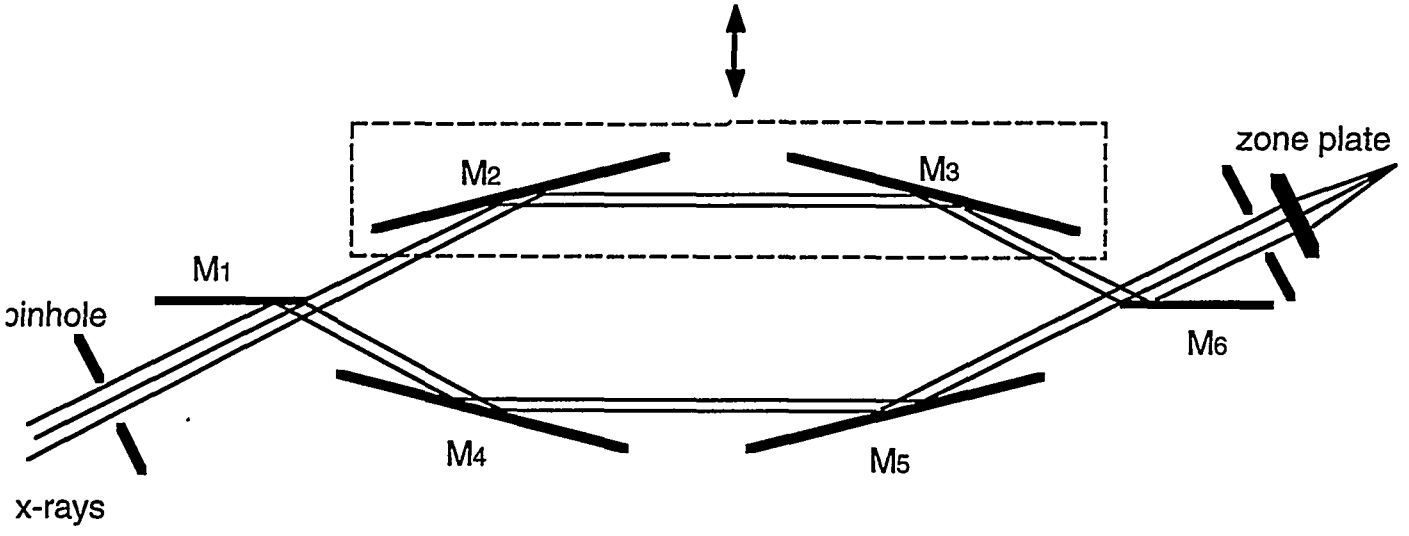

Fig. 2. Schematic of a wavefront-division Fourier transform x-ray interferometer. A spatially coherent x-ray beam is incident on and physically split into two beams at mirror M_1. Each of the two beams is reflected by a two-mirror element. When the six mirrors are properly arranged and aligned, the two beams combine into one after the mirror M6. A variable phase delay of one beam relative to the other can be introduced by moving one of the mirror sets along the direction normal to the beam splitter. While the spatial coherence of either beam is reserved, the two beams are recombined after a linear zone plate and the resulting power of the interference of the two beams is recorded as a function of the phase delay.

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93-041R1 -- DEVELOPMENT OF SYNCHROTRON RADIATION ANALYTICAL CAPABILITIES AT THE CENTER FOR ADVANCED MICROSTRUCTURES AND DEVICES

Associate Laboratory Director Area: Engineering Research

Principal Investigators: L. Leibowitz, Chemical Technology
M. C. Petri, Fuels and Engineering

Funding Profile:

FY 1992	$ -0-
FY 1993	$137.9K
FY 1994	$223.6K
FY 1995	$350.0K
FY 1996	$ -0-

Purpose: The purpose of this work is to develop a micro-analytical facility that will allow X-ray diffraction and X-ray fluorescence examination of materials on a microscopic scale. For this work a dedicated beam line is being developed at the synchrotron radiation source at the Louisiana State University (LSU) Center for Advanced Microstructures and Devices (CAMD). This work will result in a permanent facility for the microscopic X-ray examination of a wide range of technologically important systems.

Approach: A vast array of technologies face fundamental materials issues related to small-scale structures. In particular, chemical interactions between bonded materials can degrade the materials over time and can cause local precipitation of phases that can weaken bonds. Alternatively, improved bonds can be made by controlling local interactions. This control, however, can only come about from an understanding of the kinetics and the thermodynamics of the chemical interactions. The present work employs synchrotron sources to extract structural and compositional information from bonded materials that can lead to a better understanding of the processes involved. In contrast to scanning electron microscopy, synchrotron radiation sources can reveal both composition (via fluorescence) and structure (via EXAFS and diffraction), providing an ideal tool for studying materials and their interactions on a microscopic scale.

This work involves developing high-resolution collimated X-ray beams and focused X-ray beams for micro-diffraction and micro-fluorescence analyses. These capabilities for synchrotron radiation analytical techniques will be developed at CAMD, a facility owned by the state of Louisiana and operated by LSU. CAMD, which began operations in 1992, consists of a 1.5 GeV electron storage ring with 16 X-ray beam line ports. Up to three insertion devices can be installed for higher energy and higher intensity radiation. Earlier work by us at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) has shown that these novel techniques have great promise, giving results unobtainable by other means. The proposed project will adapt the methods used at NSLS to the CAMD facility. CAMD offers distinct advantages to the development of microscopic X-ray capabilities. In particular, the ready availability of beam time and a dedicated working space are attractive features of working at CAMD.

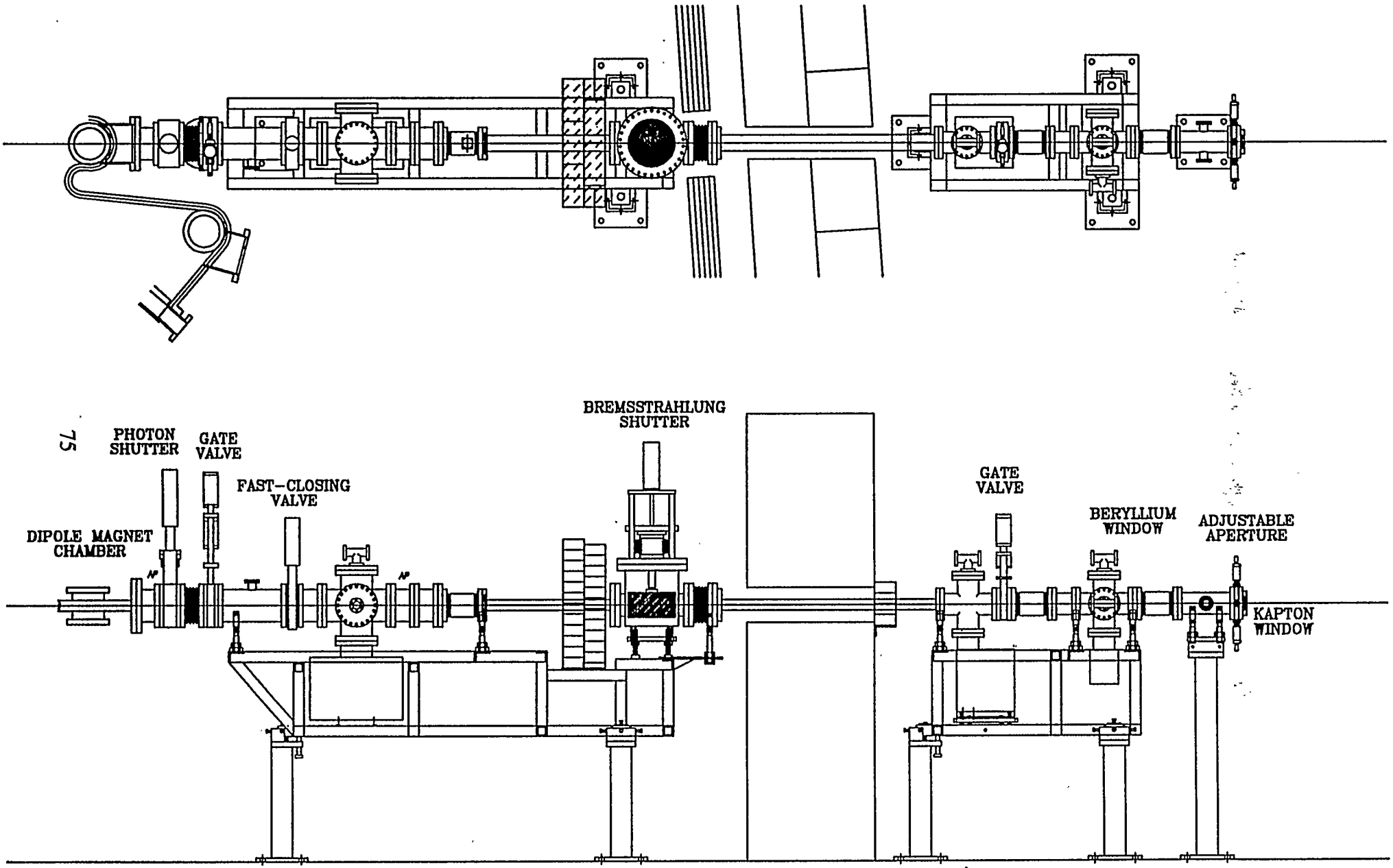
The kinetics and thermodynamics of material interactions can be studied by conducting isothermal diffusion couple experiments. These experiments consist of bonding two materials under controlled conditions and examining the interdiffusion of the chemical elements. In such a study, a collimated or focused synchrotron X-ray beam can be translated in steps across the diffusion zone. At each step, diffraction patterns or fluorescence spectra can be collected to provide structure and composition profiles along the diffusion path. Similar techniques can be applied to other interfaces of interest such as welds, braises, and battery or fuel-cell connections to name just a few. Our recent work at NSLS focused on developing equipment and techniques to study material interactions on a microscopic scale. Because of the work in this proposal, CAMD will be the first dedicated facility to take advantage of the progress made at NSLS.

Technical Progress and Results: Earlier work by us at NSLS in FY 1992 and 1993 showed the great value of having a dedicated beam line for micro-analysis. In that work, a team of FE, CMT, IPNS, and APS-XFD researchers developed techniques to examine small-scale structures in diffusion zones of a variety of materials. These materials included IFR fuel/cladding and lanthanide/cladding interfaces, and aluminum-coated iron-based alloys. Three separate NSLS beam lines were used, because no single beam line allowed simultaneous X-ray fluorescence and diffraction experiments. As a result, efforts supported by this program began in FY 1994 to develop a dedicated beam line at the CAMD facility that would allow simultaneous micro-fluorescence and micro-diffraction. The CAMD synchrotron is unique in that it could provide essentially unlimited availability for this dedicated use. Over the past year, Argonne National Laboratory has been collaborating with LSU in constructing such a synchrotron X-ray beam line at CAMD, shown in the attached figure. Significant progress has been made in designing and constructing a white-beam facility for X-ray fluorescence work. Thus far, the beam line and experiment hutch have been installed, a vibration-control kinematic table has been delivered, and an X-ray detector system has been procured and is being tested. During FY 1995, a major upgrade of the ANL/CAMD beam line will take place. Specifically, focusing optics will be added to intensify the X-ray flux on the sample and a monochromator will be added to tune the beam to a single X-ray wavelength.

Specific Accomplishments:

Phase Identification in U-Zr Fuel Diffusion Couples Using Synchrotron Radiation, M. C. Petri, L. Leibowitz, M. H. Mueller, J. W. Richardson, and D. D. Keiser, *Trans. Am. Nucl. Soc.*, **70** 143, 1994.

Phase Identification in Nuclear Materials Using Micro-Diffraction, M. C. Petri, L. Leibowitz, M. H. Mueller, J. W. Richardson, P. Zschack, and M. C. Nelson, BNL-52415, April 1994.


PHOTON SHUTTER
GATE VALVE
FAST-CLOSING VALVE
DIPOLE MAGNET CHAMBER
BREMSSTRAHLUNG SHUTTER
GATE VALVE
BERYLLIUM WINDOW
ADJUSTABLE APERTURE
KAPTON WINDOW

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94-193N -- DEVELOPMENT OF X-RAY SCATTERING TECHNIQUES WITH μeV-meV RESOLUTION

Associate Laboratory Director Area: Advanced Photon Source

Principal Investigators: E. E. Alp, W. Sturhahn, and R. Rohlsberger, Experimental Facilities Division

Funding Profile:

FY 1992 $ -0-
FY 1993 $ -0-
FY 1994 $ 84.5K
FY 1995 $160.0K
FY 1996 $180.0K

Purpose: To develop new hard X-ray scattering techniques with μeV to meV resolution. Currently this region is virtually unaccessible with X-rays. This is one area in which neutron scattering is ahead of X-ray scattering. The energy resolution attainable in the hard X-ray regime (≈ 5-100 keV) of the electr omagnetic spectrum is limited to a few meV when Bragg reflections near 90 degrees are used. On the other hand, with the introduction of nuclear resonant scattering of synchrotron radiation, it is possible to measure interactions at neV levels via time filtering. However, there is a large gap in the μeV-meV regime that cannot be measured with either diffraction or time-filtering techniques. Successful completion of this project will give us an unparalleled capability in which inelastic scattering studies from eV to neV can be pursued in one of the two experimental stations of the SRI-CAT, dedicated to high-energy-resolution X-ray scattering.

The development of meV tunable, μeV resolution X-ray scattering techniques will allow study of low level excitations in condensed matter for the first time with X-rays. These include librons, rotons, soft phonons, as well as excitations in liquid He, and similar weakly bound matter, like polymers or molecular solids. It also extends the application of nuclear resonant scattering techniques beyond the media containing Mossbauer nuclei.

Approach: We are proposing a new program to close this aforementioned energy gap by using interferometry and high-speed Doppler shifting in combination with nuclear resonant scattering. It is well known that energy and time are two canonical variables connected via the Heisenberg uncertainty principle, $\Delta E^{\bullet}\Delta t \approx h/2\pi$. Thus, a resonance with 1 nsec lifetime would correspond to an energy uncertainty of 0.66 μeV. The lifetimes of Mossbauer isotopes observed to date via synchrotron radiation are 141 nsec for ^{57}Fe, 25 nsec for ^{119}Sn and 6 nsec for ^{169}Tm, corresponding to energy uncertainties of 4.6 neV, 0.026 μeV, and 0.1 μeV, respectively. There are other considerations that limit the energy resolution range. For example, the time resolution of current fast detectors (APDs) are limited to around 1 nsec, enabling detection of energy differences of up to fraction of a μeV level via time-based interferometry. Currently, no existing method can go beyond this level. A limitation also exists for time-filtering techniques imposed by the bunch duration of the synchrotron pulse. At the APS, the bunch length is

17.5 mm corresponding to 58 psec, which would limit the resolution of the time filtering technique to 11 μeV, provided that such fast detectors are available.

In order to extend this energy range from the μeV to the meV domain, we are proposing to develop Doppler shifting and/or interferometry techniques. This would enable one to reach from 1μeV to 10 meV levels. In the next two sections, we will discuss our approach to cover this "no man's land" of X-rays.

High Speed Doppler Spectroscopy - The Doppler shift experienced by photons upon scattering is described by the equation $\Delta E = vE_o/c$, where v is the velocity along the beam direction, E_o is the photon energy, and c is the speed of light. For 14.4 keV X-rays, linear velocities up to 100 m/sec can be obtained by a disk spinning at 10,000 rpm, which corresponds to a 10-meV energy shift for a disk of 100-mm radius. One advantage of the spinning disk concept is the fact that it is continuously tunable. A conceptual experimental setup is shown in figure 2. The photon beam after passing through the high-heat-load monochromator and high resolution, nested monochromator has about 5-50 meV bandpass (5). Photons then scatter off the disk coated with nuclear-resonant medium (GIAR, resonant/non-resonant multilayer or uniformly coated single layer) to bring the bandpass to the μeV level. Finally the beam hits the sample, and the scattered beam is analyzed by a "black" absorber. This arrangement has the inherent advantage that both coherent and incoherent inelastic scattering can be studied.

Long-coherence-length-based interferometry - Interferometry in the 1 Å wavelength X-ray regime was first realized by Bonse and Hart (6). Since then many different interferometers have been designed and built (7-9). The applicability of interferometry in the X-ray regime is limited by the lack of coherent sources. The coherent volume of the radiation source is given by the transverse coherent area of the incident beam and longitudinal coherence length. The latter is limited by the degree of monochromaticity of the X-ray beam and is given by

$$l_c = \lambda^2/\Delta\lambda \ . \qquad (1)$$

Typically, X-rays are monochromatized by single crystal monochromators with $\Delta\lambda/\lambda \sim 10^{-4}$. Then, the longitudinal coherence length, l_c is around 0.1 μm for λ=1 Å. When the monochromaticity is pushed to higher values by using back reflection or higher order reflection planes, it is possible to increase the l_c to 10 μm. This short coherence length puts severe limitations on the applicability of this technique. Further monochromatization by crystal diffraction seems to be limited by crystal imperfections at the level of $\Delta d/d = 10^{-8}$.

In the last decade, however, tremendous progress was made in nuclear resonant monochromatization of synchrotron radiation. Experiments performed on ^{57}Fe (10-12), ^{169}Tm (13), and ^{119}Sn (14) demonstrated the possibility of reaching $\Delta\lambda/\lambda \sim 10^{-10}$-$10^{-14}$. This is a three-to-seven orders-of-magnitude improvement over crystal monochromators, increasing the longitudinal coherence length to several tens of meters. The new interferometric techniques we will take advantage of these long coherence lengths. Much of the instrumentation and various

optics components developed for other purposes are now operational. Our group at Argonne is among the world leaders in this field.

The essence of interferometry relies on the simple principle of beam splitting, phase retardation or rotation of polarization in one branch of the beam, and recombining the beams. This can be achieved in many ways, each with its advantages and shortcomings. Here we are developing some new components that have not been tried before, but offer great potential for implementation. The core of the interferometer consist of two components. The first is a monochromator that provides a clean beam of nuclear resonant photons. This is the essence of the polarizer /analyzer monochromator. The second component is the interferometer. This could be a channel cut crystal that is oriented in such a way that the beam splits, travels, and recombines in one monolith. Or, it could be a Michelson type of an interferometer in which suitable crystal with back-reflection Bragg geometry are used to recombine the beam on the beam splitter. This arrangement is shown schematically in figure 3. There is Ge (7 3 1) reflection for ^{169}Tm nuclear resonance at 8.41 keV, while Ge (5 15 15) reflection at ^{119}Sn resonance at 23.87 keV provides near back-reflection condition. For ^{57}Fe, a high order reflection in doped YAG (yttrium aluminum garnet) or double reflection from Si (840) - Si (-480) are possible schemes to implement the interferometry ideas. The beam splitter can be a thin crystal for the Bragg, and a thick crystal for the Laue diffraction geometry. Here the interferometric patterns can be obtained by moving the backscattering crystal with angstrom resolution over 10-100 μm. Such a setup will be useful to measure 0.1 to 10 meV differences.

Before such crystals are cut and polished, it is necessary to calculate the intensity and the angular divergence of each beam to optimize the interferometer. Prof. Roberto Collela of Purdue University has been working on the dynamical theory of multiple reflections for a number of years, and he has developed a general purpose program, NBEAM. This program will be utilized to identify the reflections. We, at Argonne, have enough expertise to prepare and characterize these crystals. In the last year, we have produced more than ten channel-cut crystals for monochromatization purposes. We would like to combine this expertise with our ability to use nuclear resonant scattering to produce a prototype interferometer.

This new research program should be a major advance over our current research program in the area of development of X-ray optics for nuclear resonant scattering. The preparation of clean nuclear resonant beams via a polarizer/analyzer monochromator has been described before (15). Also, development of thin film nuclear resonant optics in the form of GIAR and multilayers is a strong part of our current research. These programs are essential for what we are proposing here.

Technical Progress and Results: The key components of the system, namely, the production of a pure nuclear resonant scattered beam via a polarizer/analyzer monochromator, and broadening of the energy bandpass via grazing incidence geometry has been manufactured and tested. Si (8 4 0) for ^{57}Fe at 14.4 keV, and Si (333) for ^{169}Tm at 8.4 keV have been prepared and tested at CHESS. The need to synthesize large area GIAR films or thin film coatings on rotating disks have led us to collaborate with the University of Hamburg (Prof. E. Gerdau), where such facilities exist. We have hired a recent PhD, R. Rohlsberger, who has over 5 years of experience using these facilities for thin film optics purposes. He has prepared 3 inch long Fe-films over Zerodur™ substrates to measure the energy bandpass as a function of grazing

incidence angle. We need to have access undulator radiation as early as possible. Therefore, Dr. Rudolf Rüffer of the ESRF has joined the collaborative effort, by providing a Doppler shifter to synthesize these films. We plan to use the dedicated beamline at ESRF in early 1995 to continue develop this project.

We have started a new collaboration with Prof. R. Colella of Purdue University to build a novel interferometer based on splitting the beam using multiple reflection geometry. Prof. Colella visited ANL in May, 1994, and have agreed to dedicate a PhD student to this project. Mr. John Sutter, a third year graduate student at Purdue University is planning to join the group full time, starting January 1995. In the meantime, we are calculating the reflectivity of diffracted beams under multiple diffraction conditions to find the most suitable case for an interferometer at 14.4 keV.

Finally, we worked out an agreement to use the undulator beamline at the KEK Accumulator Ring between October 28-November 10, 1994, after intense efforts to start a collaboration with Prof. S. Kikuta of the University of Tokyo, and Dr. M. Ando of the Photon Factory. The performance of the undulator is comparable to APS undulators. We are the first ever outside group to use this beamline. We have reached an agreement for a common program to be carried out.

Specific Accomplishments:

1. Construction of polarizer/analyzer crystals for creation of pure nuclear resonant beam.
2. Testing the reflectivity and polarization selectivity of ^{57}Fe thin film under grazing incidence conditions.

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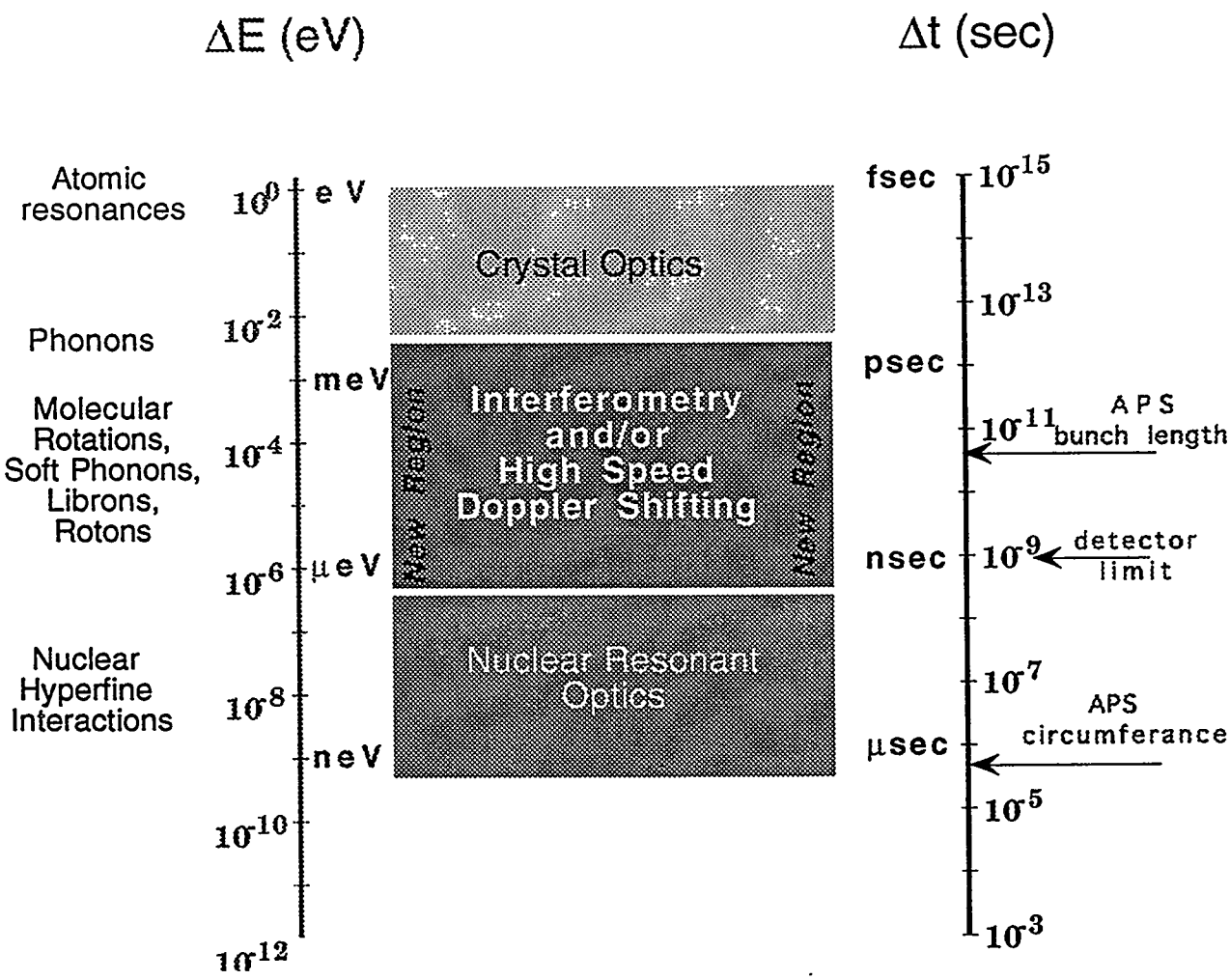

Figure 1. Energy resolution achievable with crystal optics, and nuclear resonant scattering. The 3 order-of-magnitude gap in the middle is the target of this proposal.

ADVANCED PHOTON SOURCE

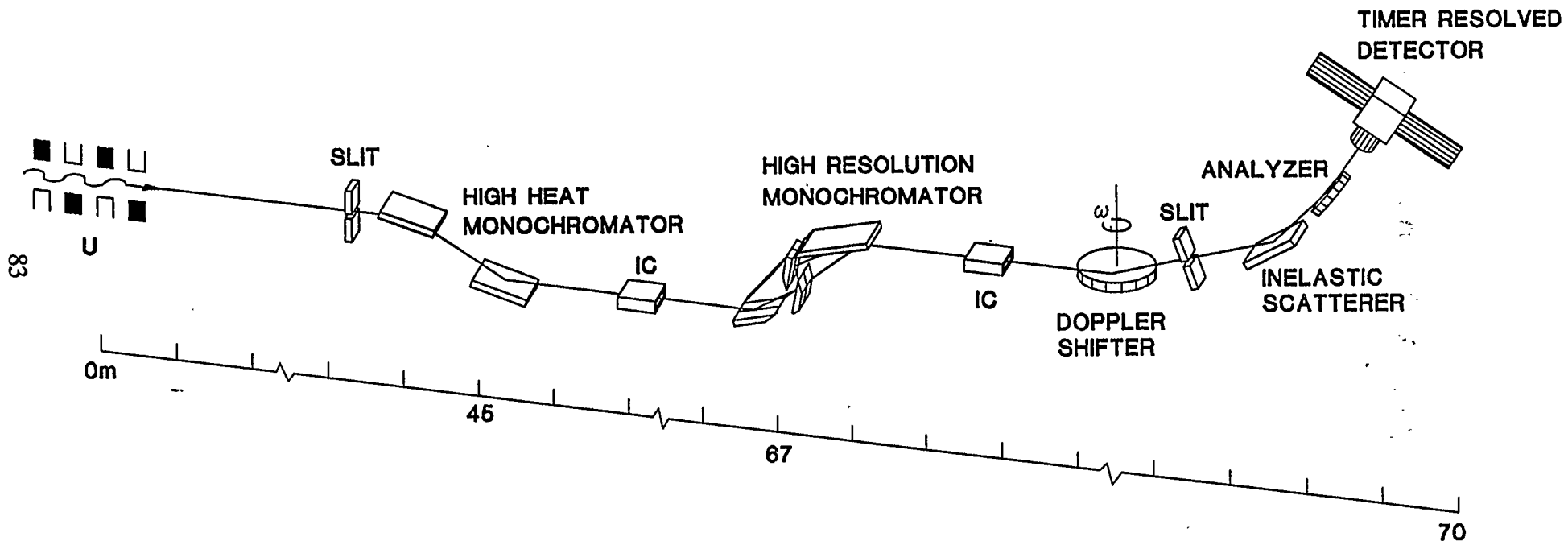

Figure 2. Conceptual layout of the Doppler shifting experiment.

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Polarizer/Analyzer Monochromator and Backscattering Interferometer

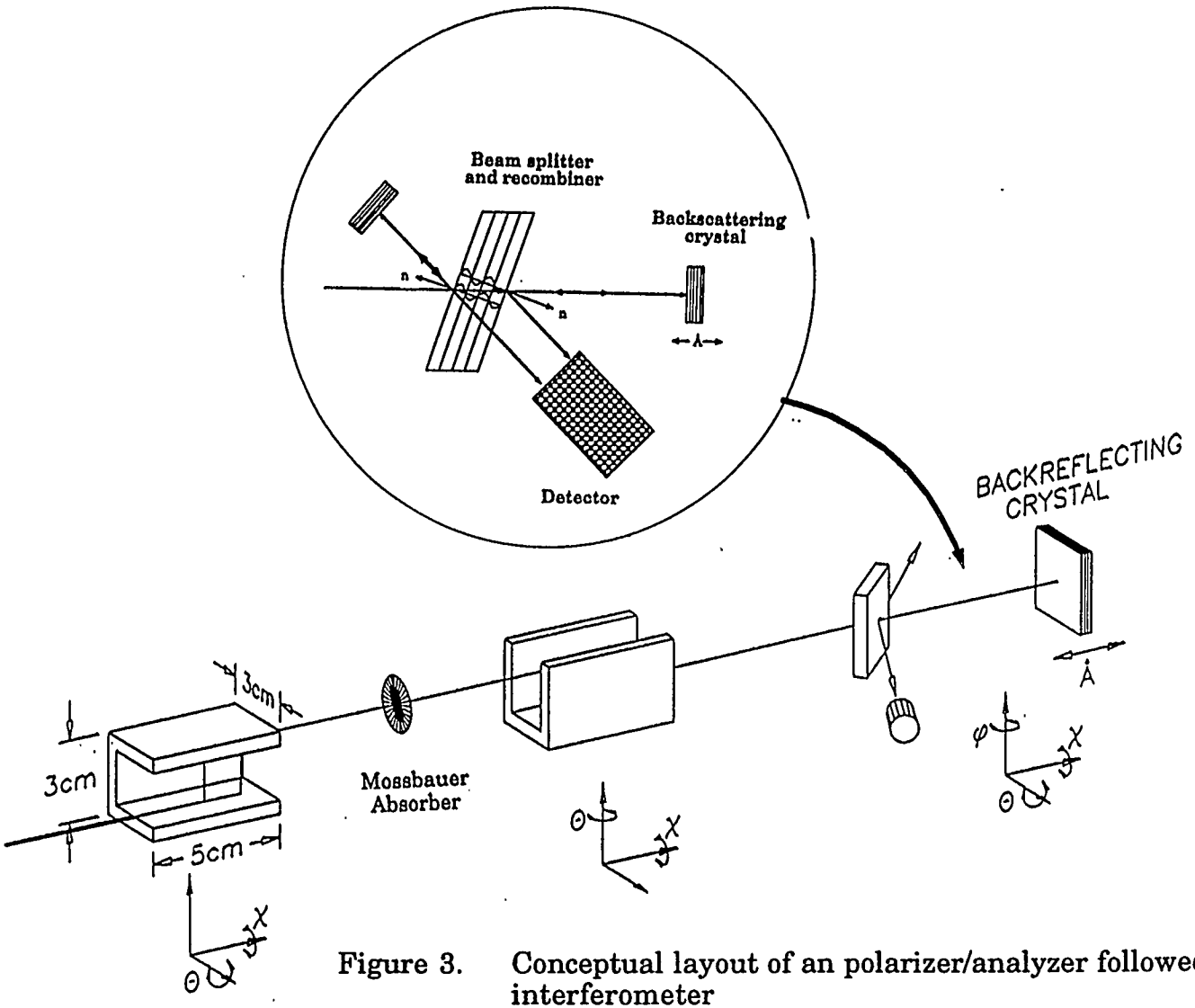

Figure 3. Conceptual layout of an polarizer/analyzer followed by an interferometer

94-002N -- NEURAL NETWORKS FOR AUTOMATED FUEL MANUFACTURING AND REPROCESSING

Associated Laboratory Director Area: Engineering Research

Principal Investigators: J. Reifman, Reactor Analysis
K. S. Gibbs, Technology Development

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$111.6K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The purpose of this project was to test the effectiveness of artificial neural networks (ANNs) as alternative classifiers for automated inspection of the welding of end plugs onto the top of remotely manufactured reprocessed nuclear fuel element jackets. The effectiveness of the developed ANN classifier was determined by comparing its classification results with the results obtained through control chart techniques used in standard statistical process control. Successful demonstration of the neural network approach could be readily transferred to other industrial applications in the area of automated quality control.

Approach: The quality control of commercial manufacturing and reprocessing of nuclear fuel has historically been performed through multivariate statistical methods that rely on estimates of population parameters such as mean values, standard deviations, and modeling techniques such as linear and nonlinear regression analysis. These statistics, however, often require assumptions on the population of measurements under study and estimation of statistical models that best fit the measured data. When these assumptions and estimations are not, or can not be properly selected, inadequate statistical models are derived resulting in ineffective process quality control. In this case, inferences based on the derived statistical models will either inadvertently reject acceptable products or accept unacceptable ones.

In contrast, ANNs provide a robust general purpose modeling technique that does not require assumptions on the population of measurements, the underlying statistical model, and the estimation of modeling parameters. Neural networks acquire these properties by analyzing the underlying structure of the data itself. For instance, there is no need to provide the network with the order of the polynomial that should best fit the data. The network finds the best model through training based on an existing database of examples. Furthermore, neural networks have proven to be quite robust in the presence of faulty data which would prevent outlying data measurements to distort the inference provided by the network model.

Neural networks have become very popular over the last few years due to their general purpose modeling capabilities. They have been widely used as a pattern recognition modeling tool for recognizing written characters, estimating signal values based on other measurements, classifying faults based on symptoms, and many other applications. In spite of the recent success of the application of neural network in these areas, the application in statistical quality control has been limited.

The scope of this project involved the use of neural networks as the classifier for the on-line automated visual inspection of welded fuel element jackets. Based on classificatory data obtained through measurements performed on pre- and post-weld images of fuel element jackets captured and processed by an off-the-shelf vision system, neural networks were used to classify welded jackets as acceptable or unacceptable. In this project, we investigated the use of a multilayer feedforward perceptron with a conjugate gradient-based backpropagation training algorithm as the ANN classifier. In addition, we compared the results, characteristics, advantages, and disadvantages of ANN classifiers with standard control chart techniques used in industrial quality control. J. E. Vitela from the Reactor Analysis Division was the lead collaborator in the development and application of the ANN classifier.

Technical Progress and Results: The research conducted under LDRD auspices during FY 1994 was composed of three tasks: database generation, neural network training, and validation of the ANN classifier. For the generation of the database, used in both the ANN classifier and control chart classifier, a total of 167 dummy stainless steel (HT9) fuel element jackets were welded in a test facility outside the argon cell of ANL's Fuel Cycle Facility (FCF) in Idaho. Based on visual inspections performed by an operator, of the 167 welds, 51 were labeled as unacceptable and the remaining 116 were labeled as acceptable. For each weld, pre- and post-weld measurements performed by the vision system were collected and used to define feature variables which, in turn, were applied in the classification of the weld.

The database of 51 unacceptable welds was purposely generated to duplicate possible failure modes of the welding system. For example, welds with off-centered domes or "slumpers" caused by an eccentric electrode towards the front, back, left, and right sides of the jacket, and welds with flat domes or "flat-tops" caused by an incorrect amount of energy deposition during welding, including the limiting case of no weld.

For the second task, ANN training, software was written to represent a multilayer feedforward perceptron with a conjugate gradient-based backpropagation learning algorithm. The neural network classifier was trained and tested numerous times with varying ANN architectures, feature variables, and training data. Software was also written to classify welds with standard control charts and to interface the collected pre- and post-weld measurement data with both classifiers.

In the last task, validation of the ANN classifier was performed by applying it to classify welds not used during the training phase. In addition, the results of the neural network classifier were compared with the results obtained using control charts. The various ANN classifiers tested correctly classified 78%-94% of the acceptable welds and 56%-64% of the unacceptable welds. The control chart classifier correctly classified 85% of the acceptable welds and 76% of the unacceptable welds. In both cases, almost all misclassified unacceptable welds were either front or back slumpers, whose occurrence is very unlikely due to mechanical constraints in the welder.

By experimenting with different architectures and training data, the ANN classifier allows us to gain insight into the classification problem and determine that the cause for misclassification of a few front and back slumpers as acceptable welds is the lack of information-rich features capable of characterizing such failure mode. The performance of any classifier is highly dependent on the information content of the user-specified feature variables. Future work should

include the design and testing of additional feature variables that are capable of characterizing this unlikely mode of failure.

The overall results indicate that multilayer feedforward neural networks and standard control chart techniques used in industrial quality control provide comparable results in the classification of welded fuel jackets. However, unlike control chart techniques, ANNs intrinsically take into account the possible relationships among all feature variables in the classification. This is a key advantage of ANN classifiers in the case where successful classification requires on the representation of the dependency of the feature variables.

Liaison was established with a number of U.S. companies that develop and manufacture automated visual inspection systems regarding future joint efforts with ANL in the area of automated quality control.

Specific Accomplishments: Artificial neural networks were successfully implemented to classify the welding of nuclear fuel elements jackets using data collected in a test facility outside the argon cell of ANL's FCF in Idaho.

A technical paper entitled "Automatic Inspection for Remotely Manufactured Fuel Elements," by J. Reifman, K. S. Gibbs, J. E. Vitela, and R. W. Benedict, was prepared and will be presented at the ANS Topical Meeting on Robotics and Remote Systems, Monterey, California, February 5-10, 1995.

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94-015N -- DEVELOPMENT OF REAL TIME X-RAY EXAMINATION FOR HOT CELL APPLICATIONS

Associate Laboratory Director Area: Engineering Research

Principal Investigator: F. L. Yapuncich, Technology Development

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$111.3K
FY 1995	$100.0K
FY 1996	$ 85.0K

Purpose: The project objective was to investigate real time X-ray systems for nuclear and non-nuclear examinations. Specimens would include sodium bonded metal fuel elements (steel substituted for fissile material). Successful examination of the sodium bond would enhance quality control of metal fuel fabrication. Determination of applicable non-nuclear applications would allow for future possible technology transfer of nuclear processes to the private sector.

Approach: The examination of metal fuel elements by real time X-ray systems was introduced to replace eddy current examinations due to the speed and clarity of the X-ray systems. The initial testing of the X-ray system on dummy and depleted uranium fuel elements were highly successful with respect sodium meniscus level, fuel pin liftoff, and weld interrogation. The basic reason for these specifications is to ensure a good sodium bond with respect to the fuel pin. Due to this success it was decided that direct examination of the sodium bond may be possible. However, the existing X-ray system was not equipped with the correct image analysis software to locate the sodium bond.

Real time X-ray technology is a rapidly expanding scientific area with applications in every field that must maintain a high standard of quality control. The scope of the investigation included evaluating various nondestructive tools which might have a possibility to locate the sodium bond, recreating a simulated sodium bond in a quartz jacket to study the bonding phenomenon, and applying this technology to suitable non-nuclear products.

The project methodology involved the use of several different types of NDE tools including reverse geometry X-ray system, X-ray tomographic system, neutron examination, and conventional real time X-ray system. Dummy fuel elements which substituted a steel pin for the actual fuel pins were used as test specimens. C. Solbrig was the lead technical consultant for the project and B. Forsman was the Chief Technician.

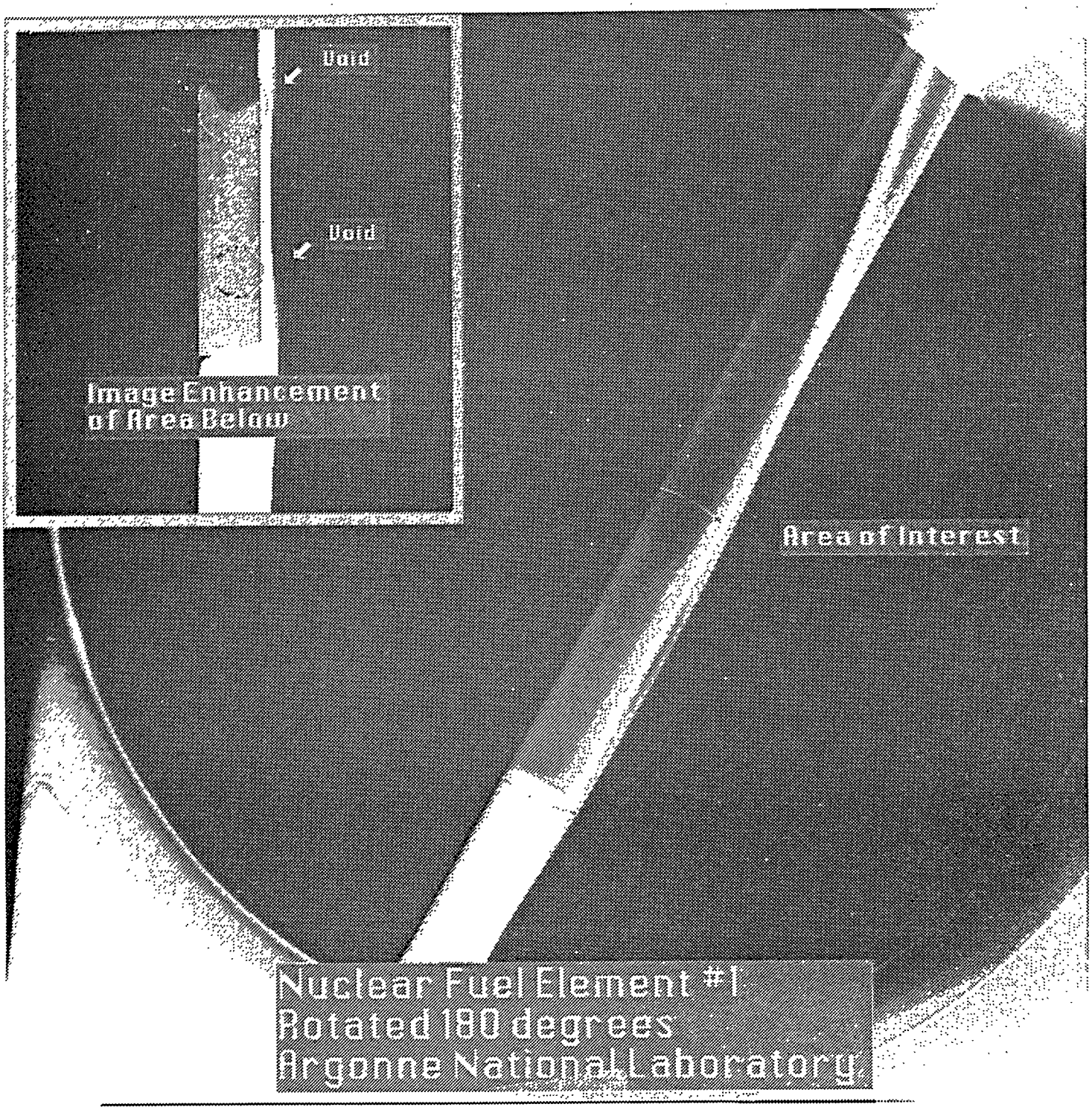
Technical Progress and Results: Real time examinations of dummy fuel elements were conducted under LDRD auspices during various times of FY 1994. The initial examinations were conducted by Digiray Corporation. Problems encountered included inability to clearly delineate the fuel pin from the sodium bond. Voids in the sodium bond above the fuel pin were very distinct (see print 1). X-ray tomography was then selected and testing was carrying out in conjunction with Scientific Measurement System, Inc. The mathematical mapping of the cross section could identify regions of lower sodium density but the visual examinations were

inconclusive. The major drawback identified with the tomographic X-ray system is the length of time to examine one fuel element and the large footprint of the system. Concurrently, solidification/melt tests were carried out by C. Solbrig to examine the bonding phenomena under transient conditions. Tests conducted on wax bonded steel pins (encapsulated in quartz jacket to allow for visual examination) showed that there is little linkage between examinations done when the bond material is solidified and when the bond is molten. A majority of the voids that were prevalent in the solidification phase were degassed into the plenum area of the quartz tube during the melt phase. Upon resolidification, voids would randomly reappear. Collaborative efforts continued with Digiray, Inc. to optimize the reverse geometry X-ray system. Dr. Richard Albert (Digiray) was able to detect a small inclusion/void near the inner diameter of the fuel jacket wall (see print 2).

In the area of non-nuclear applications, the Technology Development Division collaborated with the University of Idaho Agricultural Department (Dr. John Ojala was the U of I principal investigator) to determine how real time X-ray systems could be used in the area of examination of potato defects. A proposal was submitted to the State of Idaho including an oral presentation but funding was denied because the proposal did not fit the grant's guidelines. Meetings with potato consultants and equipment vendors were held throughout FY 1994 to establish the needs of the private sector. A CRADA proposal was submitted through the auspices of the ER/LTT process to commence research in the area of NDE of currently undetectable potato defects.

Specific Accomplishments: The reverse geometry X-ray system was found to adequately locate sodium voids located above the fuel pin but showed only marginal success at locating and analyzing the sodium bond area. Dr. M.D. Silver of Bio-Imaging Research has combined tomographic capabilities with the reverse geometry X-ray with the added bonus of extremely fast examination times. This breakthrough could enhance the system's ability to locate the sodium bond area. Examination of solidified sodium bond for the sole purpose of void detection is, at best, a highly conservative procedure in fuel elements.

Based on the combined efforts of the Technology Development Division, the University of Idaho, and private potato equipment vendors, a CRADA (C9405900) was successfully funded for FY 1995. This grant will allow basic research to continue in the area of NDE of currently undetectable potato defects.



Digiray Corp
San Ramon, CA

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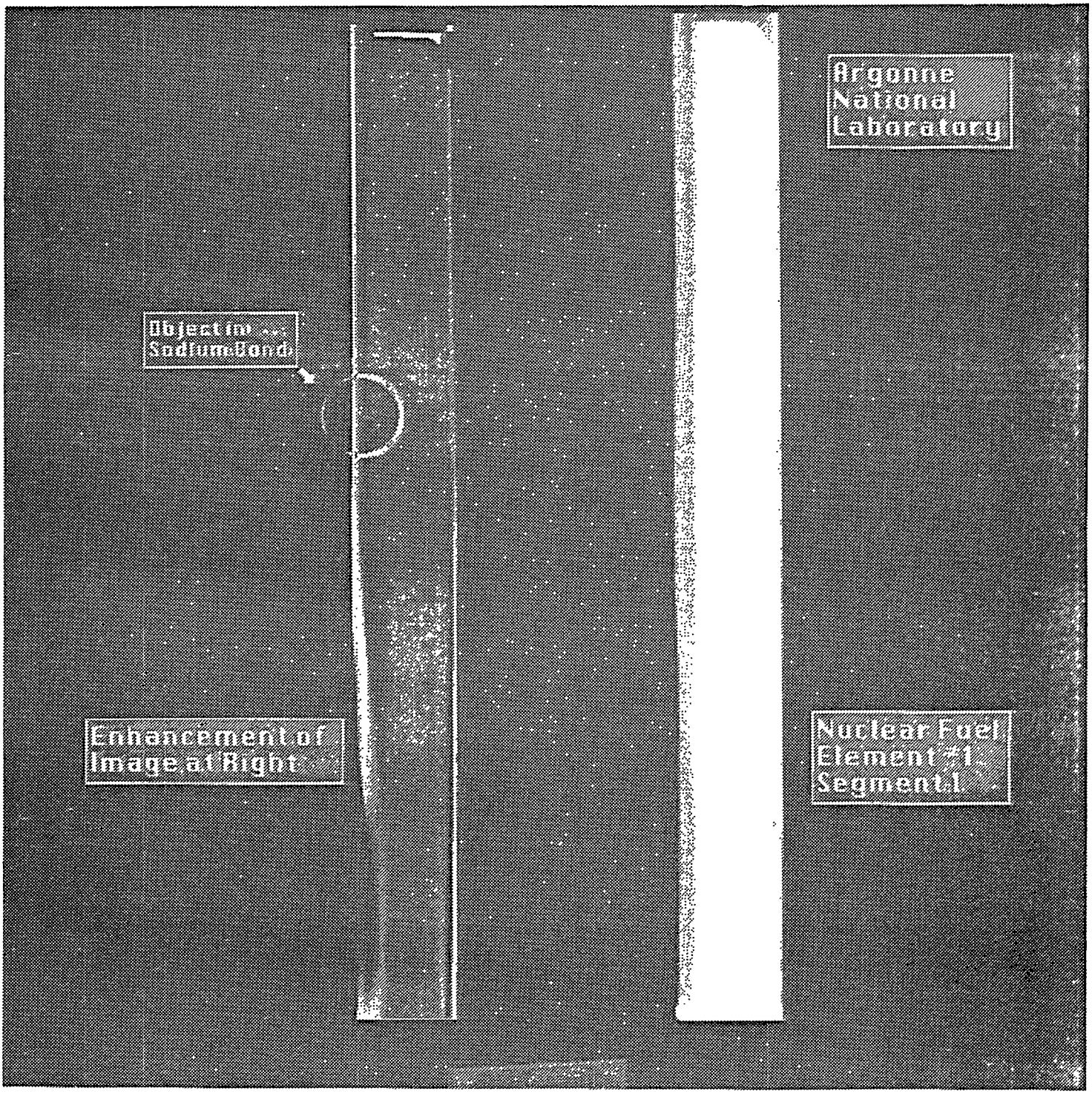

Digiray Corp
San Ramon, CA

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93-047R1 -- ONLINE IFR FUEL BURNUP DETERMINATION VIA STABLE-GAS MASS SPECTROMETRY

Associate Laboratory Director Area: Engineering Research

Principal Investigator: K. C. Gross, Reactor Analysis

Funding Profile:

FY 1992	$ -0-
FY 1993	$207.5K
FY 1994	$190.2K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: To develop a low cost, fast response, accurate method to measure burnup of IFR fuel pins upon completion of irradiation and prior to reprocessing, with an analysis turnaround time suitable to support mass flow rates for a commercial IFR. This project specifically seeks to explore the feasibility and practicability of a gas-sniffer system connected to an online mass spectrometer in the Fuel Cycle Facility. The mass spectrometer will quantify, to a precision better than 1%, multiple ratios of stable noble-gas isotopes whose compositions vary monotonically with fuel burnup. This new capability may provide an alternative to the lower accuracy, time-consuming and costly wet chemistry techniques for fuel burnup determination in future IFRs and in other fuel processing facilities outside the US.

Approach: Accurate tracking of plutonium and other fissile specie inventories in the IFR Fuel Cycle Facility requires a precise knowledge of fuel-pin burnup levels at the end of their irradiation. The current approach for burnup determination involves wet chemistry analysis in the Analytical Chemistry Lab. Although this method provides sufficient accuracy for burnup and fissile-inventory assessment, it is time consuming and impacts the economics of the IFR reprocessing concept at the commercial scale.

The scope of this project was to identify noble gas isotopic ratios that could be measured with an online mass spectrometer to accurately infer pin burnup; develop an analytical approach for computing optimal estimates of burnup given mass spectrometer measurements; and perform a preliminary technical analysis of the gas sniffer subsystem hardware. Scientific collaborators included M. T. Laug (STA consultant with Fuels & Engineering), S. Frank of Fuels and Engineering, and A. M. White of the Reactor Analysis Division.

Technical Progress and Results: During the previous year's LDRD project, the ORIGEN-2 point depletion code was employed in a detailed parametric sensitivity investigation to evaluate dynamic variations in noble gas isotopic compositions as a function of fuel burnup for prototypic IFR fuel pins. ORIGEN output data sets were analyzed with 3-D response surface methodology to identify candidate isotopic ratios that would maximize the accuracy of the gas-sniffer system for burnup determination. Analyses were performed on thirty ratios of stable isotopes from the four species xenon, krypton, argon and neon. During the present year a stepwise linear regression code was developed to identify which combinations of the 16 ratio trajectory curves would contribute the maximum information in a maximum likelihood estimator model to produce an optimal estimate of fuel burnup given a mass spectrometric measurement of the nine ratios.

A design was made of the gas sniffer system hardware and its interfaces to the fuel chopper subsystem in the Fuel Cycle Facility. A new noble gas recovery and concentration system was conceived and designed that will significantly improve our capability for obtaining high accuracy measurements of all noble gas isotopes of interest. Preliminary experiments were conducted in the Analytical Laboratory at ANL-W using isotopes of Kr to make a realistic assessment of the accuracy attainable using quantities of gas that are comparable to those expected in the FCF. The experimental results demonstrated 1-sigma error levels of 0.2%, 0.2%, 0.4%, and 0.2% for the isotopes Kr-83, -84, -85, and -86, respectively. These results are very satisfactory and are conservative insofar as the present Analytical Lab mass spectrometer is a 20-yr old instrument with considerably lower resolution capability than modern instruments.

As a direct result of these experiments, a new process was discovered for separation and concentration of noble gases. This process has been embodied in several new inventions that will (1) reduce complexity and costs and enhance safety in the fuel cycle facilities of future IFRs (fission gas recovery system); (2) significantly enhance the economics of gas tagging for failed fuel identification in IFRs and for the commercial nuclear industry; (3) improve the economics of production of xenon and krypton for industrial, medical and research uses; (4) remove indoor radon from homes, schools, and office buildings, thereby mitigating an environmental health problem the EPA says kills 20,000 U.S. citizens per year; (5) allow depressurization of the hundred million spent fuel rods stored in fuel pools around the U.S., thereby decreasing their source term and enhancing their integrity and safety during storage and eventual transport to a long-term repository; and (6) a new noble-gas surveillance methodology for Pu storage canisters.

Specific Accomplishments:

K. C. Gross and D. C. Wade, "Method and Apparatus for Online Nuclear Fuel Burnup Determination," Case No. ANL-IN-92-101 (Invention Disclosure Filed).

K. C. Gross, M. T. Laug, S. Frank, J. C. Braun "Neural Net Controlled Automated Tag Gas Sampling System for Nuclear Reactors," Case No. ANL-IN-93-113 (Invention Disclosure Filed).

K. C. Gross, M. T. Laug, and J. C. Braun, "Apparatus for Separation of Heavy Noble Gases from Mixtures of Lighter Gases," Case No. ANL-IN-93-104 (Patent Application Pending).

K. C. Gross, M. T. Laug, S. Frank and J. C. Braun, "Laser Device for Depressurizing and Resealing Spent Nuclear Fuel Pins," Case No. ANL-IN-93-114 (Invention Disclosure Filed).

J. C. Braun, K. C. Gross and D. J. Hill, "Device for Removal of Radon and Other Heavy Noble Gases from Air," Case No. ANL-IN-94-057 (Invention Disclosure Filed).

L. C. Walters, J. Krsul, K. C. Gross, S. Frank, D. Crawford, "Gas Tagging Method for Surveillance of Plutonium Storage Canisters," (Invention Disclosure Filed).

93-043R1 -- IMPLEMENT RELIABILITY CENTERED MAINTENANCE AND CONDITION MONITORING AT THE ANL-W SITE

Associate Laboratory Director Area: Engineering Research

Principal Investigator: J. C. Braun and R. E. Nietert, Reactor Analysis
H. P. Planchon, Integral Fast Reactor Operations

Funding Profile:

FY 1992	$ -0-
FY 1993	$248.2K
FY 1994	$225.2K
FY 1995	$225.0K
FY 1996	$ -0-

Purpose: Expand the practices used in the maintenance activities at the ANL-W site to become as sophisticated as the best practices in the civilian industry today and then advance the state of the art by introducing innovative data collection, coordination and computer technology. Develop processes that can be used to expand the state of the art in maintenance practices throughout the DOE complex as well as other civilian industries.

Approach: The aviation industry has made major improvements in the areas of maintenance and condition monitoring of critical components. The nuclear industry has followed these practices slowly, and is now only beginning to implement some of the practices that are appropriate to maintain complex, expensive systems in top operating condition without performing unnecessary maintenance. The military has realized significant benefits and cost savings by implementing reliability centered maintenance (RCM) and condition monitoring techniques. It is very appropriate for a national laboratory to assume a position of leadership in the advancement of this technology.

The first phase of this study identified a number of promising areas where the application of advanced monitoring practices, such as vibration monitoring, can substantially enhance the performance of important equipment. We also studied the twelve ANL-W emergency diesel generators (EDGs). These studies examined the maintenance practices carried out at ANL-W. This involved a review of the types of equipment maintained, the procedures utilized in the effort, national consensus standards, and the identification of worthwhile improvements.

In addition to hardware improvements, we judged that major improvements at ANL-W could be made by adding, modifying, and upgrading software to automate such things as the trending of data taken from preventive maintenance inspections, procedures, procedure review, spare parts identification and ordering, and maintenance planning and scheduling.

In this second year of the project, the scope was expanded to involve not only the EBR-II facility, but also the entire ANL-W site; the software development mentioned above was also added.

In the second phase of the study we designed a modern client/server database for maintenance management of large facilities. We then examined various software packages and computer

hardware and procured the equipment and software required. A software development laboratory was established at ANL-E and similar equipment and software, which forms the initial building blocks of a complete site wide system, was deployed at ANL-W.

We conducted tests of some of these automation tools; specifically we demonstrated an on-line paperless procedure via wireless-networked notebook computer, and implemented preventive maintenance planning and scheduling modules for use by the work control department of the ANL-W site. In the final phase, we will complete the development of the automation tools initiated in the second year of the project and demonstrate a methodology which could be used for transferring the entire cadre of analytical database tools, for example, to U.S. industry.

By using probabilistic risk analysis (PRA) techniques, we also intend to assess the impact on overall safety and reliability resulting from maintenance improvements. One of the final outputs of this LDRD effort will be a system for feeding maintenance information into the relevant PRA analyses to determine the new risks associated with the new maintenance practices. This will enable the determination of risk reduction or increase that results from improved or degraded maintenance practices, and allow a benefit vs. cost analysis to be performed on maintenance practices.

Finally, we intend to again expand the original scope to develop intelligent algorithms for optimizing spare parts inventories, and apply these algorithms to the spare parts inventory used for a target system. The reduction of spare parts inventories at nuclear and other high technology facilities has become an issue of growing importance due to increasing pressures to lower the costs of operation and maintenance (O&M).

Technical Progress and Results: The main thrust of this year's activities has been the development of analytical tools in support of the following maintenance activities:

- schedule maintenance,
- provide and get approval for maintenance procedures (including procedure changes),
- deploy job performance aids (JPAs) for the conduct of complex or unusual maintenance,
- track and record completed maintenance,
- track and trend critical parameters which signal the degradation of key components.

We defined analytical tools that could improve these activities. These tools would use state of the art computer hardware and client/server database software via the following modules:

1. ***Work Control,*** which consists of:
   corrective action logger: logs new, off-routine work to be performed.
   work planner: identification of preventive, predictive, and corrective actions.
   scheduler: applies project management techniques to scheduling and prioritizing work.

2. ***Procedures,*** which consist of:
   procedures library: holds all maintenance procedures on-line as electronic documents, makes them easier to revise, and simultaneously places them under configuration control.

procedure viewer/data logger: eliminates use of the usual procedures printed on paper by viewing procedures on notebook computers. This methodology also places data directly into the database and makes it available for further use (e.g., modules 3, 4, and 5 below). The data links between the notebook computers and the database server are through state of the art wireless ethernet connections.

3. ***Trender:*** pictorially displays selected data from the database in order to identify undesired trends. This module helps to identify when predictive maintenance should be performed and minimizes not only corrective maintenance but also preventive maintenance by selecting the "best" time to perform the next preventive maintenance activity.

4. ***Availability Minimizer:*** predicts value of maintenance work and effect on plant availability via an intelligent link between the PRA and the database.

5. ***Inventory Manager:*** optimizes spare parts inventory levels against acceptable variables via intelligent algorithms and links to the database data.

In the second phase of the study we defined the computer architecture required to develop this maintenance database and identified the hardware and software required to develop and interoperate with these analytical tools. We also designed a modern client/server database for maintenance management of large facilities. We then examined various software packages and computer hardware and procured the equipment and software required to automate the items mentioned above. An important consideration in the design was that the computer hardware and software be chosen such that the analytical tools developed would be compatible not only with the ANL-W computer architecture, but also with the widest combination of possible hardware and software architectures presently on or projected for the market. A software development laboratory was established at ANL-E and similar equipment and software, which forms the initial building blocks of a complete site wide system, was deployed at ANL-W during FY94.

The major accomplishment of FY94 was implementation of an on-line paperless procedure. A procedure was implemented in software and utilized during a monthly load test of the FCF Class 1E (safety grade) EDGs. Technical transfer of the "paperless procedure" to the maintenance personnel was performed with minimal training. Data, which could later be trended or utilized for other purposes, was automatically loaded into the database as it was collected by the electricians. The link between the electrician's notebook computer and the database, which was centrally located elsewhere on the ANL-W site, was accomplished via a state-of-the-art spread spectrum radio "wireless" network.

Specific Accomplishments:

1. "Integrated Maintenance Management," presentation to the IFRO/RA coordination meeting, R.E. Nietert, May 10, 1994.

2. "Preparation for University of Chicago Review of IFRO, Demonstration of Paperless Procedure Data Base System," internal memo, R.E. Nietert to W.S. Barak, May 12, 1994.

3. "A State of the Art Client/Server Data Base System for Maintenance Management," R.E. Nietert and J.C. Braun, paper presented at the DOE Nuclear Facility Predictive Maintenance Symposium, Atlanta, Ga., May 18, 1994.

4. "Project Status, Integrated Maintenance Management Data Base," internal memo, R.E. Nietert and W.S. Barak to D.J. Hill and H.P. Planchon, June 16, 1994.

5. "Maintenance Development," project status and wireless, paperless procedure demonstration presented to the University of Chicago Board of Governor's Review of the IFRO Division, B.C. Gay and R.E. Nietert, August 18, 1994.

93-040R1 -- LASER BASED HOT CELL ELEMENTAL AND ISOTOPIC ANALYSIS SYSTEM

Associate Laboratory Director Area: Engineering Research

Principal Investigators: S. G. Johnson and S. M. Frank, Fuels and Engineering

Funding Profile:

FY 1992	$ -0-
FY 1993	$216.2K
FY 1994	$124.4K
FY 1995	$140.0K
FY 1996	$ -0-

Purpose: The objective of this proposal is to introduce laser based analytical methods for direct elemental quantification at trace, minor and major levels in a hot cell environment. The ultimate goal being to reduce the need for complex labor intensive sample dissolution techniques, while providing accurate, rapid analyses of irradiated fuel, salt, cadmium and various waste samples. Direct chemical analysis of solid samples, without the need for dissolution and separations, would reduce the waste generation in the Analytical Laboratory, and demonstrate that the same could be done in future applications, i.e., hot cell based spent fuel or waste characterization facilities. Moreover, the end product of this effort would be to demonstrate techniques that could be adapted directly to the production floor of a DOE radiological waste characterization facility. This concept would reduce facility construction costs and provide for more timely analysis for input to process and material balance controls.

Approach: Sample analysis procedures used currently in the Analytical Laboratory (AL) hot cells at ANL-W require the sample be converted into solution form. Further chemical separations are necessary in order to obtain accurate elemental and isotopic analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Mass Spectrometry (MS). This is due to the extreme spectral congestion for ICP-AES and isobaric interferences for MS of the actinide and lanthanide elements present in these samples. Additionally, the removal of radioactive fission products is required for MS analysis outside the hot cells. Procedures presently used to prepare the samples for ICP-AES and MS analyses generate a variety of waste forms including mixed hazardous waste which presents problems in terms of waste disposal.

Laser ablation has the following advantages. First, the use of organic solvents and concentrated acids during the separation procedure to prepare a sample for ICP-AES or MS analysis will be eliminated. This reduces the amount of contaminated liquid waste generated by the AL and decreases the error in estimating the amount of special nuclear material (SNM) distributed in the respective waste streams. During laser ablation approximately 1 mg of the total sample may be used for both elemental analysis and isotopic assay thus greatly reducing the quantity of sample necessary and therefore the waste generated. Second, the material can be surveyed for its isotopic and elemental composition entirely within the hot cell environment reducing the risk of contamination involved with removing a sample from the hot cells. Additionally, the laser ablation technique can be performed on a sample in minimal time relative to present methods

for isotopic assay and trace elemental determinations. This has tremendous potential for decreasing the turn-around time necessary for an analysis. Determination of fission products in spent oxide reactor fuels using the technique of laser ablation-ICP-MS is currently underway at the Institute for Transuranium Elements in Karlsruhe, Germany.

The application of glow discharge sampling technologies can yield isotopic information and depth resolution directly for conductive solid samples. This additional capability can be obtained at a very nominal expense yet yield a great deal of information when coupled to a time of flight mass spectrometer (TOFMS) system which is already part of the direct solid sample analysis system. For these reasons this technology will be investigated and incorporated as part of the system.

Bench top experiments have been conducted during the past year using simulated binary metallic fuels and salt samples doped with lanthanides in order to obtain the appropriate operating parameters and analytical figures of merit for the hot cell based laser ablation (LA) ICP-AES system. These have been conducted primarily by Dr. Phillip S. Goodall a Post-Doctoral Fellow. Parallel studies have been performed on the TOFMS system using both laser ablation and glow discharge sampling methodologies with a series of standards to determine operating parameters and analytical figures of merit. Additionally, portions of the TOFMS system have been installed into the renovated hot cells in the Analytical Laboratory.

Technical Progress and Results: Technical and personnel progress has been made on several distinct fronts in FY 94. A Post-Doctoral Fellow was hired in March of 1994, to further the extent and the pace of progress on the Laser Ablation portion of the project. Dr. Goodall has an extensive background in ICP spectroscopy and has proved to be a very effective and efficient researcher. The laser ablation ICP-AES portion of project has accomplished several objectives during FY 94. First, data has been gathered for simulated reactor fuel, unirradiated metallic U-10 wt% Zr, to detail fundamental ablation characteristics, important operating parameters and analytical figures of merit. These include: optimal ablation wavelength for best precision (1064 nm), optimal ablation wavelength for best spatial resolution (532 nm), spatial resolution obtainable without special manipulation (90 micrometers), and optimal laser pulse energy range for most accurate results (matrix dependent). The experiments necessary to yield this information allowed for optimization of the ablation cell design and also for several fundamental revelations in the ablation characteristics of binary fuel. These developments are quite complex in nature and will be presented as a paper during the upcoming year in the open literature. Briefly, at this time we wish to state that detailed information has been obtained on two distinct ablation mechanisms that occur during different laser fluence regimes and that these differing mechanisms may result in preferential ablation of matrix constituents. Additionally, experiments were conducted using salt samples doped with lanthanides, and soon uranium, which allowed for similar parameters and figures of merit to be determined. The salt samples provided an additional challenge since their ablation characteristics necessitated a constant raster of the sample to minimize the drilling effect of the laser.

The TOFMS system has progressed greatly in the last year. A complete functional system has been assembled in a mock-up laboratory. The configuration is as planned for the hot cell version of the instrument. Both laser ablation and glow discharge sampling methods have been tested and optimization activities are on-going. Several standards have been used including,

copper, several types of steels and a tin-bismuth alloy. The tin-bismuth alloy provides a reasonable surrogate for binary fuel, U-10Zr, without contaminating the interior of the TOFMS until all optimization studies are complete. Figure 1 displays a TOF mass spectrum obtained for a copper standard using the laser ablation sampling technique with the relative isotopic abundance agreeing favorably with the known reference value for the 63 and 65 isotopes ^{63}Cu (70%)/^{65}Cu (30%) versus ref. ^{63}Cu (69%)/^{65}Cu (31%)). Additionally, hot cell modifications for the TOFMS are nearly complete with the following listed as accomplishments: design, construction and installation of a exterior vacuum confinement box for the fore pump, turbo pump and gate valve, design and installation of wiring for hot cell installation of ion optics, and installation of TOFMS flight tube into a two foot thick concrete shield wall of the hot cell.

Activities for the upcoming year will include the following: 1) completion of TOFMS optimization studies and installation into the hot cell followed by in-cell testing with a variety of samples including irradiated fuels and 2) completion of optimization studies for the LA-ICP-AES system and installation of the system into the hot cells.

Three collaborators have aided in the accomplishments presented here, they are Dr. Kevin Carney, Prof. Sandra Kimbrell of University Alaska-Fairbanks and Mr. David Bunnel. Dr. Carney has aided primarily in the area of the TOFMS sampling systems and Mr. Bunnel aided in the design and modification of the TOFMS itself.

Specific Accomplishments: S. M. Frank, oral presentation and paper entitled "Hot Cell Based Time-of-Flight Mass Spectrometry," presented at the *American Nuclear Society International Topical Conference on Methods and Applications of Radioanalytical Chemistry-III*, Kona, Hawaii, April 10-16, 1994. Paper to be published in *Journal of Radioanalytical Chemistry*.

S. M. Frank, poster presentation entitled "Hot Cell Based Time-of-Flight Mass Spectrometry", presented at *Second Alfred O. Nier Symposium on Inorganic Mass Spectroscopy,* Durango, Colorado, May 10-12, 1994.

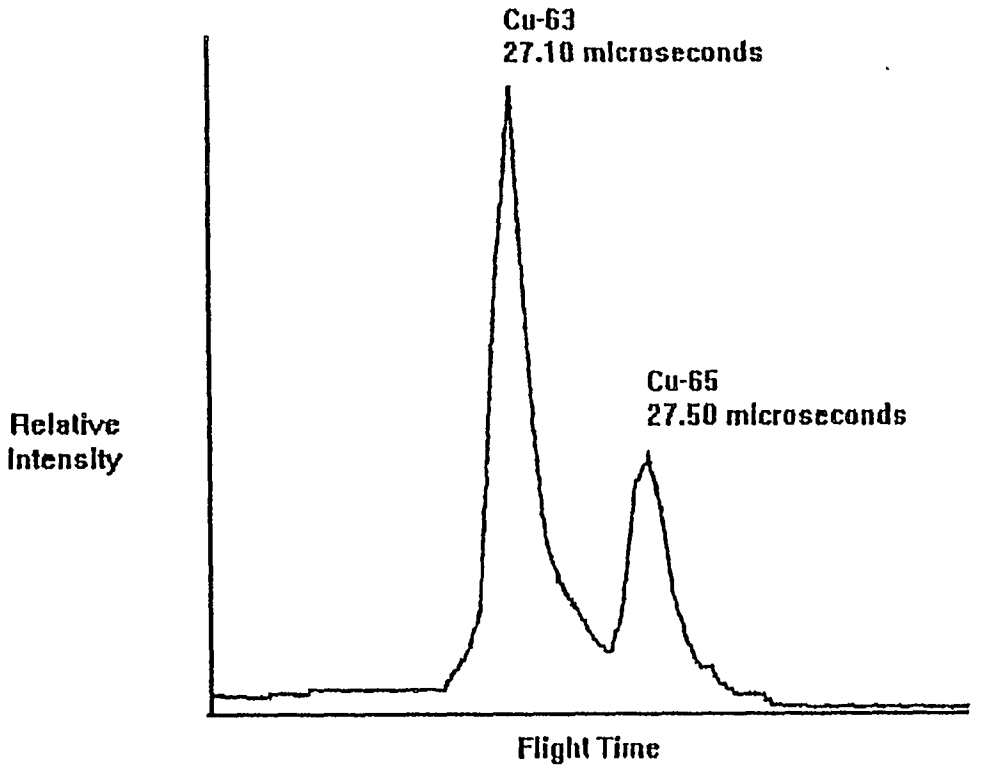

Figure 1. Time of flight mass spectrum of Cu-63 and Cu-65. Sampling by laser ablation.

92-047R2 -- COMPUTER IMAGING OF EBR-II FUEL HANDLING EQUIPMENT

Associate Laboratory Director Area: Engineering Research

Principal Investigator: G. G. Peters and L. H. Hansen, Integral Fast Reactor Operations

Funding Profile:

FY 1992	$164.6K
FY 1993	$125.9K
FY 1994	$170.0K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: This project develops imaging techniques that provide a computerized three dimensional real-time display of fuel handling equipment submerged in liquid sodium and operated in the EBR-II primary tank. The final goal of the project was to develop a method for updating the model in real-time with actual plant data. The computer imaging will improve the fuel handling surveillance and troubleshooting efforts and may be applicable to other hostile environments where positioning of critical equipment must be known.

Approach: EBR-II reactor fuel and experiments are transferred into and out of the reactor vessel via remotely operated fuel handling equipment. The radioactively contaminated 700°F liquid sodium environment prevents direct visualization of the subassemblies and fuel handling equipment during transfers. The position of the fuel handling equipment is now inferred by sensors mounted outside the hostile environment of the primary tank. Observation of the equipment within the primary tank has not been possible since the initial filling with liquid sodium more than twenty-five years ago.

Computer graphics have been used for many years to present real-time data to operators and engineers. However, only recently has technology been capable of presenting real-time data as a three dimensional (3D) image. What makes this project unique is that methods are being developed to actually update a three dimensional graphics image in response to real-time data from the plant. For the first time, we are able to see the relative positions and movements of the fuel handling components as they would actually appear inside the tank.

In order to achieve these goals, two approaches were taken to the problem. The first approach uses a highly detailed 3D model of the primary tank that shows a high fidelity image of all the components and their relative positions within the tank. This model was created in an AutoCad format by C. V. Wiegand from the original EBR-II blueprints. L. H. Hansen developed the software to animate this model.

A second approach was also taken that uses a less detailed model that is more appropriate as an operator interface. This model can be easily animated in real-time with actual plant data. Additional sensors are being developed by G. G. Peters to drive the animation.

Technical Progress and Results: In 1992, the first year's efforts began with the creation of a high fidelity, 3D computer model of the existing EBR-II fuel handling equipment. The model

was constructed by C. V. Wiegand from the original EBR-II blueprints using AutoCad™. Also initiated was the development of an acoustic sensor echo-location technique to detect the position and relative movement of the fuel handling equipment. The data received from these sensors would drive the animation. Software programs were developed by L. H. Hansen using the SDRC I-DEAS™ software application.

In 1993, the 3D AutoCad model was completed and imported into the I-DEAS™ software but found to be unmanageable because of the intense detail of the model. Until this problem could be solved, another approach was initiated using a less detailed 2D model. At this time, it was determined that the design costs of acoustical sensors would be exorbitantly high and would not provide the accuracy and reliability needed. Therefore, other types of position sensors more conducive to the visualization needs were necessary. The I-DEAS™ software application was reviewed by A. Brown-VanHoozer from a human factors perspective and was found to be neither usable nor practical as an operator interface. The software was also incapable of accessing shared memory for real-time display of fuel handling operations.

In 1994, a new software application, Designer's Workbench™, was purchased for model reconstruction of the EBR-II fuel handling equipment. Designer's Workbench™ is now used to display and animate the new 3D model in real-time. The data to drive the animation originates from instrumentation located outside the primary tank on critical fuel handling equipment. These positions are digitized and transferred over a computer network where they are used to update the 3D graphics model. The animation will be in real-time to simulate the fuel handling operations as they are occurring during fuel handling sequences.

Since the purchase of Designer's Workbench™, a new 3D computer model has been constructed by L. H. Hansen and G. G. Peters of the critical fuel handling components. The new software application is more graphically and visually oriented, so the model can be managed more effectively. Levels of detail were added to eliminate polygons that were too small to be seen. This trimming technique reduced the overall model structure making it more efficient. The original AutoCad™ model is currently being used by another research project and the I-DEAS™ software is being applied to other engineering applications.

The final goal of this project is to incorporate the 3D real-time display of the fuel handling equipment into an upgrade of the operator control console to improve fuel handling surveillance. Instrumentation located outside of the primary tank will sense the positions of moving components. New position sensors for the storage basket and transfer arm have been designed and will measure the elevation and rotation of each component. Signals from these instruments will interface directly with a SUN Sparc 20 workstation via A/D boards installed in the backplane of the computer. These signals will be indicated as readouts on a 2D graphics display and sent over the ethernet to a Silicon Graphics Indigo2 computer for updating the 3D model.

Specific Accomplishments: Visualization of the transfers of fuel and experiments into and out of the reactor using real-time data has been achieved. Critical components directly related to fuel handling operations were modelled. Dynamic behavior of the moving components was incorporated into the model by creating links to database elements that define the translational and rotational movements of each component. Actual plant data from shared memory can be used to animate the model in real-time or data can also be accessed from a file for replaying particular transfer sequences.

Important factors were considered in the design of the 3D computer model for both manageability and performance. One consideration was the number of sides or facets to apply when creating a cylindrical object. A large number of sides improves the smoothness of the curve but results in a degradation in performance during animation. When proper shading is applied, very few sides are required in order to achieve a cylindrical appearance, especially when the object is relatively small. Large objects required more facets in order to appear smooth. We found that many of the objects in our model required as few as five to seven sides in order to appear round when proper shading was used. This resulted in a significant reduction in the number of polygons required to create the model as compared to the AutoCad version. A partial model consisting of the major fuel handling components was reduced from 500,000 polygons in the AutoCad version to 1500 polygons in the new model.

Constructing 3D objects using polygons involves a number of other important performance considerations. For example, polygons should be limited to three or four vertices. This restriction greatly improves the graphics performance since triangles and four-sided polygons will draw several times faster than polygons containing five or more vertices. This is because the Silicon Graphics computers are designed with dedicated graphics engines that are optimized for triangles and four-sided polygons. It is also advantageous to use only planar polygons which have vertices that are all in the same plane. Non-planar polygons are difficult to render properly and can slow down the graphics speed considerably.

A database hierarchy was generated in which groups of polygons, vertices, strings, levels of detail, etc. are placed at different levels of the hierarchy tree. These groupings allow special attributes or behavior to be applied to entire groups of polygons. Levels of detail switches, for example, were placed on small details of the model, so that these polygons are drawn only when the eyepoint is zoomed in close enough to see them. Thus, the same object was sometimes modeled two or three times, each with a different amount of detail. When the switch points are placed correctly, the observer is not able to detect the transition points and the model transitions smoothly as the zoom scale is increased.

This database hierarchy is also important when adding dynamics to the model. Polygons were grouped together so that a common dynamic behavior could be applied to an entire object. Since link dynamics can be at any level of the hierarchy, the structure of the tree controls the particular section affected. Some objects, such as the core gripper structure, have an entire hierarchy of objects at different levels. This allows the gripper jaws to open and close, the gripper shaft and jaws to raise and lower, and the entire gripper structure to move with the rotating plugs.

The 3D graphics model of the primary tank has been used to show the feasibility and practicality of visualizing real-time operation of complex systems. This project has demonstrated that real-time data can be used to drive a detailed 3D model allowing visualization of complex processes as they are occurring. The methods that were developed could be applied to other situations where visualizing orientation and interactions between mechanical components in three dimensions is important. The visualization provides a more tangible means of understanding current situations or even preparing for more critical operations. Three dimensional computer models like EBR-II can be used to simulate positions and movements of real-world components that either cannot be seen or exist in environments where human visualization is not feasible.

The newly developed 3D computer graphics model and the visualization work were presented at a visualization session at the 8th Annual INEL Computing Symposium, October 1994. The computer visualization work on this project will also be published in the proceedings and presented at the International Conference on Fuel Management and Handling in Edinburgh, UK, March 1995.

94-046N -- SODIUM IMAGING SYSTEM (SIS)

Associate Laboratory Director Area: Engineering Research

Principle Investigators: S. A. Brown-VanHoozer and H. P. Planchon, Integral Fast Reactor Operations

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$ 89.7K
FY 1995	$200.0K
FY 1996	$ -0-

Purpose: The goal of this project was to research the feasibility of using ultra-violet(UV)/ultrasonic lasers and optical technology in detecting cracks, flaws, and the position and movement of equipment under a liquid sodium medium where direct visualization is not possible. The laser approach was selected because it provides more resolution in both the spatial and temporal regions in comparison to the conventional ultrasound technique. Since the laser beam can be focused on a specific spot diameter on the order of microns, high resolution scanning of acoustic wave amplitudes on an object surface may be performed using optical detection; thus allowing both noncontact and remote sensing of acoustic signals. These signals can then be converted into images for analyzing cracks, flaws, movement and so forth.

Approach: The investigations of this project concentrated on understanding the fundamentals of laser generation and detection, UV-lasers and laser ultrasonics, lasers and liquid metals, development of a mathematical model for using lasers in liquid sodium, and development of a simulation program to compute and simulate an avoustic wave propagation of laser generated ultrasound to be used for viewing under sodium.

The first phase of the project was to conduct a literature search on UV and ultrasonic lasers, laser research involving liquid sodium and the transparency property of sodium.

The second phase was to develop a mathematical model that could determine the electromagnetic wavelength at which liquid sodium will be transparent, could be used to analyze or characterize the ultrasound wave progagation in both the time and frequency domain, and provide the characteristics required in the development of a prototype device. This mathematical model was developed by Dr. Arun Majumdar of Laser/Electro-Optics Concepts Research, and was based on the Drude-Zener formula and Green's function.

The final phase of the project was to develop a computer simulation program to test the theoretical model. The program used was developed at the National Institute of Standards and Technology (NIST) by N. N. Hsu. The simulation program computed acoustic waves from an impulsive point source in a fluid/solid configuration in terms of a dynamic Green's function involving both a source and detector in a liquid medium. It was found that the time domain solution from the simulated program could be applied to arbitrary test configurations using a small point source and point detector for modeling a general ultrasonic scanning system.

Dr. McWhirter, of Idaho State University, and a third member of the research project, assisted with the investigation in defining specific parameters for the mathematical model, and in the testing of the simulation program.

Technical Progress and Results: From the study, it was determined that a laser with a wavelength of $\lambda=0.21\mu m$ can transmit through liquid sodium without much loss, and therefore, can be used to generate ultrasound on the surface of the metals that are under sodium. It was determined that the beam would have to be focused on the surface of the metal or as close as possible.

Two mathematical models were formulated based on frequency and time-domain analysis, Green's function and the power spectral density. Results of the investigations found that in some situations the power spectral analysis gave information about the cracks or flaws when the material was excited by a laser pulse generated by ultrasound.

A computer simulation program developed at NIST was implemented and used to model, in terms of Green's function, a liquid/solid interface with both source and detector in a liquid medium. Figure 1 shows a simulated output waveform for a point receiving sensor located 5mm away from a point source on a metal surface. Both source and receiver were calculated at 1mm above the liquid sodium-steel surface of the object. The output waveform is the result of numerical convolution in the time domain of the differentiated source waveform and the Green's function. This simulation showed that under circumstances realized experimentally, the arrivals of shear wave and the reflected main echo can be separated and the time interval between arrivals can give information about the elastic properties of the material. Furthermore, the amplitudes of the waveform will be differently displaced in terms of both magnitude and location if one compares the waveforms from a perfect plane to a surface with cracks or flaws.

Figure 2 shows a simulated output of the temporal signal based on the power spectral density analysis with respect to frequency components in the signal. This approach was determined to be important to differentiate the signals from a plane surface against a surface containing cracks or flaws.

A final aspect of progress of this project was the conceptual development of two design configurations for a prototype laser/optic system for imaging through liquid sodium. One configuration makes use of the transparency property of liquid sodium at the UV wavelength, while the other takes advantage of absorption of the laser wavelength in the liquid sodium.

Figure 3 shows the configuration of UV-lasers used to generate ultrasound on the surface of the metal using the transparency property of sodium at wavelength $\lambda=0.21\mu m$.

Figure 4 shows the second configuration based on other laser wavelengths where liquid sodium is not transparent. In this configuration, a laser is used where light will be absorbed in the sodium liquid medium, and the ultrasound is generated in the liquid and detected by another laser interferometrically.

The second phase of this project for FY1995 will involve the design of a test bed for verifying the concepts experimentally in liquid sodium. The test results will provide the parameters to

construct a prototype instrument based on the principles found in this current research effort. The significance of this research is the potential to develop new optical technology for remote sensors to characterize materials in the presence of nondirect visualization, hostile and/or high temperature environments.

Specific Accomplishments: Two internal reports have been written on the accomplishments of the projects to include specific components of the test design. A list of technical references has been compiled of laser ultrasonics and imaging techniques, and a copy of the computer simulation program has been submitted as part of the final report.

Two formal presentations have been presented at Argonne-West describing the methodologies of the project, and a paper will be submitted for scientific journal and proceeding publication in FY95. A FY95 LDRD proposal has been submitted for funding for Phase II of the project.

During the development of this project, professional relationships were established with NIST, Johns Hopkins University and the former contractor of Idaho National Engineering Laboratory, EG&G. The scientists at NIST and Johns Hopkins showed strong interest in the project since both institutes are conducting laser ultrasonic research with respect to liquid metals and nondestructive techniques for determining microstructure in a material. EG&G (now LITCO) expressed a desire to assist in developing a prototype from our results.

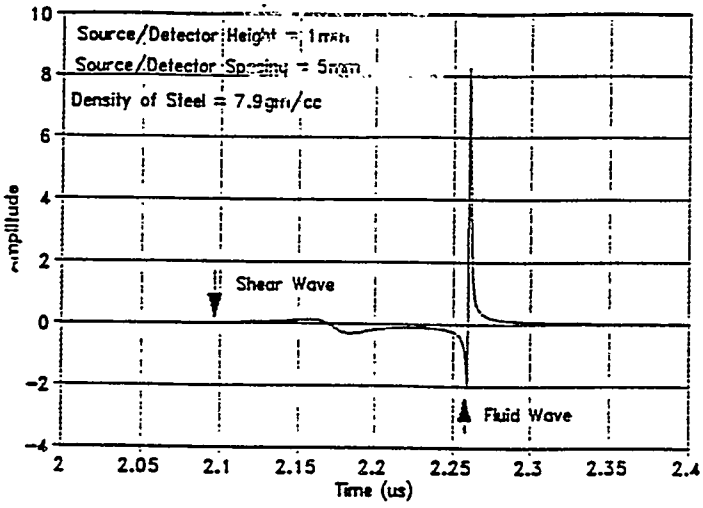

Figure 1. Simulated computed waveform for a point source and point detector 5mm apart and 1mm from a liquid sodium/ steel interface. Arrows indicate the arrivals of longitudinal, shear, and fluid waves.

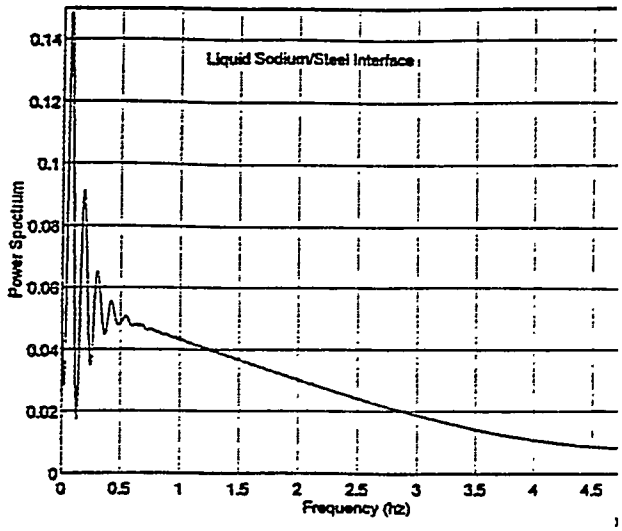

Figure 2. Power spectral density of the waveform in Fig showing the various frequency components. The values obtained by squaring the absolute values computed by F Fourier Transform (FFT) method.

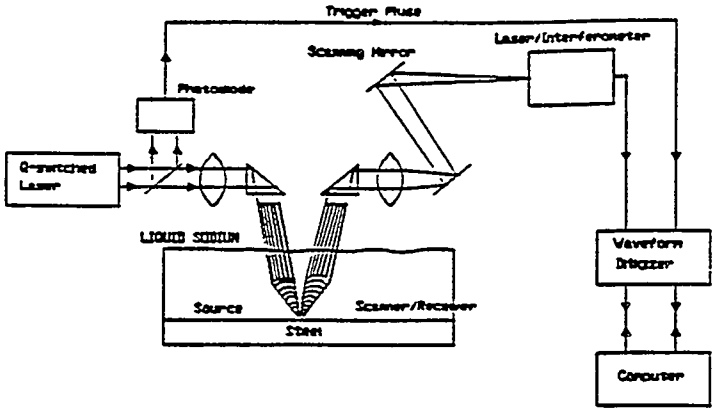

Figure 3. UV LASER CONFIGURATION

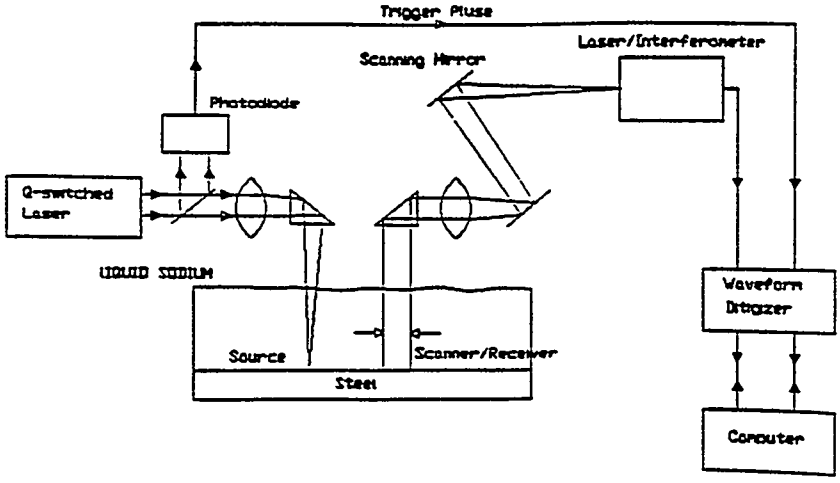

Figure 4. LASER OF OTHER WAVELEN CONFIGURATION

94-112N -- NEW METHOD FOR SEPARATION OF PLUTONIUM FROM PLUTONIUM-GALLIUM ALLOYS

Associate Laboratory Director Area: Engineering Research

Principal Investigators: Z. Tomczuk and W. E. Miller, Chemical Technology Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$212.2K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The project objective was to conduct laboratory tests to determine the feasibility of recovering plutonium from Pu-Ga alloy by using pyroprocessing that involves either electrochemical transport from a Pu-Cd-Ga anode or chemical oxidation of plutonium from the alloy via a suitable chemical oxidant. The justification for this program is that large quantities of the Pu-Ga solid alloy exist (leftover "waste" from the standard electrorefining process, which separates 85% of the plutonium from the Pu-Ga alloy), and require further treatment to recover plutonium. The proposed process, if successful, will demonstrate that plutonium can be recovered in a one-step electrorefining process, rather than a process which requires a second process (waste treatment of the anode heel) to recover all of the plutonium.

Approach: In present plutonium production involving Pu-Ga alloys, the final purification step involves electrorefining of plutonium. In the production cells, the impure Pu-Ga alloy (usually 1 to 3 atom % Ga) is made the anode, and pure plutonium is transported to a liquid plutonium cathode (cell operation is above melting point of plutonium). This transport is continued until approximately 85% of the plutonium is transported, and then operation is stopped because the anode becomes solid and further electrochemical transport is not possible with the cell design used. The solid remaining in the anode (the anode "heel") requires additional processing by a different method to recover the residual plutonium.

In this program, we will apply new methods of separating the plutonium from the solid Pu-Ga alloy. The primary method chosen was electrorefining from a molten cadmium anode. We base this approach on theoretical calculations which indicate that dilute solutions of plutonium in Cd-Ga would behave in a fashion similar to dilute solutions of plutonium in cadmium. We have already demonstrated greater than 99.99% transport of plutonium from cadmium (as part of the Integral Fast Reactor Program).

In the first phase of the program, we needed to establish that the addition of Pu-Ga alloy to molten cadmium covered with a molten salt at 500°C did not corrode the low carbon steel electrorefining cell, which is normally employed in processing metallic fuel generated in the IFR Program. If corrosion was a problem, we would then change the material of construction for the containment vessel and related hardware.

In the next phase of the program, the Pu-Ga alloy would be dissolved in the cadmium pool, which then becomes the cell anode. Plutonium then would be transported into a liquid cadmium cathode in the cell. The plutonium collected, in this cathode, would then be recovered by distilling the cathode cadmium. Composition of this plutonium compared to the original alloy (Pu+1-3 atom % Ga) would reveal the degree of separation achieved.

During the transport, the concentration of gallium in the anode should (if not transported) remain unchanged. This operation could be repeated until the limit for gallium buildup in the cadmium was reached.

The estimated limit is 0.1 mole fraction gallium in Cd-Ga. This limit is dictated by the corrosive properties of gallium toward ferrous metals. If 0.1 mole fraction of gallium in cadmium is the limit of operation, then 7.6 kg of plutonium would be recovered for every kg of cadmium requiring distillation separation from gallium (non-volatile). This cadmium would be used to make a fresh anode for recovering more plutonium, and the gallium would be returned to the process to make original Pu-Ga alloy.

If the above approach failed, we would use the solid Pu-Ga alloy directly as a moving anode and transport plutonium to a cathode. This approach is similar to that already being used to anodically dissolve metallic fuel. In the final approach considered to be investigated, if the first two were unsuccessful, the Pu-Ga alloy would be contacted with a suitable oxidant, such as $CdCl_2$, to extract the plutonium into a molten salt phase. This salt phase would be separated, and the plutonium in solution would be reduced to the metal by using a sufficiently strong reductant, such as lithium.

As discussed above, we considered three approaches for the recovery of <u>all</u> the plutonium from the Pu-Ga alloy. We ranked these in the order discussed above, and in our experimental work we intended to investigate the latter two methods only if the first approach failed.

Technical Progress and Results: Our analysis showed that Ga-Cd alloy containing less than 10 mol% Ga should not cause serious corrosion problems, especially in these short- term tests. Accordingly, laboratory-scale tests were conducted using a new steel crucible to contain the Pu-Ga-Cd solution. Filtered samples of the salt and metal phases were taken, and analytical results indicated that all of the Pu and Ga added were in the metal (anode) phase, as predicted by thermodynamic calculations. Four electrotransport tests were carried out to separate the plutonium from the metal phase. The number of tests was limited to four because of the total amount of plutonium available for transport and the amount of plutonium that would be contained in any one test by the liquid cadmium cathode, which collected the transported plutonium. The plutonium contained in the cathode product was then recovered by distilling off the cadmium in the available retort. Chemical analyses indicated that gallium <u>did not</u> accompany plutonium during electrotransport. Typical analyses of the cathode product indicated $\leq$30 ppm Ga (the actual amount is probably lower than 30 ppm, which represents the lower detection limit of the analytical method used).

Before the experiments were initiated, it was necessary to shut down the electrorefiner used for work in the IFR Program. After this shutdown, the old crucible had to be removed and the new steel crucible installed. After the electrochemical experiments were carried out, it was

necessary to restart the induction furnace (retort). A number of trial runs were conducted (after new insulation pieces were fabricated and assembled for the retort in the glovebox) to calibrate the apparatus. Afterward, a control test with pure cadmium was conducted to establish conditions needed for distillation of cadmium. (In this test and subsequent tests, we obtained cadmium recoveries >98% in the condenser-conductor.)

The electrochemical tests were completed without difficulty. The time vs cell voltage curves for these tests were similar to those obtained in the absence of gallium in the cadmium pool. The amount of plutonium transported, based on the coulombs passed, equaled 124.7 g, an amount equal to that available for transport. Chemical analysis of filtered samples after the final electrorefining test verified the above value, as the amount of plutonium left in the cadmium pool was <10 ppm. Thus, >99.9% of the plutonium transported from the Cd-Ga anode.

The experimental results were compared to those predicted with a thermodynamic model developed for the Pu-Ga-Cd system by I. Johnson of the Chemical Technology Division. Our results were consistent with his calculations. The model predicts how the activity of plutonium in the cadmium anode is affected by addition of gallium. From this, the transport voltage required can be estimated. The voltage estimated from the model is consistent with what was found in the experiment (<-1.0 V). Extrapolation to higher concentrations of gallium than those tested, using the model, indicated that plutonium could be reduced to ≤10 ppm in Pu-Cd-10 atom % Ga.

Specific Accomplishments: The test results indicate that plutonium can be completely separated from gallium by dissolving the solid Pu-Ga alloy in cadmium, using this Pu-Ga-Cd solution as an anode in an electrorefining cell, and separating the plutonium by electrotransport to the cell cathode. Pure plutonium is recovered without generating any waste. This electrorefining method is suitable for plutonium production and also for processing the large quantities of Pu-Ga alloy waste in the U.S.

A patent entitled, "Recovery of Plutonium from Plutonium Alloys" (ANL-IN-93-026), by W. Miller and Z. Tomczuk, is pending.

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94-114N -- WEAPONS PLUTONIUM DISPOSITION - AN EVALUATION OF FUEL CYCLE AND TECHNOLOGY OPTIONS

Associate Laboratory Director Area: Engineering Research

Principal Investigators: R. N. Hill, H. S. Khalil, R. A. Wigeland, G. Palmiotti, and J. J. R. Liaw, Reactor Analysis

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$314.7K
FY 1995	$150.0K
FY 1996	$350.0K

Purpose: The project objective is to evaluate a variety of weapons plutonium disposition options. The comparison of alternative technologies and fuel cycle strategies is expected to indicate potential refinements of proposed disposition systems; and to identify the waste forms associated with alternative weapons plutonium disposition strategies. The primary focus in FY 1994 was the development of refined strategies for application of the IFR metal fuel form and closed fuel cycle.

Approach: Large quantities of weapons plutonium currently exist in US and CIS weapons stockpiles. Arms reduction treaties call for the disassembly and disposition of many or these weapons. The disassembled weapons material must be closely safeguarded to prevent its diversion to produce new nuclear weapons. For U.S. arms reduction policy, the short-term goal is to quickly transform the weapons-grade material into a form which is not readily usable for weapons. This goal is accomplished by making the weapons material extremely difficult to handle. In most proposed disposition techniques, the weapons material is denatured by dilution and the introduction of radioactivity; thus, chemical separation and remote handling would be required to recover the weapons-grade material. Direct disposal of extensively denatured material is one potential disposition option; however, even extensive denaturing does not remove the necessity for active safeguarding in perpetuity. Therefore, other disposition options (e.g., use as fuel in nuclear reactors) which actively safeguard the denatured weapons material in the short-term and eventually destroy the material are also being investigated.

A wide variety of technology options have been proposed for weapons plutonium disposition, ranging from long-term storage to long-term energy production. The scope of this investigation is to evaluate the strengths and weaknesses of these alternative strategies; and to propose improvements to the promising scenarios. Particular attention will be given to the potential application of fuel cycle technology recently developed at ANL as part of the IFR program.

The project methodology involves the construction of computer simulations modeling the various weapons plutonium disposition proposals. The calculations are designed to perform detailed tracking of weapons material (plutonium) during its transmutation and/or chemical processing. In addition, other parameters such as reactor performance characteristics and radiological impact (dose) must be evaluated. The impact of key design variables is evaluated in a parametric manner.

Technical Progress and Results: The main focus in FY 1994 was the development of refined disposition strategies for the integral fast reactor (IFR) fuel cycle technology recently developed at ANL. Several unique advantages of the IFR closed fuel cycle were identified: the transuranics are repeatedly recycled to the reactor for eventual destruction, in the recycle processing 99.9% of the plutonium is returned to the core (the waste stream is essentially free of plutonium), and plutonium is preferentially fissioned (not converted to higher actinides) in the hard neutron spectrum associated with the metallic fuel. However, conventional IFR cores actually maintain or even increase the plutonium inventory (conversion ratio of 1.0-1.3); this allows sustained power production, but does not destroy the plutonium inventory. Therefore, alternate IFR core designs with conversion ratios between 0.5 and 1.0 were developed; these partial burner core designs are referred to as conventional burner designs because they utilize conventional IFR metallic fuel alloys (plutonium enrichment of less than 30 weight percent Pu/HM). For a conventional burner with a 0.5 conversion ratio, the net plutonium consumption rate was roughly 0.5 g/MWd (half the maximum theoretical value of 1 g/MWd). To allow more rapid destruction of the transuranics, a non-conventional metal fuel alloy containing no uranium was developed. This fuel form is based on the use of a binary Pu-Zr alloy. It was shown that introduction of a diluent neutron absorber was necessary to improve performance characteristics; and Hf was chosen from a wide variety of candidate materials. The resulting non-uranium core design was called a pure burner because it achieves the 1 g/MWd maximum plutonium destruction rate.

A comprehensive comparison of the weapons material evolution, neutronic performance characteristics, and reactivity feedback coefficients was performed to evaluate the impact of weapons plutonium introduction into the conventional, partial burner, and pure burner core designs described above. For each design, two fuel cycle models were evaluated; cores using weapons material as the sole source of transuranics in a once-through mode, and recycle cores using weapons material only as required for a make-up feed. It was shown that weapons plutonium does not have an adverse impact on IFR core performance characteristics; and favorable performance can be maintained for a wide variety of fuel cycle strategies. However, it was also concluded that pure burners are not an attractive option because of several undesirable reactivity feedback features and the need for a significant fuels development program.

A variety of conventional IFR burner design deployment strategies for weapons disposition were assessed. An option using low discharge burnup (to increase the short-term weapons plutonium introduction rate) was developed. A recycle option focusing on plutonium destruction and waste minimization was also pursued. In addition, trade studies were performed to develop favorable burner configurations. Layout development in the burner design was complicated by the impact of large reactivity changes; significant control rod movements would be required each cycle and must be accounted for in the configuration development.

Several evaluations of other technologies proposed for weapons disposition were also initiated in FY 1994. As an example, methods for the generation of cross sections for the evaluation of mixed-oxide (MOX) fuel in LWRs were investigated. A preliminary evaluation of the impact of MOX on LWR core performance and mass flow characteristics was conducted; and results generally agree with data given in the open literature. In addition, techniques for quantifying the proliferation hazard posed by mixtures including plutonium were developed; and a

preliminary evaluation of the proliferation characteristics of fuel and waste materials resulting from a variety of fuel cycle scenarios was performed.

The proposed focus for FY 1995 continuation of this project is the development of refined strategies for application of pyroprocessing technology to denature and dispose of weapons material. Fuel cycle options for blending of the weapons material with (existing) spent fuel will be investigated; a wide variety of potential spent fuel sources and processing techniques will be evaluated. In addition, the proliferation resistance of the resulting denatured weapons material and waste forms will be assessed.

Specific Accomplishments: A technical paper "Physics Studies of Weapons Plutonium Disposition in the IFR Closed Fuel Cycle" summarizing the comparisons of conventional, moderate burner, and pure burner IFR core designs was prepared for the 1994 ANS Topical Meeting on Advances in Reactor Physics. The results were presented at this meeting in Knoxville, Tennessee, April 12, 1994. This paper was subsequently invited for submission to the *Journal of Nuclear Science and Engineering* for a special issue based on this conference (to be published in 1995).

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94-186N -- PRECONCEPTUAL DESIGN OF A PREPROCESSING FACILITY FOR IFR-BASED RECYCLE OF SPENT NUCLEAR FUEL

Associate Laboratory Director Area: Engineering Research

Principal Investigators: J. E. Battles, Chemical Engineering
L. W. Deitrich, Reactor Engineering

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$371.8K
FY 1995	$300.0K
FY 1996	$480.0K

Purpose: The objective of this joint Reactor Engineering (RE) and Chemical Technology (CMT) project is to prepare a pre-conceptual design for a spent nuclear fuel (SNF) facility using the pyroprocess developed at ANL. The effort in FY 1994 has been on a plant that will treat DOE-owned SNF currently stored at the INEL site. The study focusses on use of existing facilities at INEL -- the Fuel Processing Facility (FPF) and the Fluorinel and Storage Facility (FAST) -- which are evaluated for use in order to minimize overall facility costs. Conceptual designs of major equipment for treatment of SNF and immobilization of by-product waste have been developed to allow development of tentative building layouts for the process in these existing buildings. During the second year of the project, a pre-conceptual design of a pyroprocess plant located in the Hanford Fuel Manufacturing and Examination Facility (FMEF) will be completed. That facility will be used to condition N-reactor spent fuel. This effort is under the general direction of D. R. Pedersen (RE) and J. E. Laidler (CMT).

Approach: To develop layouts of the pyroprocess equipment in the FPF and the FAST buildings, it was necessary to construct preliminary process flow charts delineating the equipment and other space requirements for the front end, electrorefiner operations and the waste treatment portions of the process. Designs were begun on major equipment items and estimates were made of building space and atmosphere requirements. Other related needs, such as shielding, cooling, etc., will be addressed in FY 95.

Technical Progress and Results: During FY 94, site visits to the FPF and FAST facilities at INEL by ANL personnel involved technical discussions with WINCO engineers and facility operations managers. Copies of pertinent documentation for these facilities -- drawings, system design descriptions, safety analysis reports -- were obtained and carefully reviewed to gain an understanding of the buildings and processes associated with each facility. A list of pros and cons was prepared for each facility showing its adaptability to house the ANL pyroprocess equipment to treat DOE spent nuclear fuel at INEL.

The quantity and types of spent nuclear fuel stored at INEL was evaluated to specify process equipment size and other features. Based on estimates of the actual total quantity of heavy metal in the DOE-SNF at INEL, it was determined that a throughput rate of 400 kg/day would treat this inventory over a reasonable time period (of about 15 years).

Flow charts were developed for the front end of the process (i.e., fuel assembly dismantling and fuel chopping), the electrorefiner operations, and the back end of the process (waste treatment) (see attached figure). In addition, work began to identify key equipment characteristics such as size, shielding, and inert gas atmosphere needs. These parameters establish building requirements. Estimates of floor space requirements were made for equipment and other related functional items.

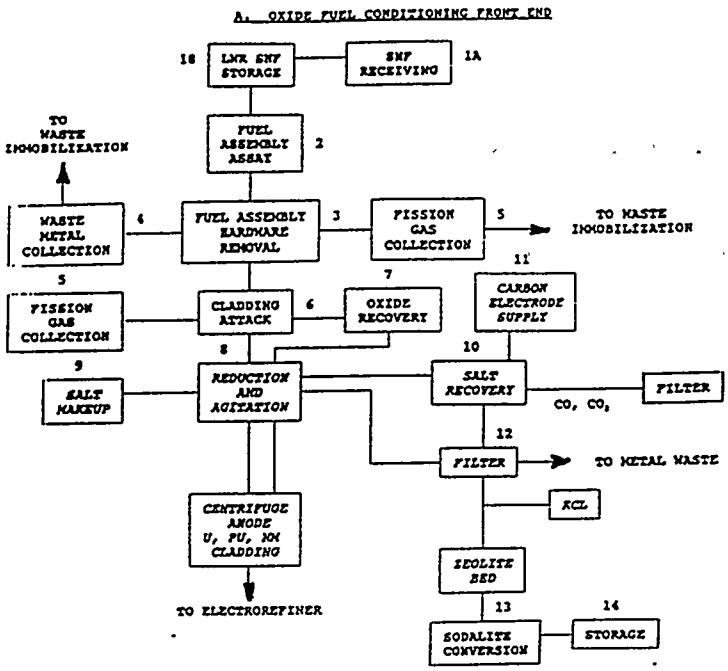
Concurrent with the flow chart development, preliminary ideas were pursued and documented relating to the design of certain components, such as the electrorefiner, cathode processor and oxide reduction vessel. These preliminary designs were developed after review of the existing equipment being installed in the Fuel Cycle Facility (FCF) at Argonne-West (ANL-W) for use in the pilot plant demonstration of the use of the pyroprocess to treat spent nuclear fuel.

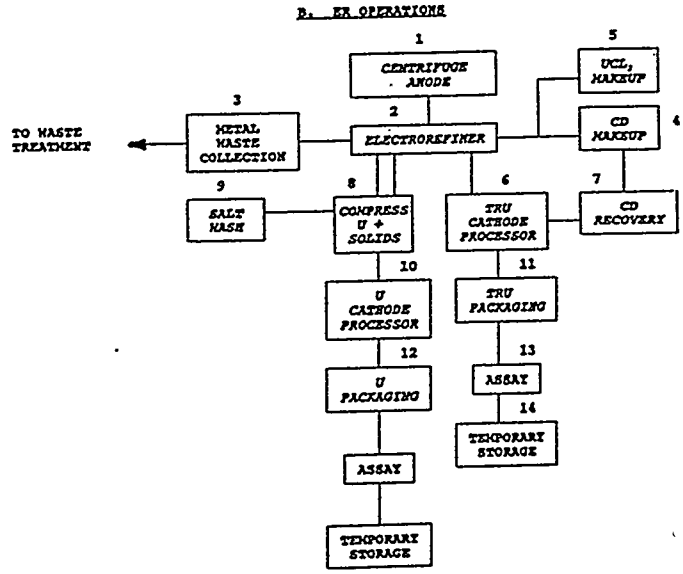
Using space requirements estimated for each equipment or functional item, physical layouts were made of the entire pyroprocess located completely in (1) the FPF facility, and (2) in the FAST facility. Restricted availability of specific areas of each facility suggest that the best arrangement is to use some portions of each facility. This combined facility approach will be finalized in FY95. Required modifications to each facility will also be identified in FY 95.

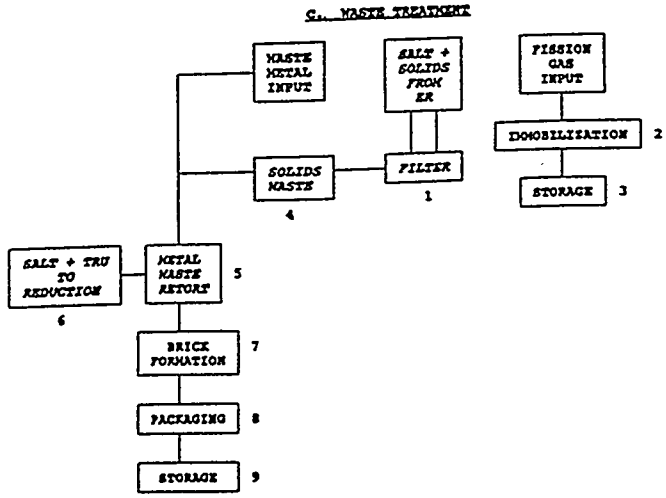
Preliminary ideas were discussed as to how best to "inert" the hot, shielded cell in the FAST facility and several shielded cells in the FPF facility. Two methods are under consideration to achieve the required leaktightness needed for an inert atmosphere: (1) constructing a new continuous, leaktight steel liner within the cells, and (2) applying an epoxy coating on all interior concrete and steel surfaces. The FPF is a new, though not completed, structure, without any contamination, and either method appears feasible. This is not true for the hot cell (FDP) in the FAST facility, which has radiation levels of 200 mr/hr in most areas and up to 200 R/hr at one end of the cell. This contamination complicates the decision as to which method would be better--steel liner or epoxy coating. In either case, however, considerable effort will be needed to decontaminate the cell before work can begin on applying the sealing treatment.

Preliminary conclusions from this study indicate that it is physically possible to locate all of the pyroprocess equipment in either the FPF facility or in the FAST facility. It appears, however, that a layout using parts of each of the two facilities will be the most effective way to utilize these existing facilities. Considerable modifications are needed in any event to achieve a leaktight, inerted atmosphere in any of the existing shielded cells. More detailed study is needed, however, coupled with preliminary cost estimates in order to select the best approach.

Specific Accomplishments: Flow charts were developed depicting each item of equipment and function required to complete the pyroprocess-based treatment of spent nuclear fuel. Floor space requirements (i.e., "footprints") of each item were developed or estimated to allow preparation of layouts of the equipment for the FPF facility and also for the FAST facility. The strengths and weaknesses of each facility -- FPF and FAST -- were identified and evaluated with regard to suitability for housing the ANL pyroprocess. This effort on INEL SNF treatment will be completed early in FY 95 as work starts on a similar evaluation for use of the pyroprocess to treat SNF at the Hanford site (N-reactor fuel).







FLOWCHARTS FOR USE OF PYROPROCESS TO TREAT LWR SPENT NUCLEAR FUEL

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94-187N -- NUCLEAR DECONTAMINATION AND DECOMMISSIONING CUTTING TECHNOLOGY DEVELOPMENT

Associate Laboratory Director Area: Engineering Research

Principal Investigators: A. E. Knox, D. R. Henley, R. K. Ahluwalia, and V. J. Novick, Technology Development

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$226.0K
FY 1995	$200.0K
FY 1996	$200.0K

Purpose: The long-term objective is to establish a center at the Laboratory for evaluating and developing hazardous material removal and cutting technologies. The primary effort focuses on Laboratory based R&D to evaluate existing cutting technologies in order to recommend or suggest methods to decrease the risk of cutting hazardous material. Further efforts will be made to enlist industrial participants to provide equipment and access to facilities to obtain additional test data and broaden the database for a hazardous materials cutting handbook. This information and test data acquired by the center would increase the efficiency of DOE/EM D&D and other clean-up efforts that involve cutting hazardous materials. No such center currently exists in the United States and no other organization or facility is as uniquely qualified to host such a center because of the combination of the Laboratory's ongoing D&D efforts, research programs in the areas of aerosol characterization and mitigation, waste stream analysis, pollution control and recent experience in evaluating cutting technologies.

Approach: It is estimated that more than 400 radioactively-contaminated facilities such as nuclear plants, manufacturing facilities, commercial and government laboratories, are scheduled for decontamination and decommissioning in the next decade in the U.S. In order to minimize costs and effort, most D&D operations resort to cutting structural materials to facilitate handling and to compact the waste. The choice of cutting tool is determined by the material composition, space or geometry considerations and thickness as well as speed, cost and concerns for workers and environmental safety. While a significant body of knowledge is generally available to aid in tool selection based on material, speed, cost, etc., there is a definite lack of information on many of the safety issues, particularly the quantity and size of particles formed during the cutting process. Recent incidents at the EBWR facility have demonstrated the need for this type of information. Airborne particles or aerosols are particularly important because they can be inhaled and deposited in the workers' air passages or they can be transported great distances across site boundaries. Therefore, in order to quantify the level of risk included in a particular D&D operation and to properly design protective or control systems, the aerosol size distribution and quantity that is generated by a particular cutting technique must be known.

This need is approached in three phases. The first phase is to develop a data base of information on aerosol production from laboratory controlled cutting operations. The second phase is to compare the controlled methodology with field sampling to broaden the applicability to the end users. Part of this task would also include measurements of particles released into the

atmosphere during underwater cutting operations. Finally, a compilation of the data will be presented in a reference handbook format allowing the user easy access to the information to aid in the design of pollution control and waste minimization strategies as well as appropriate tool selection and personal protective devices.

Technical Progress and Results: An experimental test chamber was designed and fabricated. A schematic of the test assembly is shown in figure 1. The chamber allows cuts up to one meter in length on structural pieces weighing as much as 75 kg. The material being cut travels under a fixed cutting tool to allow the aerosol source to be stationary and directly below the aerosol sampling port. The motor driving the material being cut is computer controlled to precisely define the cutting speed and length of the cut. The chamber is presently instrumented with a cascade impactor for particle size determination and High Efficiency Particulate Air (HEPA) filters for mass quantification.

A literature survey was conducted to uncover any pertinent work that might be incorporated into the data base. It was learned that the Commission of European Communities (CEC) has also determined that a need exists for a data base of cutting technologies. Their approach was to send out surveys to entities performing D&D operations and make these experiences available to others. Even though many of their respondents did not measure or report aerosol production rates or other data, collaborative efforts were initiated to share data and avoid duplication of effort.

A 100 amp plasma torch was installed in the test chamber and a series of cuts were made on various thickness of stainless steel. Results indicate that the mass median aerodynamic diameter of the aerosol produced by the plasma torch is 0.40 μm $\pm$ 0.08 μm and is not a function of cutting speed, thickness, length or kerf width. The data obtained in these initial tests suggest that a linear relationship exists between the quantity of aerosol produced and the thickness of the material times the length of the cut. If this relationship holds under further testing, it will be a relatively simple task to extrapolate a correlation to specific-user conditions and accurately predict the amount of aerosol that will be produced. This in turn will enable the risks of the particular operation to be assessed and allow for the design of a suitable pollution control system.

Specific Accomplishments: An experimental test chamber was established and a series of test cuts on stainless steel with a plasma torch were conducted. A schematic of this test assembly is shown in figure 1 and data on the quantity of stainless steel aerosol, released by plasma torch cutting, is given in figure 2.

The first series of tests using a plasma torch to cut stainless steel formed the basis of a senior thesis by C. J. Brodrick of the California Polytechnic Institute.

Preliminary work was reported at the American Association for Aerosol Research Conference, Los Angeles, California, August 29-September 2, 1994.

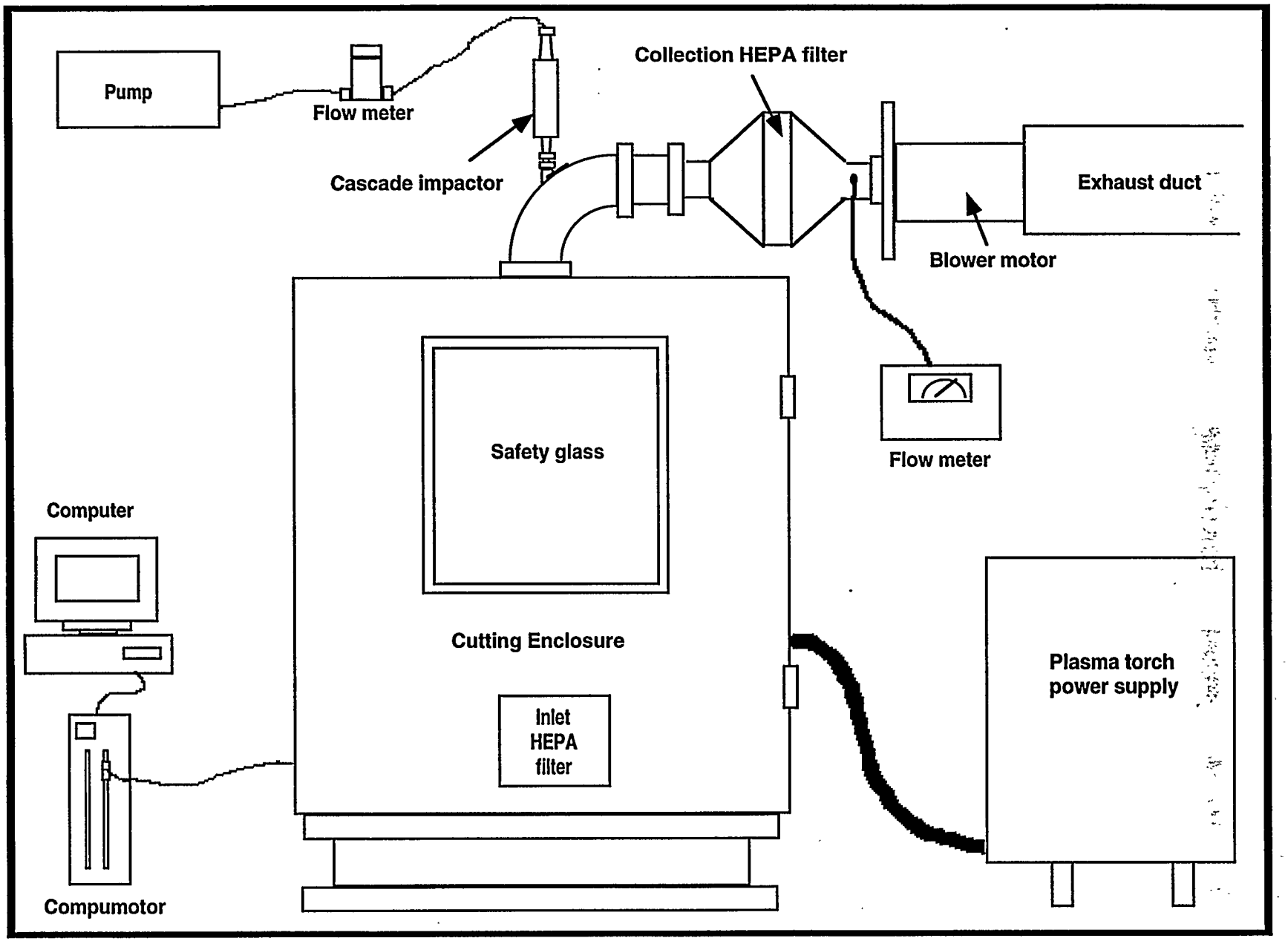


Figure 1. Experimental Test Apparatus

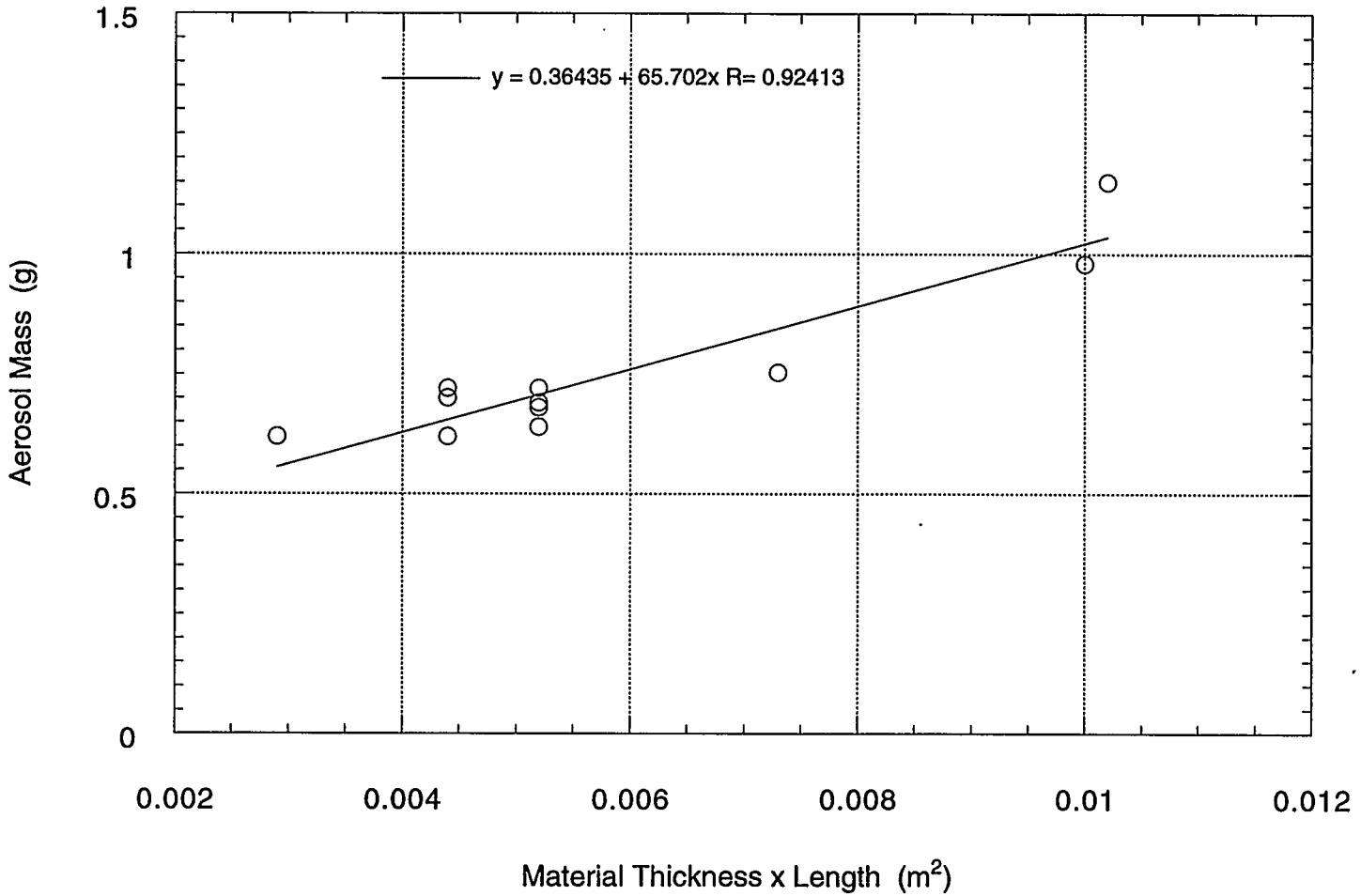


Figure 2. Mass of Aerosols Produced as a Function of Material Thickness and Cut Length

94-032N -- INTERPRETING CRACK PROPAGATION IN CRITICAL COMPONENTS OF MECHANIZED SYSTEMS

Associate Laboratory Director Area: Engineering Research

Principal Investigators: J. M. Kramer and R. J. DiMelfi, Reactor Engineering

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$160.8K
FY 1995	$140.0K
FY 1996	$141.0K

Purpose: The objective of this research was to develop a scientific methodology for sensing and gauging the remanent life of flawed mechanically-loaded components critical to the operation of mechanized systems. The development of this capability would provide the basis for replacing time-based maintenance schemes with safer and more economical condition-based maintenance procedures in many technologies, including transportation systems and power-plant components. Researchers from both the Navy and railroad R&D communities have expressed explicit interest in this work with regard to helicopter gearboxes and railroad rails, respectively.

Approach: In recent years, many key industries, e.g. the transportation and power generation industries, have expressed a desire to switch from time-based maintenance to condition-based maintenance of their machinery and structures. The latter implies the ability to electronically track the condition of critical components in service, and to understand the meaning of detected signals with regard to remaining component life. For the mechanically loaded components that are of interest to this research, life-ending failure occurs when initiated flaws (i.e. cracks) propagate to some catastrophic extent at which the component can no longer sustain nominal design loads.

A reliable condition-based maintenance scheme consists of three interdependent parts: sensing the existence of a flaw, "knowing" the nature of the sensed defect, and interpreting this information in terms of remanent life expectancy. The ever advancing fields of sensor materials and sensor technology are providing increasingly refined tools to detect critical flaws. With regard to the first part of the above triad, current sensor technology is certainly adequate for many important maintenance applications. With regard to the second problem, current artificial intelligence research has resulted in the ability to teach an artificial neural network to recognize a wide array of flaws of differing nature and configuration in a given system. Once again, it has been demonstrated that this ability is sufficient to handle rather complex systems and certainly adequate for the demands of many industrial situations. However, the third part of the puzzle, the physical connection between what is materially and mechanically happening in the flawed component and its relation to component life is lacking in attention. It is this part that is the focus of this research project.

When flaws are introduced into a component, its compliance changes, which in turn alters the natural and forced vibrational spectra of the part. It is the image of these spectra that the

artificial neural network is taught to recognize relative to the base signature of an unflawed component. Above some limit of signal detection, flaw initiation can be identified. Then, since larger flaws produce different spectra, the neural network can be taught to monitor flaw growth. Interpreting the underlying meaning of these artificial perceptions relative to component life involves performing both the mechanical analyses that relate crack configuration and size to vibrational spectra and the material property investigations that allow the prediction of crack propagation rate and component failure. The main focus of this research is the extraction and formulation of the mechanical properties of component materials in relation to component life prediction models. Secondarily, necessary work on the mechanical analysis of flawed components has been planned for this project so that the connection can be made between flaw growth and vibrational mode changes.

With the main focus on materials and component mechanical properties, it was necessary to choose a system for study. Both the U.S. Navy and the railroad industry are strongly interested in condition-based maintenance schemes for helicopter gearboxes and railroad rails, respectively. Similar steel alloys and cyclic loading geometries prevail in both cases. Inasmuch as it is our desire to investigate the behavior of material extracted from real components and relevant systems, and since railroad rails are a readily available source of material fabricated into a simple geometry, we decided to perform our mechanical property analyses on railroad rail steels. Samples of as-fabricated rail and rail that was heavily deformed in service were provided by the Association of American Railroads, Chicago Test Center.

In ductile materials, like railroad steels, crack initiation and propagation occurs because large plastic strain, microscopically localized at flaws within the steel's microstructure, becomes so intense that the material separates at the flaw. Therefore, in order to understand crack propagation in rail steel, it is necessary to know its flow behavior to large values of plastic strain. A rail failure mode typical of what we propose to monitor through the results of this research involves the nucleation and growth of cracks ("shell defects") that start roughly parallel to and ¼" below the rail top surface, running in the direction of travel. Dangerous consequences occur when these defects turn upward or downward, perpendicular to the direction of travel ("detail fractures"). This failure mode is also typical of many mechanical systems. We hypothesize that flaw development results from the interaction of the initial mechanical state in the rail head, produced during forming, with strains produced during service loading including localized plastic strain in the presence of irregularities in the rail steel microstructure itself. Since cracks evolve from intense localized plastic flow, it is necessary to have a full model of the flow behavior of the material. The project plan was to measure the flow behavior of specimens extracted from rail samples, noting any consistent difference in behavior associated with specimen location within the rail caused by the fabrication process or service loading. Dr. E. E. Gruber was the lead collaborator in this experimental mechanical test program. We further planned to formulate the material flow behavior mathematically based on the experimental data. This large-strain flow law would then be incorporated into a model for crack propagation in the material. Also, in order to map out the mechanical state of the railroad rails as a function of position, a fine network of microhardness measurements was made on the faces of the railheads from which the mechanical test samples were extracted. These tests were conducted with an eye toward revealing and contrasting the state of the virgin and used rail samples. Hardness testing was performed by personnel at Buehler Ltd., Lake Bluff, IL, using the automated, computer-controlled Omnimet MHT system.

Technical Progress and Results: With LDRD support in FY 1994, we completed a series of mechanical tests on virgin and used rail samples provided by the Association of American Railroads. Testing consisted of micro-hardness scans of the surfaces of railhead cross-sections exposed by cuts perpendicular to the travel direction along the rail, and tensile tests on standard ASTM (small) flat samples cut so that the tensile axis was parallel to the travel direction. The data was used to fix the parameters of a physically-based model for plastic flow of the rail steel. The results of this formulation are incorporated into a mechanistic model for crack advance during cyclic loading, modified to be consistent with the flow law.

The figure shows the results of the tensile testing of the rail steel specimens. There was a modest indication that the samples closest to the rail surface were the strongest, but the difference was not statistically significant. The flow curves agree within a 10% variation, and obey a flow law (stress, σ vs strain, ε) of the form:

$$\sigma = \sigma_S - (\sigma_S - \sigma_1) \exp(-\varepsilon/\varepsilon_c),$$

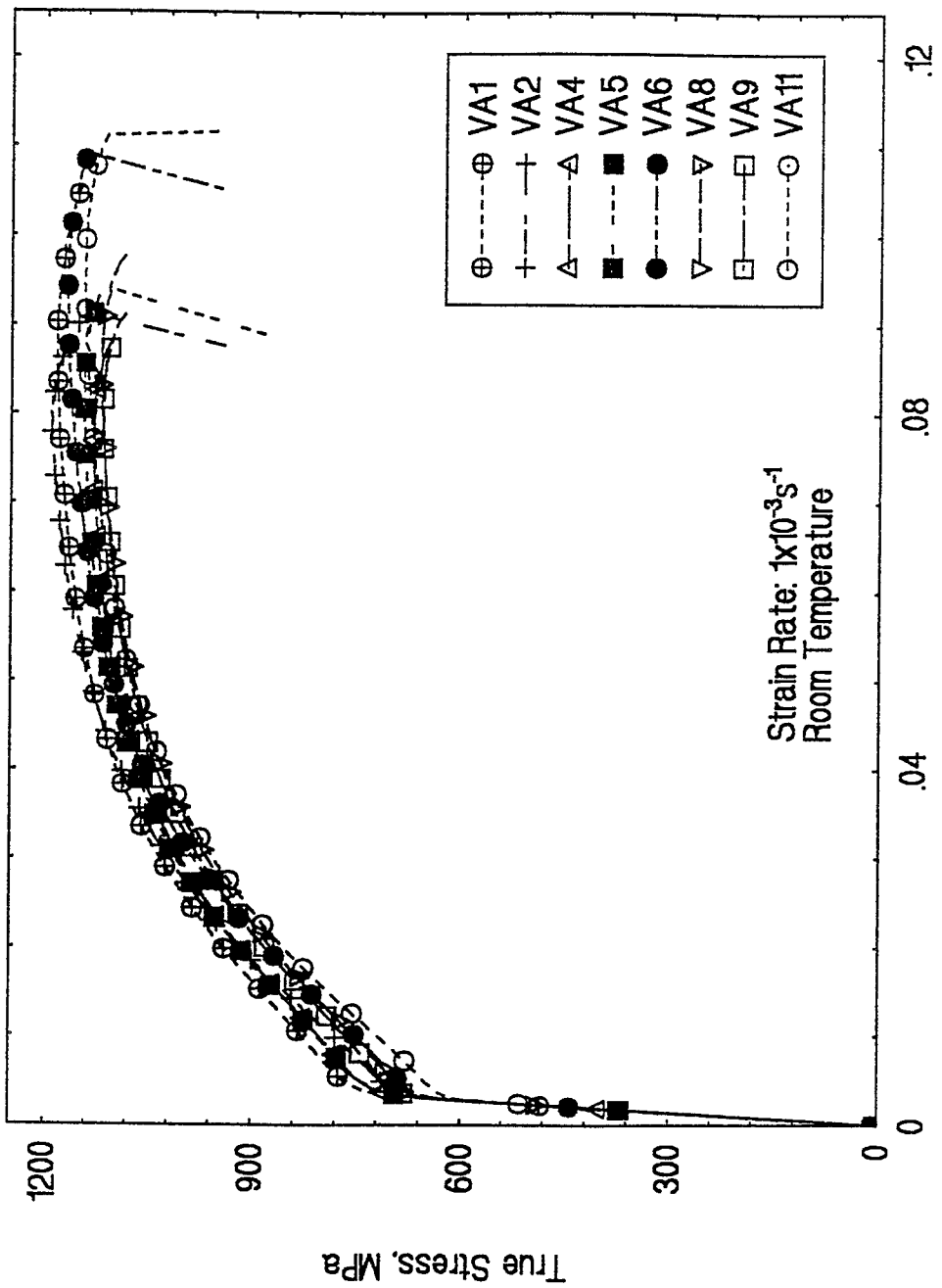
where σ_1 is the yield stress, σ_S is the stress associated with infinite strain (strain exhaustion), and ε_c is a parameter associated with the hardening rate of the material. When σ_S is achieved locally via microscopically confined cyclic plastic flow produced by loading, the materials ability to strain is exhausted and a crack nucleates or advances. The crack propagation rate per cycle (da/dN) is given mechanistically by:

$$da/dN = (\pi/96)(\Delta K)^4[(\sigma_S/2)^2(K_{Ic})^2(1-\upsilon^2)]^{-1},$$

where ΔK is the stress intensity loading range, K_{Ic} is the critical stress intensity factor for the material, and υ is Poisson's ratio. This formula can be used to determine crack advance and in predictions of remanent life as indicated above.

With regard to hardness measurements, the highest values occurred nearest the top surface of the rail samples in both virgin and used material. However, there was no consistent trend in hardness as a function of position in the cross sections, nor was there a statistically significant difference between the hardness of virgin and used materials revealed by these tests.

Specific Accomplishments: A mechanistic flow model was developed for rail steel that is useful in predictions of crack propagation and life prediction. Base hardness data profiling the mechanical state of fabricated and used rail has been established for future reference. Official contacts have been made with railroad representatives to have future work in this project incorporated into Argonne's newly formed partnership with the industry. Discussions with Navy researchers in the area of artificial neural network detection systems have led them to express serious interest in supporting our work on the mechanical aspects of component failure, pending increases in their own funding levels.


True Stress, MPa
1200
900
600
300
0
0
.04
.08
.12
True Strain
Strain Rate: 1x10^{-3}s^{-1}
Room Temperature
VA1
VA2
VA4
VA5
VA6
VA8
VA9
VA11

94-053N -- COMPTON SCATTERING FROM FERROMAGNETS USING SYNCHROTRON RADIATION

Associate Laboratory Director Area: Physical Research

Principal Investigator: P. A. Montano, Materials Science Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$205.8K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: To design a new Compton scattering experiment from ferromagnets using synchrotron radiation at the National Synchrotron Light Source (NSLS). This experiment will serve as a prototype for our research program at the BESSRC beam lines.

Approach: It has been shown[1,2] that hard X-rays can be used to measure the momentum distribution of magnetic electrons in magnetic materials. It has been demonstrated[3] that the value of the magnetization due to the negative or positive spin polarization can be extracted from Compton scattering and that accurate comparison with band structure calculations is possible. Similar results were obtained in polarized positron annihilation experiments[4] and on polarized neutron diffraction experiments. Comparison with the band structure calculations was not straightforward for those experiments. With a strong source of circularly polarized radiation, it will be possible to study the spin density variations for transition metals and alloys as a function of temperature. We are proposing to measure the momentum distribution of electrons in magnetic materials using Compton scattering. When experiments are performed with linearly polarized light or unpolarized light, the Compton profile measured represents the sun of spin-up and spin-down bands. With circularly polarized radiation, the measured Compton profile would represent the difference of these contributions. Therefore, a combined measurement with linearly polarized and circularly polarized radiation would allow one to differentiate spin-up and spin-down contributions. The study of the electron momentum distribution in solids is of considerable scientific interest. The technical challenges in Compton profile measurements are in obtaining statistical accuracy of the collected data in a reasonable time, and high momentum resolution ($\sim$ less than 0.1 atomic units).

Technical Progress and Results: The progress on the magnetic measurements has been very slow in part due to the fact that to study magnetic Compton scattering in Ni/Fe alloys requires energies well above the K-edges of iron and nickel. We had two options to use off axis radiation from the bending magnet to obtain circularly polarized radiation or to use crystal optics. The two techniques at NSLS are very difficult to fulfill in the impulse approximation regime. First off axis the amount of photons above 15 keV is very small and will not provide enough statistics for a good magnetic scattering experiment. The crystal approach is more favorable, but we were unable to complete the construction of the phase plates in time to run in 1994. Even using the phase plates at 15 keV energy the NSLS does not provide enough photons due to the optical constraint imposed by the phase plate optics.

We decided to use materials with low Z values, at least in cases where the conduction electrons come from light atoms. We decided to investigate the effect of dimensionality in the Compton scattering experiment. We carried out a preliminary study of one and two dimensional organic conductors. The samples were provided by J. Williams' group. We studied the scattering from single crystals of $(TMTSF)_2ClO_4$ and $(BEDT\text{-}TTF)_2I_3$. This work is still in progress and more measurements are planned for the next NSLS cycle. We will write a full report when the measurements are completed and analyzed.

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94-055N -- NEW MATERIALS SYNTHESIS STRATEGIES FOR HIGH-TEMPERATURE SUPERCONDUCTORS COMPOSED OF Cu-O PLANES SEPARATED BY SILICATE-BASED LAYERS

Associate Laboratory Director Area: Physical Research

Principal Investigators: K. A. Carrado and L. Soderholm, Chemistry
D. Hinks, Materials Science Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$155.1K
FY 1995	$ 25.0K
FY 1996	$ -0-

Purpose: This initiative explores new synthetic strategies for the assembly of the superconducting Cu-O planes that are essential to the class of so-called 1-2-3 high temperature superconductors. The unique link underpinning these strategies is the use of silicate-based layers to separate the Cu-O planes. The use of silicate-based layers allows for control of electron dopants and flexibility in spacing between the planes. This research represents a distinctly new approach to preparing materials of potential as high-temperature cuprate superconductors. The initiative offers the opportunity to explore alternative mechanisms to the formation of high-T_c compounds, an area in which any advancement could have critical technological importance.

Approach: High-temperature cuprate superconductor materials are most often prepared by traditional ceramic methods. These "shake and bake" techniques involve mixing and grinding of the component oxides, carbonates or other salts, and heating the mixture at a very high temperature. While the procedures are relatively simple, the products suffer the disadvantages of inhomogeneity with a loss of chemical control over the reaction mechanism. The exploration of strategies that offer more direct ways to monitor and control the synthesis is therefore warranted. All known copper oxide superconductors contain two-dimensional CuO_2 layers. These layers are separated by metal oxygen layers, AO, which form AO-CuO_2-AO structural blocks. When large amounts of gallium or aluminum are incorporated, the new single-layer copper compounds $LaSrCuAlO_5$ and $LaSrCuGaO_5$ are formed. These structures reflect the preference for tetrahedral coordination by the group 13 elements in these materials. The occurrence of oxide tetrahedra as "spacer" blocks has been demonstrated by the gallate materials, which serves as a precedent for the consideration of silicate tetrahedra.

There are many naturally-occurring layered silicate minerals for which laboratory synthetic procedures have been developed. Minerals made up of single sheets of silica tetrahedra linked together include magadiite, kenyaite, and layered silicic acid. In mica-type layered silicates, two tetrahedral silicate layers sandwich a central metal octahedral layer. The structure of the mineral chlorite is based upon a such a mineral, where the interlayer region is composed of another entire layer that is brucite-like. The scope of this work is to create two-dimensional arrays of pre-existing minerals composed of SiO_2 tetrahedra in sheets that are modified with the precursors to superconducting oxides. Such an approach allows for variability between superconducting Cu-O planes since minerals consisting of one, two, or more silicate sheets can be used for

separation. The proper firing conditions for creating a Cu-O plane must then be determined, followed by characterization of the resulting materials physical properties.

The project methodology involves the systematic application of known clay modification procedures to precursors of superconducting oxides. Both single-layer and double-layer silicates continue to be examined. Once materials are made, the materials are characterized by X-ray powder diffraction, scanning electron microscopy with energy dispersive X-ray analysis, thermal gravimetric analysis, and microanalysis. Crucial thermal information regarding firing conditions is expected from differential thermal analysis, a newly acquired technique in our laboratories.

Technical Progress and Results: We have ion-exchanged Cu(II) ions into magadiite, layered silicic acid, and a series of smectite clay minerals. The silicate interlayer becomes filled with hydrated copper(II) in this process. The layer charge density of most of these minerals is such that the distance between Cu(II) ions at full loading is approximately 12 Å. This distance is too long to favor the formation of continuous Cu-O sheets; therefore, a variety of synthetic strategies was developed to increase the Cu loading. In one method, differences in layer charge density of clay minerals were utilized. This variable resulted in a dramatic increase in Cu-loading from a montmorillonite (3%) to a fluorohectorite (20%). Another strategy involved using different Cu-containing precursor species in order to favor the successful incorporation of Cu-hydroxy complexes.

The next crucial step involves gathering critical thermal parameters to obtain the proper firing conditions. Thermal gravimetric analysis and differential thermal analysis data have begun to be collected in order to determine the conditions necessary for creating a Cu-O plane within the layered silicate materials. Copper metal clusters are made under reducing conditions and copper oxide clusters are made under oxidizing and inert atmospheres. The next step is to determine the stability of these clusters within the clay layers, and to inhibit their migration to the outside surfaces.

We also propose to use X-ray absorption spectroscopy to probe, in situ, the effects of heating on the copper coordination sphere. Samples will be sintered in a controlled atmosphere while monitoring the oxidation state and coordination of copper within the silicate layers. Optimally, the formation of either Cu-O or Cu-metal sheets will be observed depending on the atmosphere over the clay. For example, by changing the gas environment over the clay from reducing to oxidizing after metal clusters are formed, we hope to control the formation of M-O sheets. Such a process can also be monitored in part by in situ X-ray powder diffraction methods, a capability already in-house.

The use of smectite-type minerals also allows for the incorporation of other transition metal ions within the interlayer. Ions of such metals as Ca, Y, Ln, etc., are all known to be stable within this region, and will be added to vary the electronic properties of the Cu-O plane. These dopant ions also provide the benefit of compensating the charge on the silicate layers once the Cu(II) ions become incorporated into a Cu-O sheet and are no longer capable of doing so. In all of the synthetic scenarios, the silicate mineral acts as a pre-existing spacer group, and also a template for Cu-O plane formation.

92-023R2 -- INNOVATIVE THEORETICAL STUDIES IN THE SOLID STATE

Associated Laboratory Director Area: Physical Research

Principal Investigator: A. A. Abrikosov, Materials Science Division

Funding Profile:

FY 1992	$153.1K
FY 1993	$239.2K
FY 1994	$175.2K
FY 1995	$ 50.0K
FY 1996	$ -0-

Purpose: This project took advantage of visiting well-known scientists from republics of the former Soviet Union (FSU) to plant seeds of new programs based on innovative approaches in theory that are usually not used in the U.S. This program allowed us also to engage people with a higher level of capability and reputation in theoretical work than we could normally attract to ANL and create new programmatic foundations. The idea was also to continue the new developments with our existing theoretical staff, as the new methods were taught to the existing staff. Funds were also used to support the post doctoral appointee for the Laboratory's Distinguished Senior Scientist, Dr. A. A. Abrikosov, who is from the FSU.

Approach: Before 1991, the members of the Theory Group were interested mostly in computer simulations. This was due to the presence of such outstanding experts as Anees Raman, Priya Vashishta, et al. At the same time, this trend became common among the younger generation of theorists in the U.S., at the expense of the analytical approaches which led in the past to such important discoveries as the Bardeen, Cooper, Schrieffer theory of superconductivity and the Wilson theory of phase transitions. After the strongest computer experts left the group, and particularly after Dr. A. A. Abrikosov became its leader (1992), analytical methods of theoretical analysis started to play an equal role with computational methods. The idea of the project was to stimulate analytical approaches inviting the best theorists of the FSU, where these approaches were dominant, to arrange collaborative work between them and the members of the group (e.g., M. Randeria), and to encourage their work with experimentalists of the Division (M. Grimsditch, G. Crabtree, U. Welp, W. Kwok). In FY 1994, the invited physicists were Dr. L. P. Pitaevskii, P. L. Kapitza Institute for Physical Problems, Moscow; Dr. A. I. Larkin, L. D. Landau Institute for Theoretical Physics, Moscow; Dr. V. L. Gurevich, A. F. Ioffe Physico-Technical Institute, St. Petersburg. The post doctoral appointee was C. Sa de Melo.

Technical Progress and Results:

A. Superconductivity. In recent years, many experimental and theoretical results appeared on the Hall effect. However, the microscopic theory exists only for pure substances at low temperatures. Therefore, a theory of the Hall conductivity was constructed for the vicinity of Tc in the "dirty" case and in arbitrary magnetic fields. In the limit of a high concentration of magnetic impurities, the results coincide with those obtained with the time-dependent Ginsburg-Landau equation.

A theory was constructed for the collective pinning in intermediate magnetic fields of magnetic vortices in superconductors. Due to the long range of the interaction of vortices the elastic moduli have a space dispersion, and the problem becomes effectively four-dimensional. This gives the possibility of obtaining the exponent of the dependence of the critical current on the magnetic field and the preexponential factor. A renormalization group equation for the viscosity of the vortices was obtained and the current-voltage characteristic was found.

An innovative idea was suggested of "vortex cooling." The central point was that the "normal" electrons inside the vortex core of a Type-II superconductor could be excited by electromagnetic radiation. Through a process of directional absorption and spontaneous emission, photons can resonantly transfer momentum to the vortex core center of mass, thus affecting the vortex motion. As a result, a scattering force (light pressure) acts on the vortex core and changes the vortex motion, producing decreased dissipation (vortex cooling) or increased dissipation (vortex heating) depending on the direction of the scattering force and on initial conditions of the vortex motion. The most natural candidates for such an effect are thin films of short coherence type-II superconductors with s-wave symmetry at low temperatures.

B. Mandelstam-Brillouin Scattering. A theoretical interpretation was derived of experiments on light scattering in substances undergoing a liquid-glass transition, performed by M. Grimsditch (MSD-ANL). The ideas of elasto-viscous theory by S. M. Rytov were used. This theory, assuming a single relaxation time and nothing concerning the C_p/C_v ratio fits the results on scattering from longitudinal sound waves in $ZnCl_2$.

C. Microstructures. A theory of non-ohmic ballistic resistance in quantum wires was developed. A variation of ballistic current was calculated through a spatially uniform conductor with a weak electron-phonon scattering. A non-Ohmic regime takes place, if $eV > kT$ due to the dependence of the rate of electron-phonon collisions on the electron distribution which is dependent on voltage in a ballistic regime. Resonance phenomena were predicted when the frequency of optical phonons became equal to the transverse quantization level spacing. The latter can be varied by the gate voltage.

D. Quantum Liquids. A theory of quantum evaporation in superfluid He was constructed. This is a process reciprocal to the birth of quasiparticles in He due to absorption of a He atom at the surface. The method was based on the time-dependent equation for the condensate wave function. The scattering theory for such an equation was developed.

In a two-dimensional system there exists a possibility of "transmutation of statistics," i.e., passing from Bose to Fermi statistics and vice versa. It was shown that after this all the characteristic features of the momentum distribution were wiped out, e.g., the delta-functional distribution for an ideal Bose-gas produced a homogenous momentum distribution in the corresponding Fermi-gas.

E. Magnetic Multilayers. The effect of indirect magnetic coupling between layers mediated by bound states was studied. In many systems the indirect coupling between magnetic impurities is assumed to be mediated by non-interacting electrons, where the many-body effects are completely neglected. This may be correct for metal spacers but proved to contradict the experimental data for semiconductor spacers. Therefore, the main idea was to consider the

many body effects ont he indirect magnetic coupling. The Coulomb interaction between electrons in the conduction band and holes in the valence band were considered, and real bound states of electron-hole pairs (excitons) were found. The energy of these bound states lies inside the semiconducting gap. Excitons, although chargeless, can transfer spin information between two magnetic impurities or two magnetic layers separated by a semiconductor. The indirect exchange coupling introduced by such a mechanism is strongly temperature dependent and increases with increasing temperature. In addition, the sign and the magnitude of the indirect exchange coupling were classified according to the internal angular momentum states of the excitons. The relevance of these results to experimental systems of current interest, which involve ferromagnetic metal-semiconductor multilayers like Fe/FeSi, MnTe/CdTe and EuTe/PdTe, was analyzed.

F. Ferroelectricity. A macroscopic quantum phenomenon in ferroelectrics was studied which can be called "quantum echoes." The system is a collection of grains of tetragonal distorted cubic lattices with permanent unit cell anion-cation dipoles. A collection of independent grains was considered, where the intergrain dipole interaction was negligible in comparison with the intragrain dipole interaction. Due to the crystallographic structure and to the long range interaction of the dipoles within a single grain, there are two distinct macroscopic ground states. The first "ground state" occurs when all the microscopic dipoles point in the +z direction, and the second occurs when all of them point in the -z direction. The energy barrier between these two degenerate states is very high in most ferroelectrics, and the higher energy states are well separated from these two since the interaction between dipoles is long ranged, which introduce a high energy cost for flipping individual microscopic dipoles. Each individual grain can be thought of as a macroscopic two level system. The application of an external constant electric field along the +z direction biases the system and introduces a tunable energy difference between the two macroscopically distinct ground states. If a pulsed electromagnetic field with frequency that matches the energy difference between the macroscopic two level system is applied, it acts as a resonant switching field; thus, as time evolves there is a time dependent probability of quantum tunneling between the "ground states" which is resonantly driven. This may be used to produce an "echo" similar to the spin-echo in magnetic substances.

Specific Accomplishments: The following manuscripts were published or submitted to scientific journals.

1. Hall-Effect in Superconductors, by A. I. Larkin and Yu Ovchinnikov. Submitted to *Phys. Rev. B.*

2. Renormalization Approach to Collective Pinning in Intermediate Magnetic Fields, by G. Blatter, V. Geshkenbein, and A. Larkin. To be submitted to *Phys. Rev. B.*

3. Density-Functional Theory of the Sticking Coefficient for He4 Surface, by A. Lastri, L. Pitaevski, and S. Stringari. To be submitted to *Phys. Rev. B.*

4. Electron Emission n Plasma Wave Decay, by L. Pitaevski. To be submitted to *Phys. Rev. B.*

5. Phonon-Enhanced Landauer Resistance, by V. Gurevich, JPCM, 6, 8363 (1994).

6. Phonon-Assisted Landauer Resistance, by E. Fenton, V. Gurevich and V. Pevzner, *Proc. 22nd Int. Conf. Semicond.* (1994, Vancouver, Canada) World Sci. Publ., Singapore.

7. Non-Ohmic Phonon Assisted Ballistic Resistance, by V. Gurevich, K. Hess, and V. Pevzner. NATO Advanced Study Institute on Quantum Transport in Ultra-Small Devices (1944, Il Ciocco, Italy), eds. D. Ferry, J. Barker, C. Jacoboni.

8. Electrophonon Resonances in Mesoscopic Structures, by V. Gurevich, G. Iafrate, and V. Pevzner. To be submitted to *Phys. Rev. B.*

9. Theory of Femtosecond Photon Echo in Semiconductors, by S. Gantsevich, V. Gurevich, M. Muradov, and D. Parshin. Submitted to *Phys. Rev. B.*

10. Vortex Cooling, by C.A.R. Sa de Melo, *Phys. Rev. Lett.* 73, 1978 (1994).

11. Vortex Cooling: A New Photovoltaic Effect, by C.A.R. Sa de Melo. Submitted to *Phys. Rev. B.*

12. Magnetic Exchange Coupling Mediated by Bound States, by C.A.R. Sa de Melo. Submitted to *Phys. Rev. B.*

13. Macroscopic Quantum Echoes in Ferroelectrics, by C.A.R. Sa de Melo. To be submitted to *Phys. Rev. Lett.*

94-058N -- X-RAY SYNCHROTRON RADIATION STUDIES OF SEMICONDUCTOR/ SEMICONDUCTOR HETEROPHASE EPITAXY

Associate Laboratory Director Area: Physical Research

Principal Investigators: K. Huang and M. J. Bedzyk, Materials Science Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$209.5K
FY 1995	$140.0K
FY 1996	$ -0-

Purpose: The project objectives are to study the structure and growth mechanism of surfactant mediated growth of Ge on Si[1] with the X-15A NSLS synchrotron X-ray beamline and its UHV surface science chamber. The surfactants in this heterophase epitaxial strained layered structure are to be Sb and As. Here we are interested in developing insights into how the above surfactants are incorporated in the Si surface structure before Ge thin film growth commences and in the Ge strained film during the growth process. This would improve our understanding of how to grow lattice mismatched epitaxial films and thus avoid 3D island nucleation.

Approach: Prior to achieving the final goal of studying surfactant mediated growth in this strained layer heteroepitaxial structure, we need to lay the ground work of studying the individual constituents of this complicated structure in a step-by-step manner. Our approach has been to first study the surface structure of individual pentavalent adlayers of As, Sb, and Bi on Si(001) with X-ray standing waves. Next we would study epitaxial Ge thin film growth on Si(001) without a surfactant, and then study it with Sb or As or Bi as a surfactant.

The UHV surface preparation and X-ray measurements are made with collaborators Y. Qian (Northwestern /ANL graduate student), P. Lyman (Northwestern postdoc), and G. Franklin (Harvard postdoc). Theoretical cluster calculations of the surface structures are made by our NU/Physics collaborators S. Tang and A. Freeman.

Technical Progress and Results: We have continued to develop our UHV surface science MBE capabilities for deposition of and in-situ X-ray characterization of highly ordered monolayer and submonolayer phases of metal atoms on semiconductor surfaces.

This past year (FY94) we have completed the first stages of this research program by solving the surface adlayer structures for one monolayer coverage of Sb[2] and Bi[3] on Si(001). (1 ML of As/Si(001) was solved at X15A under another LDRD project in FY93.[4]) All of these group V adsorbate species form saturated ordered adlayers on Si(001) which remove the 2x1 dimerized reconstruction of the clean Si(001) surface and reform a 1x2 surface structure with group V ad-dimers aligned orthogonal to the preexisting Si dimers. The Si(001) 2x1-As (or Sb or Bi) surface is non reactive in comparison to clean Si(001) 2x1 surface because unlike the quatravalent Si atoms, the pentavalent As, Sb and Bi atoms in this dimerized structure lead to a filled-shell electronic configuration, leaving no unsaturated surface dangling bonds. Upon these group

V element adsorbed Si(001) surfaces, we have undertaken X-ray standing wave (XSW) measurements using the Si (004) and (022) Bragg reflections. As an example, figure 1 illustrates the (004) XSW measurement on the Sb/Si(001) surface. From these measurements, ad-dimer structural parameters such as ad-dimer bond length L and ad-dimer height h' above the Si(001) bulk like surface plane have been determined with very high precision (see Table 1). These results have been compared with first principles molecular cluster calculations performed by our collaborators Tang and Freeman.[3,5] Good agreements between experiments and calculations were achieved.

Table 1. Results of XSW measurements. The coherent fraction f_H and the coherent position P_H are parameters determined from XSW experiments. h' is the height of ad-dimer above the bulk like Si(001) lattice plane. L is the ad-dimer bond length. Si(001) lattice plane. L is the ad-dimer bond length.

	f_{004}	P_{004}	f_{022}	P_{022}	h'(Å)	L(Å)
As	0.80 ± 0.01	1.03 ± 0.01	0.47 ± 0.02	1.03 ± 0.01	1.40 ± 0.01	2.61 ± 0.04
Sb	0.73 ± 0.02	1.21 ± 0.01	0.52 ± 0.01	1.10 ± 0.01	1.64 ± 0.02	2.81 ± 0.09
Bi	0.79 ± 0.01	1.27 ± 0.01	0.66± 0.01	0.66± 0.01	1.73± 0.01	2.94± 0.06
Ga	0.61 ± 0.01	0.77 ± 0.01	0.35 ± 0.01	0.91 ± 0.01	0.77 ± 0.01	2.58 ± 0.04

We also did preliminary studies of ad-atom's thermal vibrational amplitude on the Si(001) surface. The thermal vibrational amplitude of surface ad-atoms is rather important since it contains valuable information about surface bonding chemistry. Precise measurement of thermal vibrational amplitude at room teperature is also a necessity for determining the ad-dimer bond length with higher accuracy. Under prior LDRD funding in FY93, we studied the temperature behavior of the As thermal vibrational amplitude on Si(001) and indirectly determined its value at room temperature.[4] In FY94, we tried to directly measure the thermal vibrational amplitude of Sb and Bi on the Si(001) surface at room temperature by combining the fundamental Si(004) reflection with the 2nd-order harmonic (008) reflection.

In FY94, we also solved the related and relevant structure of group III Ga on Si(001).[6,7,8] This surface saturates at one-half monolayer, forming a much less stable and more reactive 2x2 structure which has Ga dimers lined up parallel to the underlying Si dimers which remain unbroken in a 2x1 surface reconstruction (figure 2). Previous STM and LEED studies on this surface had concluded that the Ga dimers were orthogonal to the underlying Si dimers. This incorrect conclusion is a result of the inability of these two very important surface structure techniques to resolve the direction of the Ga dimer bond. We did XSW measurements on the Ga/Si(001) surface at various coverages of Ga below 1/2 ML. Our (004) XSW measurement precisely determined the height of Ga ad-dimer above the Si(004) bulk-extrapolated lattice plane and the excellent agreement between our measurements with pseudopotential calculations[9] and cluster calculations[6,7] concludes that the Ga forms parallel ad-dimer on the Si(001)2x1 dimerized surface. On the same surface, we have achieved the first direct measurement of ad-atom's thermal vibrational amplitude on the Si(001) surface at room temperature.[8] This achievement

improved the uncertainty of the Ga ad-dimer bond length measurement from ± 0.06Å[6,7] to ± 0.04Å.[8]

Specific Accomplishments: Our combined XSW results for Ga and As on Si(001) add to the body of experimental evidence concerning the growth of GaAs on Si(001). One particular property that our results address is that the growth of GaAs on Si(001) always starts with an As terminated Si surface. This growth mode property leads to the undesired formation of antiphase domain defects at a real surface with monatomic steps. We have also made the surface chemically sensitive structural measurements for 1 ML coverages of the pentavalents Sb, and Bi on Si(001). These measurements lay the ground work for studying the more complicated surfactant mediated growth structures.

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3. "High Resolution Structural Study of Bi.on Si(001)," G. E. Franklin, S. Tang, J.C. Woicik, M.J. Bedzyk, A.J. Freeman, and J.A. Golovchenko, in preparation.

4. "Thermal Vibration Amplitudes and Structure of As on Si(001)" G.E. Franklin, E. Fontes, Y. Qian, M.J. Bedzyk, J.A. Golovchenko, and J.R. Patel, *Phys. Rev. B* **50**, 7483 (1994).

5. S. Tang, and A. J. Freeman, *Phys. Rev. B* **47**, 1460 (1993).

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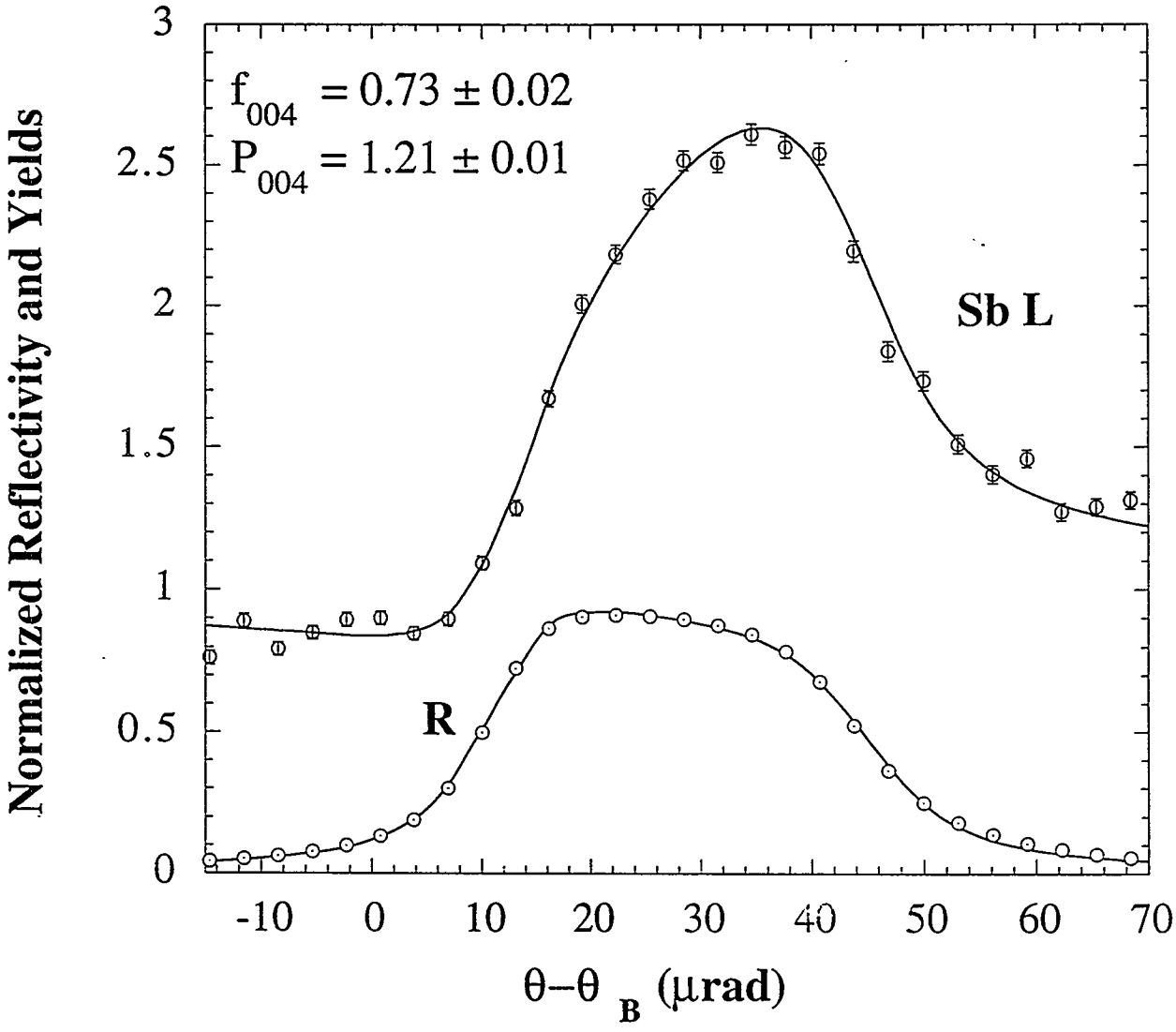
7. "Combined Theoretical and Experimental Investigation of the Adsorption Geometry of Ga on Si(100) at Low Coverage," S. Tang, A. J. Freeman, Y. Qian, G. E. Franklin, and M.J. Bedzyk, accepted by *Phys. Rev. B*.

8. "Structural and Ad-atom Thermal Vibrational Amplitude of the Ga/Si(001) 2x1 Surface," Y. Qian, M.J. Bedzyk, submitted to *JVST*.

9. J.E. Northrup, M.C. Schabel, C.J. Karlsson, and R.I.G. Uhrberg, *Phys. Rev. B* **44**, 13799 (1991).

Fig. 1 1 ML Sb on Si(001). Normalized Si(004) reflectivity and Sb L fluorescence data and best fit to the theory.



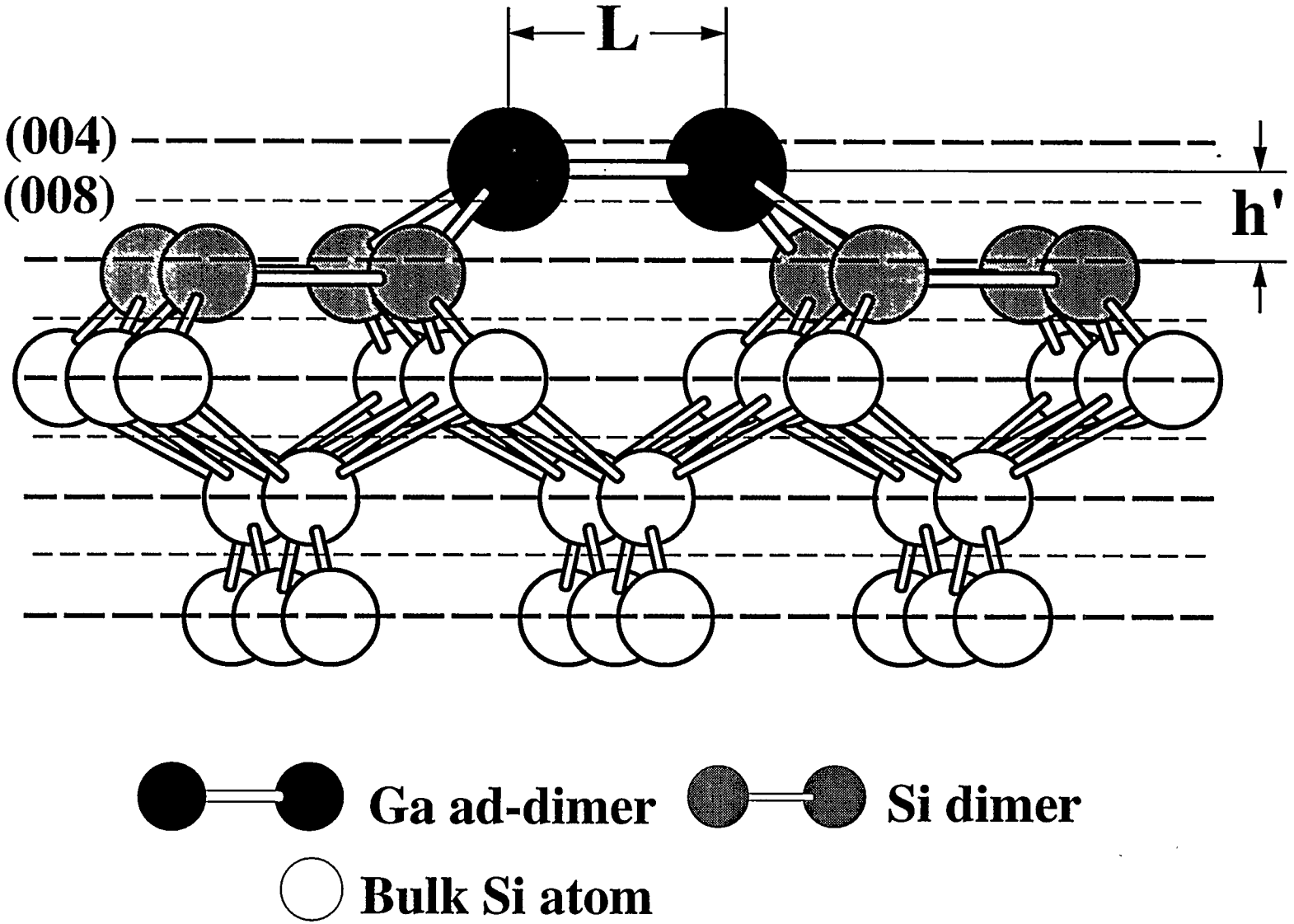


Fig. 2 Sideview of Ga/Si(001)2x2 surface.

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94-059N -- X-RAY-STANDING-WAVE STUDIES OF BURIED ELECTRIFIED INTERFACES

Associate Laboratory Director Area: Physical Research

Principal Investigator: Z. Nagy, Materials Science/Chemical Technology

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$ 88.9K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The purpose of the proposed research was to establish a novel and valuable capability for in situ investigations of the structure of electrified interfaces buried under aqueous solutions. X-ray-standing-wave (XSW) techniques can be used to investigate several aspects of the electrified interfaces; among them are (i) the structure of the diffuse electrochemical double layer extending hundreds of angstroms into the solution, (ii) Langmuir-Blodgett layers, (iii) self-assembled monolayers, (iv) chemically or physically adsorbed monolayers (and submonolayers) of ions and molecules, and (v) the Helmholtz layer. We plan to demonstrate the usefulness of this technique in investigations of the structure of electrified interfaces as a function of solution composition, electrode potential, and the nature of the metal, and to compare with predictions obtainable from available theories. A further purpose is to lay groundwork for the comprehensive XSW measurements to be carried out at an APS undulator beamline, where we project a one-hundred-fold increase in sensitivity as compared to presently available synchrotron beamlines.

Approach: We have an ongoing project, within the Aqueous Corrosion Program, for the investigation of the structure of the double layer using X-ray-reflectivity techniques. The principal investigator of this LDRD, in cooperation with Hoydoo You of the Synchrotron Radiation Studies Group of the Materials Science Division, has developed a novel X-ray/electrochemical cell for reflectivity studies in the transmission geometry (1). Preliminary investigations of the double layer at the platinum(111)/cesium fluoride aqueous solution interface gave encouraging results, and we expect that in the future we will be able to obtain detailed information on the ionic distribution at the interface near the metal surface (5-10 Angstrom distances) in relatively concentrated ($\sim$0.1 M) solutions. On the other hand, the reflectivity technique is not suitable for investigations of the structure of the diffuse double layer extending hundreds of angstroms in low concentration (mM and less) solutions. For these conditions, the X-ray-standing-wave technique is uniquely suitable, and the development of a capability for these measurements would strongly complement and extend our present program without any duplication of existing capability or effort.

M. J. Bedzyk, a key collaborator in this project, has been a pioneer in the application of the X-ray-standing-wave (XSW) technique to interfacial problems through his work carried out at Cornell University (2-7). In these investigations, the XSW is generated above a reflecting surface by the interference between an incident X-ray beam and a reflected X-ray beam, resulting in XSW nodal planes that are parallel to the reflecting surface. In conventional XSW

measurements, the XSW is generated by dynamical Bragg diffraction from a perfect single crystal. In this case, the period of the XSW is equivalent to the d-spacing of the diffraction planes. A new method developed recently uses total external reflection (TER) from a mirror surface to generate an XSW (2). Since the critical angle for TER is only a few milliradians, an XSW generated by TER will have a long and variable period ranging from 70 to 1000 angstroms. In these experiments, the incident angle is varied, which changes the XSW period (and phase). This in turn varies the fluorescence yield from ions or atoms that reside above the reflecting mirror surface. The angular response of the fluorescence yield is directly related to the Fourier transform of the distribution profile of the fluorescent species.

This TER-XSW technique was recently shown to be an ideal probe for investigating the structure of Langmuir-Blodgett (LB) multilayers (3-5) and the diffuse double layer at a membrane/aqueous solution interface (6-7). The diffuse-double-layer-XSW measurement, which was made during the first APS/CHESS undulator run at Cornell, was of major importance, since it represented the first detailed structural measurement of an electrostatic double layer. These measurements were carried out at a membrane/solution interface where the control of the excess surface charge density is difficult, being influenced by the solution and membrane composition. Measurements at a metal/solution interface are advantageous because the surface charge density can be controlled easily by controlling the potential of the metal, though at the price of some complexity of the cell design.

The longstanding problem of double-layer structure in electrochemistry has remained unsolved until now because of the buried nature of this interface. X-rays, which can penetrate through low-Z materials, are ideal for probing the liquid/solid interface. However, the angstrom wavelength of X-rays is too fine of a scale for measuring the diffuse double layer that forms at a charged surface/aqueous solution interface. The solution to this problem is to use X-ray standing waves with a 70 to 1000 angstrom period.

Technical Progress and Results: We have designed and built an X-ray/electro-chemical cell suitable for XSW use. The design principles are shown in the sketch on figure 1. Essentially, it is a thin-layer cell, with a solution layer thickness on the order of 10^{-4} cm between the working electrode surface and the covering membrane. Laboratory testing of the cell gave satisfactory results.

We have carried out detailed literature search and feasibility calculations to establish the best systems to be studied initially from the standpoint of X-ray technique, electrochemical feasibility, and importance. We have selected the zinc perchlorate solution/gold mirror electrode combination for our tests to prove technique viability, followed by the cesium perchlorate/gold mirror electrode combination to initiate the detailed comparison of double-layer theories. We have identified the competing theories to be included in our study.

We developed two computational methods for analyzing the TER-XSW data that will be obtained from our diffuse double layer studies. This theoretical work provides the basis for interpreting the results from this novel method with confidence and with a better understanding of the underlying physical phenomena.

The first method is an inverse Fourier transform method, which makes use of the fact that the XSW method directly solves the phase problem, which is inherent to other X-ray scattering methods, such as diffraction and reflectivity. Through various conversions and approximations we can create a reduced data set that is a Fourier transform for the density profile of the fluorescence selected ionic species. This method has the advantage of being a direct structure determining method. In other words, no model-based intermediate step is required to quantitatively interpret the results.

The second method, which is based on Parratt's recursion formulation, does require a layered model at the initial step, but is more rigorous than the inverse Fourier transform method. We will use both methods. The Fourier method will be used to estimate a starting model. The recursion formulation-based method will then be used to refine that model. The computer programs have been implemented on the Quadra 650 Macintosh computer system installed at the X15A NSLS X-ray beam line.

Specific Accomplishments: We have identified the competing double-layer theories to be examined and the electrochemical systems to be studied to obtain a meaningful comparison amongst the theories. We have designed, built, and laboratory tested the X-ray/electrochemical cell to be used for the XSW studies of the electrochemical double layer structure, and we developed the computer software needed to carry out the experiments and analyze the results. With all the preparatory work accomplished, we are now ready to begin the synchrotron X-ray experiments.

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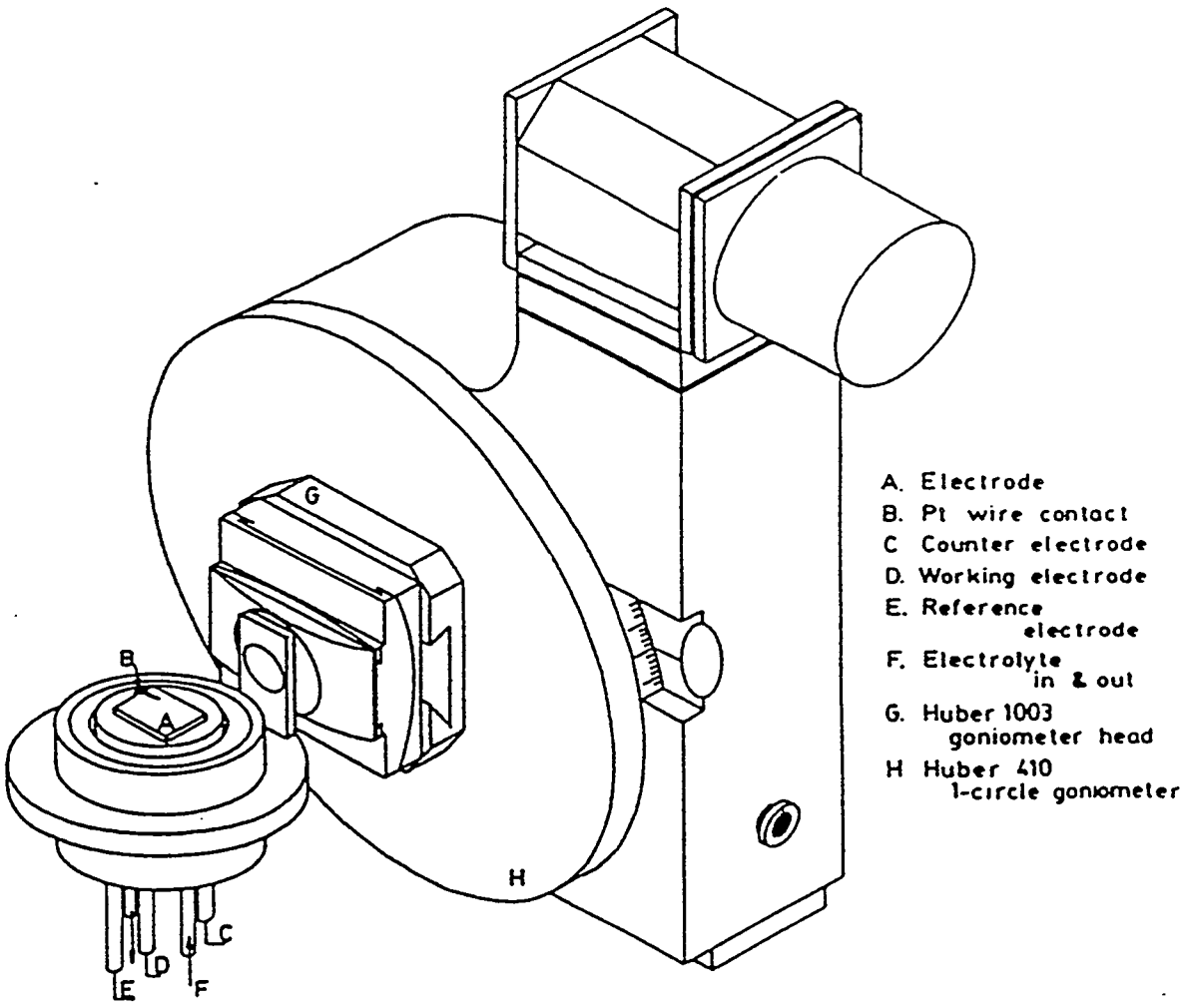

Figure 1. Electrochemical cell assembly and goniometer. (Membrane cover of the cell is not shown.)

94-060N -- INVESTIGATIONS OF TIME-RESOLVED AND ANOMALOUS SAXS STUDIES FOR CRITICAL PROBLEMS IN ADVANCED MATERIALS RESEARCH

Associate Laboratory Director Area: Physical Research

Principal Investigators: K. A. Carrado and R. E. Winans, Chemistry
P. Thiyagarajan, Pulsed Neutron Source

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$ 56.3K
FY 1995	$ 60.0K
FY 1996	$ -0-

Purpose: This initiative seeks to explore the mechanism of formation of technologically important disordered systems. Synchrotron X-ray scattering techniques have begun to be employed to gain an understanding of the critical structural features present. Such understanding will lead to fundamental knowledge regarding structure-activity relationships and also help to make the synthesis of these materials more precise, systematic, and predictable. Time-resolved small angle X-ray scattering (SAXS) studies are suited for monitoring the mechanism of formation *in situ* of such disordered materials as clays because of the inherent crystallization times for this system. Anomalous SAXS (ASAXS) allows a heavy metal ion to be tracked in terms of its disposition within a disordered framework, and this feature will also be exploited. These approaches will provide pioneering information in the near term, and set the stage for more detailed studies of many classes of materials in the long term.

Approach: Disordered systems constitute some of the most technologically and industrially important materials. This disorder, which is in most cases essential for the materials' activity, inherently precludes their detailed characterization by conventional techniques like X-ray diffraction. Current limitations towards understanding the important structural features of disordered systems can now begin to be overcome by using synchrotron radiation scattering methods. Initially, layer silicate clays will be examined because of their microcrystalline nature. Although these minerals are crystalline, their inherent disorder is so high that their particle size is extremely small. Of special interest is their mechanism of formation, which is as yet unknown but of relevance to their use as catalysts, binders, etc.

We have recently developed a new synthetic procedure for preparing clays under mild hydrothermal conditions. The gels can also contain a wide variety of organic and organometallic spacer molecules. Among the direct methods available for structural characterization of these colloidal systems, small angle scattering proves to be among the most powerful. Small angle neutron scattering (SANS) studies of the gels quenched at several different reaction times revealed that within the first few hours the repulsive interactions between the colloidal silica particles decrease and larger colloidal systems are formed. Layered systems are observed after 24 hours by SANS, when the particles are too small and dilute to be observed by X-ray powder diffraction. It is, however, not possible to monitor the growth and formation of the hectorite *in situ* by SANS because the signals are quite weak. In addition, the growth of the particles can

be seen only in a small part of the low q-region of SANS spectra. Monitoring these reactions thus requires high-flux sources and powerful small angle scattering instruments that can access much lower q-regions, which points to the use of synchrotron small angle X-ray scattering (SAXS).

The presently available SAXS instruments at NSLS (National Synchrotron Light Source) and SSRL (Stanford Synchrotron Radiation Laboratory) have very high fluxes, but they do not access q-regions smaller than what one can achieve at the SANS facilities. However, SAXS experiments done at these facilities help us to develop and test the equipment necessary for studying the slurries at high temperature. This is done while information on the type of scattering signals at various times of the synthesis is obtained. In addition, we can develop the anomalous SAXS (ASAXS) methodology for studying these systems. The variation of distances between, and disposition of, metallic centers during crystallization can be examined using ASAXS. When the energies of X-rays are in the immediate vicinity of an absorption edge of a heavy scattering atom, the scattering becomes strongly wavelength dependent. With a tunable intense X-ray source, it is possible to selectively alter the contribution (contrast variation) of a particular element to the SAXS scattering profile, and thus derive information on the disposition of those elements.

Technical Progress and Results: The SAXS instruments at SSRL and NSLS are capable of yielding adequate SAXS signals in the very low q-region (0.01 to 0.2 $Å^{-1}$) within a five-minute time frame. It is our intent to follow the structural aspects of the clay colloids during their synthesis *in situ*. Within just a few hours, the colloids have been observed to grow enough in size from the initial sol-gel to settle to the bottom of the reaction vessel. Hence, a specially-designed sample cell was developed in order to insure that a representative sample stays in the beam during the entire synthesis. Initial experiments performed at SSRL showed that there was very little change in morphology after reaction at 95°C for 13 hours *in situ*. This temperature is slightly lower than the 100°C temperature usually employed, wherein layers have been seen within 24 hours by SANS. The fragile glass sample cells used are not able to hold the pressures generated at 100°C, hence the need to use a slightly lower temperature. It will be necessary to repeat these experiments using other sample cell designs and perhaps longer crystallization times. These studies will yield kinetic information in terms of both structure and morphology of the reactive colloids during the onset, growth, and the final formation of layered silicate materials.

We are also interested in delineating information on the disposition of Ni(II) incorporated within the inorganic framework. Specifically, Ni(II)-containing synthetic mica-montmorillonite (Ni-SMM) is known to be an active hydroisomerization catalyst. We have prepared gels, and powders from these gels, of this synthetic clay quenched at several different reaction times. Inital ASAXS measurements were collected at SSRL but, due to instrumental problems, much better data was obtained soon thereafter at NSLS. Traditionally, the best ASAXS results have been collected on rare earth systems because these metals have such large cross-sectional areas. However, these systems have been very dilute. Analysis of Ni(II) in our silicates is adequately compensated by the high concentration; there is 20 wt% nickel in the final Ni-SMM catalyst. Collection of X-ray absorption spectroscopy data was also done in order to derive the structural environment within the immediate vicinity of the metal ion. This complements the longer range distance information provided by SAXS and ASAXS. Data analysis of the results collected

during the year is currently underway. The acquisition of a new more data-intensive computer system will aid in this analysis. In general, these studies will offer insight into the mechanism of formation of disordered materials such as clays that can be useful in the developing new synthetic strategies.

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94-103N -- DEVELOPMENT OF A CODE FOR SIMULATING WELDING PROCESSES

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: R. A. Valentin and H. M. Domanus, Energy Technology

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$218.4K
FY 1995	$130.0K
FY 1996	$ -0-

Purpose: Modify Argonne's recently developed casting simulation code, CaPS (Casting Process Simulator), to model gas-tungsten-arc (GTA) and gas-metal-arc (GMA) welding. Both GTA and GMA welding are used extensively in the heavy equipment fabrication industry. Creation of a simulation tool that could quickly evaluate how variations in process variables such as current and voltage, fill-wire feed speeds, and component motion alter final weld geometry, residual strain, and distortion would have great value in improving weld quality and reducing process time. Because a major component of such a simulation concerns formation, motion, and solidification of the weld pool, the CaPS code is a natural starting point. In particular, the convective fluid dynamics of the pool and its solidification are already available through CaPS. This project concentrates on modifications needed to add mass transfer, evaporation, surface tension, and electrodynamic effects. Also, because the process of adding molten material to build the weld involves a constantly changing computational region, it is necessary to make certain basic changes in the structure of the existing code. At the end of FY 95, development is to be at a point where a convincing demonstration of feasibility could be made to those industrial concerns that have already indicated interest in the project.

Approach: In developing the CaPS code and applying it to various problems of mold filling and solidification, it became evident that many of the technical issues being addressed for casting did not differ greatly from those associated with the weld process. In particular, the formation and behavior of the weld pool could certainly be modeled by an extension of the simulation techniques employed when developing CaPS.

In discussing the subject of weld simulation with various industrial contacts, it became clear that there are two coupled but distinct areas of concern. The first concerns local effects, that is, physical processes that are local to the weld pool, its solidification, and evolution of final material properties and local stresses. The second area concerns more global features such as distortion of an entire structure due to the strains induced during welding. Because CaPS was well suited to the study of local effects, it was decided that only weld pool dynamics would be considered during the early stages of this feasibility study. A link to global structural concerns and perhaps to other computer codes is to be left for later development if an eventual industrial partner is found after the feasibility work has been completed.

While the methods used in developing CaPS will be those used in the welding code, the latter will not be a simple extension of CaPS. Instead, it will build on lessons learned during that development, together with a modified code structure needed to simulate the complexity associated with the dynamics of the evolution of the weld pool.

The welding process is simulated by computing detailed transient, three-dimensional distributions of volume of fluid, velocity vectors, pressure, temperature, and solid mass fraction. The spatial variable distributions are computed for a large but finite number of hexahedral cells arranged in an Eulerian structured mesh framework. Integral forms of the conservation of mass, momentum, and energy equations, along with temperature-dependent physical properties, are used. The finite-volume formulation involves approximating the various terms of the integral conservation equations with respect to a cell and its six adjacent neighbors. The finite-volume approach gives rise to a set of algebraic equations, one per variable for each cell. The coefficients of the linearized algebraic equations are assembled into matrices. A segmented-solution algorithm employing sparce matrix solvers is then used to determine the cell values. The terms of the algebraic equations can be identified as transient terms, flux terms (convective and diffusive), and source terms. Transient results are obtained by repeating a time-stepping algorithm in which each variable distribution is advanced over a time increment.

The geometry is described by a collection of parametric cubic volumes (hyperpatches) that are an extension of Hermite curves. It is assumed that the model space is completely described by this set of hyperpatches. Commercial software is used to define the geometry and obtain the set of hyperpatches.

Technical Progress and Results: Due to the heavy computational requirements needed to perform welding simulation, the SUN SPARCstation platform on which CaPS was developed was determined to be inadequate. Development of the welding process simulator software was ported to an HP 735 with 112 Mb of memory. Benchmark comparisons indicate a factor of 13 increase in computational speed over the SUN system.

The momentum and energy routines in the simulator module were restructured to accommodate the addition of new source terms. The matrix coefficients are now built modularly to facilitate implementation of new physical models. In the momentum routines, there are now options for new source terms to model the forces due to surface tension and electromagnetic effects. Heat loss from the weld pool by evaporation and heat added from the arc can now be considered as sources in the energy routines.

Practical welding process simulations can be expected to involve more than 1 million computational cells. In contrast, CaPS simulation has been demonstrated with up to approximately 30,000 cells. While the algorithms and storage schemes were designed to (at least theoretically) automatically scale to any size problem, practical limits were observed in test cases. A 1-million-cell rendering required more than 35 cpu hours to determine. Several modifications to the automatic mesh generator module were therefore made. These sped up the mesher so that a 1-million-cell rendering can now be done in less than 11 minutes and a 2-milliion-cell rendering in less than 25 minutes. The simulator module was found to be even more constrained. A major revision was made to the storage allocation scheme that explicitly distinguishes between potential fluid/phase change cells and cells that will always be solid

throughout the simulation. Typically, less than one-tenth of the cells have the potential of melting and becoming fluid cells during the course of a welding simulation. The new storage scheme had implications for virtually every subroutine in the simulator module, so the modifications were extensive. A 1-million-cell simulation has recently been demonstrated, and further tests are underway.

During FY 1995, the effort will shift from changes in code architecture to testing of the various physical models needed to provide an accurate simulation of the solidification of the weld pool. These include a free-surface treatment that models surface tension so as to account for electromagnetic field effects. Sufficient capability will exist by the end of FY 1995 to demonstrate code feasibility to potential industrial sponsors.

Specific Accomplishments: A basic code structure has been developed for the welding simulation to allow computation in sufficient spatial detail to model weld pool dynamics to the degree necessary for industrial applications. To broaden the potential interest in such models, interactions with staff in other program areas have been initiated to couple the CaPS-derived code with structural codes capable of modeling global and local strain and distortion.

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94-165N -- DEVELOPMENT AND APPLICATIONS OF NOVEL BIOMIMETIC TiO_2 PHOTOCATALYSTS FOR SELECTIVE HEAVY METALS REMOVAL

Associate Laboratory Director Area: Energy and Environmental Science and Technology and Physical Research

Principal Investigator(s)

Basic Component: M. C. Thurnauer, D. M. Tiede, and D. Meisel, Chemistry
Applied Component: R. W. Peters, J. M. Wu, and N. K. Meshkov, Energy Systems

Funding Profile:

FY 1992 $ -0-
FY 1993 $ -0-
FY 1994 $176.9K
FY 1995 $140.0K
FY 1996 $200.0K

Purpose: The purpose of this project is to develop and test advanced, new photocatalysts that have the unique capability of both sequestering and converting heavy metal ions from aqueous solution to their less toxic, readily recoverable metallic forms. This project exploits a strategy to enhance the reactivity of semiconductor photocatalysts for selected toxic compounds by derivatization of the photocatalyst surface with biomimetic polymers. This study will result in identification and development of potential biomimetic photocatalysts for simultaneous heavy metal recovery and organic destruction, and in identification of treatment conditions which minimize the residual metal concentration(s) contained in the effluent (even in the presence of complexants and interferences), development of appropriate scale-up criteria, and determination of system performance including an economic analysis which will be compared to conventional technologies (such as pump-and-treat using metal hydroxide precipitation or ion exchange).

Approach: Oxidative degradation of pollutants by photocatalysis using semiconductor particles such as TiO_2 has been the subject of numerous recent studies. The principle behind semiconductor-assisted photocatalysis in the aqueous phase containing organic pollutants and semiconductor particles involves the photoexcitation of the semiconductor particles by ultraviolet (UV) light causing the energy state of the electrons to change from the valence band of the solid to the conduction band, resulting in the formation of electrons and holes at the surface of the semiconductor particle which can either recombine, producing thermal energy, or interact with other molecules. The radicals generated can either oxidize organic pollutants or reduce heavy metals at the solid/liquid surface. The focus of the majority of laboratory studies involving TiO_2-assisted photocatalysis to date has been on the destruction of organic pollutants in solution using photocatalytic oxidation, with little attention devoted to recovery of heavy metals.

The current study seeks to enhance the performance of TiO_2-assisted photocatalysis to sequester and recover heavy metal ions in their metallic form while simultaneously destroying organic compounds, potentially in a single step. To achieve our goal a dichotomous approach was taken: (1) the development and design of the photocatalytic system and (2) their application to contaminated waste streams. The development and design work is focused on determining the mechanism of the photocatalytic process in order to design catalysts that are specific and

efficient. In this respect the passive sorption of the metal ion to the surface modified colloid is investigated as well as the photochemical reduction of adsorbed metal ion in the presence of different surface modifiers. The influence of the surface structure on the efficiency of the photochemical reduction of metal ion and/or decomposition of organic wastes is being investigated. The application task involves batch, bench-scale studies involving parametric testing.

The experimental approach of this project is based on the methods developed and studied by Dr. O.I. Micic (Boris Kidrich Institute - Vinca, Belgrade, Yugoslavia) during the year 1992 at Argonne National Laboratory as a Maria Goeppert Mayer Scholar for synthesis of small semiconductor particles. In collaboration with Dr. Micic a new technique for the study of the photochemistry of colloidal semiconductors by electron paramagnetic resonance (EPR) was carried out. This method allowed direct observation of both reduced and oxidized intermediate species formed during semiconductor illumination.

Technical Progress and Results: In the Chemistry division, a colloidal reactor for controlled synthesis of nanoscale colloidal particles was developed and demonstrated, producing consistently reproducible feedstock for the applied research in the Energy Systems division and for fundamental mechanistic studies. During the first year cysteine was selected as the model derivative for surface modification of TiO_2 nanoparticles. Infrared spectroscopy suggested that cysteine is bound to the TiO_2 particles at pH$\sim$5 with a carboxyl group. Addition of lead into cysteine modified colloid resulted in the bidendate complexation of lead ions with the mercapto group and an oxygen from a carboxyl group of cysteine, covalently linked to the titanium atom at the surface of colloidal TiO_2. After lead ion reduction, the recovery of the carboxyl group was observed. The presence of excess cysteine resulted in the photooxidation of cysteine. Preliminary work was undertaken on other bidendate ligands acting as surface modifying species such as thiolactic acid, 1-mercaptopropionic acid, l-alanine and cysteamine. Preliminary results support the fact that a charge transfer complex between ligands and surface titanium atoms is one of the requirements for successful reduction of lead ions. Using electron paramagnetic resonance (EPR) spectroscopy, the Chemistry division characterized the trap sites for electrons and holes in underivatized, derivatized, and derivatized plus metal-complexed colloids. Adsorption of cysteine on the TiO_2 surface, changes the $g<2$ region of the TiO_2 EPR spectrum normally associated with surface oxygen species which are generated by trapping of holes at oxygen lattice and surface adsorption sites. Following irradiation of the cysteine-coated TiO_2 particles, hole transfer to cysteine occurs. This charge transfer is seen in the TiO_2 system EPR spectrum as a disappearance of the $g<2$ EPR features associated with trapped holes, while leaving a large surface electron EPR signal in the $g>2$ region. In the absence of metal ions, evidence for the formation of cysteine radical reaction products was obtained by observation of their characteristic EPR spectra. Oxidation of cysteine was not observed in the presence of lead and mercury ions which are bound to the sulfur functional group of cysteine. In this case photoinduced electrons were transferred to reduce metal ions, and the precipitation of metallic lead was observed. The changes in the REDOX properties of derivatized colloids support the IR result that cysteine modifies the TiO_2 surface structure. In the presence of methanol, holes were converted into methanol radicals which can inject electrons into TiO_2, shown with EPR spectroscopy. Therefore, the presence of methanol can potentially double the yield of reduced metal. Meanwhile degradation of methanol occurred simultaneously. These results suggest that the reduction of metal ions can occur simultaneously with degradation of some organics on surface modified TiO_2.

Testing in the Energy Systems division demonstrated that adsorption of lead (Pb^{+2}) and mercury (Hg^{+2}) ions occurred in the systems using either untreated (virgin) or treated (modified using cysteine) TiO_2. Adsorption rates of metal ions in the systems using treated TiO_2 photocatalysts are ~3x faster than those using untreated TiO_2 photocatalysts in both cases. (See figure 1 for the case of Pb^{+2}.) Pb^{+2} and Hg^{+2} concentrations in the irradiated solutions decreased as the UV irradiation time increased; greater metal removals were achieved at longer irradiation times. The removal rate of Pb^{+2} ions in the system using treated TiO_2 photocatalysts were 2-3x faster than that using untreated TiO_2 photocatalysts (see figure 2).

Experiments were also performed in which organics (naphthalene) and heavy metals (Pb^{2+}) were treated with the TiO_2 photocatalysts. The presence of lead did not interfere with removal (destruction) of naphthalene from solution. The presence of naphthalene resulted in "lag-time" effect on the photoreduction of lead from solution; after the majority of naphthalene had been removed, the lead was then removed by photoreduction. In both cases (lead and naphthalene), the cysteine-modified TiO_2 photocatalyst resulted in removal rates which were faster and more effective than the untreated TiO_2 system (see figures 3 and 4). This technique has resulted in the simultaneous photocatalytic removal of naphthalene and lead.

LDRD funding has been requested to continue this research during FY 95. This study seeks to enhance the performance of TiO_2-assisted photocatalysts to sequester and recover heavy metal ions in their metallic form while simultaneously destroying organic compounds in a single step. The tasks to be performed during next year are listed below:

Task 1: Develop and design new photocatalyst (TiO_2 photocatalysts that have been modified using different mercapto-reagents).

Task 2: Continue preforming batch, bench-scale experiments to determine process kinetics and optimum treatment conditions (pH, temperature, TiO_2 dosage, and ligand dosage, UV optimum wavelength, addition of oxidation accelerants, etc.).

Task 3: Conduct continuous flow experiments to better simulate industrial and field treatment.

Task 4: Conduct batch and continuous flow experiments in the presence of various organic co-contaminants.

Task 5: Perform scale-up design and preliminary systems analysis, economic analysis of the processing.

Task 6: Model the behavior of the photocatalytic oxidation systems.

In addition, in order to commercialize this technology, efforts will also focus on the recovery of the TiO_2 photocatalysts. Efforts will be made to secure one or more industrial partners to conduct a field demonstration in the third year of this project.

Specific Accomplishments: Three papers have been accepted for presentation at national technical conferences during this next year, based upon the results obtained during FY94. These papers are listed below:

"Use of Cysteine-Modified TiO_2 Photocatalysts for Treatment of Combined Organic/Inorganic Wastestreams", by R.W. Peters, J.-M. Wu, N. Meshkov, M.C. Thurnauer, and A.E. Ostafin", Paper accepted for presentation at the 5th International Symposium on Chemical Oxidation: Technology for the Nineties", Nashville, Tenn., February 15-17, 1995.

"Conversion of Holes into Reducing Species on Surface Modified Small-Particle TiO_2", by O.I. Micic, A.E. Ostafin, T. Rajh, J.J. Sabelko, M.C. Thurnauer, and D.M. Tiede, Paper accepted for presentation at the 5th International Symposium on Chemical Oxidation: Technology for the Nineties", Nashville, Tenn., February 15-17, 1995.

"Combined Photooxidation/Photoreduction Using TiO_2 Photocatalyses to Treat Organic/Heavy Metals-Laden Wastewaters", by R.W. Peters, J.-M. Wu, N. Meshkov, M.C. Thurnauer, and A.E. Ostafin, Paper accepted for a poster presentation at the Waste Management 95 Symposium on HLW, LLW, Mixed Wastes, and Environmental Restoration--Working Towards a Cleaner Environment, Tucson, Ariz., February 26-March 2, 1995.

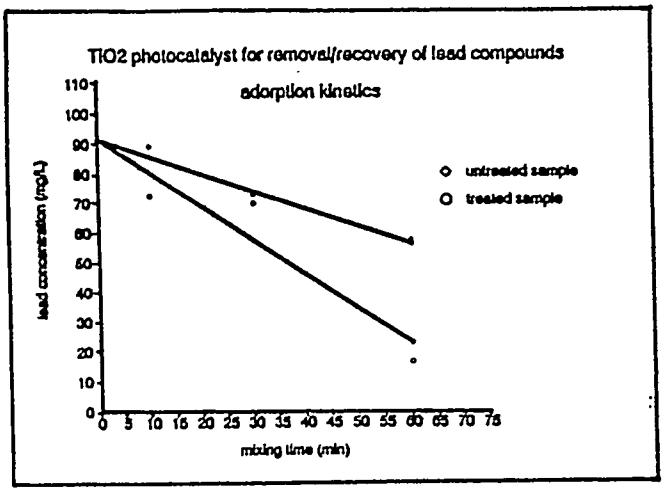

Fig. 1. Pb Adsorption Kinetics

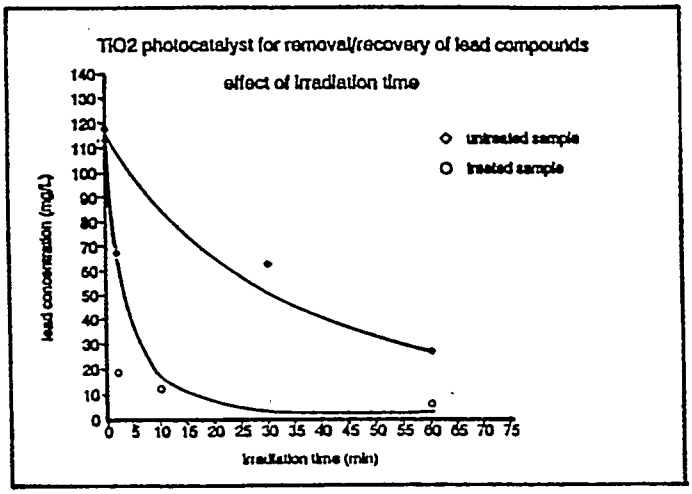

Fig. 2. Effect of Irradiation Time on Pb Removal

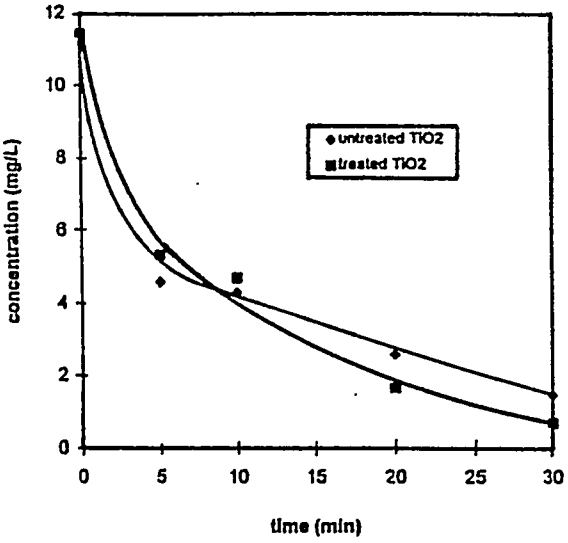

Fig. 3. Residual Naphthalene Concentration for Combined Naphthalene-Pb^{+2} System.

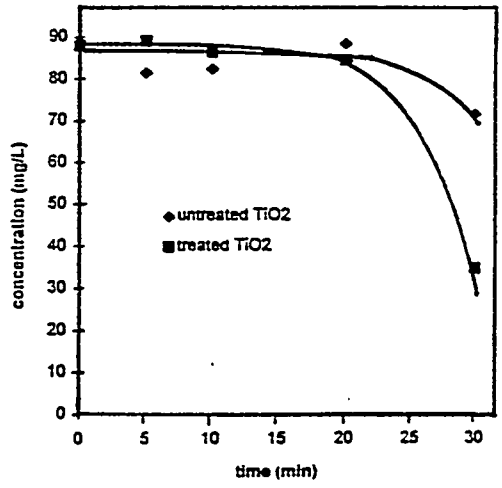

Fig. 4. Residual Pb^{+2} Concentration for Combined Naphthalene-Pb^{-2} System.

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94-169N -- PLASMA MODIFICATION AND CHARACTERIZATION TO IMPROVE MICROMANUFACTURING AND ETCHING TECHNOLOGIES

Associate Laboratory Director Area: Physical Research

Principal Investigator: K. R. Lykke and M. Pellin, Chemistry
D. Spence, Technology Development

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$162.4K
FY 1995	$140.0K
FY 1996	$200.0K

Purpose: Utilizing both the advanced concepts of plasma modification developed in the Technology Development division and the unique diagnostic techniques developed in the Materials Science/Chemistry divisions, this effort seeks to modify, characterize, and optimize gaseous plasmas to improve the manufacture of micromachines and microchips. Building on pioneering work at ANL which allows modification of oxygen and other plasmas to produce high concentrations of reactive neutrals, this project seeks to use a unique ability to independently control the plasma ion/neutral ratio as a platform for an increased understanding of anisotropic plasma etching. Key to this effort is an ability to analyze both the gaseous plasma and reactive-etched substrates rapidly and with exquisite sensitivity. The strategic purpose of this work is to develop both uniquely capable and more environmentally-benign manufacturing processes.

Approach: Micromachining and etching technologies involve the production of structural components that have dimensional tolerances of 1μm or less. Most microsystems are currently made from silicon or similar semiconductors for which advanced etching techniques from the microelectronics industry can be applied. Key to the production of these devices is the ability to etch materials with high aspect ratios. That is, to produce narrow, deep trenches.

The microscopic mechanism responsible for high-aspect ratio etching is termed "ion-neutral synergy." Although not quantitatively understood, the mechanism is basically one in which etching is performed by reactive neutral atoms that have been directed perpendicular to the surface of the material to be etched by collisions with ions that have been accelerated by a potential applied perpendicular to the working surface. Such anisotropic etching enables microstructures to be fabricated with the large depth-to-width ratios that are essential for the high-density component integration. By contrast, liquid or neutral etchants etch isotropically (and produce large quantities of hazardous materials).

At ANL, pioneering work has been made on the modification of oxygen, nitrogen, and other plasmas (similar to those used in etching), such that the degree of dissociation (producing reactive neutral radicals) can be varied at will to give yields from a few percent to more than 50 percent. This has been achieved by the addition of environmentally-benign additives such as N_2 and H_2O in concentrations less than one percent. It is important to note that these additives do not produce deleterious impurities in these plasmas. Concomitantly, the production of ionic species can be varied independently by the control of power or gas flow to the reactor.

Note that changes in power level have been found at ANL to have relatively little effect on the production of the neutral species.

Thus, our proposed technique provides independent control of ions and reactive neutrals, which will enable ready optimization of plasma conditions to then achieve optimal etching conditions. Our methods remove the "Edisonian approach." To our knowledge, application of our concepts to microengineering or microchip etching has not been performed elsewhere.

Technical Progress and Results: All of our measurements are carried out on a source test stand incorporating a high-brightness electron cyclotron resonance (ECR) source and large diagnostic chamber. In FY94, this test stand has been modified to accept the special diagnostics required for these studies. In addition:

- A unique electrostatic imaging lens whose design is based on numerical calculations performed in the Technology Development division has been fabricated and incorporated into the front end of a commercial quadrupole mass spectrometer (QMS). This mass spectrometer comprises our primary beam diagnostic and has been incorporated into the ion source test stand. Routine tune-up and calibration of the mass spectrometer has been performed using nitrogen ion beams.

- We have performed initial tests on the ion fraction population in the ion beam by monitoring the O_2^+ to O^+ ratio in an ion beam extracted from an oxygen plasma. We have made measurements of the O^+/O_2^+ ratio, both with ($\sim 1\%$) and without H_2O additives and find that the ion ratio is independent of the additive, as we argued would be the case in our initial proposal. See figure 1 for a demonstration of the capabilities of the mass spectrometer. To study the all-important neutral fraction, we have designed a modification to the ion optics on the quadrupole mass spectrometer.

- Concurrent with the above, we have anticipated the need for sophisticated surface diagnostics. To this end, Ion Scattering Spectroscopy (ISS) has been chosen as the *in situ* diagnostic of the etching and growing of the chip surface. This technique will utilize a pulsed ion microprobe using time-of-flight techniques designed and modeled in the Chemistry and Materials Science divisions. One of the extraordinary features of this technique is the capability to detect elemental constituents on the surface in real time and at ambient pressure, a very elusive capability for the plasma-etch and growth community at present.

- Towards this end, we have designed a new ion source for the ISS portion of our studies and have begun construction. This unique pulsed ion source is based on laser desorption of metals and other species. The major improvement over existing ion sources for ISS is that the source is inherently short-pulsed ($\tau < 10$nsec) and provides extremely high intensity (space-charge limited). In addition, the source can be used as an ion microprobe and one has the advantage of using many different types of ions, simply by changing the target. This will allow a careful examination of the elemental composition of the surface to be probed.

- We have begun construction of the xyzθ sample stage that will allow positioning the sample in front of the plasma modified ECR source. This stage will also allow for heating of the substrates.

- We have designed and constructed an all-reflecting microscope objective that will allow for high-resolution imaging ($<1\mu$m, *in situ*) of the surface. This feature will be useful in studying the ion-neutral synergy in forming steep walls with high aspect ratios.

Specific Accomplishments: "Production of high-proton fractions from plasma modification in ECR sources," by D. Spence and C. L. Fink, LINAC Conference, Tsukuba, Japan, October 1994.

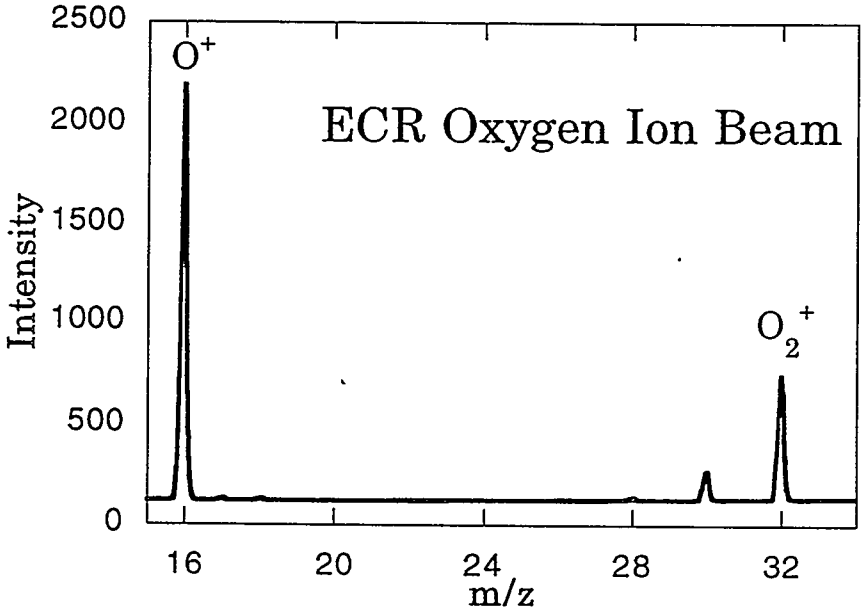

Figure 1. Mass spectrum of oxygen ions extracted from the ECR source. The microwave power was 200W, total extracted ion current was 10mA, oxygen gas flow rate was 1sccm.

94-179N -- APPLICATION OF ADVANCED MATERIALS AND METHODS TO CERMET GAS SENSOR DEVELOPMENT

Associate Laboratory Director Area: Energy Systems Division

Principle Investigators: M. C. Vogt and E. L. Shoemaker, Energy Systems Division; C. Foster and M. Chang, Materials Science Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$140.2K
FY 1995	$140.0K
FY 1996	$200.0K

Purpose: The extensive research in advanced materials at ANL, along with its exploration in applied computer science, can be focused to make marked improvements in existing gas sensing technology, and can also be used to produce unique gas sensing capabilities as well. Recently, new electrocatalytic gas (ECG) microsensors have been produced at ANL that employ ceramic metallic (cermet) materials and advanced computer analysis methodologies. In addition, recent advances in the growth of high-quality oxide thin-film materials have been made at ANL based on Metal Organic Chemical Vapor Deposition (MOCVD). By building on this proven platform and tying the improvement of the current microsensors more closely to specialized advanced materials development, more capable microsensors can be constructed and can serve as an additional development platform for further gas microsensor research.

Approach: Typical gas microsensors in the current market and under development focus on a narrow and dated method for processing their signals. They produce an electrical signal proportional to some physical phenomena. The burden of development of these microsensors has been constrained by these dated signal processing systems. The techniques to be employed for this study capitalize on the greater amount of information that can be supplied by a gas microsensor if its signal is more completely analyzed. The same gas microsensor that can detect only oxygen if processed using past methods, can be used to identify multiple gases in a mixture if its signal is processed in a more complete way. In cyclic voltammetry analysis, a ramped voltage is applied to the sensing and reference electrodes of the microsensor and the electrical current passing through the microsensor is recorded. Gases on the surface react as a function of the voltage applied and affect the measured current. This builds a unique voltage-current signature for the reactions on the microsensor's surface. ANL expertise in neural network pattern recognition methods, combined with cyclic voltammetry chemical analysis techniques, can be used to isolate and identify chemical phenomena not possible before. This ability also allows more complex microsensors to be produced without the constraint of dated processing systems.

Current ANL studies have shown proof-of-concept by producing a thick-film cermet gas microsensor. These studies also identify the need for improved sensitivity and selectivity to gas mixtures. These problems can be well addressed by taking advantage of the on going advanced materials work at ANL. This materials research has developed synthesis methods for high-

quality thin-film growth on many substrate materials using MOCVD. While the proof-of-concept studies have focused on thick-film-only devices for their low cost and ease-of-construction, thick-film/thin-film hybrids should yield a higher sensitivity and faster response time than possible in the thick-film-only devices. In addition, optimizing the materials used in the prototype microsensor could improve the response and the sensing range of the device. The Energy Systems Division focused on improving existing microsensor materials and produced partially completed microsensors for the Materials Science Division thin-film addition. The Materials Science Division produced and characterized chemical vapor deposited thin-films of various electrolytes on these "under-construction" microsensors. The Energy Systems Division completed microsensor construction and characterized the hybrid thick-film/thin-film gas microsensors.

Technical Progress and Results:

Materials/Measurement Optimization:

SOLID ELECTROLYTES - Intensive film tests were conducted with alternate solid electrolyte materials: yttria stabilized bismuth oxide YO-Bi_2O_3 and tungsten stabilized bismuth oxide WO-Bi_2O_3. The Bi_2O_3 electrolytes should exhibit ionic conduction comparable to yttria stabilized zirconia (YSZ) but at much lower temperatures between 50 - 100°C. This would bring the operational cost of the microsensor down as well as decrease drift of the microsensor with change in temperature. Several dozen microsensors were made with the doped Bi_2O_3 electrolytes and are currently being tested.

CATALYTIC ELECTRODES - Work was done to determine the effectiveness of using alternate catalytic electrode materials in place of platinum in the prototype microsensor. Microsensors were constructed with ruthenium (Ru) and palladium (Pd) electrodes and were tested for response and reproducibility. As expected, the microsensors responded uniquely and reproducibly to the different catalysts tested (see figures 1, 2, and 3). The uniqueness of response from each catalyst could be used to differentiate dissimilar gas species.

REFERENCE ELECTRODES - The buried metal oxide reference electrode acts as a source of free oxygen anions in the microsensor which (theoretically) enhances response by carrying ionic charges transferred at the catalytic surface through the solid electrolyte layer. Several different metal oxide systems which have (calculated) high partial pressures of oxygen anion formation were studied: FeO, CuO_2, VO, MnO, and Ta_2O_5 . Intensive film tests were conducted. Of these, two alternate reference metal oxides systems, Ta_2O_5 and MnO, were tested in place of the nickel oxide (NiO) reference used in the prototype microsensors. In addition, microsensors constructed without a metal oxide reference layer were tested. These tests were conducted to determine the function (experimentally) of the reference electrode and whether response could be modified by changing its composition. The MnO, Ta_2O_5 and no reference microsensors responded virtually the same. In 100% N_2, the microsensors were unresponsive, generating non-uniform signals in the fraction of a micro-amp range (see figures 4, 5, and 6). As oxygen was slowly introduced, the signals began to resemble the standard prototype waveforms (see figure 7). When exposed to 100% N_2 again, the response decreased as oxygen anions were depleted irreversibly from the system. As a result of this oxygen dependence, the change in microsensor response with oxygen concentration was markedly enhanced for these microsensors as compared to the NiO prototype microsensors, however, the responses were less reproducible and tended to drift within a short period of time (minutes). This data implies that the

microsensors require a constant reference of oxygen anions to maintain stability and that the metal oxides of MnO and Ta_2O_5 do not reversibly generate adequate partial pressures of oxygen anions.

MEASUREMENT TECHNIQUES - Three different methods of cyclic voltammetry : sinusoidal, differential pulse, and stepped, were tested along with the standard triangular wave to determine if more information could be extracted from the voltage-current signatures generated by the microsensors. It was found that the most reproducible and useful cyclic voltammetry method was the triangular wave. The pulsed voltammetry technique generated unstable and unreproducible currents (see figure 8) and the sinusoidal technique generated curves very similar to the standard triangular wave without providing any additional information (see figure 9). Experiments were also conducted at various voltage amplitudes to determine the ideal range to test the microsensors within. Tests were conducted in the range from 0.5 VDC to 8.0 VDC. It was found that beyond 3.0 VDC, the microsensors become irreversibly altered and could not return to their steady-state condition (see figure 10). In addition, tests were conducted to determine if damaged microsensors could be regenerated by re-sintering the YSZ. Results showed that most damaged microsensors could be restored effectively by re-firing at 1350°C (see figure 11).

DEVELOPMENT OF SCREEN PRINTED THICK-FILM/MOCVD THIN-FILM HYBRID MICROSENSORS - The Materials Science Division successfully produced pure-phase YSZ thin-films, by MOCVD, on a variety of highly-polished substrates including Si, MgO, Pt/Si etc. One of the most critical parameters for the microsensor, the ionic conductivity of the electrolyte, depends greatly on the microstructure of this film. Initial result indicated that a wide range of conductivity's were obtainable by manipulating the microstructure of the YSZ films. Several YSZ thin-films were also deposited by MOCVD on the partially completed thick-film microsensors provided by the Energy Systems Division. Initial tests of the YSZ films measuring 0.2 microns and 0.6 microns respectively were unsuccessful in providing an insulative layer between the upper and lower thick-film platinum electrodes. Thin-film multi-layers of Pt/YSZ/Pt on silicon substrates were made to determine whether the problem was arising from the roughness of the thick-film Pt or the incompatibility between the thin-film and thick-film preparation techniques. The thin-film multi-layer structures showed adequate insulation between the lower and upper layers of Pt, but the films did not have the mechanical strength needed to be mounted and tested in the current experimental apparatus. An alternative mounting process was designed. The fragile pads of the thin-film upper electrode were lead bonded with a Bausch and Lomb ultrasonic lead bonder to a ceramic substrate screened with thick-film conductive stand-offs. This device was not yet tested completely. The Materials Science Division also conducted intensive cross sectional SEM studies of prototype thick-film microsensors to analyze their film structure. These studies showed that microsensors with substantially (25%) thicker layers of YSZ required higher temperatures to generate distinct waveforms (see figures 12 and 13) and exhibited less stability as compared to the microsensors with thinner YSZ layers.

NEURAL NETWORK DESIGN AND IMPLEMENTATION - This stage of research has looked at identifying the physical limitations of implementing neural networks to drive and process the complex response from the ECG microsensor.

Work was performed by Scott Carpenter in the Chemical Technology Division to use their chemical data processing system, SAGE, to process the ECG microsensor response data in several ways to identify any possible data reduction schemes that would allow simplified processing. Work is still underway, but initial results of CO response signatures have shown that some data reduction techniques can transform the voltage-current envelopes into straight lines of various slopes.

Collaborative work was begun with Jon Hawkins in the Electronics and Computing Technologies Division to begin planning a neural "chip" to support the ECG microsensor. The Electronics and Computing Technologies Division's past work produced a single application-specific integrated circuit (ASIC) that implemented a crude but effective trainable neural network. Public domain circuit routing software was used along with a DARPA-funded low-volume IC manufacturing facility available to the DOD/DOE labs (called MOSIS) to actually model neurons in silicon, instead of representing the neurons mathematically in software. The work to bridge the gap between the existing, trained, prototype software artificial neural networks (ANNs) and the neural chip has begun by rebuilding and remodeling the existing networks with a limited number of discrete values available for the network weights to take on. Current Energy Systems Division prototype networks have used single precision integer numbers to store the network connecting weight values. This gives them a range of 0 - ~65,000. The Electronics and Computing Technologies Division's original neural chip used only a single bit, 0 or 1, to implement weight values. It is expected that the current networks can be remodeled with weights having values between 0 and 255. If this range of values can store the needed information to differentiate gas signatures, then the new neural chip should be able to be made using 8-bit registers in silicon instead of single binary digit bit-flags. This would allow the construction in the Electronics and Computing Technologies Division of a complex, trainable, ASIC for both sensor support and other purposes. The retraining of the Energy Systems Division prototype networks has begun and looks very favorable. Smaller networks have been created, with <25 inputs (compared to >100 inputs in early prototypes CO networks), and code has been written to limit the number of weight values to 256. Work in this area will finish in January 1995 and be the topic of an IIT graduate masters thesis on the subject.

Work has also been done to miniaturize the software aspects of the neural net processing. With advice from a local industrial collaborator (The Seatt Corporation), several industrial standard microcontrollers were identified and obtained (Philips 80C51 and PIC 16C7X). These microcontrollers are single self-contained computers that have a microprocessor, I/O ports, analog/digital converters, and memory all on a single 18 pin DIP IC (see figure 14). Code has been developed and tested to use these chips to perform all the expected support functions the ECG microsensor needs to operate independently. Code has been written to output a sinusoidal or triangular excitation signal, as well as sample and measure the corresponding change in current and voltage of the sensor output. Early results indicate that a chip of this kind should be able to support the microsensor, though the capability of the chip (speed and amount of on-board memory) is a factor in any given application. Work is still being done to reduce and integrate the neural net processing code to a size suitable for the microcontroller. This feed-forward identify/quantify processing is simple compared to the training of the network, and should fit well on a chip with 32K - 64K on -board memory. It is the desired goal to optimize the feed-forward identify/quantify code to fit on a microcontroller with only 4K - 8K on-board memory. If the neural code cannot be reduced enough, it should be quite possible to use the

microcontroller in conjunction with the planned neural chip. The microcontroller would play a subordinate role to the neural chip, with the microcontroller generating the necessary excitation signal and sampling the sensor, and the neural chip processing the signal and handing back a measured gas value to be displayed by the microcontroller chip.

Specific Accomplishments: A patent is pending on an invention for the microsensor entitled: "Electrocatalytic Cermet Gas Detector/Microsensor" (ANL-IN-91-104), by M.C. Vogt, E.L. Shoemaker, A.V. Fraioli.

Two invited articles are being prepared for publication in the *Journal of Fire Science*, and *SENSORS* journal on the design and capabilities of the electrocatalytic gas microsensor.

Test facilities have been set up and collaboration established with staff at Idaho National Engineering Laboratory (INEL) to do further testing of the microsensor in selected environments. INEL staff have chosen to evaluate this technology over several others for its potential in monitoring hazardous materials under adverse conditions.

Approached by the Naval Surface Warfare Center to develop a sensing system for O_2 and CO_2 to be used in underwater breathing apparatus.

Approached by the American Textile Manufacturers Association (AMTEX) for further development of the microsensor to detect gases from industrial processes.

Approached by the Seatt Corporation to conduct research into developing a CO monitor for human-occupied spaces.

Invited presentations to AMTEX and Northwestern University were made on the thick-film oxide microsensors work.

Partnerships with Northwestern University and Northern Illinois University have been established to guide continued research in the cermet microsensor area.

A CRADA has been initiated upon invitation from the NeuralWARE Corporation to develop new applications for neural network technologies (hardware and software). The NeuralWARE CRADA will aid several on-going ANL programs that use neural processing.

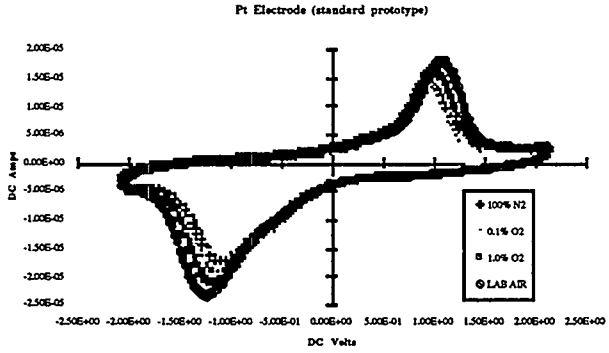

Figure 1. Standard Pt electrode response to O_2

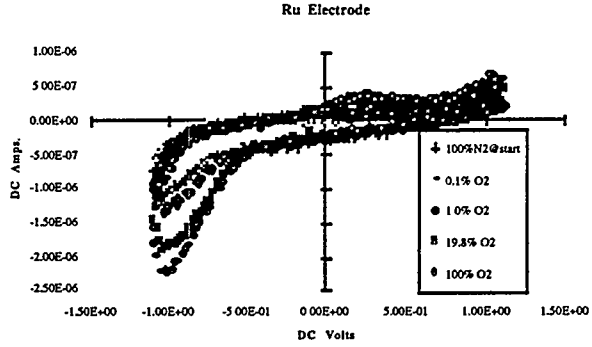

Figure 2. Ru electrode response to O_2

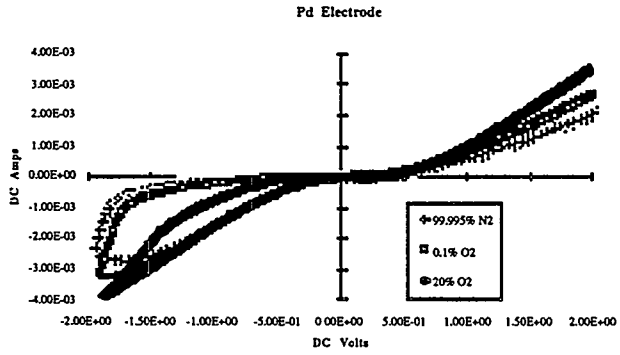

Figure 3. Pd electrode response to O_2

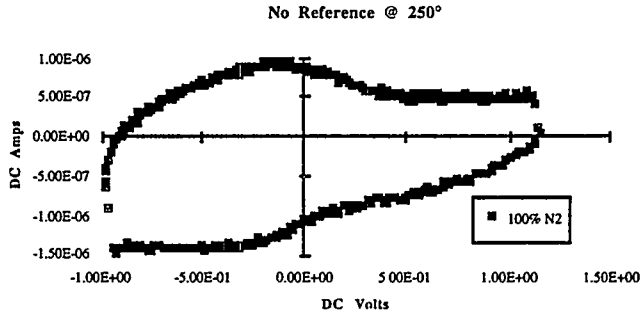

Figure 4. Microsensor response - no reference electrode

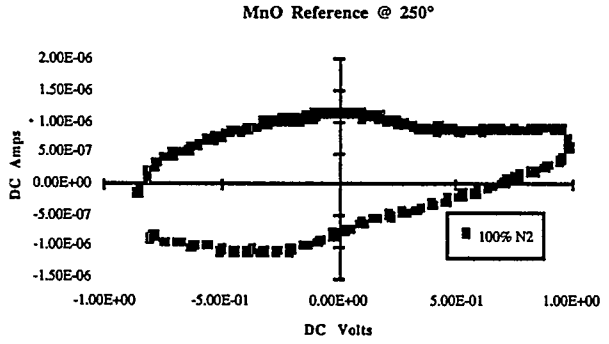

Figure 5. Microsensor response - MnO reference electrode

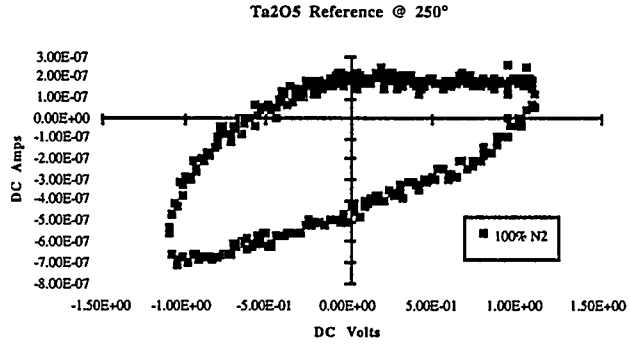

Figure 6. Microsensor response - Ta_2O_5 reference electrode

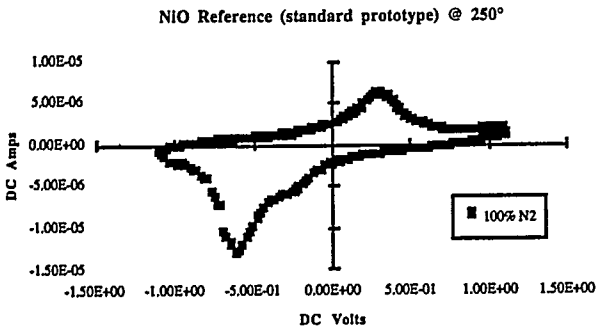

Figure 7. Microsensor response - Pt reference electrode

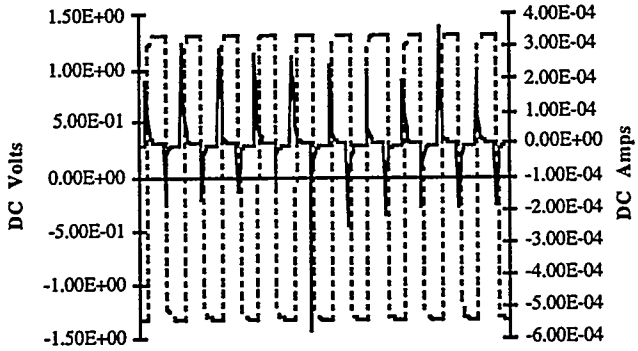

Figure 8. Pulsed voltammetry method.
(current peaks should be equal for each pulse)

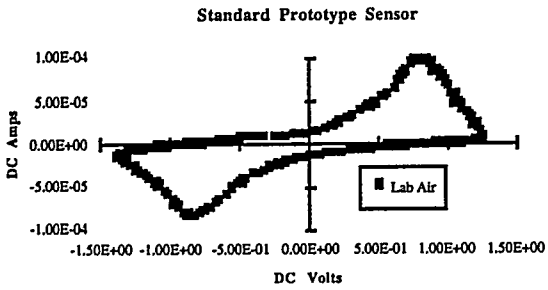

Figure 9. Sinusoidal voltammetry method.

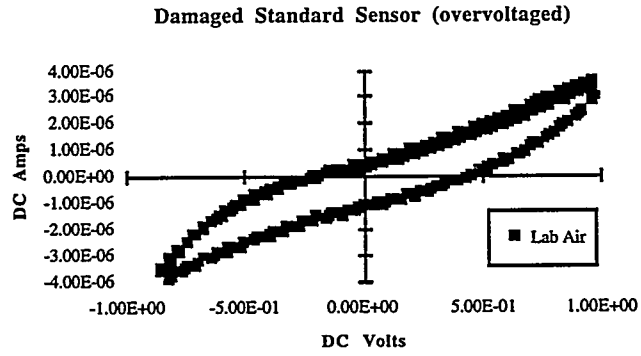

Figure 10. Microsensor response to large applied voltages

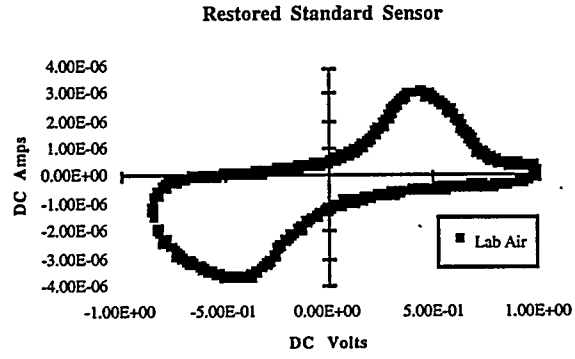

Figure 11. Microsensor response after re-sintering YSZ.

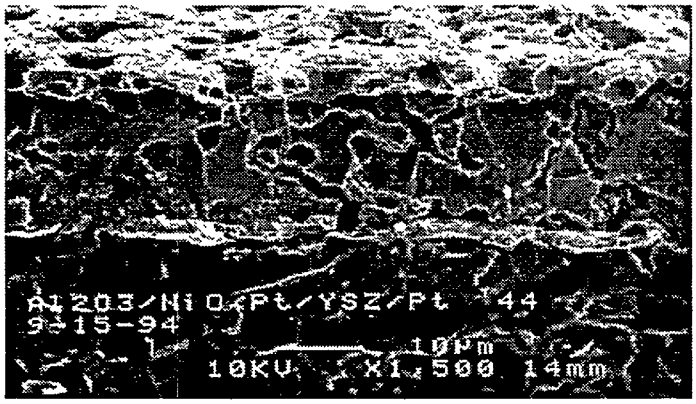

Figure 12. Magnified (1500X) cross section of a microsensor

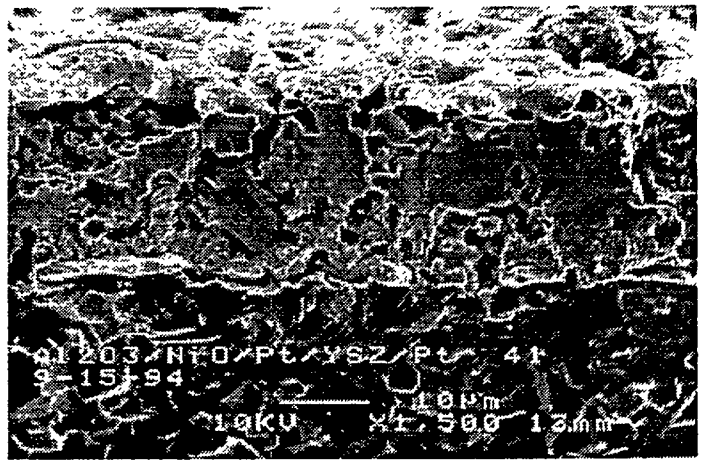

Figure 13. Magnified (1500X) cross section of a microsensor with 25% thicker YSZ layer.

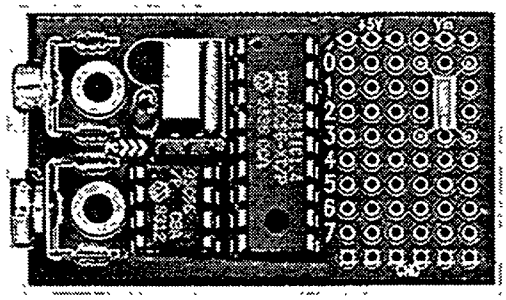

Figure 14, Actual Size of Current Microcontroller and ECG Microsensor

94-182N -- REMOVAL OF CONTAMINANT CU FROM REMELTED STEEL SCRAP

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: M. Blander, Chemical Technology
D. R. Diercks, Energy Technology

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$144.4K
FY 1995	$140.0K
FY 1996	$190.0K

Purpose: The purpose of this science and technology LDRD-funded project is to examine an approach which uses aluminum-sulfide or alumino-silicate based slag for the removal of copper from molten scrap. Copper is a major contaminant of steel scrap, and its presence in steels at levels greater than 0.10 wt.% can adversely affect the mechanical and fabrication properties of the resulting steel. No economically viable process for Cu removal is currently available, and the demand for high quality scrap is increasing as mini-mills expand into the production of high grade steel sheet. The development of a practical method for removing copper from scrap would allow for the use of a significant portion of our nation's uniquely large (about 750 million ton) scrap pool and provide the raw material for expanded domestic production of high quality products such as steel sheet at reduced cost. In addition, the increased use of scrap would result in significant environmental benefits and energy savings.

Approach: Slagging of molten scrap to remove copper would be the method preferred by steel manufacturers because it is consistent with methods used to remove other contaminants. However, the thermodynamics for reactions such as:

$$FeS + 2Cu = Fe + Cu_2S \qquad (1)$$

are not favorable for oxides (K=7.8E-4 at 1600°K) and only slightly favorable for sulfides (K=2.9 at 1600°K). The distribution coefficient for copper between a slag phase and molten steel (in units of (wt% Cu in slag/wt% Cu in steel)) can be written as:

$$L_{Cu} = \frac{W_{Cu^+}}{W_{Cu}} = \frac{X_{Cu^+}}{X_{Cu}} \cdot \kappa = \sqrt{\gamma_{Cu}^2 K_1 \frac{\gamma_{FeS} \cdot X_{FeS}}{\gamma_{Cu_2S}}} \cdot \kappa \qquad (2)$$

where κ is a constant to convert mol.% to wt.%, γ_i is the activity coefficient of element or compound i (e.g., copper, cuprous-sulfide, iron sulfide), X_i is the mole fraction of element or compound i, and K_1 is the equilibrium constant of equation (1). Several factors have small effects on increasing L_{Cu}; however, a decrease in the activity coefficient of cuprous-sulfide has

the potential for a large increase to L_{Cu}. Experimental work in the field of molten salts has shown that the activity coefficients of a given salt can be significantly decreased in binary mixtures, and the change is a function of both relative cation size and charge. The activity coefficient of a given monovalent solute (e.g., Cu^{+}) can be decreased in a binary mixture by increasing the charge and decreasing the cation radius of the solvent. To make cuprous-sulfide more stable relative to ferrous-sulfide, use of a binary slag containing aluminum-sulfide would lower the activity coefficient of cuprous-sulfide. The Cu^{+} ion has a radius of about 0.96Å, Fe^{+2} has a radius of 0.75Å, and Al^{+3} has a radius of 0.45Å.

A natural extension of the above discussion suggests that the use of a solvent with a polyvalent, small radius cation could make the use of an oxide-based slag favorable for the removal of copper from steel. In other words, the use of alumina and silica as a solvent may make the formation of cuprous-oxide more favorable than iron-oxide. In addition, there is a charge compensation effect in silicates in which Al^{+3} ions bond strongly (i.e., forms a complex) with a monovalent cation in the presence of a silicate network in acid solutions. Estimates have been made that indicate the activity coefficient of cuprous-oxide may be quite low. Further complexing by the addition of a complexing anion, such as S^{2-}, to the silicate melt could also help make the oxide slags favorable.

Experiments are designed to systematically study the effects of compounds with polyvalent cations on the removal of copper from molten steel; they are conducted by Adam Cohen, who is a full-time staff employee in the Energy Technology Division and is pursuing a PhD in Material Science on a part-time basis at Northwestern University. The experiments involve heating a crucible with copper-bearing steel and the slag composition of interest to the desired testing temperature and maintaining the temperature until equilibrium between the metal and slag phases is reached, usually with the aid of mechanical agitation. The sulfide slag experiments are run in a controlled, low oxygen environment under an inert gas (argon) atmosphere to minimize the adverse effects of oxygen on the sulfide slagging process. The furnace tube assembly for the alumino-silicate slag experiments is less elaborate because the potential for oxygen contamination does not exist.

Technical Progress and Results: The project builds upon preliminary results obtained by ANL during the U.S. DOE Steel Initiative in 1987 during which a distribution coefficient for copper in a binary Al_2S_3-based slag as high as 31 was found. The use of Al_2S_3-based slags to remove copper from steel was patented in 1990 (U.S. Patent No. 4,925,488). The new work on the sulfide-based slags was designed to eliminate oxygen interference, which likely affected the experiments in 1987. By eliminating oxygen, higher distribution coefficients were theorized.

During the period from March 1994 through December 1994, twenty-one experiments were completed: sixteen using a sulfide-based slag and five using an alumino-silicate based slag. The sulfide-based slag experiments resulted in final copper levels in the steel below 0.1 wt.% for every test and a distribution coefficient for copper as high as 40, which is the highest found to date for a sulfide-slagging system. The results also show that higher oxygen lowers L_{Cu}, consistent with what was theorized from the 1987 experiments. Additional tests are planned for 1995 to better optimize the composition and further improve the distribution coefficient.

Five alumino-silicate based slag experiments have been completed. Thus far, the experiments have not yielded satisfactory results. However, one experiment did result in a distribution coefficient of ~ 0.5. While the copper content was not reduced below 0.1 wt.% and the distribution coefficient is significantly below that necessary for a viable process, it is encouraging to see such a high value for L_{Cu} considering the extremely low equilibrium constant for the ferrous-oxide - cuprous-oxide reaction ($\sim 10^{-4}$). Such a result indicates that the activity coefficient for Cu_2O can be made very low, and the result is enough to warrant further testing of slags designed to further lower the activity coefficient of Cu_2O. Compositions with higher silica contents and with added sulfide should have higher distribution coefficients.

Specific Accomplishments:

1. We have measured the highest distribution coefficients ever found for the extraction of copper from steel (40).

2. We have shown that the activity coefficients of cuprous oxide are very low in acidic aluminosilicate melts and that aluminosilicate melts high in silica content and containing some dissolved sulfides might be suitable for copper removal from steel.

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94-133N -- DYNAMIC LASER CLADDING

Associate Laboratory Director Area: Engineering Research

Principal Investigator: K.H. Leong, Technology Development

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$181.3K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The project was to demonstrate proof of concept of an innovative idea in laser cladding that combines laser and aerosol technology. Success will overcome the constraint of conventional laser cladding technology that requires a horizontal surface for the placement of the clad powder material and advance this manufacturing technology in the application of advanced materials for high temperature, corrosion and wear resistance.

Approach: Laser cladding is a process that is used to deposit a hard and thermal, corrosion or wear resistant alloy layer on a relatively soft substrate. Distortion and thermal damage to the substrate are minimal. The process involves the deposition of a layer of powder on the substrate and the subsequent melting and fusing of the powder with a laser beam. The nature of the process as currently applied constrains the substrate to be in a horizontal position. Consequently, cladding of nonhorizontal surfaces and components cannot be done *in situ*. It should be noted that the availability of high power Nd:YAG lasers with fiberoptic beam delivery removes the constraint on the physical proximity of the laser.

Basically, the concept is to produce a jet of the powder to be cladded and melt the particles in transit with a laser beam that illuminates the jet and the substrate. The molten particles impact on the molten substrate and cladding results. Preliminary computations carried out on beam intensity and time for melting the particles indicate that the concept is feasible.

B. Hunter, Technology Development, carried out the experimental cladding experiments and E. Keppler, Reactor Engineering, prepared the metallurgical samples.

Technical Progress and Results: A powder resuspension system (atomizer) was designed and constructed to deliver the aerosolized powder to a custom-designed beam delivery system. This special delivery system is attached below a faceted transmissive integrator optic that produces a top hat profile beam for cladding. Aerosol enters below the integrator optic and flows down a tube and nozzle assembly concurrent with the propagating high power laser beam. The particles are melted in transit and impact on the substrate that is also illuminated by the laser beam.

Three different powders (boron nitride, glass, and stellite) were used. Glass powders were the most easy to aerosolize; stellite powder tended to clump; the boron nitride was in the form of flakes in paint or paste form and was not aerosolized. Laser cladding was performed with a layer of powder or paint on 3/8" thick 1045 steel plate. Clads obtained provided a baseline for

comparison with clads obtained using aerosolized glass and stellite. The aerosol output using stellite powder was less stable than that using glass. Improvements to the atomizer system are expected to produce a more stable output. A stable output is required for a good clad because the aerosol particles absorb and scatter part of the total laser beam power. A constant power of the beam to the steel plate is essential for a uniform clad surface. Consequently, a more uniform clad layer was obtained with the glass powder.

Figures 1a and 1b are profiles (15x magnification) obtained for glass powder cladded to 1045 steel by placing a layer of the powder on the steel surface and using the aerosol method respectively. The micrographs show the glass layer on top of a laser glazed transformed steel underneath and the parent steel substrate. The clad and glazed and heat treated layer exhibit the fine microstructure typical of laser cladding. Closeups of the region around the cladding showed excellent alloying of the two materials for both methods. No porosities were present. Figure 1c is a 130x magnification of a corner of the cladding obtained by the aerosol method showing the good quality of the clad.

Figures 2a and 2b are for the case of stellite with the latter using the aerosol method. Uniformity with the aerosol method is not good because of the problem in generating a stable aerosol. The etching method used to bring out the grain size was for steel and hence, do not show the grain structure of the stellite very well. Figure 2c (260x magnification) is a higher magnification of the right side of the clad in figure 2b. It shows good adhesion, penetration of the stellite into the cracked steel surfaces and no porosities.

Less success was obtained with the boron nitride paint, as shown in figure 3a and 3b (15x and 65x magnification). The boron nitride is a thermal insulator and thick coatings tend to give poor results. It was difficult to produce an optimal layer to result in good cladding. Other investigators have improved boron nitride clads by remelting resulting in lower porosity. It was not feasible to aerosolize the flaky boron nitride.

Specific Accomplishments: Dynamic laser cladding using an aerosol method was demonstrated. Refinement of the technique would produce more uniformed cladding and advance laser cladding technology in that cladding on a component for production or repair could be achieved in any orientation.

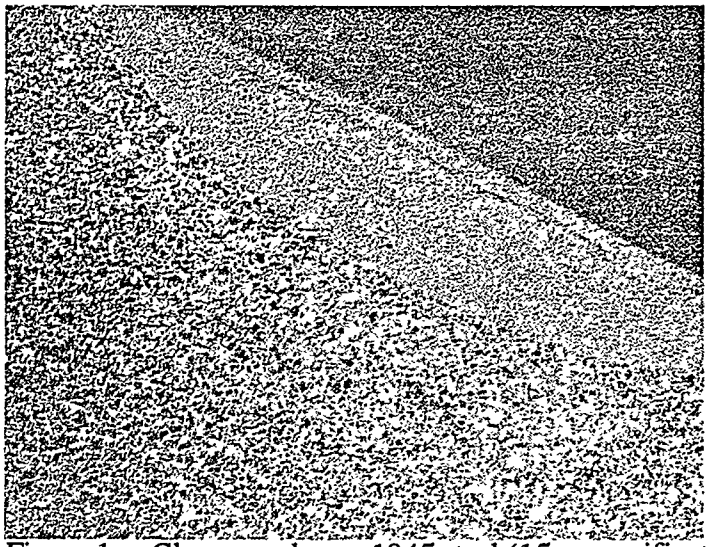

Figure 1a: Glass powder on 1045 steel (15x magnification). The glass was applied as a thin layer.

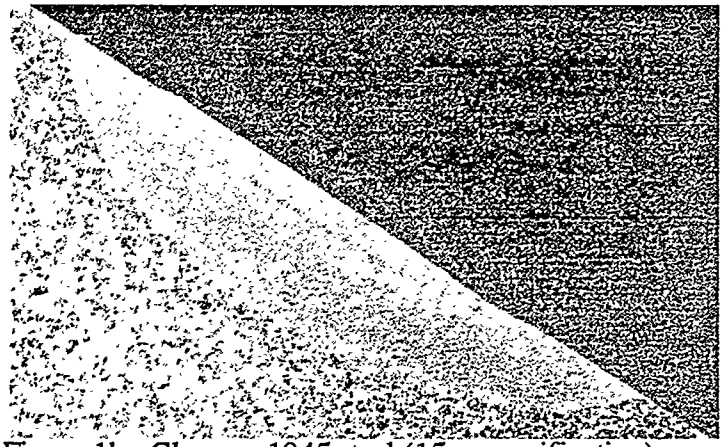

Figure 1b: Glass on 1045 steel (15x magnification). The glass was applied as an aerosol.

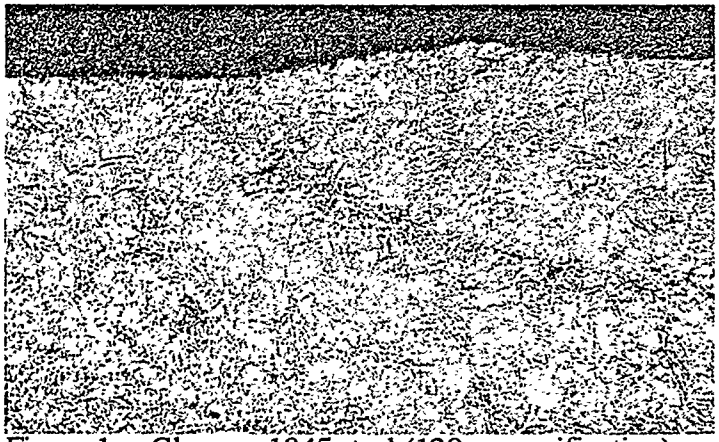

Figure 1c: Glass on 1045 steel (130x magnification). Closer view of Figure 1b.

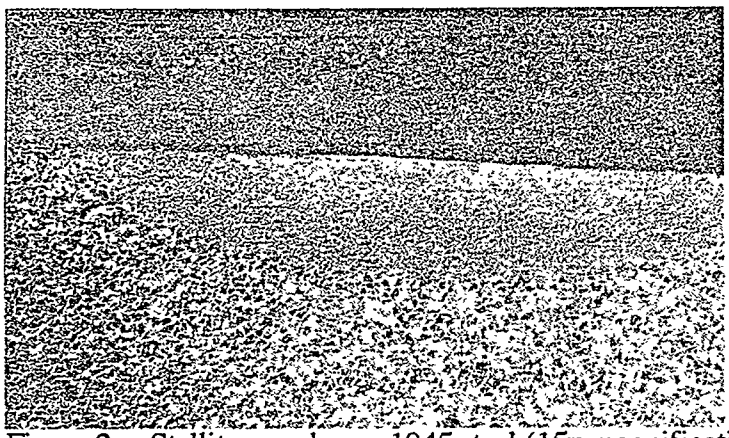

Figure 2a: Stellite powder on 1045 steel (15x magnification). The stellite was applied as a thin powder.

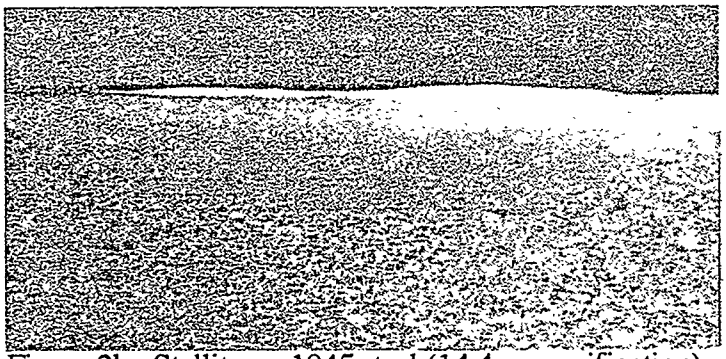

Figure 2b: Stellite on 1045 steel (14.4x magnification). The stellite was applied as an aerosol.

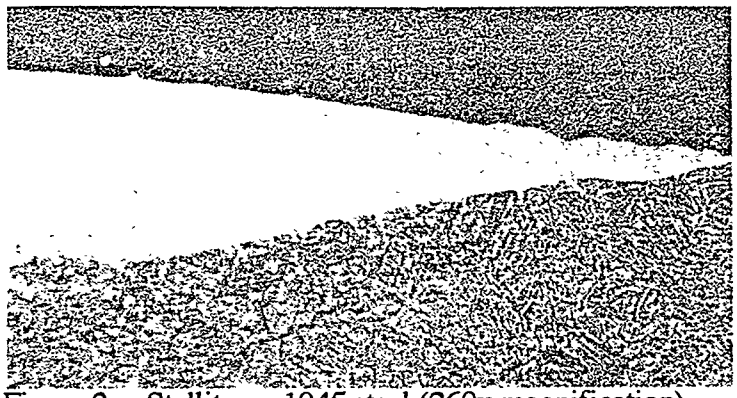

Figure 2c: Stellite on 1045 steel (260x magnification). Closer view of Figure 2b.

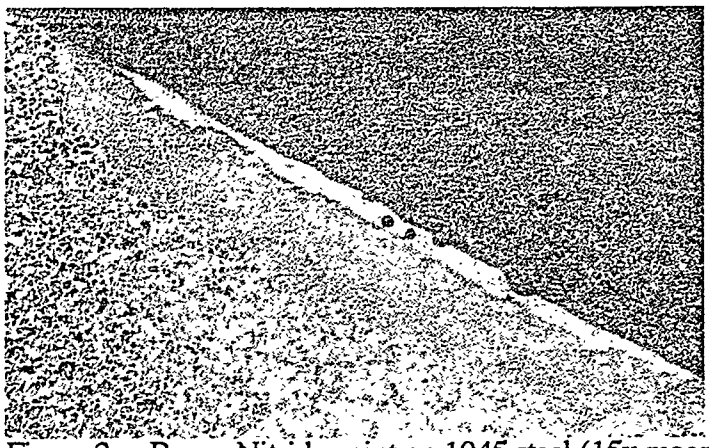

Figure 3a: Boron Nitride paint on 1045 steel (15x magnification).

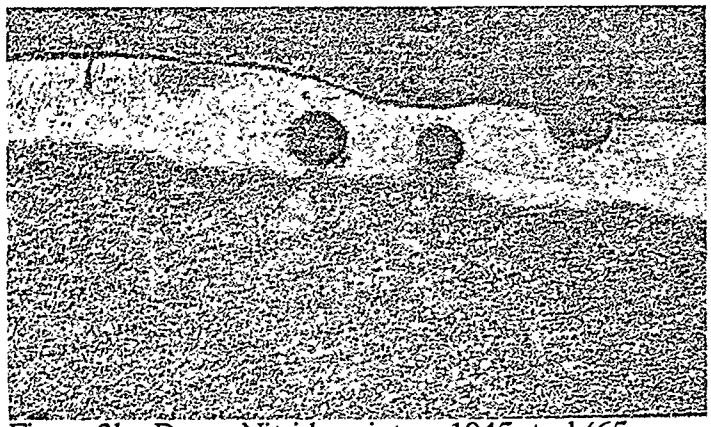

Figure 3b: Boron Nitride apint on 1045 steel (65x magnification).
Closer view of Figure 3a.

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94-047N -- 2D/3D/HOLOGRAPHIC IMAGES AND VIRTUAL REALITY PROJECTIONS FOR CONTROL ROOM/SIMULATOR DESIGN

Associate Laboratory Director Area: Engineering Research

Principle Investigators: S. A. Brown-VanHoozer and R. W. King, Integral Fast Reactor Operations

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$179.8K
FY 1995	$200.0K
FY 1996	$250.0K

Purpose: It has been hypothesized that a virtual reality system can be used to visualize inherently complex dynamic structures, processes, and human related behavior. The study tested this hypothesis. The feasibility and practicality of using two and three dimensional images with virtual reality (VR) modeling for presenting information in a training and operational environment was determined.

Approach: The project was divided into three stages: development of a model for a VR environment, projection of a realistic, dynamic model in VR format, and user evaluation of the VR model.

The test model chosen for the project was a three dimensional (Ideas/AutoCAD) model of the EBR-II primary components. It was developed by Linda Hansen and Chuck Wiegand of ANL-W. The AutoCAD files were converted to a file format that was compatible for virtual reality projection by the University of Illinois-Chicago. All files were eventually transferred to the Math and Computer Science Division at ANL-E when their VR-CAVE was installed.

The VR image was developed on a Silicon Graphics Interface and projected into what is known as a CAVE environment by an ONXY computer. The CAVE is a 10ft x 10ft x 10ft projection-based environment that surrounds the viewer with four screens, three rear-projection screens for walls and a down-projection screen for the floor. A head tracking device is attached to the viewer and as the viewer moves inside the CAVE, the correct perspective and stereo projections are calculated for each wall. A hand-held wand provides the human-interaction with virtual environment.

Conversion of AutoCAD files to the appropriate CAVE simulation files required special software. Randy Hudson of UIC/ANL-E and Nihar Gokhale of ANL-E were the VR programmers of this project.

In stage two, the model was refined from the original AutoCAD files so that the image more closely resembled the EBR-II primary tank, primary vessel and fuel handling components, and demonstrated dynamic movement of the fuel handling system.

In stage three of the project, a human factor's study was designed for nine EBR-II operators to evaluate the EBR-II VR model.

Technical Progress and Results: Three of the four basic virtual reality areas were implemented into the design of the EBR-II VR model: a static computer-generated world of a CAD model, simple dynamics of the physical properties of the model, and simplistic behavioral control of the objects.

Dynamic movement of the fuel handling equipment and simulated lighting effects were added to the model. This provided a more realistic metallic visual effect and depth perception of the equipment displayed in the model. The fuel-handling dynamics were activated by a menu selection, e.g., rotation of transfer arm through a 180-degree arc; full transfer sequence of core-to-basket.

Transparency was incorporated into the model which allowed the user to see the primary tank without the tank occluding the internal components of the reactor.

Selective culling of scene elements was used to make the primary tank and neutron shield disappear entirely, and "control of rendering mode" allowed the control of the model of rendering of individual reactor components.

Sound was programmed for effect, however, due to an update on the ONXY system configuration, this aspect was never assimilated into the model. Another aspect that was considered for the model was radiosity. UIC had attempted to integrate this element into the model in order to provide a more detail surface lighting effect; however, shortage of staff delayed this implementation.

A final outcome of the project was the possibility of further research through the support and interest of commercial utilities, instrumentation and control enterprises, education, and medical.

Specific Accomplishments: The EBR-II VR model can be displayed in the CAVE environment using a version of the CAVE software that incorporates the Performer software, which is used to model the VR images. The components are dynamic with realistic metallic effect. With the use of a hand-held wand, one can navigate anywhere in the VR model, rotate and move the transfer arm, storage basket, hold down mechanism and gripper, and rotate the entire reactor about its vertical axis so that the image can be viewed from all sides.

An informal human-interactive VR study evaluation was conducted, which involved two former EBR-II operators. The result was very positive and informative with respect to training and operational applications. It was concluded that a more in-depth and formal study was required and will be pursued in FY 1995.

The annual SIGGRAPH conference was attended which involved hands on experience of the different levels of virtual reality systems, e.g., 3D/stere-optic visual monitors, head-mount displays, CAVEs, and so forth.

A final demonstration of the project was given in September of 1994 at ANL-W in Building 221, that showed the level of achievement of the VR model. The demonstration was conducted in two sessions. Approximately twenty people (scientists and engineers) attended the two sessions. A contact was established with Westinghouse-Hanford, who expressed strong interest in the outcome of this project for training applications at Hanford.

A paper has been submitted for the 1995 British Nuclear Energy Society Conference on Fuel Handling Management, on the findings of the informal study with respect to virtual reality models and user interaction. Two other papers are being submitted for scientific publication and proceedings on the overall project.

What was concluded from this project is that the VR-CAVE environment is practical for in-depth training, research and development of two and three dimensional models and human-interaction of advanced visual technology.

The replacement of models by the routine translation of 3D-CAD drawings of a design into VR projections is possible, however, because of the level of detail in the 3D-CAD drawings, VR-CAVE modeling is not practical for routine design of systems with today's computing capacity. Nor, is it practical in an operational environment. However, as future advances are made in the hardware and software VR-application could become a more viable way for routine design of any system.

Three-dimensional modeling has immediate usefulness in engineering design evaluations and for training and operational evaluation.

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94-054N -- LARGE-SCALE WAVELET-BASED SIGNAL PROCESSING

Associate Laboratory Director Area: Physical Research

Principal Investigators: M. K. Kwong and P. T. P. Tang, Mathematics & Computer Science

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$160.6K
FY 1995	$160.0K
FY 1996	$ -0-

Purpose: The project objective is to explore the application of wavelet techniques in large-scale signal processing, with the goal of devising new motion estimation and video and image compression algorithms and implementing them on high-performance computer architectures. Successful demonstration of these techniques would contribute, in particular, to the advancement of high-definition television technology, scientific computation, and medical imaging.

Approach: Large-scale signal processing--for example, in HDTV technology, postprocessing of large-scale scientific computation, and advanced medical imaging--requires the computing power of the most advanced computers. Known algorithms are either too slow or too inaccurate to compress data effectively, either in the spatial domain by transform coding, or in the temporal domain by motion estimation. To address these limitations, we are combining the new and exciting field of wavelets with our experience in applied mathematics and parallel computing to devise more efficient algorithms that increase the speed and quality of video and image compression and enhancement. A longer-term goal is to build a parallel wavelet library for image processing on high-performance computer architectures, in particular, on the IBM SP1 massively parallel machine.

The project methodology involves design of parallel wavelet-based algorithms and multiresolution motion-estimation techniques to enhance compression. Additionally, a study of dyadic wavelet decomposition and histogram analysis of MRI images has been initiated (with B. Lin), with the objective of improving data archiving with feature-based indexing.

The project has involved contact and collaboration with various universities and industry, including Professor M. Giger and Dr. Hiro Yosida (University of Chicago Radiology Department, on medical imaging), Professor Tom Bielecki and Professor Stephen S. T. Yau (University of Illinois Mathematics Department, on denoising and enhancement), P. T. Peter Tang (on sabbatical at the Chinese University of Hong Kong Mathematics Department, on image compression), Herb Taylor (David Sarnoff Research Laboratory, on HDTV codes), and Peter Heller (Aware Ltd., on image compression and PDEs).

Technical Progress and Results: Several accomplishments can be reported. We developed a new concept, called W-matrices, that generalizes discrete wavelet transforms. Unlike classical wavelet theory, our approach allows much more freedom--nonorthogonality and nonuniformity--thus leading to new and better transforms. Moreover, the algorithm is easy to implement and, because it uses only matrix theory for most parts, it is easy to understand.

We then used this concept of W-matrices to design a nonorthogonal multiresolution analysis (MA) technique, called quadratic spline MA. The new technique handles signals of even or odd length (classical transforms can handle even-length signals without introducing unnatural artifacts) and provides good signal compression. Additionally, it outperforms existing transforms for compressing reasonably smooth signals and images.

To enable researchers to apply the new MA to a wide variety of image-processing applications, we implemented the new algorithms and developed a user-friendly software environment. The environment includes an integrated numerical capability and tools for personally tailoring the environment to individual needs.

A working prototype code for parallel video compression has been developed and successfully run on the SP1. The next stage in this work will be devoted to improving the speed of execution.

Specific Accomplishments:

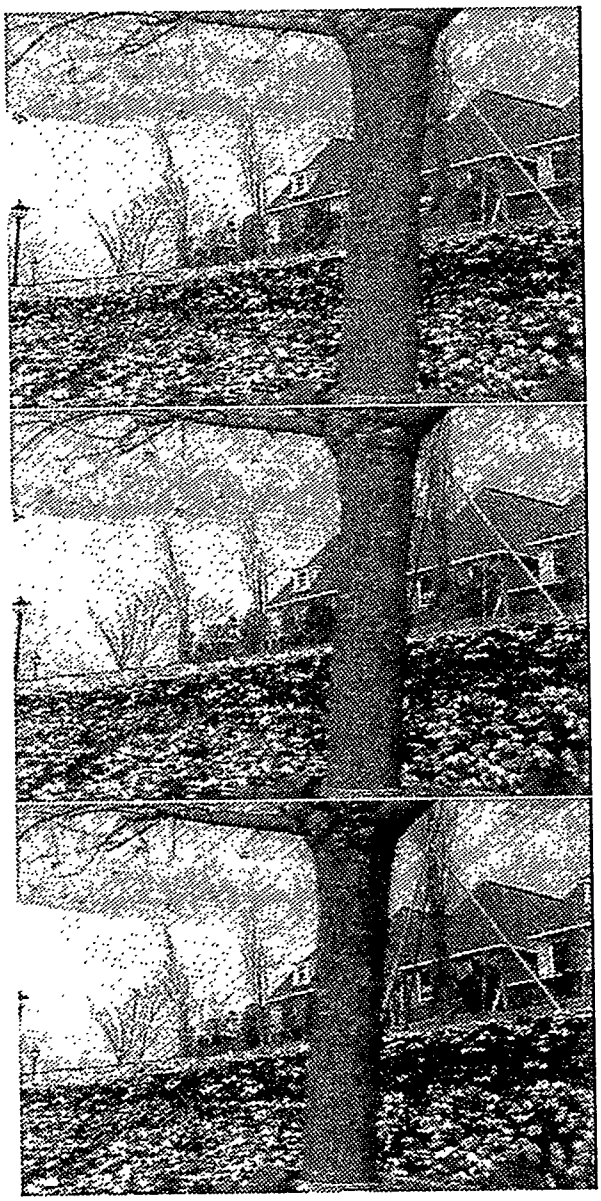
Preprints:
M. K. Kwong and P. T. P. Tang, "W-Matrices, Nonorthogonal Multiresolution Analysis, and Finite Signals of Arbitrary Length," MCS-P449-0794.

M. K. Kwong, "MATLAB Implementation of W-Matrix Multiresolution Analyses," MCS-P462-0894.

Conference Organization and Proceedings Editor:
Workshop on "Gigabyte Image Processing and Visualization -- Challenges and Opportunities," Argonne, Ill. (July 1994).

SIAM/ICIAM minisymposium on "Wavelets and PDEs," San Diego, Calif. (August 1994).

Large-Scale Processing and Compression of Time Sequence of Images



The standard for encoding motion pictures is MPEG II. It makes use of:

- RGB to YUV, UV subsampling
- Discrete cosine transform
- Motion compensation
- Run-length compression
- Variable length (Huffman) coding

Real-time software encoding is still not within reach. Our objective is to tackle the even harder problem of 3D time sequence encoding/decoding. We propose a massively parallel implementation of the encoding and decoding algorithms based on a dispatcher-processor-collector model. We have started to build our programs on the IBM SP1, using the following facilities:

- Parallel programming tools – p4 and Chameleon
- 128 SP1 nodes available
- Message passing using high speed switch, EUI, and EUI-H
- Fiber channels
- HIPPI channel
- Frame buffer
- Scalable I/O project (future)

The above pictures are frames # 0, 2, and 5 in the MPEG-coded sequence titled "Flower Garden". The pictures were produced from a coded input bit-stream using a parallel program running on the SP1, and displayed on a high resolution graphics terminal using a frame buffer.

M.K. Kwong, Peter P.T. Tang
MCS, Argonne National Laboratory

94-190N -- INTEGRATING MULTIMEDIA WITH HIGH-PERFORMANCE COMPUTING AND COMMUNICATIONS

Associate Laboratory Director Area: Physical Research

Principal Investigator: R. Stevens, Mathematics and Computer Science

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$158.9K
FY 1995	$150.0K
FY 1996	$150.0K

Purpose: The project objective is to explore the close coupling of multimedia technology (images, sound, and text) and high-performance computing architectures and applications. By enabling systems such as the IBM SP to process voice and image data along with scientific data resulting from computations, we hope not only to expand the types of applications suitable for parallel computing (e.g., digital libraries) but also to facilitate the use of modern interface technology for those using the SP system for scientific applications (e.g., coupling animation and voice annotation with scientific data sets).

Approach: Current parallel supercomputer systems like the IBM SP are well suited for "traditional" scientific computing (i.e., rapidly evolving a simulation described by a set of numerical partial differential equations forward in time and periodically capturing the state of the system). Future uses of supercomputers will include not only numerical computations but also the reduction of output data to meaningful statements about reality (virtual or otherwise). Specifically, in the future one would like to use the supercomputer as a general-purpose tool for computational science, including the use of the system for supporting visualization, collaborative development of systems, collaborative exploration and analysis of experimental and computational data, and the storage and archiving of such data and collaborative experiences. These uses of massively parallel processing systems require additional hardware and software support. One of the purposes of this project is to evaluate ways of expanding the capabilities of the IBM SP system.

The project involves exploration and development of the features and architectures needed to support digital libraries and interactive multimedia use of parallel supercomputers. Six subprojects are being investigated: audio/video storage and retrieval, support for parallel image processing and analysis, support for remote visualization via high-speed fiber channel networks, development and testing of a multimedia node concept for future IBM SP systems, demonstration of multimedia to enhance scientific applications, and demonstration of integration of wireless communications technology with high-performance computing and communications. It is anticipated that one of the outcomes of this project will include software and architectures that will enable Argonne to successfully compete for federally supported work on the National Information Infrastructure.

Technical Progress and Results: As part of an effort to evaluate the use of scalable parallel systems for the integration of multimedia and supercomputing we have:

- Developed a multimedia research laboratory space in the Mathematics and Computer Science division, building 221
- Configured into the Multimedia Laboratory a 12 node SP2 complex with ATM, HIPPI, and audio/video adapters, installed 3 IBM 41T workstations with ATM and audio/video adapters and installed wide variety of consumer-grade audio and video source, display, and editing gear. (note the IBM hardware is on loan from IBM for this project). The multimedia laboratory will allow a variety of experiments to be conducted that were not possible before at ANL.
- Installed loaner Synoptics ATM switch, an important strategy for the multimedia supercomputing project is the integration of ATM technology. The Synoptics switch has enabled us to test various networking configurations and to measure video and audio bandwidth requirements. Video tests have sustained over 40 Mb/s for 24 hours over this early switching hardware.
- Demonstrated video tunneling over Ethernet and ATM networks, thereby allowing comparisons between the network media and the effects of hardware video compression---A major task in the multimedia supercomputing project is the development of a multistream archiver capable of supporting recording and playback of multimedia data from a variety of sources. The video tunnel is the first type of point-to-point video server the project has developed. This tunnel technology has allowed us to test various server designs.
- Demonstrated video tunneling from the CAVE environment to the multimedia laboratory --- We have demonstrated the ability to integrate CAVE visuals into the video archiving process and have demonstrated this tunneling between the CAVE lab in the Mathematics and Computer Science division to the multimedia laboratory.
- Demonstrated use of SP2 as a backend computational engine for the CAVE environment using HIPPI connectivity to the CAVE---A crucial task in the project is to link the CAVE virtual environment to the IBM supercomputer. This was demonstrated in June 1994 and is being used in a number of applications projects currently under development at ANL.
- Performed early experiments with the SP2 as a video archive machine--- Early work has been demonstrated on the SP2 showing that the SP2 parallel disk structure can be used to support a multistream video archiver.

Specific Accomplishments:

"Multimedia Supercomputing: Science Television," Mardi Gras '94 Teraflop Computing Conference, February 10-12, 1994.

"Integrating Multimedia, Virtual Environments and High-Performance Computing," High-Performance Distributed Computing Conference, Invited Lecture, August 1994.

"LabSpace: Building the Electronic National Laboratory," a proposal submitted to DOE-ER call for proposals to build Distributed Collaborative Environments, September 26, 1994.

"LabSapce: Building the Electronic National Laboratory," presentation given to ATT, IBM, Northern Telecom, and DOE-DCCE, Sept.-Oct. 1994.

94-194N -- DEVELOPMENT OF NUMERICAL CODES TO CALCULATE ELECTRONIC STRUCTURES FOR MOLECULES OF BIOLOGICAL INTEREST

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: M. Inokuti, M. A. Dillon, and M. Kimura, Environmental Research

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$125.1K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The project is to develop numerical techniques for calculating the electronic properties of components of DNA and RNA. The immediate objective is to use the new techniques to calculate the wave functions and electron collision cross sections of two DNA bases. Our ultimate aim is to combine theoretical approaches, use the combination to characterize energy absorption from energetic electrons by nine key components of DNA and RNA (adenine, cytosine, guanine, thymine, uracil, metaphosphoric acid, 2-methyltetrahydro-3-furanol, 2-methyltetrahydrofuran, and orthophosphoric acid), and validate the results by comparison with experimental data. The resulting knowledge will be valuable in two ways. First, electronic excitation and ionization cross sections computed for each component of DNA can be used to model the sublethal damages caused by site-specific absorption of high-energy radiation, such as base deletion and bridge formation. Second, knowledge of the cross sections of the nine key components will enable us to construct the cross sections for electronic excitation and ionization of the nucleotides and subsequently of DNA and RNA. Knowledge of the cross sections for interactions of electrons with DNA is necessary if we are to understand the direct action of ionizing radiation, as opposed to indirect action mediated by hydroxyl radicals produced in the water sheath surrounding the nucleus. The project work will fill a serious gap in basic knowledge needed to quantify the role of direct action of ionizing radiation on DNA. This is a step needed for modeling effects such as radiation-induced carcinogenesis and cell death, which are key endpoints in the assessment of radiation risk, both at low doses to the public due to nuclear and other technologies and also at high therapeutic doses.

Approach: This project requires the use of two computational techniques that largely complement each other: a) for treating the ground state and lower excited states of molecules described earlier we develop an *ab initio* approach call the *multireference single and double configuration interaction* (MRD-CI) method. This technique will enable us to keep a close check on the accuracy of the energy eigenvalues and the wavefunctions generated in subsequent calculations. b) For treating the entire range of energies, including highly excited and ionized states, we propose to apply a method within the Hartree-Fock framework called the *multiple scattering* (MS) method. This procedure has proven to be extraordinarily efficient and powerful for computing the electronic properties of large molecules and clusters, far more inclusive than the traditional *ab initio* approaches, and has been applied to condensed matter. The MS method

can be applied easily and with high precision to discrete bound-state calculations of the molecules and possibly to the nucleotides themselves. More importantly, a natural extension of the calculation is the generation of continuum states required to calculate ionization cross sections [in *the continuum multiple scattering* (CMS) method].

Technical Progress and Results: The computer program of the MRD-CI method was successfully converted for the VAX version so that we could run the code by using our local workstation or even a PC locally. This was the major task for earlier months of FY 1994. Test runs for determining energy levels for simple molecules such as C_2H_2, C_2H_4, and C_3H_8 were successfully carried out and the results were found to agree within four significant figures in comparison to these data previously determined by using a different version of the code on a super computer CRAY.

The computer program based on the MS method was also converted to the VAX version for the use locally. Test calculations were again conducted for a variety of simple molecules to ensure that the conversion was correctly achieved and the machinery we plan to use provides sufficient numerical precisions for our purpose. The test results were satisfactory and we feel comfortable that our goals in these respects are met at this stage.

We initiated calculations for determining electronic levels for adenine and guanine using the MS method on our PC. In addition, we initiated compilation of data based on electron scattering and photon absorption experiments in conjunction with theoretical activities described above.

Specific Accomplishments: The programmings based on the MRD-CI and MS methods for a local VAX and PC were successfully carried out and from test runs, we believe that we established capabilities of our computations based on these methods locally.

Initial attempts to calculate electronic levels for adenine and guanine are underway in conjunction with our effort of compilation and construction of cross section data based on electron scattering and photon absorption experiments.

93-097R1 -- THE ROLE OF 3D MOLECULAR STRUCTURE IN ENERGY TRANSDUCTION AS PROBED WITH SITE DIRECTED MUTAGENESIS

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: J. R. Norris, Chemistry Division
D. K. Hanson, Center for Mechanistic Biology and Biotechnology

Funding Profile:

FY 1992	$ -0-
FY 1993	$ 18.0K
FY 1994	$ 14.4K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The objective of this project is to use genetically modified protein reaction centers to explore the relationship between 3D molecular structure and the energetics of biochemical and chemical reactions. In particular this work explores the control of the chemical free energy in biochemical and chemical reactions as the result of modifying one or two solvent molecules in the vicinity of a reactive species. Such studies are unique and are only possible with the reaction center protein found in photosynthetic bacteria. The anticipated outcomes are manifold, including a better understanding of natural and artificial photosynthesis as well as a new method to fine tune chemical reactivity with solvent molecules.

Approach: The photosynthetic reaction center protein has been widely studied because of its importance in understanding the photosynthetic process. However, because the photosynthetic reaction-center protein contains a pseudo C_2 axis of symmetry and because it can be manipulated by site-directed mutagenesis, the reaction center offers unique experimental opportunities for examining the extent and the mechanism of inert 'solvent' participation in a chemical or biological reaction. The chemical reaction explored in our work is simply the removal, by chemical oxidation in the dark, of one electron from the special pair of bacteriochlorophylls that constitute the primary donor of bacterial photosynthesis. The free energy of this chemical reaction, measured via its one electron reduction potential $E_{1/2}$ is modified by changing amino acid groups near the special pair.

Technical Progress and Results: We have developed a simple model of the reduction potential that describes the effect of amino acid substitutions on the reduction potential of the special pair. The modified reaction centers were constructed by site-directed mutagenesis at ANL and purified by a technician at the University of Chicago. Our procedure provides an improved method to measure reduction potential in these membrane proteins. But more importantly, our simple and systematic model for the reduction potential suggests that solvent effects on redox properties can, in general, be predicted and that they result from accumulative "solvent" effects that can be quantified by our procedure. This method based on C_2 symmetry and genetic manipulation appears promising for studies of other reactions and should have implications for chemistry in general. Future work will be necessary to establish the detailed nature of the correlation between amino acid and redox potential.

Specific Accomplishments: Table 1 summarizes the six amino acids analyzed to date. In addition to F, H, T and Y, K (lysine) and E (glutamic acid) have been measured. However the E(K) and E(E) have not been verified by additional combinations containing K or E and thus serve as predictions only. The T_L-T_M value is based on a protein in which a third amino was also modified. A simple trend is observed for the reduction potential modifications listed in the table. The effect of the amino acids reflects the polarizability and polar nature of the interacting solvent group. Highly polar or polarizable amino acids stabilize the cation while less polar or polarizable ones destabilize the cation.

Table 1. Special pair reduction potential modifications

Amino Acid	Reduction Potential Change (meV)
E(F) -E(F) Phenylalanine	0 ±5
E(T) -E(F) Threonine	-6 ±5
E(K) -E(F) Lysine	+3 ± 5
E(E) -E(F) Glutamic Acid	-21 ± 10
E(Y) -E(F) Tyrosine	-27 ± 10
E(H) -E(F) Histidine	-44 ± 10

where E(F) = +11.9 and E and K have been observed in only one combination each.

Publications

Y. Jia, T. J. DiMagno, C.-K. Chan, Z. Wang, M. S. Popov, M. Du, D. K. Hanson, M. Schiffer, J. Norris and G. R. Fleming, "Primary charge separation in nutant reaction centers of Rb. capsulatus," *J. Phys. Chem.* **97**, 13180-13191 (1993).

Z. Wang, R. M. Pearlstein, Y. Jia, G. R. Fleming and J. R. Norris, "Inhomogeneous electron transfer kinetics in reaction centers of bacterial photosynthesis," *Chemical Physics* **176**, 421-425 (1993).

92-180R2 -- MOLECULAR BIOLOGY AND BIOTECHNOLOGY OF HYPERTHERMOPHILIC ORGANISMS: THE CHAPERONE RELEASE FACTOR

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigator: Jonathan D. Trent, Center for Mechanistic Biology and Biotechnology

Funding Profile:

FY 1992 $ 47.5K (start July 1992)
FY 1993 $337.7K
FY 1994 $296.0K
FY 1995 $105.0K
FY 1996 $ -0-

Purpose: The long-term research goal of the hyperthermophilic research group is to understand the molecular basis of hyperthermophily, i.e. the molecular adaptations that hyperthermophilic organisms have evolved to be able to thrive at temperatures above 80°C. Our intention is to use this knowledge to ply problems in biotechnology, using either the hyperthermophiles themselves or their unique biomolecules. We anticipate that an understanding of the intrinsic properties of hyperthermophilic macromolecules, the extrinsic factors within the cell that help impart thermostability, and the adaptations of cellular processes that allow them to function at high temperatures will have a significant impact in biotechnology. This is not a completely new idea. Some thermostable enzymes, for example, are already in use in industrial processes and are being widely considered for new applications in both the enzyme and pharmaceutical industries. Beyond this limited use, knowing the range of thermostable enzymes available in nature, the properties that make them intrinsically thermostability and the cellular factors that contribute to their stability will greatly expand the horizons of biotechnology. In addition, researchers in structural biology, the Center for Mechanistic Biology and Biotechnology (CMB), and other divisions are interested in exploring the potential of hyperthermophilic macromolecules.

LDRD funds have been used to develop methods for understanding the function of the hyperthermophilic chaperone in folding and stabilizing enzymes and for searching for other protein factors that may be critical for its function. In all organisms "molecular chaperones" are influencing the solubility and proper folding of proteins. While it is known that many proteins correctly fold spontaneously in vitro, there is mounting evidence that this process requires the intervention of molecular chaperones in vivo. We have discovered a hyperthermophilic chaperone and we are convinced that understanding its function will provide important insights in both basic and applied science. Using what is known about chaperones from other organisms we are trying to find the necessary components of the archaeal system.

Approach: The necessary first step to be able to study molecular chaperones or any aspect of hyperthermophilic organisms, is to be able to grow large quantities of these organisms to provide sufficient quantities of protein for biochemical investigations. Techniques have been established for purifying large quantities of chaperone proteins to homogeneity and this purified material was used to make 'affinity' columns. Basically, these affinity columns contained chaperone bound

to a matrix and by passing total cellular proteins over these columns factors that associate with the chaperone were isolated. These factors were analyzed by polyacrylamide gel electrophoresis and partially sequenced. These sequences were used to screen for their corresponding genes by polymerase chain reaction (PCR) techniques.

Technical Progress and Results: Significant progress has been made in all of the chaperone research, despite significant set-backs in our culturing facility. Using small-scale culturing methods, we have improved our cell yields and increasing growth rates of our test hyperthermophilic organism. The construction of a prototype, low-cost, 20 liter culture vessel gave excellent yields and a scale-up version of 150 liter was constructed in May 1994. Unfortunately, we have been forced to cope with long logistical delays.

Despite these delays, we have produced enough cell material to make significant progress with both our chaperone and thermophilic enzyme projects. The columns have been made and two chaperone binding proteins have been isolated. Partial amino acid sequence was obtained and cloning the respective genes is underway.

Specific Accomplishments:

Publications:

Trent, J.D., M. Gabrielsen, B. Jensen, J. Neuhard, and J. Olsen, "Acquired Thermotolerance and Heat Shock Proteins in Thermophiles from the Three Phylogenetic Domains," *Journal of Bacteriology*, *176*:6148-6152 (1994).

Manuscripts in Preparation:

Trent, J.D., R. de Salvo, and R.W. Georgantus, "A Large Volume, Low Cost, Glass-Lined Culturing System," to be submitted to *Biotechnology and Bioengineering*.

Kagawa, H., J. Osipiuk, N. Maltsev, R. Overbeek and J. D. Trent, "A Second Heat Shock Protein in a Hypthermophilic Archaeon Defines the Ancestors to the Eukaryotic Chaperonins," to be submitted to *Cell*.

Quaite-Randall, E., J.D. Trent, A. Joachimiak, "The Role of Conformational Changes to the Function of the Archaeal/Eukaryotic Chaperonin," to be submitted to *Science*.

93-090R1 -- ADVANDED MOLECULAR DYNAMICS METHODS, PROTEIN FOLDING SIMULATIONS AND CRYSTALLOGRAPHIC STRUCTURE REFINEMENT

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principle Investigator: P. A. Bash, Center for Mechanistic Biology and Biotechnology

Funding Profile:

FY 1992 $ -0-
FY 1993 $284.8K
FY 1994 $270.8K
FY 1995 $165.0K
FY 1996 $ -0-

Purpose: The purpose of this program is to develop and utilize theoretical/compu-tational methods to characterize the atomic and electronic events associated with enzyme reaction mechanisms. Applications of this methodology will focus on understanding the basic physical-chemical aspects of enzymes, and provide a practical interface to genetic engineering experiments for the design of enzymes with novel catalytic properties. This Computational Structural Biology Program will interface with the following ANL projects (1) the High Performance Computing Center, (2) the APS and (3) the Structural Biology Center.

Approach: This project is motivated by the Advanced Photon Source (APS) and the High Performance Computing capabilities that exist at Argonne National Laboratory. The APS will provide an evolutionary advance in the ability to determine the atomic structures of biological macromolecules as well as a revolutionary capability to investigate the dynamic behavior of proteins in atomic detail. When the APS comes on-line, time resolved crystallographic experiments will be carried out to depict structural events that occur during an enzyme reaction. This structural data is necessary but insufficient to completely understand all the structural and electronic processes that occur during the bond making/breaking events that define an enzyme reaction mechanism. To study these important processes, methods that rely only on first principles from chemistry and physics must be implemented and utilized. During the next 2-3 years, Argonne's High Performance Computing Center (HPCC) will scale to Teraflops capability. The enzyme mechanism theoretical program will interface with APS protein crystallographic experiments by utilizing derived structural data as a basis for computer simulations optimized to run on the HPCC's parallel computers consisting of hundreds computational units.

The combination of advanced quantum physics and chemistry methods, efficient numerical and computational algorithms, and the most advanced computers will enable the study, through computer simulation, of the essential elements of any enzyme reaction whose structure is known in atomic detail. These methods, which are designed to simulate the mechanisms of enzymes, will have chemical accuracy (1-2 kcal/mol) for the characterization of (1) relative energetics for alternative reaction mechanisms, (2) energetic effects on the absolute enzyme reaction mechanism due to the solvent environment of the surrounding protein, and (3) the effects of site-

specific amino acid substitutions for enzyme redesign. We have applied our methodology to characterize the mechanism of the enzyme reaction in malate dehydrogenase, which is an essential enzyme in the citric acid cycle.

The goal of this project is to develop methods and associated computer code to simulate the structural and energetic events that characterize enzyme reactions. The methods utilized combine (1) *quantum mechanics* methods to characterize the electronic structure of the reacting components of an enzymatic reaction, (2) *classical molecular mechanics* to model the protein matrix that acts as the solvent environment for the reaction, and (3) *a massively parallel computer implementation.* The resultant method and computer code is able to simulate the essential chemical events involved with an enzyme reaction utilizing Argonne's High Performance Computing Facility.

Technical Progress and Results: In FY 1993, computer code consisting of a combination of computational quantum mechanics and classical molecular mechanics techniques was created and critically tested on well defined small molecular systems. These tests defined the range of applicability of our methods for use in the computer simulations analysis of complex enzymatic systems.

In FY 1994, the High Performance Computing Facility in the Mathematics and Computer Science Division came online with a 128 node IBM parallel computer system. Our methods were implemented to run on this parallel computer, and we carried out a series of simulations to characterize the enzyme reaction in malate dehydrogenase. This work was done in collaboration with Len Banaszak, who is a professor at the University of Minnesota and a member of the ANL structural biology CAT that will use the APS for protein crystallography experiments. He provided the atomic structural data that is the necessary input for our calculations. We used this data to determine the entire energy profile for the bond making and breaking events that characterize the atomic mechanism for this reaction. This was the first such calculation on an enzyme system, and it provided mechanistic insights that are not possible to obtain from traditional experiments. This work is highlighted in the upcoming ANL annual report as an example of the combined use of state-of-the-art experimental and computational resources at Argonne to solve complex real world biological problems.

With the basic technology now in place to simulate the fundamental properties of enzyme reactions, we hope to see further extensions of our methods to increase their range of applicability and for their practical use in enzyme design. This would include the implementation of advanced *ab initio* quantum chemical methods and procedures to calculate thermodynamic and kinetic parameters associated with enzyme reactions.

Specific Accomplishments:

Invited Lectures:

- Physics Department, University of Illinois, Champaign-Urbana, May 1994
- Computational Sciences Department, University of Kentucky, November 1994
- Methods in Drug Design, San Francisco, April 1995

Abstracts:

P. A. Bash and L. Ho, "Computer Simulation of the Enzyme Reaction in Malate Dehydrogenase"
- Biophysical Society Meeting, March 1994
- American Chemical Society Meeting, August 1994
- Enzymes Gordon Research Conference, July 1994

Manuscripts in Preparation:

- P. A. Bash and L. Ho, "Calculation of the Energy Profile in Malate Dehydrogenase"
- P. A. Bash and L. Ho, "Simulation Analysis of Solvent Effects on Hydride and Proton Transfers in Malate Dehydrogenase"
- S. Panigrahy and P. A. Bash, "Critical Evaluation of a Density Functional Method Using a Divide-and-Conquer Approach"

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92-160R2 -- DESIGN ENZYMES FOR EFFICIENT AND EFFECTIVE CONVERSION OF BIOMASS INTO CHEMICAL FEED STOCK AND FOR OTHER INDUSTRIAL APPLICATIONS

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principle Investigators: M. Donnelly, Environmental Research
F. Stevens, Center for Mechanistic Biology and Biotechnology
J. Frank, Energy Systems

Funding Profile:

FY 1992	$329.5K
FY 1993	$302.6K
FY 1994	$239.7K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: Naturally occurring enzymes are very effective catalysts but their potential for industrial applications is often limited by their specificity. Often they do not catalyze certain specific reactions of potential commercial value even though they catalyze closely related reactions. This project seeks to develop the capability at Argonne to modify naturally occurring enzymes to create novel catalysts, in particular catalysts of use in the production of chemicals from renewable feedstocks. The intent of this work is also to provide general information which will allow predictable alterations of enzymes' specificity by combining advanced computational approaches, experimental modification of enzymes' structures, and the enhanced crystallographic capabilities that will be made available through the Advance Photon Source. The enzymes chosen for study in this project satisfy both objectives; their study will provide fundamental insights into the modification of specificity, and successful modification will provide novel catalyst of potential commercial value. Additional activity on the immobilization of enzymes and their reaction in non-aqueous solvents will establish critical bioengineering expertise in the Laboratory, as well as evaluate the potential of the specific targeted enzymes for use in advanced catalytic processes.

Approach: The enzymes malate dehydrogenase (MDH) and fumarase (FH) catalyze the conversion of a common intermediate, malate. Thus, they both bind the same chemical, malate. Published 3-dimensional structural data for MDH provides a basis for designing alterations of this enzyme, and commercially available substrates will allow thorough evaluation of the changes in specificity. Alterations of MDH should be able to generate enzymes with activities similar to those of lactate dehydrogenase, another enzyme of well known structure, thereby increasing the insights into the determinants of structure/function relationships to be gained by investigation of the altered enzymes.

Similar alterations of FH, if successful, could generate a novel enzyme, an "acrylase" capable of adding water to acrylic acid to give either lactic acid or 3-hydroxypropanoic acid. These novel catalysts will created a link between the current chemical industry and an emerging industry based on renewable feedstocks and biodegradable polymers. Enzymatic interconversion

of lactic and acrylic acid could permit the production of acrylic acid, a major petrochemical, from renewable feedstocks, whereas conversion of acrylic acid to 3-hydroxypropionic acid would produce a monomer of a biodegradable polymer.

Immobilization of the fumarase and evaluation of its reactivity in organic solvents will determine the potential of the natural enzyme for use in an advanced catalytic process more compatible with existing processes of the chemical industry. In particular, the effect of these procedures on stability, reactivity and the reaction equilibrium will be determined.

Technical Progress and Results: The genes for both MDH and FH were cloned and the enzymes overexpressed in high yields. The unmodified proteins were purified to homogeneity and their specificity with respect to compounds converted were determined. Both enzymes displayed high specificity; neither catalyzed significant conversion of reactants other than the natural substrate, one exception which MDH converted with moderate efficiency. Alternative forms of both enzymes were cloned to improve the purification and characterization of the proteins.

We have had considerable success in modification of the model enzyme, MDH. The enzyme cloned was that *E. coli*, the MDH for which the highest resolution crystallographic data is available. We have successfully created a series of mutants with altered reaction specificity. Seven different mutants were generated based on evaluation of sequence homologies, features of the three dimensional structure evaluated through computational modeling, and chemical considerations. In most of the mutants an arginine residue at position 81 was changed to glutamine, the residue found in this position in all examples of the related enzyme, lactate dehydrogenase (LDH). Proteins were purified by affinity chromatography and analyzed for activity toward malate, the normal substrate for MDH, pyruvate, the homologous substrate of LDH, and related α-keto acids. The mutants were found to be essentially devoid of MDH activity, but now had measurable activity toward lactic acid and other α-keto acids (table 1). Thus, we have successfully created an "LDH" from an MDH. However, the activity of the modified MDH was low relative to the original enzyme, and secondary mutants were generated in the critical region of the protein around the altered residue to attempt to impart greater activity. Some of these mutants produced minor enhancement of the activity, but further changes are needed to yield a highly active enzyme. The insights gained from these less obvious changes should provide exactly the type of information which will be needed to help construct a generalized, rational approach to the modification of enzymes' specificity.

Another set of mutants of MDH was generated in collaboration with Dr. Louise Anderson of the University of Illinois, Chicago. Sulfhydryl groups were introduced into the *E. coli* enzyme in locations homologous to those of certain sulfhydryls in MDH from plants. In plants, MDH and other enzymes are regulated by light in a process that involves the oxidation of sulfhydryls to disulfides. Three mutant forms of the *E. coli* MDH were compared and the activity of one was demonstrated to be modulated by conditions which affect formation or breakage of disulfides. Molecular modeling of this mutant indicated that rotation of a C-terminal helix could allow formation of the expected disulfide (figure 1). This data offers the promise of a general

approach to creation of enzymes whose activity can be modulated by the oxidation-reduction conditions of the reaction.

Computational analysis of the MDH reaction, using a combination of quantum mechanical and molecular mechanics approaches, has provided general insights into the effect of the protein on the reaction as opposed to the reaction in solution or in the gas phase. These results provides information on the importance of specific residues to catalysis which can be used to direct future mutagenesis. Energy profiles of the reaction have defined the transition states for hydride and proton transfers, details of catalysis which are not accessible experimentally.

Fumarase (FH), the target enzyme which could form the basis for novel commercial catalysts, was cloned from two organisms, *E. coli* and *B. subtilis*. Expression of the *E. coli* enzyme was extremely good, consistently over 200 fold, both for the natural enzyme and for a variant with a terminal tail of five histidine residues which permitted purification of the enzyme in a single step. Both forms of the enzyme have been provided to Dr. L. Banaszak of the University of Minnesota who determined the structure of the *E. coli* MDH and had initiated determination of the structure of fumarase. Banaszak's laboratory is now using our overexpressed fumarases in crystallographic studies. The modified enzyme could accelerate determination of the enzyme's structure since the tail bind metals, providing well defined metal derivatives of the protein which are needed for solution of protein crystal structures. Unfortunately, however, the structure has not yet been fully determined. Nonetheless, we have generated a limited number of mutants in highly conserved arginine residues based on comparison of known FH sequences. These mutations potentially could effect binding of substrate and catalytic specificity in an analogous manner to the effects observed in MDH. Preliminary analysis of these mutants reveals loss of activity toward fumarate, but additional work on the purified mutants will be required to determine if new catalytic activity has been produced.

Immobilization and organic solvent studies were performed using commercial fumarase from pig heart. Several methods of immobilization were evaluated, including ion exchange, adsorption to diatomaceous earth, and covalent attachment to chitosan. The ion-exchange immobilization was found to give the best result, yielding an activity of about 1,400 U/mg. The activity of lyophilized fumarase in organic solvent was evaluated. Methyl-t-butyl ether (MTBE) was selected as the preferred solvent. UV absorption data showed possible presence of activity.

Specific Accomplishments:

Patent Applications:

- F. J. Stevens and S.-P. Tsai, "Preparation of acrylic acid from lactic acid via modified fumarase"

Applications for Funding:

- Application to DOE in conjunction with Dr. L. E. Anderson, U. of Illinois, Chicago

Publications:

- D. Li, F. J. Stevens, M. Schiffer and L. E. Anderson, *Biophys. J.* 67, 29 (1994).
- L. E. Anderson, N. Prakash, D. Li and F. J. Stevens, Planta, In press (1994).
- E. H. Muslin, D. Li, F. J. Stevens, M. Donnelly, M. Schiffer L. E. Anderson, manuscript submitted.
- M. E. Pacrld, L. E. Anderson, D. Li and F. J. Stevens, manuscript submitted.
- W. E. Boernke, C. S. Millard, P. Wilkins-Stevens, F. J. Stevens and M. I. Donnelly, manuscript submitted.
- L. Ho and P. Bash, manuscript in preparation (primarily supported under LDRD Project 93-090R1).
- P. Wilkins-Stevens, K. Champion, J. Gaspar, F. J. Stevens and M. I. Donnelly, manuscript in preparation.

Table 1. Activities of Native Malate Dehydrogenase and A80P/R81Q Mutant Toward Various 2-Ketoacids

Substrate	Parameter	Native	Mutant
Oxaloacetate	K_{cat}	881.	NM
	K_M	0.04	NM
	k_{cat}/K_M	1.	--
		21,100,000.	
Pyruvate	k_{cat}	NM	6.3
	K_M	NM	19.
	k_{cat}/K_M	--	331.
2-Ketobutyrate	k_{cat}	NM	10.2
	K_M	NM	62.
	k_{cat}/K_M	--	64.
Phenylpyruvate	k_{cat}	2.6	1.9
	K_M	7.9	4.2
	k_{cat}/K_M	329.	443.

Units: k_{cat} = (s-1), K_M = mM, k_{cat}/K_M = s-1M-1
NM: Not Measurable

k_{cat} is the catalytic rate constant for the formation of product.
K_M is the apparent binding constant for substrate.
The ratio of k_{cat}/K_M reflects the catalytic efficiency of the enzyme.

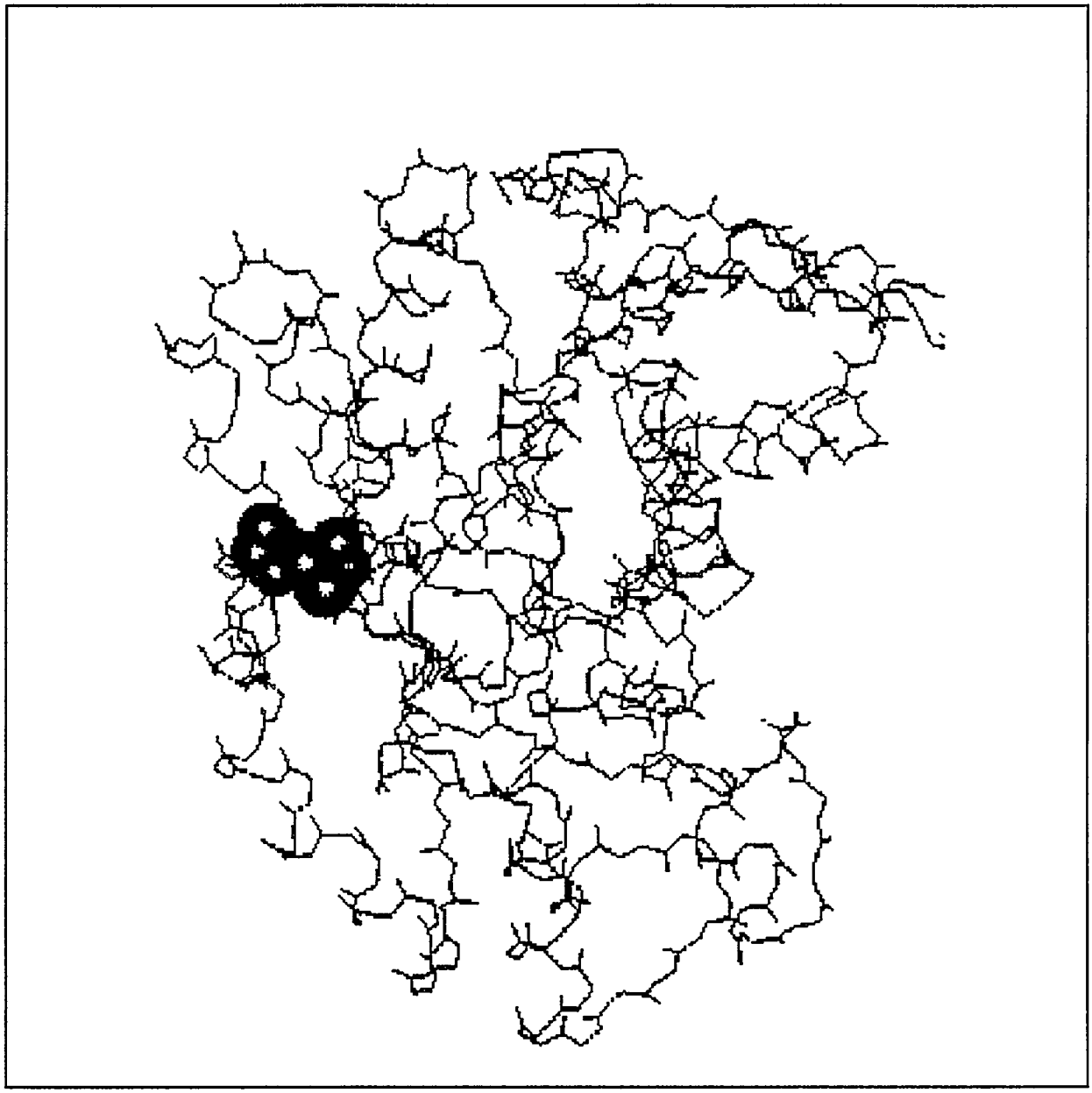

Figure 1. Molecular Modeling of the Disulfide Bond Introduced into Malate Dehydrogenase to Create a Regulatable Enzyme

Dark spheres represent introduced cysteine residues which are postulated to form the disulfide bond illustrated here under oxidative conditions. This bond formation requires rotation of a helix and minor alterations in the active site, resulting in inactivation of the enzyme. Reduction of the disulfide restores activity.

92-108R1 -- STRUCTURAL BIOLOGY AND THE HUMAN GENOME: CRYSTAL STRUCTURES OF PROTEIN-NUCLEIC ACID COMPLEXES

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigator: Andrzej Joachimiak, Center for Mechanistic Biology and Biotechnology

Funding Profile:

FY 1992	$242.1K
FY 1993	$ -0-
FY 1994	$290.4K
FY 1995	$190.0K
FY 1996	$ -0-

Purpose: The program is intended to take advantage of the synchrotron radiation sources that the Structural Biology Center (SBC) has at the National Synchrotron Light Source (NSLS) and will build at the Advanced Photon Source (APS) during the coming years. This program is also highly relevant to the DOE/OHER Human Genome Initiative.

Approach: The main goal of this project is to study the structure of biologically important protein-nucleic acid complexes (DNA and RNA) in humans, other eukaryotes, bacteria and archaebacteria, in order to better understand protein/nucleic acid interaction. The primary experimental method we use will be X-ray crystallography using synchrotron sources. We expect to subsequently verify our observations and hypotheses by cocrystallization of the altered proteins with their targets.

Technical Progress and Results: DNA repair enzymes — *E. coli* 8-oxoguanine DNA glycosylase. We have developed large-scale purification procedures that enable us to produce milligram quantities of pure, highly active 8-oxoguanine DNA glycosylase from overproducing *E. coli* strain. This is an important DNA repair enzyme known also as a FPG protein. This protein specifically recognizes DNA duplex containing 8-oxodG, and excises modified base from DNA. The recognition process is highly specific. We designed DNA targets that contain an abasic site or an analog of 8-oxodG for cocrystallization and purified synthetic oligonucleotides. We began crystallization experiments with a free protein and with complexes of FPG with target DNA containing an abasic site or an 8-oxodG analog, 8-oxonebularine, that is recognized by FPG protein but is cleaved very slowly. Crystallization experiments are in progress with DNA targets containing nebularine and furan. Although FPG provided for us an excellent substrate for chaperonin binding studies, so far it has not yielded good crystal specimens for X-ray diffraction analysis.

Transcription repressors — *trp* repressor of *E. coli*. A new crystal form of the tandem *trp* repressor-operator complex that diffracts to high resolution (> 2.3 Å) has been grown that addresses directly the issue of water-mediated interactions. Parallel binding experiments have been conducted to verify the role of the *trp* repressor N-terminal arm in DNA binding. We have shown that the N-terminal arms of the *trp* repressor do not affect specific operator binding. We

have found that these arms are dispensable and have no effect on the repressor interaction with α- and β-centered operator targets.

Restriction enzymes — *Eco* RII endonuclease from *E. coli*. We grow in our laboratory *E. coli* strains that overproduce *Eco* RII restriction enzyme and methylase. Endonuclease is a 46 kD polypeptide that forms dimers in solution and specifically recognizes two related DNA sequences, CCAGG and CCTGG. The DNA cleavage reaction is relatively slow ($t_{1/2}$ = 200 min) providing the opportunity to study the mechanism of enzyme action using X-ray crystallography with synchrotron radiation. In addition *Eco* RII requires binding of an enhancer sequence to cleave specific DNA target and shows a sequence homology with integrases (mutation of Tyr 308 to Phe abolishes DNA cleavage but not recognition). We purified to homogeneity the endonuclease in milligram scale and set up initial crystallization experiments, that have so far produced two crystal forms of the free enzyme (see figure 1). Evaluation of these crystals is in progress. We designed DNA fragments for cocrystallization experiments and purified synthetic oligonucleotides in milligram scale. We are in the process of crystallizing the specific *Eco* RII/DNA complexes.

Protein-RNA recognition — RNA inhibitors of basic fibroblast growth factor and α-thrombin. Basic fibroblast growth factor (bFGF) is a multifunctional effector that stimulates cell proliferation and migration, induces plasminogen and collagenase, and plays a role in tissue remodeling, wound healing, tumor proliferation and metastasis, diabetic retinopathy, and rheumatoid arthritis. Systematic evolution of ligands using an exponential enrichment procedure (SELEX) has been used at NeXagen to produce high-affinity nucleic acid ligands that bind to basic fibroblast growth factor. Similar RNA fragments have been obtained that interact specifically with human α-thrombin.

We have purified synthetic RNA fragments for cocrystallization with bFGF and thrombin. Initial crystallization experiments yielded small crystals of free RNA that inhibits bFGF (see figure 2). Crystallization of protein-RNA complexes is in progress.

Sequencing of archaebacterial genome. This effort in collaboration with Dr. Jonathan Trent and Dr. Carol Giometti is aimed at selected sequencing of *Sulfolobus shibatae* genome. We sequenced a number of clones from the genomic library in order to find potentially important enzymes and nucleic acid binding proteins for structural and functional studies. So far several enzymes and nucleotide binding proteins have been identified and partly sequenced. Sequencing and cloning of selected genes is in progress.

Specific Accomplishments:

1. We have developed milligram-scale purification procedure of highly active 8-oxoguanine DNA glycosylase from overproducing *E. coli* strain for crystallization and binding studies.

2. Crystals of the tandem *trp* repressor-operator complex that diffracts to high resolution (> 2.3 Å) have been grown.

3. We have shown that the N-terminal arms of the *trp* repressor do not affect specific operator binding.

4. We purified to homogeneity the *EcoRII* endonuclease in milligram scale and produced two crystal forms of the enzyme.

5. We have purified synthetic RNA fragments for cocrystallization with bFGF and thrombin. Initial crystallization experiments yielded small crystals of free RNA that inhibits bFGF.

6. We partly sequenced a number of clones from the genomic library of *Sulfolobus shibatae* and identified by sequence homology several enzymes and nucleotide binding proteins.

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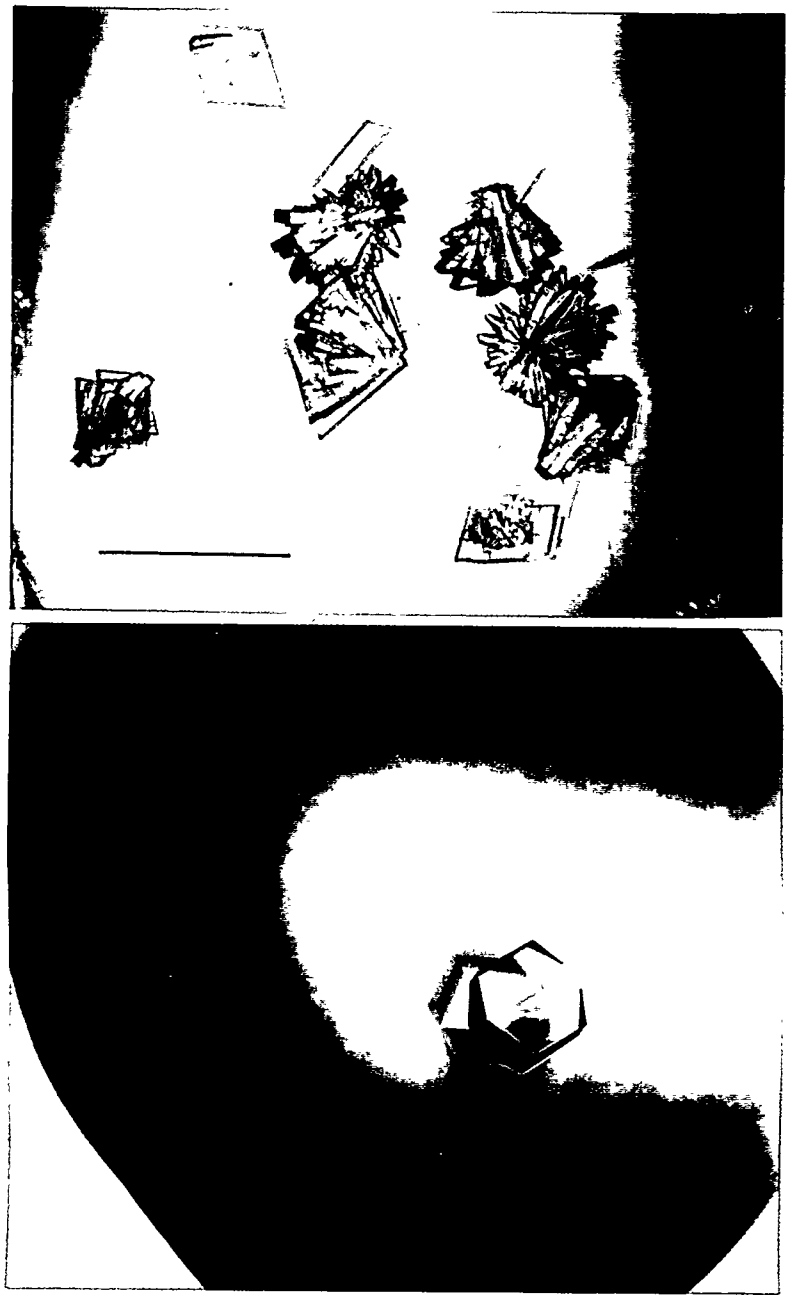

Figure 1. Crystals of EcoR II from *E. coli*

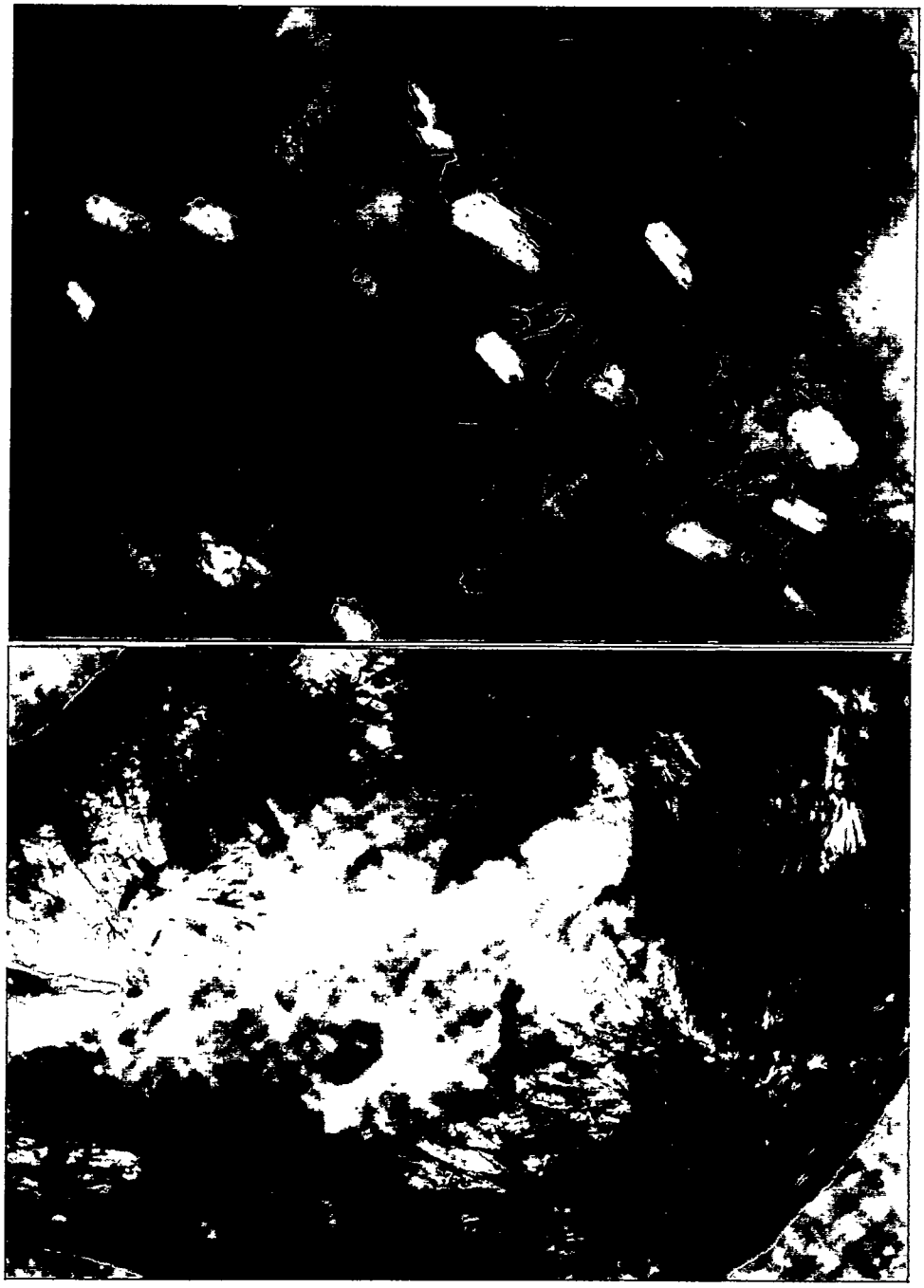

Figure 2. Crystals of bFGF Inhibitor - 26at RNA

93-156R1 -- NATIONAL EARTH MONITORING DATA REPOSITORY

Associate Laboratory Director Area: Decision and Information Sciences

Principal Investigators:
A. P. Campbell, J. H. Christiansen, and
D. G. Zawada, Decision and Information Sciences
C. Loehle, Environmental Research
J. R. Krummel, Environmental Assessment
J. Lee, Energy Systems

Funding Profile:

FY 1992	$ -0-
FY 1993	$189.8K
FY 1994	$143.7K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The overall objective was to demonstrate that the management of multispectral imagery and other data can be used to map and characterize complex land surfaces, and that data can be managed cost-effectively using this technology as a tool for tracking changes on a global scale.

Approach: Efforts this year continued the development of the concept of a National Earth Monitoring Data Repository aiming to allow its presentation as a Laboratory-wide initiative. Our approach involved mounting efforts in three technical areas. In the first, we used the neural network-based Hyperspectral Data Exploration Workbench (HIDEW) software system prototype developed at ANL to deduce surface cover type across portions of the Cadiz Township (Wisconsin) study area. In the second, we identified a proper paradigm for modeling forest response. This capability is required to allow prediction of forests response to land management changes, forest fragmentation, and climate change. The final part of our approach was to model the effect of landscape pattern on process dynamics using a spatio-temporal approach.

Technical Progress and Results: For the HIDEW component of work, we employed both pixel spectra from Landsat Thematic Mapper multispectral imagery data and fractal image texture metrics derived by HIDEW from aerial photographs as input to a HIDEW neural network surface classifier process. We began by enhancing the research-grade HIDEW prototype to make it more robust and convenient to use. The code was then used to perform the surface classification analyses.

Considerable effort was spent to transform HIDEW into a useable product that requires minimal training. Achieving this aim necessitated software engineering research and development work in several areas:

1. Complete revamping of the user interface. The new HIDEW graphical user interface (GUI) supports multiple platforms, and user interaction with HIDEW is now more convenient and intuitive.

2. Neural network process enhancements. Until recently, creation and training of neural networks has been a separate, labor intensive task outside of HIDEW. To eliminate such awkwardness, process objects were developed that allow training set library creation for supervised learning, neural network architecture specification, net training, and activation of trained neural nets to be performed interactively while within HIDEW. In essence, the complete character-based NASA NETS system has been incorporated into HIDEW and given a convenient GUI.

3. HIDEW data infrastructure improvements. HIDEW is an object-based software system, intended to be driven by a true object database (ODB). As part of the FY94 work, HIDEW has been made compliant with the latest version of the Versant ODB. In addition, a Message Dispatch System was added that allows any object within HIDEW to send and receive messages to the whole system. Process objects were made more robust and now allow any number of Image Data Packets to be specified as input.

The second area of effort was to estimate forest response to various types of stresses. Three major components necessary to a forest modeling paradigm were successfully identified. First, a methodology for modeling forest spread from remnant fragments was identified. It involves use of a contagion model to simulate spread to zones adjacent to remnant patches. Next, a spatially explicit approach to modeling forest growth was identified. This was accomplished through a detailed analysis of the adequacy of existing modeling approaches and the identification of model improvements necessary to obtain realistic forest response simulations. Finally, the lag in forest response to changing conditions was found to be an important issue. A model from the literature was adapted to increase realism for cases involving periodic disturbance of forests and results were written up. In the next year of funding it is expected that these general results can be applied more specifically to the Cadiz Township case study data to predict forest response and biodiversity under different scenarios.

The last major element of our work was development of spatially explicit catchment models that provide us a way to link landscape patterns to ecosystem processes. These distributed-parameter models have been designed to forecast water and material movement over single watersheds or catchments. The approach we used was to develop a set of spatial elements (or cells) for the watershed in which all process events (e.g., interception and infiltration) in an individual element are uniform. However, between elements parameter values are allowed to vary in an unrestricted manner to reflect a heterogeneous landscape. With further development and modification of this basic modeling approach, one can begin to quantify the effect of known pattern changes on known process fluxes across defined landscapes.

While this task focussed on modeling the effect of landscape pattern on process dynamics using a spatio-temporal approach, technology development was required to efficiently simulate complex spatial phenomena. This involved development and integration of a distributed-parameter computer code, a geographic information system (GIS) database, and analytical tools to construct the spatial element file. Also required were visualization methods (i.e., a graphical user interface) to efficiently manipulate large arrays that contain model parameters.

We have developed an enhanced distributed parameter model that simulates the flow of water and material over a watershed with hydrologic parameters distributed in an array of elements

or cells. Equations describing material and water flow processes use parameters such as surface roughness, rainfall rate, vegetation type and cover, soil type and erodability, and slope. The primary output from the model is the amount of sediment lost or deposited from each element and a hydrograph quantifying the dynamics of water and sediment movement out of the watershed. Correlations and spatial statistics are calculated by comparing input data with soil and nutrient movement.

Because the parameters controlling the dynamics of water flow and material transport are site-specific, a critical aspect of model development was to construct the input data set (i.e., the element file). For many landscape system boundaries, thousands of elements are required to approximate the scale of surface flow dynamics. For example, a 100 km^2 landscape with an element resolution of 0.25 hectare will have 40,000 elements, each of which contains geo-referenced parameter values that are a function of soil type, land cover (e.g., deciduous forest, pasture, concrete), and topographic conditions that vary over the landscape. Thus, while the model can be a powerful tool to analyze process-pattern interactions, an efficient, cost effective method is required to develop the data input file. This effort is planned as part of the FY 1995 effort.

File transfer algorithms have been incorporated to utilize the spatial database capabilities of a GIS. A GIS provides an efficient method to construct the digital elevation model and input land cover and soil information from other digital databases (e.g., Landsat images) or cartographic products (e.g., aerial photographs or topographic maps). The construction of the topographic data file provides an example of how our GIS technology improved the efficiency and accuracy of the modeling technology. To accomplish this task we: (1) digitized topographic maps with AutoCad software, (2) sent vector files to ARC/INFO (a GIS) software and used the TIN algorithm to produce a digital elevation model, (4) with the GRID algorithms in ARC/INFO we produced a "cell" file of slope and aspect, and (4) the cell file was then sent to the model code where the surface drainage was initialized. With this process accurate and precise topographic data, which is fundamental to the dynamic process, was developed for model. Another example is the direct import of satellite data to initialize all land cover and vegetation parameters required by the model. As discussed earlier, HIDEW was used for this purpose.

Coupled to the use of a GIS to construct the data input file, we have developed a set of visualization tools that allow the analyst to edit the data layers on the computer screen. The tools simplify data editing and visualization of data input and model output.

Specific Accomplishments: We have applied the model and associated GIS tools to evaluate sustainable development in a Wisconsin landscape. The landscape has changed from deciduous forest and prairie to corn and soybean production over the last 100 years. We incorporated digital aerial photographic data and Landsat satellite information to quantify the effects of deforestation and intensive agriculture on long-term soil and water fluxes from this 10,000 hectare area. Results show that our tool is capable of evaluating changing equilibrium conditions related to fundamental ecosystem dynamics. These changes are indices of long-term sustainability.

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94-106N -- COUPLED OPTIMIZATION/GROUNDWATER MODELING TECHNIQUES FOR THE DESIGN OF GROUNDWATER REMEDIATION SYSTEMS

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: R. Johnson, Environmental Assessment
C. Swietlik, Decision and Information Sciences

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$106.6K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The project objective was to investigate the applicability of coupled optimization/groundwater modeling techniques to the design of an actual groundwater remediation system. This project attempted to establish potential remedial action cost savings from using this type of design approach, and attempted to identify any technical/computational obstacles to wide spread adoption by the private sector. Successful demonstration of coupled optimization/groundwater modeling techniques applied to the design of groundwater remedial actions would provide a new set of tools for designing remedial systems with significantly reduced capital and operational costs.

Approach: Environmental programs within DOE and DoD are shifting from site assessments to remedial actions. Almost all groundwater remedial actions involve the placement of injection/extraction wells, whether for pump-and-treat systems, in-situ bioremediation, or soil gas extraction methods. Such systems are extremely expensive to install and operate. Traditional design technique have used trial and error methods for locating and sizing injection/extraction wells. Studies by Shoemaker et. al at Cornell University of hypothetical problems suggest cost savings on the order of 50% over the life of a remediation system can be obtained if optimization techniques combined with transport models are used to improve traditional design methods.

There has been considerable academic work in the last ten years that focuses on the application of coupled optimization/transport modeling techniques to the problem of optimal location and sizing of wells. This has included work at Stanford in non-linear mathematical programming, at the Univ. of Vermont in simulated annealing techniques, and at Cornell in optimal control techniques. Cornell's methodology, in particular, has shown promise because it accommodates highly non-linear systems, and is computationally feasible for systems where time varying policies are required. Cornell's methodology has been demonstrated on small hypothetical problems, but computational burdens and the lack of off-the-shelf software for generic applications has hampered its application to real world problems.

The objective for this project was to demonstrate the applicability of Cornell's methodology to real groundwater remedial action problems. In the context of this objective, work in FY94

focused on three tasks. The first task was to adapt Cornell's methodology (originally cast as a Grand Challenge problem) to commercially available Unix workstations, replicate published results, and benchmark performance. The second task was to document the methodology's efficacy in reducing pump and treat remedial action costs by applying it to the design of a pump and treat remedial system at a DOE/DoD site where ANL is active. The final task was to identify the technical and computational constraints inherent in the approach that hinders its widespread application to groundwater remedial action design. The last task, in particular, sets the stage for proposed LDRD work by this project in FY95.

Dr. Z. Wei, Decision & Information Sciences (DIS), was the lead collaborator in the porting of the Cornell code from a supercomputer platform to Unix-based commercial workstations. Dr. G. Williams, Environmental Assessment Division (EAD), was the lead collaborator in the application of Cornell's methodology to an actual remedial action design problem. Dr. C. Shoemaker, Cornell University, provided technical support for the effort.

Technical Progress and Results: Cornell's differential dynamic programming code with an embedded version of the two dimensional ISOQUAD flow and transport model was obtained from Cornell, and initially installed on ANL's IBM SP1 (high performance parallel processing research machine) for verification and benchmarking purposes. The code's results on the IBM SP1 for a published hypothetical example were verified, and the code's performance benchmarked. The code was then ported and recompiled for a multi-processor Sun workstation, and for a single processor Silicon Graphics (SGI) workstation. Because the original code was a research code specifically written for an SP1, a machine with an architecture and compiler that is different from Unix workstations, a significant amount of effort was expended to obtain working versions on the Sun and SGI Unix platforms. Once compiled successfully on the Sun and SGI workstations, the code was again verified successfully for the published hypothetical example, and its performance benchmarked against the SP1. Initial run times for the hypothetical example ranged from 8 minutes on the SP1 to 30 minutes on a Sun 690 workstation.

A review of pertinent DOE/DoD sites where ANL is active was conducted to select the most suitable case study. The site selected was J-field at Aberdeen Proving Ground (APG). This site was selected for several reasons. First, EAD has completed the design of a pump and treat system for the site using design techniques commercially available now. Second, a well documented subsurface conceptual model existed for the site, simplifying the application of Cornell's methodology. Third, the site is interesting and complicated from a technical perspective with groundwater contaminated by volatile organics, and an environmentally sensitive marsh ecosystem threatened. Finally, APG is an important sponsor for ANL, and the J-field work is high profile from APG's perspective.

Cornell's methodology was used to repeat the design of a groundwater remedial action at J-field. Using Cornell's approach, a system was designed that satisfied design constraints (i.e., provided protection to adjacent wetlands), and could be operated at half the cost of the system obtained from the traditional design process. The primary source of cost savings were the strategic

placement, sizing and operational rules for the extraction wells used by the system, as derived by the optimal control techniques.

The computational model used for the J-field problem was simplified as much as possible without compromising model results, including reducing the model from full three dimensions to two dimensions. Despite this, workstation run times for the actual problem were on the order of days, not hours. This highlights one of the primary technical hurdles to commercial application of this technology — for real applications coupled optimization/fate and transport modeling techniques are computationally onerous.

Several opportunities for removing this obstacle were identified in the FY94 work. First, some preliminary attempts at optimizing the code in single processor mode resulted in a performance increase of 1.6, suggesting that significant performance gains might be obtained through further code optimization efforts. Second, a review of the method's implementation suggests that in several areas the code might benefit from recasting as a parallel processing model. Finally, decoupling the optimization portion of the code from the flow and transport model using automatic differentiation techniques developed in the Mathematics and Computer Science division could result in further performance improvements, while also expanding the approach's realm of applicability. These are areas proposed to be addressed by FY95 LDRD funding.

Specific Accomplishments: In the area of program development, the work in this LDRD to date has resulted in contacts with private sector software companies (Dynamic Graphics, Inc. and Stratamodel, Inc.) interested in potentially commercializing this approach to remedial action design; planned presentations to APG staff to expand ANL's involvement at the site in the area of groundwater remedial action design using approaches demonstrated by this LDRD; enhancements in ANL's practical high performance computing software design capabilities which can be leveraged in other programs; and finally spin-off proposals with other ANL divisions for taking the work further, including an Advanced Computational Technology Initiative proposal with the Mathematics and Computer Science division to apply these techniques to the design of petroleum extraction systems and a Small Business Technology Transfer Program proposal with a private company to explore commercialization potential.

Papers for presentation at the American Geophysical Union and Geological Society of America annual meetings are in preparation.
Two papers were prepared for publication and submitted:

Loehle, C. Habitat Destruction and the Extinction Debt Revisited. To: *Nature*.

Loehle, C. and D. LeBlanc. Climate Change Effects on Forests: A Critical Review. To: *Ecological Applications*.

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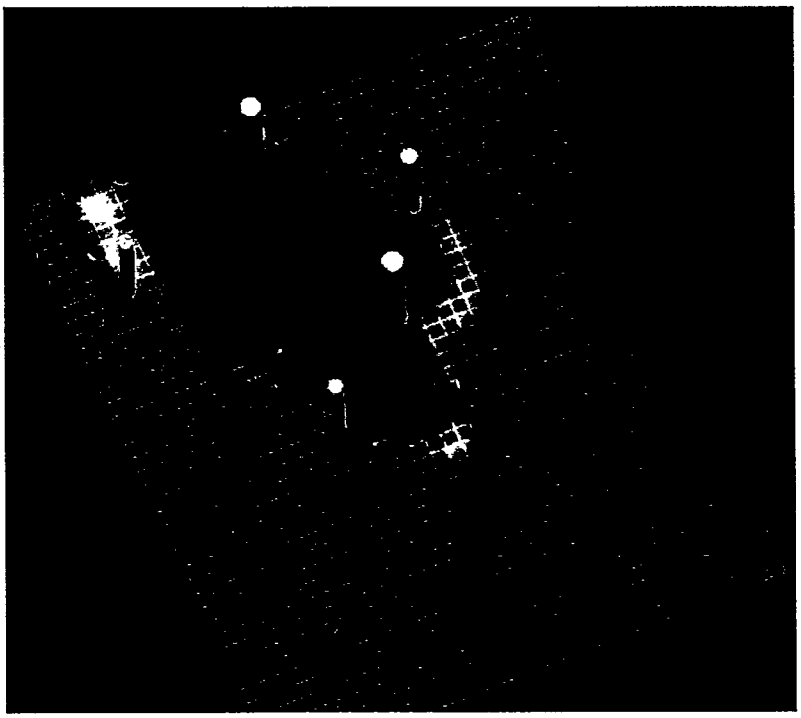
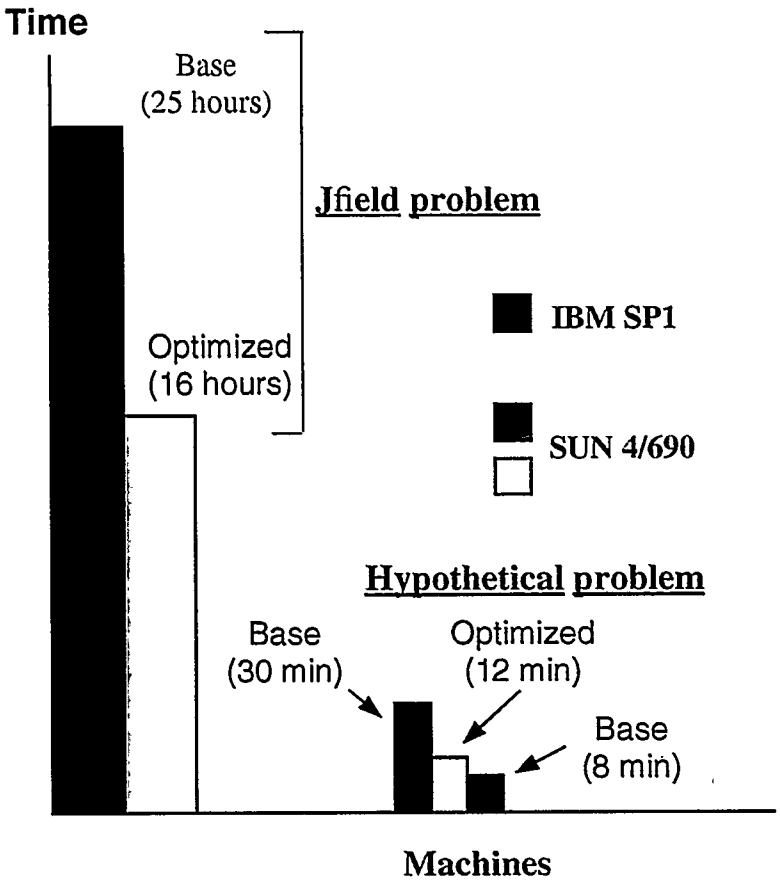
Graphic to the right shows the optimized placement of extraction wells at Jfield, Aberdeen Proving Ground. Colored surface indicates location of VOC contamination.





Bar chart to the left shows the impacts that preliminary code optimization has had on code performance for two selected platforms and two example data sets

91-034R1 -- REMOTE SENSING AND GLOBAL CHANGE

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: J. R. Krummel, Environmental Assessment
D. G. Streets, Decision and Information Sciences
H. Su, Environmental Assessment

Funding Profile:

FY 1991	$ 9.9K
FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$105.7K
FY 1995	$115.0K

Purpose: To test the applicability of Landsat satellite multi-spectral scanner (MSS) data to quantifying and monitor the spatiotemporal dynamics of global vegetation and land cover change. Determining the rate and magnitude of global land cover or vegetation change is necessary in order to link climate models to ecosystem functions and project future conditions. Our primary objective is to construct a time series of MSS data sets and measure dynamic changes in vegetation patterns over very large areas but at spatial resolutions that can explicitly connect several hierarchical scales (landscapes, regions, continents). A secondary objective is to test image processing and change detection techniques on MSS data in order to determine the accuracy and efficiency of our techniques for global monitoring.

Approach: Cumulative changes in regional land cover and vegetation associated with agricultural development, the harvest of forest products, and urbanization contribute to altered patterns of global vegetation. Global changes in natural vegetation patterns (e.g., the distribution of forest, grassland, and savanna) could alter the continental or global pattern of ecosystem functions (i.e., productivity, evapotranspiration, and water runoff). Ongoing global changes in these critical ecosystem functions caused by human disturbance must be factored into models and analyses of potential global climate change. To date, there has been no systematic analysis of global land cover changes and much of the data used to quantify global carbon storage or land cover dates from the late 1970s and early 1980s. As a potentially valuable tool in examining the dynamics of global change, we tested how image processing and pattern recognition tools applied to satellite remote sensing data collected at the same location over several decades can monitor and quantify large-scale changes in vegetation and land cover.

Our approach was to search published statistics of land use conditions in North America, Central America, Africa and Asia to develop sample regions that could serve as indicators of global or continental land cover change. Once the sample areas were selected, we would conduct computer searches of the archived MSS data that has been acquired continuously since 1972 and has world-wide coverage.

Based on the search, a time series of satellite images would be obtained for the sample regions, image processing and change detection algorithms applied to the data sets, transition matrices calculated for each sample region and rates of change determined. We proposed a classification

that would delineate forest, forest-degraded, crop land, grass land, water, and urban or built-up land based on level I classification systems for remotely sensed data (from the U.S. Geological Survey). A statistical analysis of the classification would be conducted to determine the potential error in discriminating between each land cover type.

Technical Progress and Results: We initially selected eight regions on five continents as test areas. Based on a computer search of the MSS archives in the U.S., Canada and China and data quality evaluation (cloud cover, image quality, season), we selected four areas for intensive analysis: the lower Mississippi River flood plain, Southeastern Mexico, the interior of the Ivory Coast, and a heavily populated agricultural area in China, which encompasses most areas of Jiang-Su Province. The time period for the 15 scenes that we acquired ranged from 1973-1990.

We developed a computer code to access the archived MSS data collected prior to 1976. We then employed principal components analysis (PCA), normalized difference vegetation index, and Tassel Cap transformation procedures to extract the information on urban and vegetation features from the original images and then used the resultant features to conduct a supervised classification. ERDAS image processing software operating on a Sun Sparc 20 workstation was used to conduct the land cover classification and subsequent statistical analysis (based on the degree of overlap between classes in polynomial phase space).

Table 1 shows preliminary results of our analysis of land cover change for the Ivory Coast, Mexico and China. According to the United Nations, approximately 13% of total forested area was lost between 1974 and 1985 in the Ivory Coast. Based on our analysis of the MSS data, total forested area decreased from 60% of total study area in 1974 to 35% in 1986 or a 24.5% of the total forest area from 1974 to 1986. The United Nations reported that deforestation rate in Mexico 1.3% from 1980 to 1985. Result from our study showed that total forested area decreased from 60% of total study area in 1974 to 50% in 1984 or a rate of about 1% each year. In China we estimated a 9% increase in urban and built-up land in Jiang-Su Province during the short period between 1976 to 1984. Indeed, almost 1% of the total land area was converted from agricultural land or wetland to residential, commercial, industrial and transportation areas (figures 1 and 2). Except for forested land in China, our statistical analysis showed that the MSS data in combination with our image processing and classification techniques could provide a reliable estimate of land cover change over large regions.

Specific Accomplishments: A method to monitor and detect global land use change has been established at Argonne that incorporates remote sensing data, image processing software and classification techniques. The method detects major changes in agriculture, forest and urban land cover over time at the regional or continental scale.

The LDRD researchers are submitting the results of the work to the *International Journal of Remote Sensing* and the *Journal of Environmental Management.*

The results of the LDRD work will be incorporated into a proposal that will be submitted in February, 1995 to the Office of Energy Research, U.S. Department of Energy under the Integrated Assessment Program.

Table 1. Percentage of Land Use Changes in Three Study Areas.*

Central Ivory Coast

Year	Forest	Forest-Degraded	Cropland	Grassland	Water	Urban/Built-Up Land
1974	28.5	31.2	14.6	20.2	3.7	1.8
1986	10.6	24.7	22.9	33.9	2.3	5.6

Southeastern Mexico

Year	Forest	Forest-Degraded	Cropland	Grassland	Water
1974	27.9	31.8	11.4	25.0	3.9
1984	23.5	26.2	11.2	36.8	2.3

Jaing-Su Province - China

Year	Forest	Cropland	Water	Urban/Built-Up Land
1976	6.0	61.4	28.9	3.7
1984	14.3	50.3	22.4	13.0

*Note that this is a preliminary result, percentage values may be reestimated accordingly.

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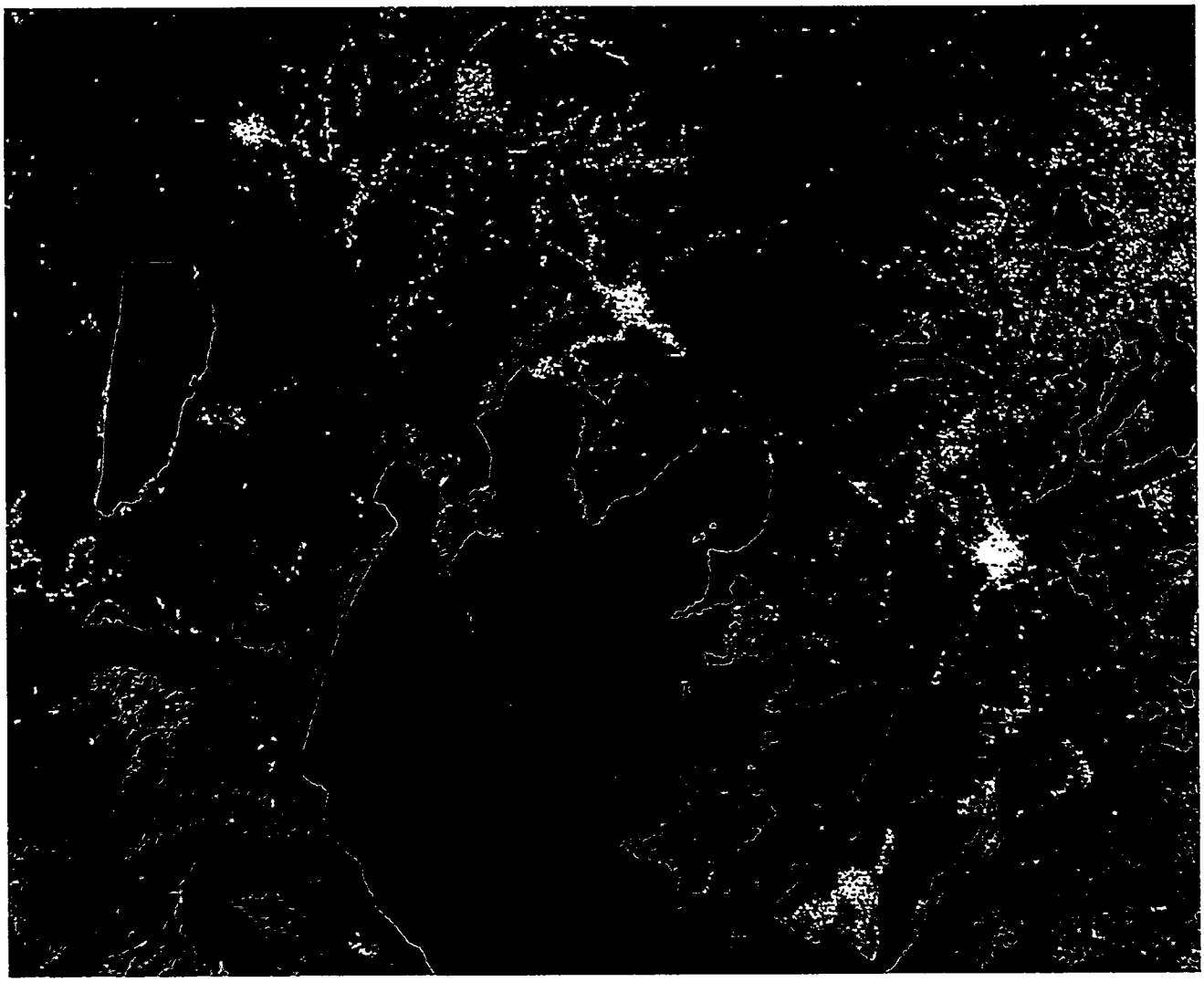

Forest land

Agricultural land

Water

Urban or built-up land

Classified Land Use Map, JiangSu, China
Landsat MSS, 11/27/76

Forest land

Agricultural land

Water

Urban or built-up land

Classified Land Use Map, JiangSu, China
Landsat MSS, 05/08/84

94-154N -- DETECTION OF GLOBAL CHANGE: LONG TERM TRENDS AND EPISODIC BEHAVIOR IN THE ATMOSPHERIC TEMPERATURE PROFILE

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigator: R. A. Reck, Environmental Research

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$184.2K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: A new approach was developed for the detection of global climate change, based upon analysis of changes in the vertical profile of temperature. The study was conducted with a number of existing temperature data sets to determine changes in the temporal and spatial variability. Special attention was focused on the region near the upper part of the lower atmosphere (the tropopause) since this region is thought to act as a thermostat for climatic changes. In particular the temperature profile and the tropopause in the tropical Pacific is believed to hold a key to early detection of human induced climate change. The primary activity of the U.S. Global Climate Change Program involves documentation of global change through establishment of an integrated, comprehensive, long-term program of observing and analyzing earth system changes on a global scale. This research contributes in a substantial way to this overall goal.

Approach: In the analysis of global change it is found that the resultant earth's surface temperature is the composite of many forcing factors. To be able to sort out human-induced effects from all these contributions is a daunting if not impossible task without a very long data set (which we do not yet have). In the present approach we look beyond the response at the earth's surface and instead look for the fingerprints of thermal change throughout the atmosphere.

The principal research activities involved (1) determination of the long-term trends and episodic behavior of the vertical temperature profile in the tropical Pacific using several sets of independent data, (2) interpretation of the behavior in terms of cause and effect, and (3) application of a radiative-convective model for confirmation of the proposed mechanisms.

The research considered variables such as cloud cover, water vapor, sea surface temperature, and column ozone. Where it was possible, two or more independent data sets were analyzed for the same geophysical quantity. The data sets used in this research included: the monthly temperature climatology of Oort for the years 1958-88 (a composite of over 20 data sets), column ozone from the Nimbus 7 Total Ozone Monitoring System, information on cloudiness contained in the TOMS data set, and related sea surface temperatures.

Technical Progress and Results: Methods have been developed to analyze temperature data as a function of altitude. Daily data for nine locations, each with values at different levels in the vertical, were analyzed to determine shifts in the thermal balance at different altitudes. Special applications of sensitivity tests were developed, specific for meteorological data (the so-called Kendall-Mann test). G. Wen, a postdoctoral (a graduate from the University of Chicago), brought his special data handling skills to the task and considerable progress was made in identifying the major factors contributing to climate change in the region.

Our results show that the principal natural driving force for change in the vertical profile of temperature in the tropical eastern Pacific is the combination of the effects of the el Nino and the Southern Oscillation, the so-called ENSO. The results show tropospheric temperatures respond concurrently to the state of the ENSO at all pressure levels within the troposphere. See figure 1. However, the temperatures in the free troposphere and in the planetary boundary layer near the surface were not strongly correlated. Our results are consistent with deep cumulus convection as the primary mechanism for transporting heat from the planetary boundary layer to the upper troposphere.

Trends in the thermal structure of the atmosphere are shown in figure 2 for the tropical western Pacific. These results indicate a shift in (1) the potential temperature at the tropopause, (2) the mean lapse rate between 500 mb and the tropopause and (3) the temperatures at the 500 and 1000 mb levels. The shifts in the thermal structure of the upper troposphere are believed to be the result of changes in ozone (as documented by the TOMS data). What we have learned is that daily variability is very important and has heretofore been overlooked in trend analyses. Our future work on detection of global change will, hence, be focused in that area. Our initial work on ozone variability indicates a strong role in the temporal variability of temperature, forced by daily ozone changes.

In this future work we will be assisted by Professor John E. Frederick of the University of Chicago, Beth L. Weinberg, a University of Michigan graduate student studying for her PhD thesis at ANL under a Global Change Fellowship, and Robert M. Bornick, another postdoctoral staff member.

Specific Accomplishments: Two papers on this work were presented this year:

"Minimal Total Ozone Amounts at Temperate Latitudes of the Northern Hemisphere in the Time Period June 1987-May 1988," at a conference on Atmospheric Chemistry.

"Interannual Variation and the Vertical Structure of Temperature in the Equatorial Region," at a Symposium on Global Electrical Circuit, Global Change and the Meteorological Applications of Lightning Information.

A talk was also presented at this year's Atmospheric Chemistry Program Review by the Office of Health and Environmental Research (OHER) of DOE, entitled: "A New Approach to the Characterization of Long-Term Changes in Total Atmospheric Ozone: Applications of Frequency and Extreme Value Statistics."

Two papers have been sent to journals for publication: "El Nino and Anomalies of the Vertical Structure of Tropospheric Temperature over the Eastern Equatorial Pacific" was sent to the *Journal of Geophysical Research* and "A New Approach to the Characterization of Long-Term Changes in Total Atmospheric Ozone: Applications of Frequency and Extreme Value Statistics," was sent to *Geophysical Research Letters*.

Two proposals were written: "Trends and Evolution of Minimal Ozone Amounts, 1979-1992," was sent to OHER of DOE and was funded at $280K for two years. The second proposal, "Time Behavior and Extreme Value Statistics of Total Ozone Obtained from the Total Ozone Mapping Spectrometer Data Set for the Period December 1979 to May 1993," was submitted to the National Aeronautics and Space Administration for three years of funding at a total of $642.4K. A decision on the latter is pending.

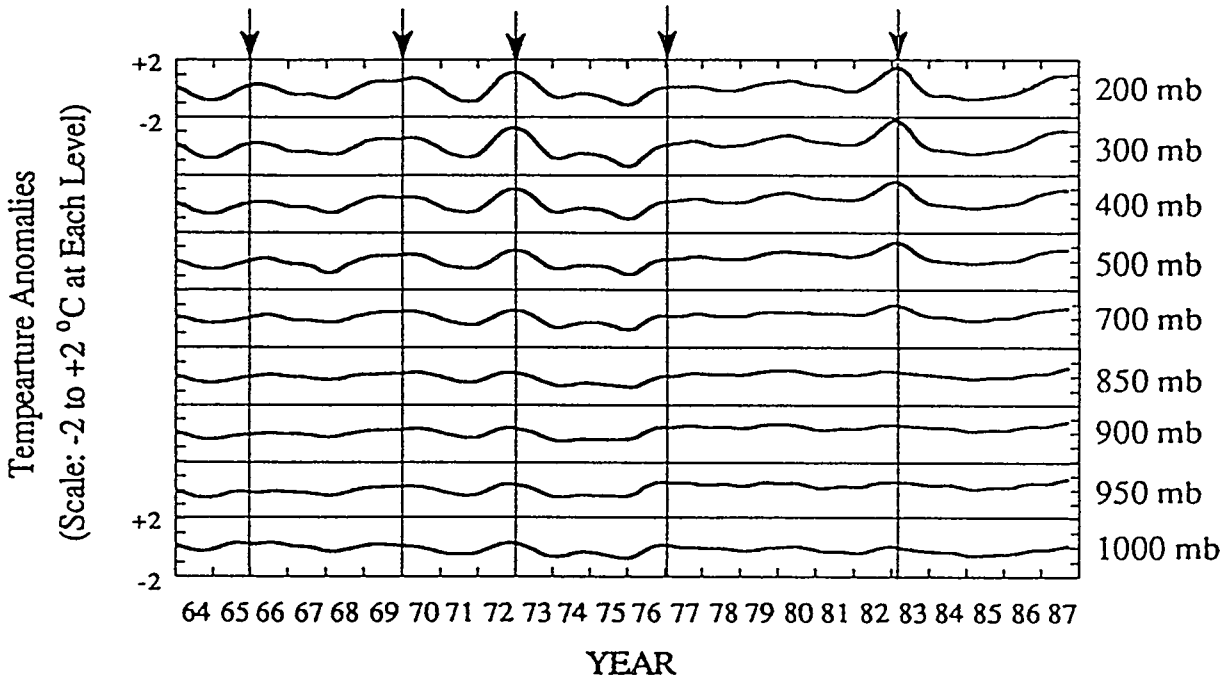

Figure 1. Time series of the 15-point running mean of monthly mean temperature anomalies with respect to the climatological (1964-1973) monthly mean values in the eastern Pacific region (10°S-10°N and 80°W-180°W). (A Gaussian-type filter with weights 0.012, 0.025,0.040, 0.061, 0.083, 0.101, 0.117, and 0.122 at the central point was applied). The major el Nino events are indicated by arrows.

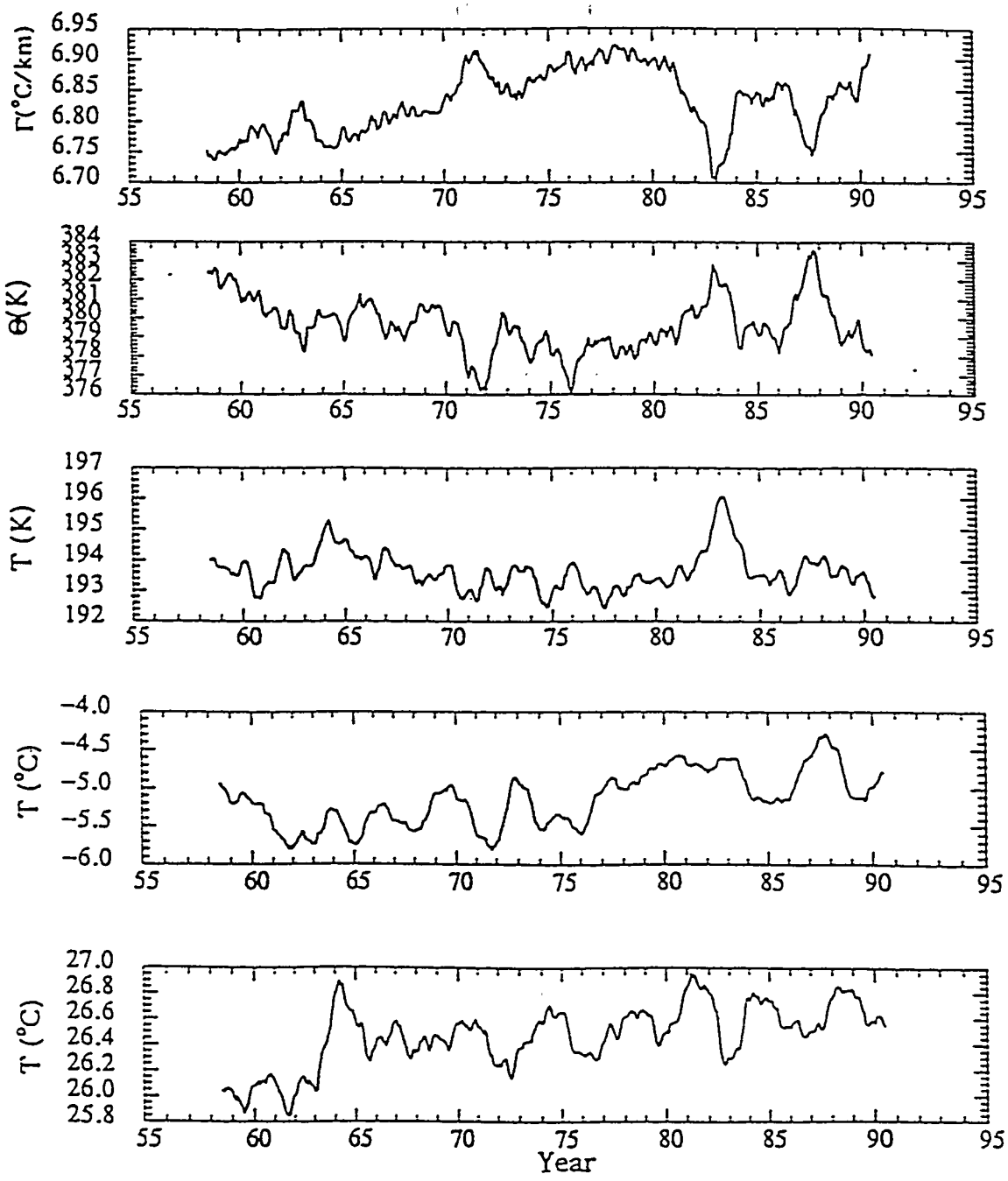

Figure 2. Plots of the mean lapse rate from 500 mb to the tropopause (Γ), the potential temperature at the tropopause (θ), and the monthly mean temperatures at 100 mb, 500 mb, and 1000 mb, respectively, for the years 1958-1992 for the same geographical area as described in Figure 1.

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94-157N -- REGIONAL CLIMATE FORCING IN MIXED LAND-LAKE REGIONS: DEVELOPMENT OF COMPONENTS OF MODELING USER FACILITY AND WORKBENCH: A HIGH-RESOLUTION ATMOSPHERE-LAND SURFACE EXCHANGE MODULE

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: W. Gao and M. L. Wesely, Environmental Research

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$144.9K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: To develop (1) a coupled atmosphere-land surface exchange model that is driven by high-resolution remote sensing data from satellites, (2) techniques to link such a model with large-scale atmospheric models, and (3) methods to estimate atmosphere-biosphere exchange rates of chemical trace gases such as CO_2, O_3, and biogenic nonmethane hydrocarbons (NMHCs) over regional scales. The accurate determination of exchange fluxes between the atmosphere and underlying land surfaces for momentum, heat, water vapor, CO_2, and chemical trace gases is a difficult task in large-scale atmospheric models. Large spatial and temporal variabilities in vegetation conditions exist. The resolution used in global- and regional-scale climate models usually is too low to allow adequate representation of subgrid fluxes. This problem is a source of major uncertainties in predicting climate change.

Approach: Use of high-resolution surface spectral reflectances from satellites to describe spatial and seasonal variations in vegetative status will allow a significant improvement in the parameterization of surface energy and gas fluxes at subgrid scales in climate models and thus will reduce uncertainties in climate change studies.

This project couples remote sensing data in multiple wavebands from several satellites with advanced surface models to form a modeling system based on satellite data for studies of climate-biosphere interactions at different scales (figure 1).

Remote sensing data in visible, near-infrared, and thermal-infrared bands of the spectrum are acquired from Satellite pour l'Observation de la Terre (SPOT), Landsat, and polar-orbiting environmental satellite series of the National Oceanic and Atmospheric Administration (NOAA). The data are processed and input to a surface radiation transfer model to quantitatively derive useful parameters that characterize vegetation's density, coverage, and biophysical conditions. These derived surface parameters then are incorporated into surface flux models that simulate the exchange of energy and mass between the lower atmosphere and vegetation canopies.

The coupled satellite data-modeling system provides capabilities for studying regional climate-biosphere interactions. For example, the system has been used to model transfer of chemical

gases and pollutants from the lower atmosphere to vegetation canopies in the eastern United States, to estimate CO_2 exchange rate at a tallgrass prairie in Kansas, and to calculate surface energy fluxes at the southern Great Plains Cloud and Radiation Testbed (CART) site of U.S. Department of Energy.

Technical Progress and Results: Methods were developed to couple Argonne's pollutant deposition model with processed normalized vegetation index (NDVI) data from the advanced very high resolution radiometer (AVHRR) on NOAA satellites. The resulting new model allows a more realistic description of spatial and temporal variations in vegetation conditions and can describe spatial, seasonal, and year-to-year changes in pollutant transfer from the lower atmosphere to different terrestrial ecosystems. Modeled deposition rates of ozone to a tallgrass prairie in Kansas agree closely with in-situ measurements. Results also show that drought conditions in the eastern half of the United States in 1988 suppressed vegetation growth and the uptake of ozone.

A computer system has been established to capture and process real-time remote sensing data from NOAA satellites. With this system, five channels of visible and infrared remote sensing data from AVHRR sensors on the NOAA-11 and NOAA-12 satellites can be captured twice a day for the area of interest. Images can be processed to produce useful surface parameters like NDVI and surface temperature. This system is being used to evaluate vegetation changes and to estimate surface energy fluxes at the southern Great Plains CART site.

A fast scheme has been developed for computing surface energy budget by using high-resolution satellite data. This scheme has two major improvements. First, an analytical solution to the surface energy budget equation is used to speed up computation of surface temperature, heat flux, and radiation flux. Second, three key model parameters (surface albedo, surface conductances, and soil heat flux ratio) are estimated with remote sensing data by using simplified functions. The new scheme can provide rapid estimates of surface parameters and energy budget at small scales but over a large area, and thus it is feasible for application in large-scale climate models to include subgrid-scale surface heat and radiation fluxes.

Specific Accomplishments: Satellite data were used to model pollutant deposition at regional scales. A presentation titled "Use of satellite data to improve parameterization of spatial and temporal variations of gaseous dry deposition in regional-scale models" was given at the American Meteorological Society's Atmospheric Chemistry Conference, January 23-28, 1994, Nashville, Tennessee. The following two manuscripts were accepted for publication in *Atmospheric Environment*: "Modeling Gaseous Dry Deposition over Regional Scales with Satellite Observations. I. Model Development" and "Modeling Gaseous Dry Deposition over Regional Scales with Satellite Observations. II. Deriving Surface Conductances from AVHRR Data."

A system for capturing and processing data from NOAA satellites was established for detecting vegetation changes in various environmental studies. An invited seminar titled "Surface reflectance modeling and satellite data interpretation for atmosphere-biosphere exchange study" was given at the Canada Centre for Remote Sensing, April 28, 1994, Ottawa. A presentation on this subject titled "Parameterizing atmosphere-land surface exchange for climate models with satellite data: A case study for the southern Great Plains CART site" was given at the American

Meteorological Society's Global Climate Change Conference, January 23-28, 1994, Nashville, Tennessee.

A manuscript titled "A simplified scheme for parameterization of subgrid-scale (PASS) land surface fluxes with satellite data in atmospheric models" was submitted to *Journal of Geophysical Research.*

A presentation titled "Modeling and scaling up of land surface fluxes of energy and trace gases with high-resolution satellite data" was given at International GCIP/MAGS Workshop on Scaling in Hydrometeorological/Hydrological Processes and Models, September 18-22, 1994, Victoria, B.C., Canada.

Two research proposals were submitted: "Surface Fluxes from Satellite Data," by W. Gao, to the Atmospheric Radiation Measurement Program, Office of Health and Environmental Research, U. S. Department of Energy; and "Surface Characterization and Radiation Modeling for Analyzing Upwelling Radiation Measured by Unmanned Aerospace Vehicles and Satellite Across the CART Site," by W. Gao, to Global Change Research with Unmanned Aerospace Vehicles, U. S. Department of Energy. Notification has not yet been received as to whether or not these proposals will be funded.

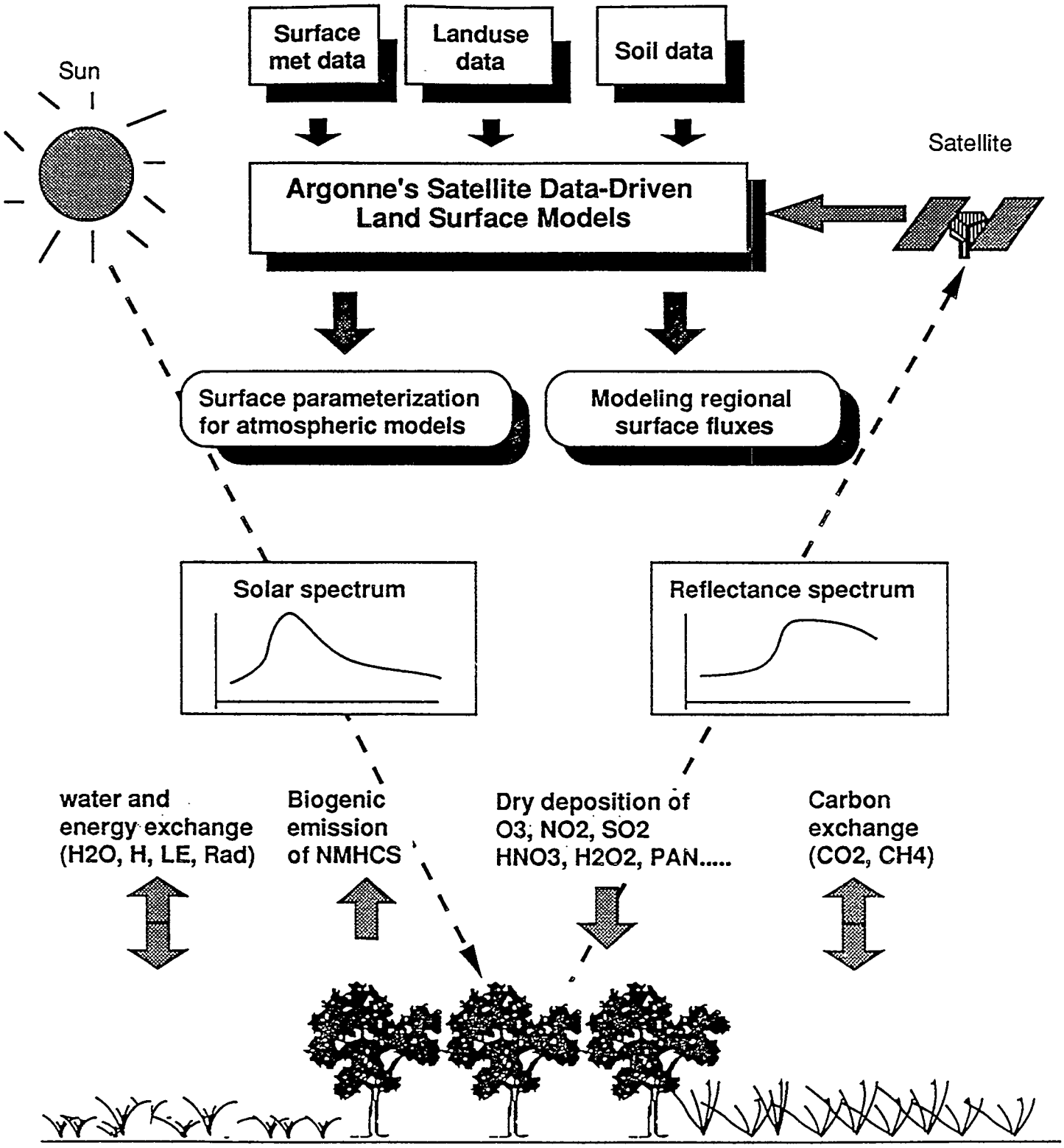

Figure 1. Schematic diagram of a coupled system for modeling atmosphere-biosphere exchange by using satellite observations

94-033N -- LIQUID-METAL-BASED METHOD FOR DISPOSAL OF TOXIC CHEMICALS

Associate Laboratory Director Area: Engineering Research

Principal Investigators: D. H. Cho and D. R. Armstrong, Reactor Engineering

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$ 87.2K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The objective of this project was to conduct a series of laboratory tests on the destruction of halogenated and other toxic organics by reacting with molten sodium. The tests would provide information on reaction products such as species and physical forms. This project would be a first step toward developing a novel technology for treatment of toxic wastes.

Approach: High-temperature incineration is currently being used to destroy toxic chemicals from industrial wastes and chemical weapons. However, a number of questions concerning the health and environmental effects of incinerators present roadblocks to broad use of this waste disposal technology. Indeed, public opposition to incineration appears to be growing. The need for developing alternative technologies is being increasingly recognized. One of the technical concerns being raised about high-temperature incineration is the emission of toxic gases during the incineration. The method being investigated in this project would minimize gaseous emissions, toxic or otherwise.

The scope of this investigation consisted of conducting small-scale laboratory tests in which selected halogenated organics react with molten sodium. The results of these tests would provide information for determination of the feasibility of the proposed method for destruction of toxic organics.

The test methodology involved contacting vapors of organics with molten sodium in a batch reactor. A measured amount of the organic sample (vaporized by boiling) was reacted over a short time with a pool of liquid sodium maintained at a constant temperature.

Technical Progress and Results: An experimental apparatus for the injection of organic vapors into a pool of molten sodium was assembled. As shown in figure 1, it consisted of a collection of four vessels (i.e., sodium sump, reactor, organic tank and expansion tank) connected by various tubes, fittings, and valves.

A total of seven tests were conducted; five tests with 1,1,1-trichloroethane and two tests with chlorobenzine. The amounts of organics injected into the sodium pool were in the range of two to four grams. The sodium pool temperature varied from 300°C to 500°C. The gaseous reaction products were sampled and analyzed.

The results of chemical analyses of the gas samples show that the organics were completely destroyed by reacting with molten sodium. Mass spectrometric analyses indicated that all chlorine compounds including elemental chlorine in the gas samples were less than the detection limit of 100 ppm. A gas sample submitted for gas chromatographic analysis was found to contain no chlorine compounds above the detection limit of 1.0 ppm.

Specific Accomplishments: A series of tests on the destruction of halogenated organics by reacting with molten sodium were completed, demonstrating the viability of a novel concept for treatment of toxic chemicals.

An invention report entitled "Liquid-Metal-Based Method for Treatment of Toxic Chemicals" (ANL-IN-93-072) has been filed, and a patent application is under consideration.

ANL-W expressed interest in the waste treatment concept of this project. It is anticipated that potential applications at ANL-W will be explored.

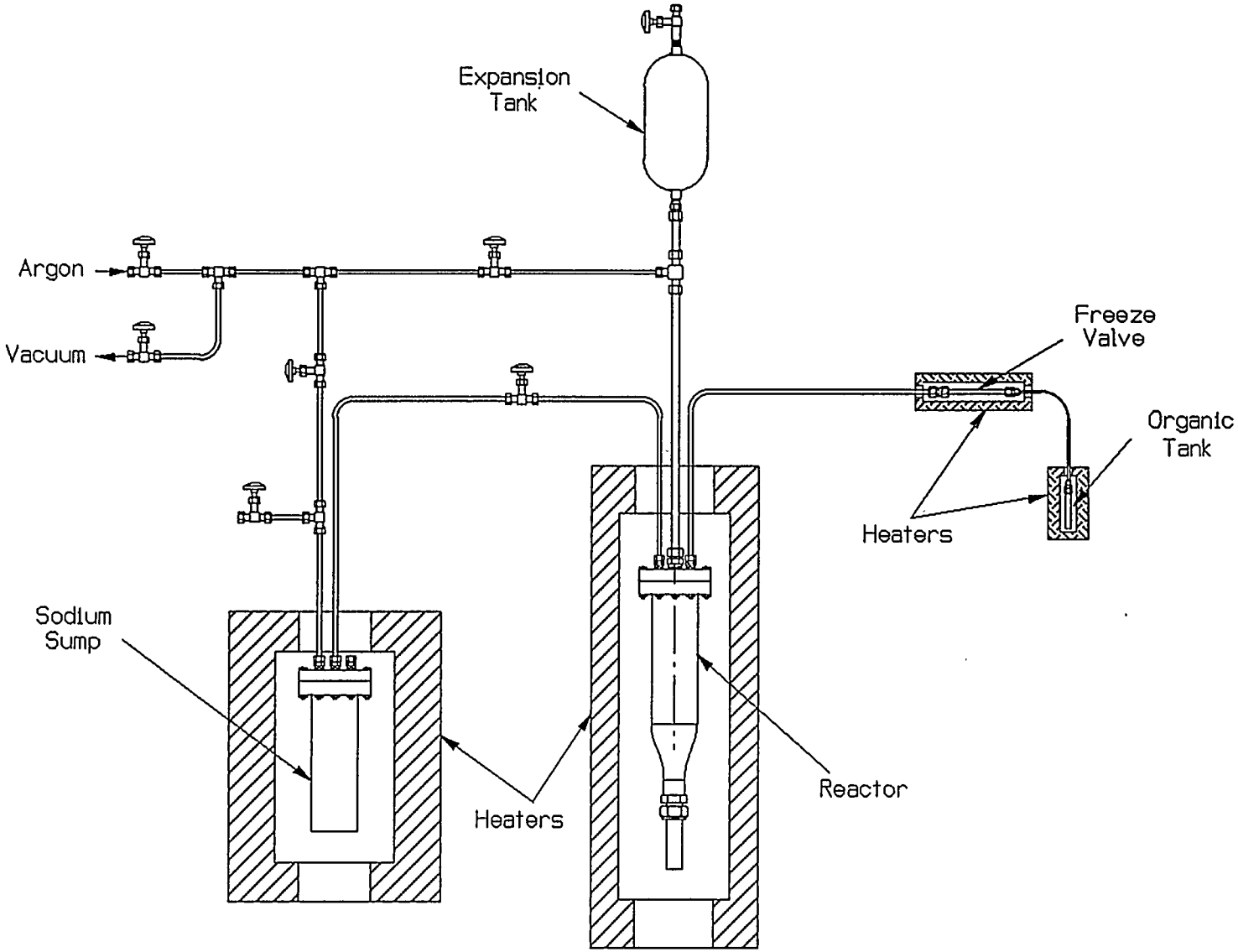

Figure 1. Sodium Reduction of Organic Halides

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93-094R1 -- NO_x REDUCTION IN DIESEL ENGINE EXHAUST USING A NITROGEN PLASMA

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: R. R. Sekar, H. K. Ng, and L. O. Hoppie, Energy Systems
V. J. Novick, Technology Development

Funding Profile:

FY 1992	$ -0-
FY 1993	$ 88.9K
FY 1994	$201.0K
FY 1995	$140.0K
FY 1996	$ -0-

Purpose: This project explores a novel, synergistic technique for the reduction of the NO_x emissions from engines that preserves all the benefits of the oxygen-enriched combustion concept. The inlet air would be separated in a hollow-fiber membrane into oxygen-rich and nitrogen-rich streams. The oxygen-enriched air would be used for engine combustion and the other stream is generally vented. The purpose of this project is to use the nitrogen in the waste stream as a source of electrically-activated nitrogen which, in turn, can be used in a proposed post-treatment process to reduce NO_x emissions dramatically. Such synergistic use of oxygen-enriched air for improved combustion and electrically activated nitrogen for post-treatment may lead to efficient and cleaner diesel and gasoline engines capable of meeting the regulations proposed for the year 2000. The proposed NO_x standards for engines using gasoline, diesel and other alternative fuels are extremely low and such novel methods will be needed to demonstrate that these levels are technically achievable.

Approach: Emissions from diesel and gasoline engines are being regulated to very low levels. Most of the criteria pollutants, such as carbon monoxide, unburned hydrocarbons, particulates and smoke require oxidation to be rendered harmless. NO_x, on the other hand, should go through a reduction reaction. ANL has been exploring the use of oxygen-enriched air for combustion in engines. This concept decreases all pollutants in the exhaust, except NO_x. If a practical means of solving the NO_x problem can be devised, it will benefit all the engine and vehicle manufacturers. This project explores a novel means of NO_x control in conjunction with oxygen-enrichment.

The principle involved here is the reduction of NO gases into nitrogen and oxygen by the use of electrically activated atomic nitrogen. While the theory behind this reaction has been known for many years, practical devices to provide electrically activated atomic nitrogen have not been developed. The scope of this project is to evaluate two electrical activation devices and select one of them for subsequent engine tests. The waste stream from the oxygen enriching device contains almost pure nitrogen, which can be the source of atomic nitrogen.

In FY 1993, two electrical activation devices were designed, built and checked out. The first device is a pulsed plasma generator producing a nitrogen corona and the second is an arc

discharge device which generates a rotating arc through which nitrogen gas is passed thereby producing atomic nitrogen. No appropriate experimental facility was available before this project was initiated in the Energy Systems Division. Hence a laboratory set-up had to be built almost from scratch.

Henry Ng and Vince Novick built-up the corona discharge device, with most of the components coming from the Engineering Physics group. The arc discharge device was designed and built by Lyle Hoppie and Raj Sekar. A suitable d.c. power supply was procured. The two devices were installed and Environmental Safety and Health (ES&H) inspections were completed.

In FY 1994, both the rotating arc and the pulsing devices were used to obtain laboratory data to quantify the NO_x reduction potential of each device. The pulsing system of producing monatomic nitrogen showed NO_x reduction efficiencies of 55% to 85%. The arc system employing direct current was better and showed efficiencies of 90%, but the electrodes were burning out after 30 minutes. At this point we believe that the pulsed arc system offers the best compromise of efficiency and durability.

Technical Progress and Results: The objectives set forth for FY 1994 were met. The investigation in this project centers around the following chemical reaction:

$$2NO+2N \rightarrow 2N_2 + O_2$$

If this reaction can be made to take place with a practical and economical device attached to an engine exhaust, then the environmental benefits are substantial, since the resultant products are harmless.

In FY 1994 the investigation focussed on collecting data from the devices built in FY 1993. This experimental data will be used in selecting one of the devices and redesign it for engine tests.

A pulsing corona (as compared to a pulsing arc) was obtained but it was too weak to be useful in reducing nitrogen oxides. Therefore all subsequent investigations were done with the arc devices. Both the pulsing arc and rotating arc were shown to be very effective in removing NO and NO_2 from a gas stream. For the rotating arc device, over 95% reduction was observed but this could not be repeated due to premature equipment failure. Typical reduction efficiency from the pulsing arc device is shown in figure 1.

During the optimization of the reaction chamber, it was noticed that when the arc hit the side wall instead of the ground electrode, the efficiency was greatly reduced due to the quenching of the reactive nitrogen. Other experiments showed that when nitrogen was replaced with air, no reduction of NO or NO_2 was observed. As far as the electrical power requirement was concerned, it was estimated that 2-5 KW will be needed for a 100KW vehicle operating with this device. If this device is used in conjunction with oxygen enrichment, then the improved vehicle fuel economy will offset this power requirement.

Based on the encouraging experimental results obtained so far, it is clear that more work is needed to further study the effects of oxygen in the needle and gas streams to define the operating limits for this device. In FY 1995, a new glass chamber will be designed so that the oxygen in the gas stream will not be exposed to the electric field (thus forming undesirable species such as ozone) while the reactive nitrogen is delivered to the stream. The test equipment has been moved from building 362 to building 315. FY 1995 efforts, if funded, will include tests with real engine exhaust gases.

Specific Accomplishments: Several presentations were made to DOE and other potential sponsors and automobile company executives who are interested in NO_x reduction technologies. The major accomplishment is the collection of experimental data. The arc discharge device was entirely designed and built at ANL. With the anticipated LDRD support in FY 1995, experimental data will be obtained from the test bench with real engine exhaust gases.

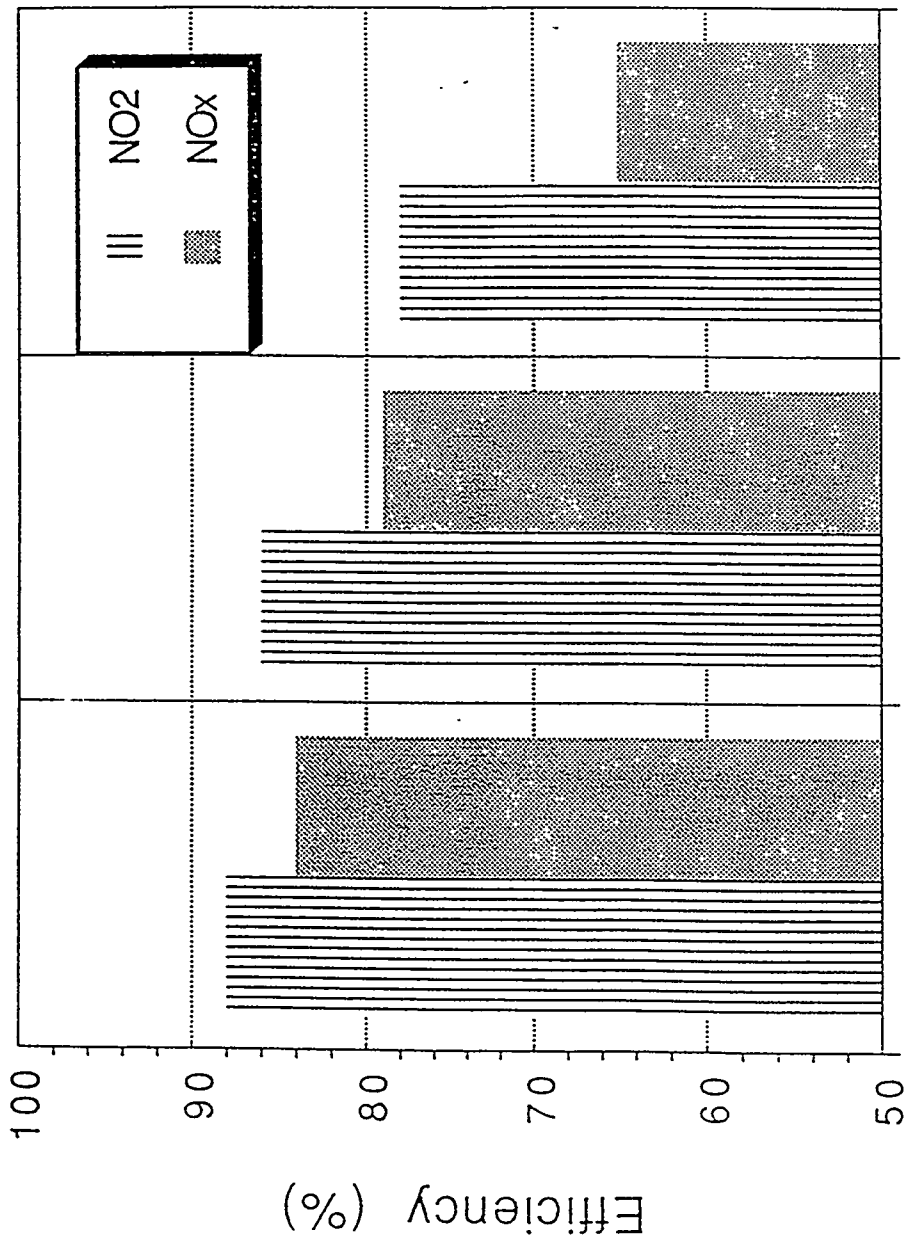


Figure 1. NO_x Concentration (ppm)

94-102N -- MILLIMETER-WAVE SENSOR FOR ENVIRONMENTAL MONITORING

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: N. Gopalsami and A. C. Raptis, Energy Technology

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$178.0K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The purpose of this project is to investigate the potential and feasibility of millimeter-wave technology for continuous emission monitoring of industrial effluents. Both standoff monitoring of wide areas and in-situ monitoring of individual stacks are of importance. Additionally, the detection sensitivities of the technique must be determined for common pollutants.

Approach: Measurement of effluent chemicals from industrial sites is important for demonstration of environmental compliance with the 1990 Clean Air act amendments, as well as for monitoring process safety and efficiency. Because its transmission properties are better than those of optics in harsh environments (smoke, dust, aerosols, steam, or adverse atmospheric conditions), the millimeter-wave technique was investigated for both standoff and extractive samples monitoring of airborne effluents from process plants.

Electromagnetic waves in the frequency range of 30 to 300 GHz are generally classified as millimeter (mm) waves. Polar molecules selectively absorb electromagnetic radiation of specific wavelengths in accordance with their rotational energy transitions in the microwave (MW) and mm-wave regions. Molecular rotational spectroscopy is a well-accepted laboratory technique that measures MW/mm-wave absorption with a gas cell under low pressure (<1 torr). The scope of this project involved development of techniques and devices for field measurement of industrial effluents.

The main scope of this work consisted of investigating the potential of mm-wave technology for both standoff and extractive samples measurement of industrial pollutants. For standoff monitoring, we investigated a novel idea that used a radar technique for spectroscopic measurement of airborne chemicals. The proof of principle of this technique was tested by releasing two simulant gases, D_2O and methanol, in open air. For extractive samples monitoring, a portable Fabry-Perot cavity was designed and built to detect specific chemicals of interest. In addition, the mm-wave detection sensitivities of commonly occurring pollutants (such as combustion products and volatile organic compounds) were measured in the laboratory and compared against those of the infrared technique.

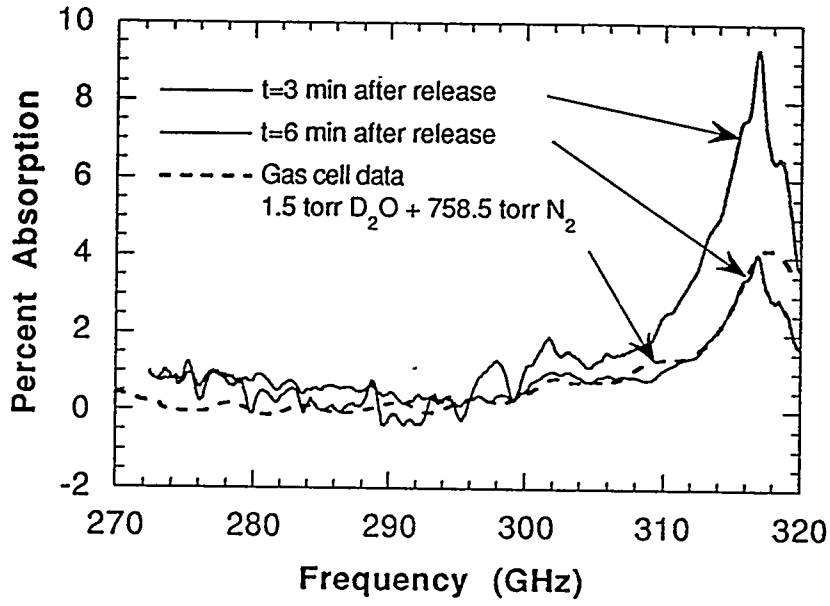
Additional participants in this work included S. Bakhtiari, a postdoctoral appointee in Energy Technology; Professor F. De Lucia, Ohio State Univ.; Professor K. Gopalan, Purdue Univ., Calumet; and M. Graham, a Lab Grad student from the Univ. of Illinois at Chicago.

Technical Progress and Results: The proof of principle of a novel idea, based on the swept-frequency radar technique, was tested for spectroscopic measurement of airborne chemicals. Using a signal sweeper in the 75-110 GHz range and a frequency tripler, we generated mm waves in the range of 225-320 GHz. A plume was created by heating the chemical under test in a beaker and releasing it under an open-ended T-shaped glass tube positioned in the path of the mm-wave beam. A corner reflector on the far side of the plume enabled monostatic (one-sided) measurements. A hot-electron bolometer was used as a detector. Two tests were conducted, one with D_2O and one with methanol. The measured absorption traces (figure 1) clearly indicated the presence of D_2O and methanol; the absorption peaks decreased as the release rate decreased with the cooling of the chemical. Line shapes and peak locations were verified with gas cell data obtained under controlled conditions.

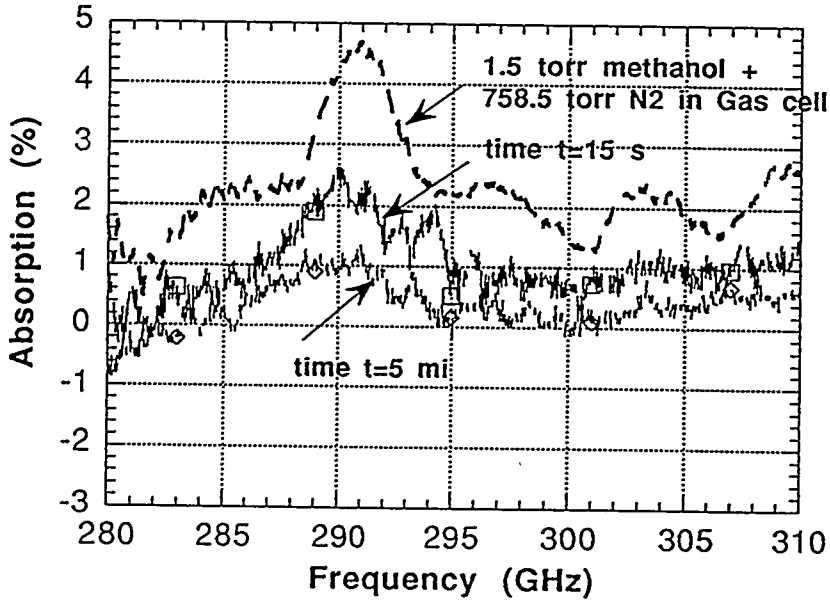
Millimeter-wave detection sensitivities of 35 common pollutant chemicals were measured with the ANL-built spectrometer in the 225-320 GHz frequency range; all measurements were made at atmospheric pressure, with nitrogen used as the carrier gas. The tested chemicals included inorganics such as sulfur dioxide, nitrogen oxides, and H_2S, as well as volatile organic compounds such as alcohols, acids, aldehydes, ketones, and organic compounds containing chlorine, sulfur, and nitrogen. Detection sensitivity depended on the dipole moment of the molecules, but for most of the above chemicals, it ranged from tens to hundreds of ppm over a one-meter path-length. In addition, the line strengths of 32 atmospheric molecules were simulated in the mm and infrared ranges by using the HITRAN data base. Except for weak dipole-moment molecules such as those with ring structures, comparable sensitivities were obtained in these ranges.

A portable Fabry-Perot cavity was designed and built for extractive samples monitoring of specific chemicals of interest (see figure 2). The cavity may be tuned by microprocessor controls to monitor different chemicals one at a time. Because the molecules are under low pressure ($\approx$1 torr), orders-of-magnitude improvement in sensitivity and selectivity are possible with this technique relative to open-air tests. Initial test results appear encouraging.

Specific Accomplishments: Feasibility of the millimeter-wave technique for open-air monitoring of effluents was demonstrated. A patent application titled "Millimeter-Wave Sensor for Monitoring Effluents" has been filed. Based partly on this work, a new source of funding ($200K) has been secured from the Department of State under the auspices of the Newly Independent States-Industrial Partnering Program (NIS-IPP). This is a joint program between Argonne and Ohio State University (in the U.S.) and the Institute of Applied Physics and ISTOK (in Russia) for development of a unique gas analyzer. As a followup, the Micro-Now Company in the U.S., jointly with Argonne and the Russian partners, has submitted a Phase II proposal for commercialization of the US-NIS mm-wave technology being developed. In addition, pursuant to interest expressed by the USCAR Environmental Research Consortium, a white paper has been submitted for low-emission measurement of vehicle exhausts. Two conference papers and one M.S. project have resulted from this work.



(a) D_2O release data



(b) Methanol release data

Fig.1. Proof of principle of open-air detection of (a) D_2O and (b) methanol

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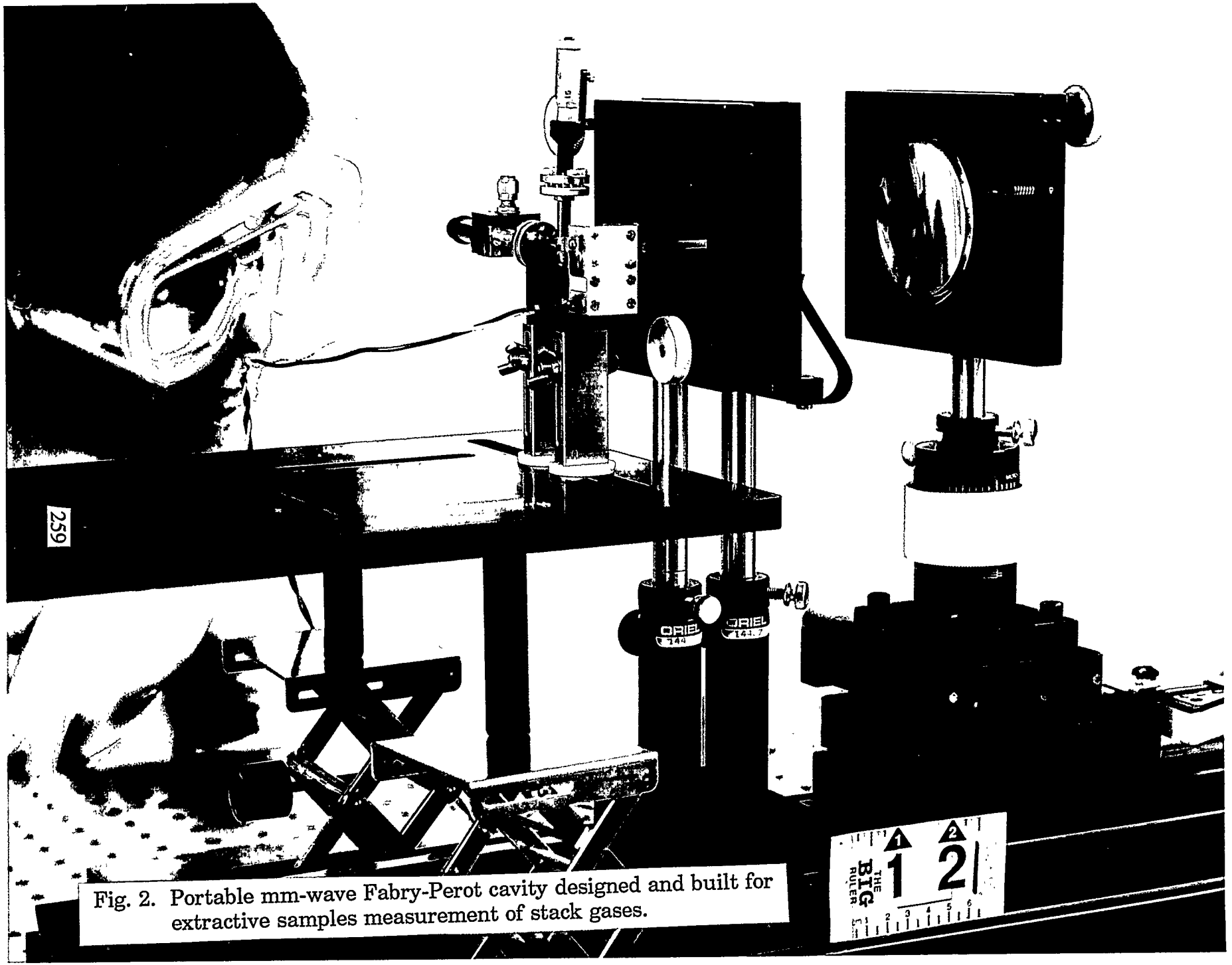

Fig. 2. Portable mm-wave Fabry-Perot cavity designed and built for extractive samples measurement of stack gases.

94-115N -- CONDITIONING OF N-REACTOR SPENT FUEL FOR ULTIMATE DISPOSAL

Associate Laboratory Director Area: Engineering Research

Principal Investigators: E. C. Gay, J. J. Laidler, and W. E. Miller, Chemical Technology Division

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$191.0K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: Determine the feasibility of applying IFR pyroprocess technology to the treatment of spent N-Reactor fuel for ultimate disposal in a geologic repository.

Approach: It is first appropriate to note the important differences between IFR and N-Reactor metal fuels. For IFR fuel, the stainless steel cladding is inert, and zirconium is alloyed with the heavy metal (HM) at HM/Zr weight ratio of about 9/1. For the Zircaloy-clad fuel of the N-Reactor, the ratio is estimated to be about 32/1 if cladding and fuel are homogenized. Therefore, in processing IFR fuel, we would have to handle about three times more zirconium compared with processing N-Reactor fuel.

In IFR research, we investigated two methods for attacking zirconium metal. One of these methods is anodic dissolution. At the appropriate voltage, zirconium metal will oxidize into the salt and deposit on the cell cathode. When the zirconium is alloyed with HM, the result is the same, even though it is not clear under what conditions zirconium in the alloy is truly oxidized or partially eroded away because of oxidation of the uranium base. The other method for attacking zirconium metal is digestion (at 500°C or less) in cadmium metal. The solubility of zirconium in liquid cadmium at 500°C is low, about 0.2 wt %. We have found, however, that cadmium vigorously attacks zirconium by forming the intermetallic compound Cd_2Zr, and that this attack is rapid and continues until one of the reagents is exhausted. [The small amount (2-4%) of tin in Zircaloy would likely have little effect on either dissolution process.]

The presence of a stable oxide film formed on the Zircaloy cladding on exposure to steam or high temperature water could have a profound effect on the above-described dissolution processes. The molten salt, containing HM and fission product chlorides, could possibly destroy this film. Its presence would block dissolution in cadmium. If it is present and inert in the molten salt, then this cladding could be treated in the same manner as the stainless steel cladding on IFR fuel. The uranium fuel would be anodically dissolved out of the cladding after it is ruptured by some mechanical means so as to provide electrolyte access inside the cladding. The ruptured clad slugs would be contained in a porous stainless-steel basket, which would be made the anode of the cell. This method works well for IFR-type fuels where >99.99% of the heavy metal is easily dissolved out of the insoluble cladding.

If an insoluble film on the Zircaloy is not present, then the porous basket anode approach would be of interest for N-Reactor fuel and will be investigated. The rate of anodic dissolution of the Zircaloy will probably be a good deal lower than the rate of dissolution of the HM; therefore, it may not be necessary to dissolve all of the Zircaloy cladding along with the HM. This would be advantageous since no further separations processing would be needed for the Zircaloy which remained in the anode basket. Ways to maximize this effect might be found through control of basket geometry and operating conditions imposed on the cell. In any event, it would be advantageous to mechanically rupture the cladding to provide immediate electrolyte access to the HM inside the cladding.

For fuel dissolution in cadmium, it would also be advantageous to rupture the cladding mechanically before the fuel slugs are added to the cadmium pool. This would allow the cadmium to attack the inner cladding surface as well as the outer. It would also provide immediate access of the cadmium to the contained HM so that electrotransport of the HM to cathodes could be conducted at the same time as cladding attack.

Our initial experimental approach to this problem is to do decladding-transport studies with the engineering-scale electrorefiner in the Chemical Technology Division. Experimental dissolution-transport equipment would be designed to fit into this electrorefiner through the vessel access parts. One important goal of the experimental program is to obtain rate data for the various dissolution-transport options so that scale-up to a production model could be done at the end of this initial study.

Technical Progress and Results: Five anodic dissolution tests with simulated (depleted uranium plates and Zircaloy tubing) N-Reactor fuel were completed in the engineering-scale electrorefiner. In one test, no Zircaloy was dissolved while 99.5% of the uranium was dissolved. In the remaining tests, between 8.3 and 81.5% of Zircaloy was dissolved, while the dissolved uranium ranged between 87.1 and 100%. The effects of operating conditions on the anodic dissolution of uranium and Zircaloy were determined from these tests.

Six anodic dissolution tests were completed with an unirradiated N-Reactor fuel slug. The fuel slug was sawed into pieces of different length and diameter. The objectives of these tests were to determine the electrorefining characteristics of these fuel segments and to determine the type of fragmentation needed to provide spent fuel segments that are suitable for a high throughput (dissolution of >10 kg uranium/h) electrorefining process.

Results of the unirradiated N-Reactor fuel anodic dissolution tests are given in Table 1. The following conclusions were drawn from these tests with the unirradiated N-Reactor fuel:

1. The highest uranium dissolution rates are achieved with direct contact between the fuel segments and the anodic dissolution baskets.

2. The highest uranium dissolution rates are achieved with minimum constraint of salt flow through the anodic dissolution baskets.

3. Current-limited operation at constant voltage showed better performance than constant-current operation. The cell voltage was maintained below 0.45 V, and the electrorefiner was operated at the highest cell current with minimum dissolution of the Zircaloy cladding.

4. The uranium dissolution rate in the end pieces of the N-Reactor fuel slugs is 70-80% lower than that measured in the inner and outer fuel segments.

5. To minimize the dissolution of the Zircaloy cladding, fuel segments of similar uranium dissolution rates should be loaded in each anodic dissolution basket.

6. Further tests are needed to determine the effect of fuel segment diameter and length on the uranium dissolution rate.

Specific Accomplishments: Based on the above results from these initial anodic dissolution tests, a conceptual design was produced of a dissolver-electrorefiner for a full-scale plant to process N-Reactor spent fuel. In this design, the diameter of the electrorefiner is about 60 in (1.5 m). A 3.062 metric ton batch of N-Reactor fuel is loaded into 42 anodic dissolution baskets and is electrorefined at a rate of 10.1 kg uranium per hour. The throughput rate is 6.124 metric tons (two batches) of uranium per month per electrorefiner. The peak current is 5073 A.

A paper entitled "Electrorefining N-Reactor Fuel" by E. C. Gay and W. E. Miller was submitted for publication in the proceedings and presentation at the DOE Spent Nuclear Fuel Challenges and Initiatives Meeting, December 13-16, 1994, Salt Lake City, Utah.

TABLE 1. Unirradiated N-Reactor Fuel Anodic Dissolution Tests

Run No.[a]	Aver. Dissolution Current, A	Maximum Dissolution Voltage, V	Electro-depoosition Time, h	Quantity of Electricity, Ah	Anodic Dissolution Baskets				Electricity Required for DissolutionA h/kg U
					Initial Metal Wt, kg		Amount of Metal D Dissolved, %		
					Uranium	Zircaloy	Uranium	Zircaloy	
148	25	0.33	91.1	2239	6.104	0.312	85.7	0	428
149	25	0.53	27.8	701	1.841	0.093	90.1	0	405
150	32	0.8	52.5	1695	4.183	0.211	100	81.2	405
151	35	0.43	41.5	1438	3.887	0.297	81.3	0	455
151A	20	0.45	17.8	357	0.727	0.297	96.7[b]	0	477
151B	3	0.37	46.2	149	0.127	0.297	100[c]	27.6	500

[a]Runs 148-150 used constant current operation; Runs 151, 151A, and 151B used current limited-constant voltage operation

[b]Based on the amount of uranium dissolved in Runs 151 and 151A.

[c]Based on the amount of uranium dissolved in Runs 151, 151A, and 151B.

94-117N -- MOLTEN-SALT TRU EXTRACTION PROCESS FOR CONVERTING TRU RESIDUES TO NON-TRU WASTES

Associate Laboratory Director Area: Engineering Research

Principal Investigators: J. E. Battles and C. C. McPheeters, Chemical Technology

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$225.1K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: Explore the feasibility of extracting transuranic (TRU) elements (Pu, Np, Am, and Cm) from oxide residues, including spent fuel, ash heel stored at Rocky Flats, and calcined high-level waste stored at the Idaho Chemical Processing Plant for feed to the pyrometallurgical process developed for metal fuels. The goal is to achieve sufficient extraction efficiency to convert the residues to non-TRU wastes, thus greatly reducing the cost of site remediation and waste disposal.

Approach: Work at ANL during the 1960s by Johnson and Wenz showed that PuO_2 can be dissolved in $MgCl_2$ molten salt by the simple reaction:

$$PuO_2 + MgCl_2 \rightarrow PuOCl + MgO + 1/2\ Cl_2$$

The reaction will not proceed under ordinary conditions; however, in the presence of a getter for the chlorine, e.g., zinc, it proceeds rapidly. A small amount of zinc can be used to react with the chlorine according to the reaction:

$$PuO_2 + MgCl_2 + 1/2\ Zn \rightarrow PuOCl + MgO + 1/2\ ZnCl_2$$

This reaction was confirmed in recent preliminary laboratory-scale experiments. Plutonium and americium were selectively extracted from an ash heel sample into a molten $MgCl_2$ salt. Because the bulk of the residue was chemically unaffected, the salt, containing dissolved PuOCl and AmOCl, can be separated from the solid residue and the insoluble MgO reaction product. The soluble oxychlorides are then easily reduced to metal to isolate the TRU product for disposal in a compact waste form.

Because PuO_2 has a much higher solubility in $MgCl_2$ salts than does UO_2, this process can separate PuO_2 from UO_2. For instance, at 800°C an equimolar mixture of molten $MgCl_2$ and $CaCl_2$ in equilibrium with solid PuO_2 contained 6.5 wt % plutonium in solution, whereas the same mixture in contact with UO_2 contained only 0.025 wt % uranium.

In these extraction processes, because the bulk matrix is not dissolved, reaction of the $MgCl_2$ with the TRU elements depends on contact of the salt with the extractable oxide. Hence, it is important that the particles be small enough for this contact to be possible. For ash heel, recent work done at ANL by Chaiko has shown that the PuO_2 is present as discrete particles, and when finely ground these particles are available for extraction. For other matrixes, such as light water reactor (LWR) fuel, it is expected that the PuO_2 would be an integral part of the UO_2 matrix and thus would not be completely extractable.

Technical Progress and Results: An experiment was conducted in which ash heel containing 0.54 g of Pu and 1250 μg Am was contacted with 300 g $MgCl_2$. Zinc (20 g) was also included as a getter for the chlorine. After two days of contact with stirring, filtered samples of the $MgCl_2$ were taken for analysis. According to the analysis, all of the Pu and Am could be accounted for in the $MgCl_2$ salt. However, as the uncertainty in analysis was estimated at $\pm$ 10%, some TRUs may have remained in the ash heel residue. The salt and residue were washed with dilute acid to remove the salt and oxychlorides, and the ash heel residue was filtered and analyzed. The results showed 0.01 g Pu and 23 μg Am in the residue. Thus, 98.8% of the plutonium and 98.2% of the americium were extracted. We have exposed the residue to an additional extraction with fresh $MgCl_2$ to see if further extraction is possible. Unfortunately, the analytical results are not yet available. This second extraction should tell us if the 1-2% residual TRUs are not extractable because they are buried in the ash heel matrix, or if an equilibrium concentration had been reached in the first extraction, in which case additional extraction into fresh $MgCl_2$ should be possible.

The ash heel, which is a variable matrix of Al_2O_3, SiO_2, Fe_3O_4, etc., contains $\sim$10% PuO_2. The test material had been ground to $\sim$20 μm particle size for our use. We are convinced that even smaller particles would ensure complete extraction; however, very fine particles present a problem, as they are difficult to separate from the molten salt. A submersible centrifuge which is being developed for other processes appears attractive for this application. We have examined a number of designs which would allow us to separate the residual ash heel from the molten salt. The principle for the device is a pump that retains particles heavier than the fluid in a region provided within its housing. The unit recirculates the liquid and suspended solids until all the solids are retained.

Experiments have been performed in which simulated LWR spent fuel (high-fired mixtures of UO_2, PuO_2, and fission products) was exposed to $MgCl_2$. In these experiments the PuO_2 is incorporated within the UO_2 matrix and is not readily contacted with the $MgCl_2$. With coarse material 35% of the plutonium and 38% of the americium were extracted. With finely ground material, $<$38 μm, the amount extracted was similar, 38% of the plutonium and 38% of the americium. When the UO_2 matrix was heated in air and oxidized to U_3O_8, which results in a reduction in particle size, 46% of the plutonium and 51% of the americium were extracted. These results indicate that, as expected, the process is not readily usable for extraction of TRU elements from LWR fuel.

Future work will concentrate on further reducing the TRU content of the ash heel, characterizing the ash heel morphology to determine the location and form of the TRU elements, and developing methods for concentrating the TRU-bearing fraction. The objective of these activities is to convert most of the ash-heel volume to a non-TRU waste for ease of

disposal. The concentrated TRU fraction can then be immobilized in a stable waste form suitable for repository disposal.

Specific Accomplishments: Greater than 98% of the Pu and Am in Rocky Flats ash heel was extracted in one contact. A submersible centrifuge shows promise for separating the fine residual ash heel from the $MgCl_2$ salt. The $MgCl_2$ extraction of TRU elements from simulated LWR spent fuel was not effective with less than 50% extracted.

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94-118N -- CHARACTERIZATION OF METALLIC FUEL ALLOYS FOR PLUTONIUM DESTRUCTION

Associate Laboratory Director Area: Engineering Research

Principal Investigators: D. C. Crawford, S. L. Hayes, and E. L. Wood, Fuels and Engineering

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$175.8K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The project objective was to perform an initial evaluation and characterization of potential metallic fuel alloys derived from the U-Pu-Zr system to be utilized for the destruction of Pu in a liquid metal reactor. Candidate alloys included U-Pu-Zr, Pu-Zr and Pu-Zr-Hf alloys made from weapons-grade Pu feedstock, which contains Ga as an alloying element. The hope was to devise a fuel form that could tolerate the Ga alloy addition, thus eliminating the need for a Ga-removal step prior to the destruction of the weapons-grade Pu in a reactor. Needed characterization would ultimately include demonstration of the ability to cast fuel slugs of the proposed alloys, measurement of the thermophysical properties needed for evaluation of core performance, fuel-cladding compatibility studies, and irradiation testing.

Approach: A metallic fuel alloy able to tolerate Ga additions resulting from the use of weapons-grade Pu as a feedstock component would reduce the preprocessing required of this material prior to its incorporation into a fast reactor fuel for destruction by fission. The three primary concerns with the use of Ga as a fuel component are (1) elemental Ga has a low melting temperature, and could therefore lead to liquid phase formation within the fuel, (2) liquid Ga has a high vapor pressure and could prove difficult to retain in the fuel alloy during casting, and (3) Ga is known to embrittle steels. The fact that Ga embrittles steels poses the most significant safety question regarding the use of Ga in a reactor. Should the Ga component of the fuel alloy become liquid, it might be readily transported to the steel cladding, where embrittlement could cause premature cladding failure. However, Ga forms stable compounds with U, Pu, and Zr, each having relatively high melting temperatures; Ga tied up in compound form in the fuel alloy would probably not be available to embrittle the cladding. For this reason it was felt that Ga could be successfully incorporated into the U-Pu-Zr fuel alloy without undue safety concerns.

The approach selected for this project was to attempt to cast a U-Pu-Zr alloy using Ga-bearing weapons-grade Pu as a feedstock component and to incorporate this fuel alloy into an irradiation experiment in the Experimental Breeder Reactor II (EBR-II). The small addition of Ga to the U-Pu-Zr alloy was not expected to alter significantly the material properties of the fuel alloy; thus, an acceptable safety case for an irradiation experiment would be possible. For the Pu-Zr and Pu-Zr-Hf candidate fuel alloys, material property information needed to prepare the safety case for an irradiation experiment did not exist. Therefore, an effort was initiated to prepare glovebox facilities in the Fuel Assembly and Storage Building (FASB) for use in

measuring the thermal conductivities and enthalpy/specific heats of these alloys. These two activities, the casting and irradiation of a U-Pu-Zr-Ga alloy, and development of a thermophysical property measurement capability inside a Pu glovebox, were conducted in parallel.

Technical Progress and Results: Injection casting of the U-Pu-Zr-Ga alloy was performed in the Experimental Fuels Laboratory (EFL) with technical guidance from C.L. Trybus of the Fuels and Engineering Division. The nominal alloy composition was U-19.8Pu-10Zr-0.2Ga (in weight percent). The liquidus temperature of this alloy was expected to be essentially the same as that for U-20Pu-10Zr (which is cast routinely in the EFL). However, a modified casting procedure was employed for the Ga-bearing alloy in an effort to reduce the expected evaporation of Ga from the fuel melt prior to casting. Relative to the normal procedure, the Ga-bearing casting employed a lower amount of melt superheat, a somewhat lower holding and pre-injection vacuum, and a reduced time at temperature prior to injecting the melt into quartz molds.

Five slugs of the U-Pu-Zr-Ga alloy were successfully cast using the modified casting procedure. These slugs were clad in HT9 and incorporated into the EBR-II irradiation experiment designated X521 along with standard EBR-II Mk-IIIA and Mk-V fuel elements. This subassembly was loaded into the reactor for Run 169A, and remained in-core until the final EBR-II shutdown following Run 170A at the end of September; no fuel failures occurred, and the subassembly achieved a maximum burnup of 1.9 atomic percent. The intention had been for the experiment to remain in-core until 5 atomic percent burnup, and then to perform destructive examinations on at least one of the Ga-bearing elements to evaluate the impact of Ga on fuel performance. Of particular interest is the form and location of the Ga in the fuel and whether fuel-clad chemical interaction is affected by the Ga additions (i.e., is Ga penetrating the cladding?). Such examinations have not yet been performed.

In parallel to the U-Pu-Zr-Ga irradiation experiment, preparation of a glovebox in FASB for Pu operations was initiated. Thermophysical property measurement apparati for collecting thermal conductivity and enthalpy/specific heat data on unusually small specimens of the Pu-Zr and Pu-Zr-Hf alloys were designed, built and tested in collaboration with H.F. Poppendiek of GeoScience Ltd. These systems will be able to measure the required property data with an error of less than 10% (with hope of achieving errors less than 5%) on small Pu-bearing samples. Installation of these apparati into the glovebox are awaiting final glovebox modifications (e.g., electrical wiring modifications, installation of thermocouple feedthroughs, etc.). These systems are necessary for the determination of the thermophysical properties of the Pu-Zr and Pu-Zr-Hf alloys prior to their irradiation testing.

Specific Accomplishments: A data package and safety analysis supporting the irradiation of a U-Pu-Zr-Ga fuel alloy was prepared and approved by the IFRO Division Experiment Safety Review Group. The ability to successfully cast and irradiate a metallic alloy fuel that directly utilizes weapons-grade Pu (containing the Ga alloying addition) was successfully demonstrated. Apparati for the collection of thermal conductivity and enthalpy/specific heat data on unusually small, Pu-bearing samples were designed, built, and tested.

94-167N -- WASTE MANAGEMENT OF CHLOROFLUOROCARBONS

Associate Laboratory Director Areas: Physical Research and Energy and Environmental Science and Technology

Principal Investigators: J. V. Michael and A. F. Wagner, Chemistry
H. S. Huang, Energy Systems

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$133.6K
FY 1995	$140.0K
FY 1996	$ -0-

Purpose: The purpose of this project is to develop a verifiable model of chloro-fluoro-carbon (CFC) incineration via a low-temperature plasma furnace.

Approach: Incineration is one of the most cost effective methods of disposing of large volumes of municipal, hazardous, and/or medical wastes. However, the environmental concern over emissions has made the field of incineration controversial. Numerous laboratory, pilot, and full scale experiments have shown that the nature and yield of organic emissions from waste incinerators is controlled by chemical kinetics. This is certainly true in the case of CFC compounds. To optimize complete destruction of these hazardous compounds and to monitor any degradation of performance, chemical models of the incineration process are needed. Such models should be based on experimental data for elementary reactions but at the same time properly describe the performance of practical incinerators. While the chemical mechanisms for destruction of CFCs at the temperatures needed for incineration are not well known, considerable progress at the elementary reaction level in both theory and experiment has occurred in recent years. At the same time, novel incineration devices, such as low-temperature plasma furnaces, are being investigated as alternatives to conventional high temperature combustors. At Argonne, considerable expertise in both elementary reaction kinetics and novel incineration is present in both the Chemistry Division and the Energy Systems Division. This project combines this expertise in a concerted evaluation of the potential of plasma furnaces as environmentally safe CFC incinerators. There are three objectives:

1. Measurements of selected unimolecular dissociation rate constants will be carried out for some important chlorocarbon molecules.

2. These processes will then be theoretically analyzed to understand the thermochemical properties of the species involved in the reactions. Also, the experience with theory will create confidence in extrapolations to other molecular systems. This will allow the development of a combination experimental/theoretical database.

3. With the information so obtained, chemical models will be constructed for use in real incinerator applications, and these models will be tested in experiments performed with a low-temperature plasma furnace incinerator.

Accurate rate constant measurements for the elementary reactions involved in the incineration process are clearly needed if successful incineration models for CFC destruction are to be developed. Prior to the work of this project, there were almost no results available for either bimolecular rate constants or unimolecular dissociation processes at the temperatures (800-1500 K) and pressures (1 atm) used in conventional incinerators. To be sure, work on OH with several chlorocarbons has appeared, and O-atom studies with the CH_3Cl, CH_2Cl_2, and $CHCl_3$ are complete; however, the rate behavior appears to be strongly non-Arrhenius for all reactions. Therefore, extrapolation beyond the T-range of a particular study is not very reliable. There are also three studies of note on O-atom and OH-radical with unsaturated CHC molecules. There are a myriad of Cl-atom with organic substrate molecule studies. In all cases the mechanism involves simple H-atom abstraction. Most of this work has been carried out in support of atmospheric chemistry and therefore does not extend to the incinerator temperature range. Again, the rate data appear to show strong curvature in Arrhenius plots making new higher temperature studies on this type of reaction to be imperative. Thermal dissociation rate data are also not extensive. There is one report on the thermal decomposition of CH_3Cl, and, due to the work of one of the investigators (Michael), new direct studies have been completed on the decompositions of CH_3Cl, CCl_4, CF_3Cl, $COCl_2$, and CH_2Cl_2, using the atomic resonance absorption spectrometric method (ARAS) for Cl-atom detection. Prior to work of this project, there was very little else known about the thermal decompositions of aliphatic chlorocarbon molecules and almost nothing known about the thermal dissociation of chloro*fluoro*carbons. The first efforts of this project have been to extend the ARAS method (see below) to such measurements.

Although primary thermochemical and kinetics rate constants must come from experiment, chemical kinetics and electronic structure theory can play an important role in expanding measurements on a few reactions into a more extensive database for modeling practical devices. In the last decade, the development of both variational versions of conventional statistical theories [e.g., transition state theory and Rice-Ramsperger-Kassel-Marcus (RRKM) theory] and accurate approximations to tunneling have provided the framework for a near quantitative understanding of non-Arrhenius curvature in rate constants. At the same time, developments in computer technology and electronic structure theory have made it feasible to calculate features of the potential energy surfaces for reactions that directly translate into thermochemical properties (e.g., heats of formation) or govern reaction rates (e.g., reaction barrier heights) within the variational kinetics theories. Most of this effort has been directed toward hydrocarbon combustion. One of the investigators (Wagner) has been extensively involved in this work. Recently has this type of theoretical analysis been applied to halocarbon chemistry with preliminary studies of CH_3Cl and CH_3F dissociation. Extension of this work to CFC thermal dissociations, with a calibration of the theory to critical experiments, has been the second objective of the project.

Low temperature (non-equilibrium) plasma destruction is a promising alternative technology for treating CFC compounds. This technology has several advantages over conventional thermal and/or catalytic oxidation processes:

- operates at ambient temperature
- eliminates sensitivity to catalyst poisoning by halogen compounds

- requires low maintenance
- compact and low cost
- can be easily retrofitted to existing equipment

Some initial investigations have been performed for applying this technology to destroying CFC compounds, with good results. As has already been suggested, however, to further advance this technology an improved understanding of the chemical kinetics steps in the reaction mechanism is required.

At Argonne, three low-temperature plasma reaction systems have been constructed. One microwave-based system has been tested for hydrogen sulfide dissociation, and one similar system has been employed for evaluating the destruction efficiency for volatile chlorinated organic compounds (e. g., trichloroethylene and trichloroethane). The third system, which is a pulse corona one, has been used for the investigation of nitrogen oxide reduction. This pulse corona system will be modified for this study.

Technical Progress and Results: The first objective of this work was the measurement of accurate unimolecular rate constants for chlorofluorocarbon molecular dissociations at high temperatures. To this end, we used the atomic resonance absorption spectrometric (ARAS) shock tube technique and facility in the Dynamics in the Gas Phase Experimental Group in Chemistry Division at ANL for measuring Cl-atom formation rates.

The work plan for the first year concentrated on thermal decomposition studies of CF_2Cl_2 (CFC-12), $CFCl_3$ (CFC-11), and CF_2HCl (HCFC-22). The thermal decomposition studies on CF_2Cl_2 and $CFCl_3$ are complete. The results for CF_2Cl_2 are shown in figures 1 and 2. Yield measurements (figure 1) indicated that molecular elimination to $CF_2 + Cl_2$ did not occur. Hence, we are able to say with confidence that the primary reaction gives $CF_2Cl + Cl$ followed by the fast decomposition of CF_2Cl to CF_2 and another Cl-atom. A similar situation exists in the $CFCl_3$ case. The initial process produces $CFCl_2 + Cl$, and the halogenated methyl radical subsequently rapidly decomposes giving a second Cl-atom and the carbene radical, CFCl. Figures 2 and 3 show the thermal rate constant data for these molecules. We have started experimental investigations on CF_2HCl. We have measured CF_2 radical formation rates, and this indicated that the primary thermal decomposition process is direct formation of $CF_2 + HCl$; i.e., molecular elimination in contrast to atomic elimination. A typical absorption profile for CF_2 radicals is shown in figure 4.

The second objective of this work is theoretical analysis of CFC dissociations using the experiments as a calibration. We have carried out theoretical calculations for CFC-11 and CFC-12 using modern unimolecular reaction rate theory. Though not complete, this work will contribute to further calculations on other systems that will not be specifically studied experimentally.

The third objective of this work is the development of a model of the plasma incineration that is verified by measurements of the incineration of CFCs. This effort will be the primary objective of continued funding FY 1995.

Specific Accomplishments: This work was the subject of an oral presentation given by S. S. Kumaran, K. P. Lim, M.-C. Su, and J. V. Michael at the 1994 Annual AIChE Meeting in San Francisco, November 13-18, 1994, as part of the Symposium on Fundamental Chemical and Physical Processes in Combustion and Incineration. We have carried out theoretical calculations for CFC-11 and CFC-12 using modern unimolecular reaction rate theory, and are currently preparing two manuscripts for publication.

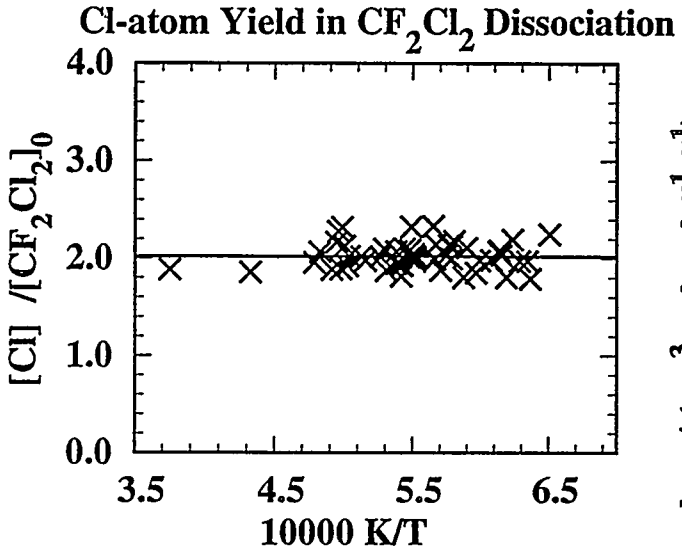

Figure 1.

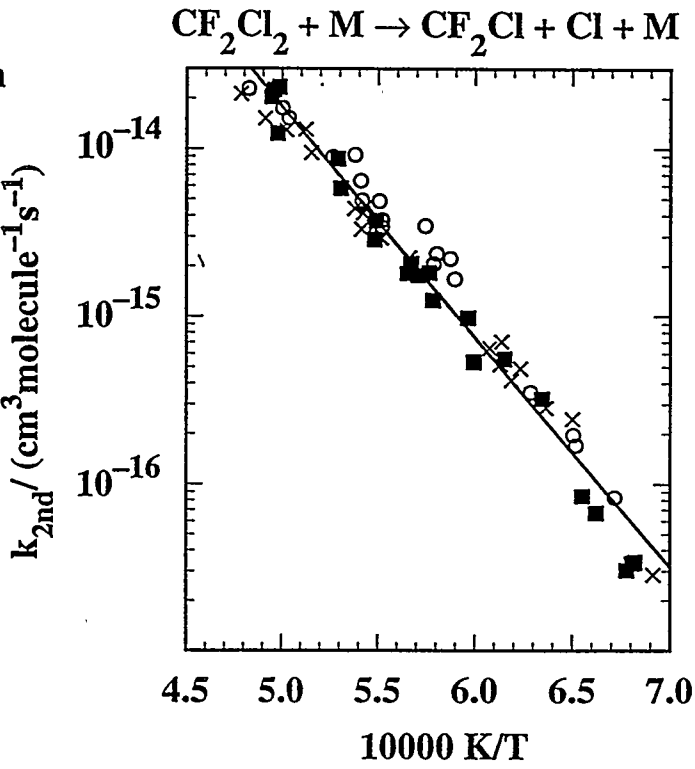

Figure 2.

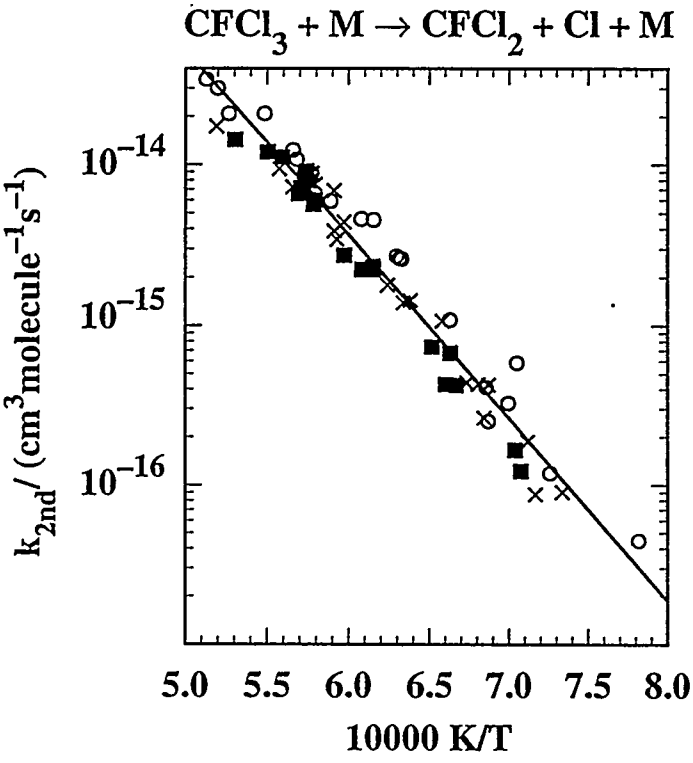

Figure 3.

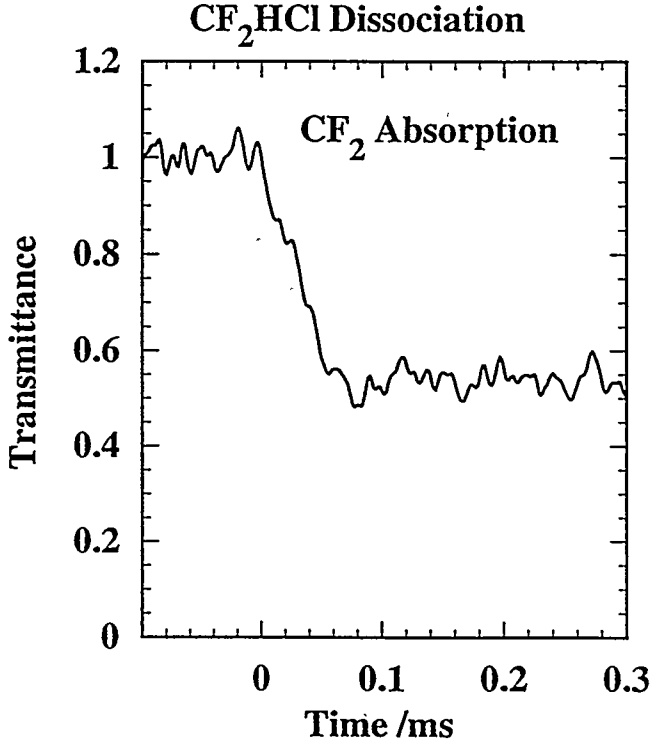

Figure 4.

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94-003N -- INTELLIGENT ROBOTICS GLOVE

Associate Laboratory Director Area: Engineering Research

Principal Investigators: T. Y. C. Wei, D. Y. C. Pan, and J. Reifman, Reactor Analysis

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$128.4K
FY 1995	$118.0K
FY 1996	$ -0-

Purpose: The project objective is to determine the technical feasibility of an intelligent robotics device using an ANL-derived approach to identify geometrical features of an object through tactile perception. The proposed system is composed of a strain-sensitive glove, a strain tomographer and a neural network. Establishment of a design would enable ANL to make a technical case to prospective industrial partners.

Approach: Current research on tactile perception devices is oriented at producing a mechanical duplicate of a human hand with fingers and intelligent sensory feedback. The limitations of this approach appear to be dictated by the need for sensors to measure the displacement of the "fingers" relative to many known reference points. In contrast the ANL-derived approach is to construct a strain-sensitive glove which can be bent over the contours of the object to be recognized. The use of bending/local curvature information together with calibration through neural network training should substantially reduce the need for known reference points, simplify the design, increase reliability and produce lower manufacturing costs.

Proof-of-concept feasibility for this ANL approach is addressed through investigating the design issues for a design which combines an intelligent glove composed of layered intelligent composites, an integrated sensor/signal mesh, strain tomography/neural networks and the plate bending concept. The top-level design issues are:

- Intelligent composite material: flexibility and resilience to adjust to different shapes; sensitivity for electrical signal processing; hysteresis should be minimum for reproducibility of object shape.

- Glove/arm design: conformance of glove to surface of object being recognized; minimal number of electrical connections/wiring for electro-mechanical interfacing; control over relative position of arm/glove.

- Image reconstruction/tomography: use of curvature for construction of image should not lead to integration of local errors into global image; functional dependence of strain-to-curvature mapping and its inverse should be unique and accurately represented.

The methods used to resolve these top-level design issues were a combination of off-the-shelf surveys, one-dimensional experiments, two-dimensional simulations and analyses. By area, the workscope was:

- Intelligent composite material: In collaboration with the University of Delaware/Center for Composite Materials, off-the-shelf surveys were conducted, samples were fabricated and one-sensor/one-unit experiments were performed.

- Glove/arm design: design studies were performed in conjunction with the selection of the intelligent glove material and the development of the image reconstruction/tomography algorithm.

- Image reconstruction/tomography: With the participation of visiting scientist J. Vitela (National Autonomous University of Mexico), two-dimensional analyses were performed to develop mapping algorithms for image reconstruction. Testing was performed first with exact curvature data for a set of two dimensional objects and then with strain data for the same set of objects using simulation calculations for the glove deformation.

Technical Progress and Results: In summary, the conclusions of this project work regarding the top-level design issues are:

- Intelligent composite material:
  - Matrix/preform fibre: RTV silicon/fiberglass yarn. This combination allows the required flexibility and resilience for the glove fabric. Ten sensors/inch in the preform is within the range of current manufacturing techniques.
  - Sensor: This is still undetermined. Conductive elastomer strands give the required signal sensitivity/material flexibility. However, hysteresis/reproduci-bility may become a major materials research project. A promising alternative is capacitive polymers. This will be tested if a second project year is funded.

- Glove/arm design:
  - Glove mechanical design: a conceptual glove design has been produced. Limited testing will be performed if a second project year is funded. Major testing will be reserved for a follow-on to LDRD support.
  - Glove electro-mechanical interfacing: a novel doubly connected mesh of sensor and signal strands woven into the preform has been proposed.
  - Arm mechanical design: a number of off-the-shelf manufacturers have been identified as possibilities.

- Image reconstruction/tomography:
  - Use of local curvature: Ten sensors/inch given enough local curvature definition that the global image is not significantly affected by the local discretization errors in 2-D. Corners will have to be treated by a piecewise algorithm. The piecewise algorithm will be investigated in the second project year if funded.

- Strain-to-curvature mapping: In order to recognize sharp changes in local curvatures, such as corners, a piecewise algorithm will have to be used. For milder curvature objects, the slender-beam neural network representation gives reasonable 2-D shape results. If funded, 3-D issues will be examined in the second project year.

Specific Accomplishments: A patent application entitled "A method and apparatus for identifying object dimensions through tactile means" (ANL-IN-93-032) by T. Y. C. Wei, D. Y. C. Pan and J. Reifman was written. An internal report entitled "Conceptual System Design Study: Intelligent Robotics Glove" was completed.

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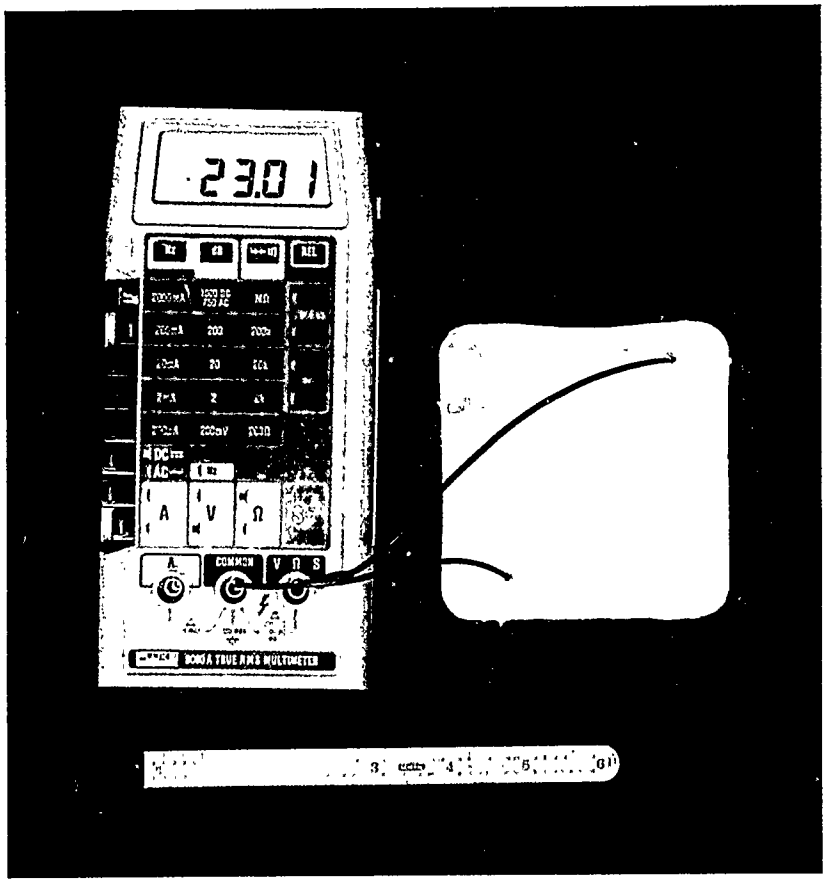

Fig. 1. Electrical Sensitivity of Undeformed Glove Piece

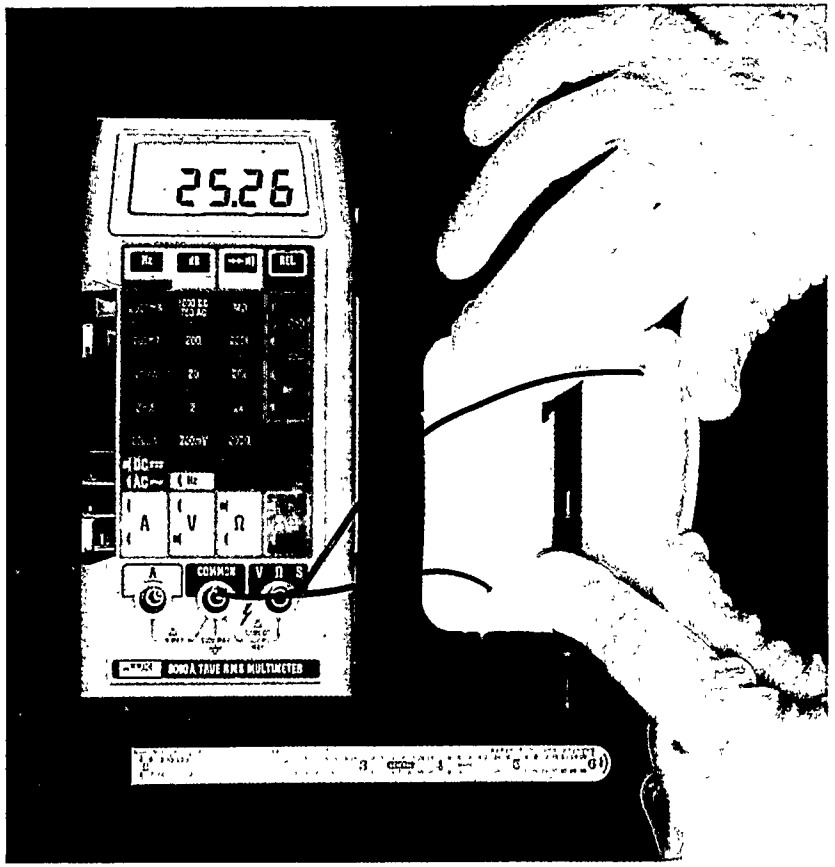

Fig. 2. Electrical Sensitivity of Deformed Glove Piece

94-056N -- LONG BASELINE NEUTRINO OSCILLATION EXPERIMENT

Associate Laboratory Director Area: Physical Research

Principal Investigators: Maury Goodman and Dan Crane, High Energy Physics

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$158.5K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: We are studying the technical, economic, and environmental feasibility of an experiment to detect and measure neutrino interactions at a distance of 730 km from an accelerator. The Soudan 2 nucleon decay collaboration had submitted a proposal (P822) to Fermilab to use the existing Soudan 2 detector as a first generation detector in conjunction with a beam from the Main Injector. Fermilab has embraced the prospect of using the Main Injector for this neutrino oscillation program with great enthusiasm. In order to take timely advantage of this special opportunity, our goal was to demonstrate the feasibility of using the existing Soudan detector, or a possible new detector designed specifically for this experiment to search for neutrino oscillations at Soudan. Success on this project will lead to funding for a substantial new program, distinct except for location from the present Soudan 2 experiment.

Approach: Work on this project involved a myriad of scientific issues related to neutrino beams and particle physics detectors. Our approach included the following efforts:

- Beam Monte Carlo simulation and design optimization.
- Study of the requirements of a detector for neutrino oscillation using the proposed Fermilab neutrino beam.
- Exploration of innovative concepts for neutrino detector technology.
- Impact of new groundwater radiation guidelines upon beam design and civil construction issues.
- Study of environmental issues connected with the necessary civil construction for a beam from Fermilab aimed towards the Soudan 2 underground physics laboratory.
- Leadership of the design of a new large "cavity filler" neutrino detector at the Soudan site.
- Development and use of Monte Carlo simulation programs to study events in the Soudan 2 detector from the proposed neutrino beam.
- Documentation of the results of the above studies in the form of conference papers, reports, and presentations to the FNAL Physics Advisory Committee.

Technical Progress and Results: The Argonne group conducted an in-depth study, together with Peter Litchfield from Rutherford Laboratory, of the systematic errors on the neutral current to charged current ratio in a two detector long baseline experiment. The major systematic errors that were identified were the uncertainties in the electron neutrino flux and the misidentification of neutral or charged current events due to differences in reconstruction failures in the two detectors. Other systematic errors which were studied and found not to

contribute a major effect were misidentification due to the energy cut, misidentification due to differences in acceptance between the two detectors, uncertainties in the energy spectrum, uncertainties in the quasi-elastic cross section, uncertainties in the cross section due to renormalization (Q-squared cutoff) and uncertainties due to the charm cross section. It was significant that the largest systematic error identified was 6 times smaller than the statistical error on P822, because this implied that a 36 times larger exposure (due to added detector or more beam) would be profitable.

The other major analysis which was provided almost exclusively by the Argonne group was in the beam simulations. Several different ways to simulate the beam were pursued, and the results with a number of different assumptions were compared qualitatively and quantitatively. We are proposing further work, particularly on the beam Monte Carlo simulations. The specific design for civil construction of the beam will be frozen within the next six to nine months. Argonne has taken a lead role on the beam simulation. The thoroughness of several aspects of those studies, including the decay pipe length and radius, background neutrino composition of the beam, and optimized horn design, will depend on the continued availability of LDRD funds. In addition, Argonne personnel are working on active element R&D for the large new detector, in particular on alternatives to Resistive Plate Chambers. Effort which would be maintained by LDRD funds would help to take maximal advantage of this program, in particular by working on detector specific Monte Carlo simulations, and identifying which parameters are most important in the detector R&D program.

Specific Accomplishments:

Argonne provided the leadership in creating and maintaining scientific interest in the long baseline neutrino project at Fermilab through many stages of activity through 1994. This included the distribution of newsletters by electronic mail, recruiting of collaborators, and the establishment of regular modes of communication regarding this project.

Argonne coordinated several scientific meetings on this project. Approximate attendance is indicated in parentheses. They included:

1. October 2, 1993 P822 collaboration meeting in Minneapolis (50)
2. February 20, 1994, P822 collaboration meeting at Fermilab (40)
3. April 11-12, 1994, Long Baseline meeting at Fermilab (10)
4. July 8-12, 1994, Snowmass Summer Study on long baseline, Snowmass, Colorado (120)
5. August 11-12, 1994, New Long Baseline Collaboration Meeting, Fermilab (50)
6. October 1-2, 1994, 2nd Long Baseline Collaboration Meeting, Fermilab (60)

The most significant milestone the project reached in the last year was the programmatic decision by the Fermilab PAC to include a long baseline experiment as part of its program when the Main Injector is built. This decision was announced by letter in June of 1994, and also included a preference for the Soudan site which this group has been advocating. Since June, that site has been settled on. The PAC had earlier called for proposals for a long

baseline neutrino oscillation experiment, which this group and two others responded to. In the June 1994 letter, they called for the three groups to coalesce on a single proposal, which we took the leadership in organizing. Several reports were prepared in FY1994, which contributed to the Fermilab decision:

1. Progress Report and Revised P-822 Proposal for a Long Baseline Neutrino Oscillation Experiment from Fermilab to Soudan, 12 October 1993 (107 pages).
2. Update to P-822: Proposal for a long-baseline neutrino oscillation experiment from Fermilab to Soudan, 8 March 1994 (34 pages).
3. P-822 response to the PAC's questions of 11th April 1994, 16 May 1994 (11 pages).
4. Expression of Interest for a long-baseline neutrino oscillation experiment from Fermilab to Soudan using a 16 kT iron calorimeter, 16 May 1994 (11 pages).
5. Expression of Interest for a Long Baseline Neutrino Oscillation Experiment Using a CERN Beam and a Large Magnetic Sampling Calorimeter at Gran Sasso, 16 May 1994 (17 pages).
6. Organization of a series of technical memos called "NuMI notes" (NeUtrinos at the Main Injector). There are 31 to date of which 16 benefitted directly from the LDRD program.
7. "The atmospheric neutrino anomaly in Soudan 2", Maury Goodman for the Soudan 2 Collaboration, to be published in Nuclear Physics B, Proceedings of Neutrino '94, XVI International Conference on Neutrino Physics and Astrophysics, Eilat, Israel; June 1994.

Collectively, the project more than accomplished its goals for the 1994 fiscal year in that we achieved strong support for a neutrino program at Fermilab from the Fermilab PAC and management. Now an even greater effort is required to achieve DOE backing and develop a successful program.

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93-006R1 -- EXCITED STATE ATOMIC STRUCTURE DETERMINATION USING SYNCHROTRON RADIATION

Associate Laboratory Director Area: Physical Research

Principal Investigators: J. R. Norris and L. X. Chen, Chemistry

Funding Profile:

FY 1992	$ -0-
FY 1993	$122.1K
FY 1994	$192.5K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: We investigated molecular structures of excited state or reaction intermediates in various systems using time-domain X-ray absorption spectroscopy. These studies will lead to a better understanding of chemical reaction mechanisms. The discovery of new intermediate structures indicates potential applications not recognized before. The technologies involved in the studies will set the foundation for picosecond time-domain experiments at APS in the future.

Approach: Many photochemical reactions occur via short-lived molecular species created by light. Knowing the structures for such species sometimes is crucial for understanding reaction mechanisms, designing effective reactions, and the discovery of new applications. Few studies have been carried out in molecular structural determinations of short lived species because the X-ray photon flux during lifetimes of these intermediates from any current synchrotron is far below the requirement for obtaining an accurate molecular structure. Compared to NSLS, the Advanced Photon Source (APS) will offer over a 1000 times more X-ray photons for performing experiments on short lived excited states. This will allow us to capture the molecular structure of short-lived species by X-ray absorption spectroscopy (XAS) or X-ray diffraction.

We have been developing our expertise in capturing the structure of short-lived species using NSLS at BNL to study some reaction intermediates with relatively long lifetimes. The lifetimes of these intermediates were further extended by lowering the temperature of the sample to near 10K where steady-state XAS measurements can be employed. We have proven that this approach is feasible for a number of systems. However, the lifetimes of many species are still too short at 10K for any steady-state technique. Thus, our next step is conducting time-domain experiments on the millisecond time scale with energy dispersive X-ray absorption spectroscopy (EDXAS).

Technical Progress and Results: Several tasks were reported in FY 1993 as ongoing projects in our last report: (1) XAS data analysis and quantum mechanical modeling for photoinduced intramolecular electron transfer intermediate structures of cyclopentadienylnitrosylnickel (CpNiNO), (2) XAS measurements on metastable structure of Fe(II) complex in photoinduced spin state transition reaction, (3) photoexcitation and temperature dependent studies of photosynthetic reaction center protein (RC) structure in the vicinity of the non-heme Fe site, and (4) XAS measurements for steady-state and photoexcited RC's with chemical

modifications. During FY 1994, much of the effort has been devoted to completing these tasks. The other important project started during FY 1994 was to investigate the capabilities of EDXAS (X6A, NSLS) for the time-domain experiments. New systems for studying photoinduced structural changes are also being explored. We also started XAS investigation of molecular structural changes during photoinduced redox reactions in a titanium dioxide surface.

(1) Molecular structural change of CpNiNO in photoinduced intramolecular electron transfer reaction. Many of the results were mentioned in FY 1993. Recent investigations indicate that the XAS results not only detected the structural change of Ni-N-O from linear to bent as the molecule was illuminated by light with certain wavelengths, but also verified the origin of the bent metastable state is the electron transfer intermediate rather than ion pair of $[CpNi]^+NO^-$.

(2) Photoinduced electron transfer intermediate of Fe(II) complex during the spin state transition. The electronic spin state transition of Fe(II) complexes are extensively studied because of its importance in understanding basic molecular properties and its potential applications in temperature sensor and optical switch. Structural changes of iron picolylamine chloride ($[Fe(pic)_3]Cl_2 \cdot$ EtOH) spin state transition were studied. The spin state transition of $[Fe(pic)_3]Cl_2 \cdot$ EtOH can be thermally activated, or photoinduced when it is in a crystalline solid. At 10K, almost all the molecules are in the low spin (LS) state, whereas at room temperature, they are in the high spin (HS) state. The metastable HS state can be generated by photoillumination and can be trapped for a definite time at 10K. The most characteristic structural change in $[Fe(pic)_3]Cl_2 \cdot$ EtOH accompanying the change from the LS state to the HS state is the elongation of Fe-N bond distances by about 0.2Å. We found a new intermediate state in the photoinduced spin state transition of $[Fe(pic)_3]Cl_2 \cdot$ EtOH in solution. This intermediate has a unique structure which differs from the conventional HS or LS state. Instead of uniform Fe-N bond distances in the LS state or the HS state, the newly discovered intermediate has two sets of Fe-N distances at 1.95Å (2 Fe-N) and 2.11Å (4 Fe-N). This severe distortion of a regular octahedral coordination geometry results from asymmetry of the electron occupation in e_g orbitals, commonly known as Jahn-Teller effect. The asymmetry in e_g is due to electron transfer between the solvent molecules and $[Fe(pic)_3]Cl_2 \cdot$ EtOH. The intermediate also has different optical properties compared to those for the conventional LS and HS states. This discovery suggested that this complex in solution has three distinguishable states instead of two as in the crystalline solid. We are also exploring other compounds with similar properties. The polarization dependence XAS of $[Fe(pic)_3]Cl_2 \cdot$ EtOH has been started on an oriented polycrystalline sample recrystallized in a magnetic field. We plan to distinguish different Fe-N bonds and find the origin of the Jahn-Teller effect.

(3) Temperature dependence of photosynthetic reaction center (RC) structures. Many hotophysical properties of the RC are temperature dependent. We probed structural changes as a function of temperature and photoillumination using XAS of the non-heme Fe. Some minor differences were observed in Fe XAS for the RC at room temperature and at 10K which are due to the Debye-Waller factor which accounts for the disorder of the system. Since the RC sample has a very low concentration of Fe, these experiments are very difficult to do with the second generation synchrotron. The sample degraded before we could collect enough data to analyze the structural change by photoillumination.

(4) Structure of chlorophyll chromophores in chemically modified RC. One of the main problems in following the structural change of the RC after photoillumination is its lack of the heavy elements in the chlorophylls and pheophytins. Currently, chemically inserting heavy metal bearing chlorophylls at certain positions is possible. This allows us to probe the structural change at these sites. We have conducted XAS studies on Zn- and Ni-chlorophyll containing RC's. The results show that these modified chlorophylls have very similar structure as the native RC. As in task (3), the XAS of photoilluminated RC is very difficult to do with the second generation synchrotron.

(5) Feasibility study of EDXAS in time-domain experiments. The next important step in our work is doing time-resolved experiments using EDXAS. EDXAS offers capabilities of collecting entire XAS spectrum simultaneously using a diode array detector, instead of scanning the spectrum step-by-step by a monochromator. The present time resolution is limited by the detector read-out time of 5 ms. From the initial experience with EDXAS, we realized that improvements are needed for data acquisition and photoexcitation in order to perform experiments for some special molecular systems. A Nd-YAG laser pumped optical parametric oscillator system will be used as the photoillumination source for our future experiments. We have made suggestions for improving the data acquisition for the time domain pump-probe experiments. A real time-domain experiment can be carried out within a few months when the laser system and improved software are installed.

(6) Photoinduced charge separation and heavy metal reduction on TiO_2 colloid surface. Photocatalyzed reduction/oxidation reactions of heavy metal ions and the organic materials on the surface of TiO_2 colloids are very important in environmental protection/remediation. The reaction efficiency is significantly improved by binding certain surface reagents on the TiO_2. The understanding of the reaction mechanism for such processes relies on structural information of the intermediates. We have conducted XAS measurements on heavy metal ions, and titanium atoms on colloid surfaces. Soon we plan to conduct sulfur XAS of the surface reagent. We have identified the special structural features of surface of TiO_2 which becomes more and more pronounced as the size of the colloid decreases. The cysteine-Pb complex has also been characterized. Further data analysis and monitoring of structural changes upon photoillumination are in progress.

Specific Accomplishments:

L. X. Chen, M. K. Bowman, Z. Wang, P. A. Montano, and J. R. Norris, "Structural studies of photoinduced intramolecular electron transfer in cyclopentadienyl-nitrosylnickel," *J. Phys. Chem.* **98**, 9457-9464 (1994).

L. X. Chen, Z. Wang, G. Hartwich, I. Katheder, H. Scheer, D. M. Tiede, A. Scherz, P. A. Montano, and J. R. Norris, "An X-Ray Absorption Study of Chemically Modified Bacterial Photosynthetic Reaction Centers," to be submitted to *Chem. Phys. Lett.* (1994).

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L. X. Chen, Z. Wang, D. M. Tiede, and J. R. Norris, "Temperature effect of bacterial photosynthetic reaction center structure probed by Fe site EXAFS spectra," NSLS Annual Report (1993).

L. X. Chen, Z. Wang, P. A. Montano, and J. R. Norris, "X-ray absorption studies on electronic spin state transitions of [Fe(α-picolylamine)$_3$]Cl_2·EtOH in different media," Poster, 18th DOE Solar Photochemistry Research Conference, Granlibakken Conference Center, Tahoe City, Calif., June 5-9, 1994.

93-091R1 -- LASER-INDUCED TRANSIENT GRATINGS

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: E. F. McCormack, J. L. Dehmer, P. M. Dehmer, and S. T. Pratt, Environmental Research

Funding Profile:

FY 1992	$ -0-
FY 1993	$ 93.3K
FY 1994	$ 91.8K
FY 1995	$ -0-
FY 1996	$ -0-

Purpose: The purpose of this work is to develop a class of nonlinear optical detection techniques with potential applications in remote gas phase chemical analysis and in the study of chemical reaction dynamics. This class of techniques is based on novel laser-induced grating (LIGS) phenomena as well as the related phenomena of degenerate four-wave mixing (DFWM) and real-time holography. These techniques have the potential for sensitive, remote detection of trace and transient species in the gas, liquid, and solid phases, and they provide a number of distinct advantages over ionization or laser-induced fluorescence techniques.

Approach: Recently a new spectroscopic method has been reported that employs a two-color, LIGS technique to detect optical transitions in the gas phase [M.A. Buntine, D.W. Chandler, and C.C. Hayden, *J. Chem. Phys.* 97, 707 (1992)]. This technique is closely related to a second recently developed technique that employs DFWM to detect transitions from excited molecular states [Q. Zhang, S.A. Kandel. T.A.W. Wasserman, and P.H. Vaccaro, *J. Chem. Phys.* 96, 1640 (1992)]. A simplified understanding of LIGS phenomena can be gained by considering the following example. The output of a single (pump) laser is split into two beams that are crossed at a small angle in the sample to be probed. When the pump laser is tuned to a transition in the species of interest, the interference pattern of the two crossed beams produces a transient grating at the intersection of the two beams. This grating is made up of excited and unexcited molecules. The output of a second (probe) laser is then sent through the sample to interrogate the grating, producing a diffracted signal beam that propagates in a readily determined direction. In the DFWM technique, the probe beam is obtained by retro-reflecting one of the pump beams back through the sample to produce a signal beam that propagates along, but in the opposite direction of, the second pump beam. The advantages of these techniques result because the signal is carried on a new, coherent "laser" beam with low divergence and high beam quality that is generated from the sample. Thus, the detection of the signal beam can be performed some distance from the actual sample, allowing remote detection even in hostile environments. This new class of techniques is also independent of the decay pathway of the excited molecular states, thus allowing the detection of molecules that do not ionize or fluoresce. These techniques therefore provide a complementary alternative to the more standard techniques of charged-particle and fluorescence detection. The considerable advantages of the LIGS techniques suggest a number of potential applications in the study of excited-state absorption spectra and photoionization and photodissociation dynamics, as well as in the remote detection of trace and transient species in a wide variety of environments.

Exploratory work on LIGS and DFWM was performed to determine their suitability for the determination of excited-state absorption spectra and their applicability to remote detection and chemical analysis. We evaluated the sensitivity of the technique for detecting and characterizing rapidly predissociating excited states, that is for detecting species independent of their ultimate fate, and we examined the time-dependence of the LIGS signal to determine if this allows any improvement in the detection sensitivity or selectivity. We are beginning to evaluate the potential of the two techniques for extracting optical properties (particularly transition moments and oscillator strengths) from the experimental data. We are also beginning to examine the feasibility of fiber-optically coupling the laser beams to and from the sample to allow the use of LIGS techniques in non-line-of-sight applications. Finally, although our initial work will focus on gas-phase species, potential applications in the liquid phase are now being assessed.

Our approach was to use a well-characterized prototype system to evaluate these techniques, and nitric oxide was chosen due to the large body of information available on its excited states and their decay processes. In our initial work we characterized three different LIGS techniques and evaluated their relative merits. Next, we examined the time structure of the two-color LIGS signal, that is, how the LIGS signal decayed as a function of the delay between the pump and probe lasers. We then applied the two-color LIGS technique to the detection of a rapidly predissociated level in nitric oxide, and evaluated the detection sensitivity. Finally, we performed initial testing on fiber-optically coupling the laser to and from the sample. This preliminary testing is being performed in the liquid phase on dissolved dye molecules.

Technical Progress and Results: In FY93 we demonstrated three different transient grating techniques for recording spectra of excited states of nitric oxide. In FY94 we extended this work to the study of the time evolution of the grating signal to obtain information on the hyperfine structure of the LIGS transitions. For suitable polarizations of the input laser beams, the time-dependence of the LIGS signal was shown to display quantum beats, which provide spectroscopic information on the sample with sub-laser-linewidth resolution. This work also illustrates that the detection sensitivity will be optimized for certain polarization configurations. We applied the LIGS techniques to both static gas samples and to supersonically cooled molecular beams. The time structure of the LIGS signal in the molecular beam is particularly informative, as it reflects the decay due to molecular motion of the laser-induced grating structure in the sample. For this reason it can be used to accurately characterize the transverse translational temperature in the molecular beam. We demonstrated this point in nitric oxide and showed that the translational temperature determined from spectroscopic analysis was somewhat higher than the translational temperature, indicating an incomplete equilibration of the translational and rotational degrees of freedom.

The LIGS technique was also applied to the study of rapidly predissociating levels of nitric oxide. The technique was applied to a complex portion of the spectrum in which four different electronic states interact, and one of these states is strongly predissociated. By using the LIGS techniques it was possible to observe all four electronic states, a feat that was not possible in earlier studies employing ionization detection. The LIGS techniques allow the unambiguous assignment of all of the rotational structure in this region and provide a consistent interpretation of the multistate interactions.

In FY94 we also initiated work using fiber-optics to apply the LIGS techniques to non-line-of-sight applications. We have demonstrated that a sufficient intensity of the grating forming laser beam can be transmitted through the fiber and we have begun to evaluate different grating geometries for the most efficient alignment and detection of the grating signal. In this work we are using a liquid sample of dissolved dye molecules, which will also illustrate the applicability of the technique for condensed-phase analyses.

In FY95 we propose that this work will progress in two directions. First, we will apply the techniques to other molecules to evaluate their generality and to determine the factors limiting the detection sensitivity of the technique. Second, we will continue to develop the fiber-optically coupled device and its potential for non-line of sight applications.

Specific Accomplishments: A paper entitled "Observation of Hyperfine Quantum Beats in Two-Color Laser-Induced Grating Spectroscopy of Nitric Oxide" describing our observations of quantum beats in the LIGS signal was published in *Chemical Physics Letters* [*Chem. Phys. Lett.* 227, 656 (1994)]. A second manuscript describing our new spectroscopic results on nitric oxide and on the ability of LIGS techniques to detect transitions regardless of the ultimate fate of the molecules has recently been completed and will be submitted to *The Journal of Chemical Physics*.

In the past year, one of us (EFM) gave invited talks on our LIGS work at the American Chemical Society National Spring Meeting and at the Gordon Research Conference on Multiphoton Processes. In addition, a contributed paper was presented at the March meeting of the American Physical Society.

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94-168N -- A COMPUTER SIMULATION OF AN INTELLIGENT VEHICLE HIGHWAY SYSTEM FOR CHICAGO METROPOLITAN AREA

Associate Laboratory Director Area: Energy and Environmental Science and Technology

Principal Investigators: A. M. Tentner, Reactor Analysis
M. W. Henderson, Mathematics and Computer Science
T. F. Ewing, Technology Development

Funding Profile:

FY 1992	$ -0-
FY 1993	$ -0-
FY 1994	$ 123.1K
FY 1995	$ 140.0K
FY 1996	$ 175.0K

Purpose: The project will develop a Computer Simulation and Simulator for an Intelligent Vehicle Highway System (IVHS) with direct application to the Chicago Metropolitan Area. This simulation will be designed to take advantage of the massively parallel computer architectures and will be implemented on the IBM Scalable POWER Parallel System SP-1 installed at the ANL High Performance Computing Facility. The proposed IVHS simulator will be designed to adapt, with relatively little effort, to the analysis of IVHS systems in other geographical areas. The development of the IVHS simulator will serve as the focal point for the ANL Intelligent Transportation Systems Initiative. It will also allow the Laboratory to become established as a leading center of IVHS research.

Approach: During the first year the IVHS System Simulator architecture has been defined and the high level structure has been implemented on the distributed computing SUN network at ANL. Active links with IVHS America, the Chicago based ADVANCE project, and other leading IVHS programs have been established. During the second year detailed models of some of the key components of the IVHS simulator will be developed and implemented. These include the Mobile Navigation Assistant, the RF Communications Network, and the Travel Information Center. A range of numerical methods will be considered in order to optimize the performance of various IVHS components. It is expected that these models will be developed in coordination with the Chicago based ADVANCE IVHS demonstration project. During the third year simulations will be conducted to assess the impact of the IVHS system on traffic patterns, as well as the impact of changes in various IVHS functions on the overall system performance and traffic flow in the geographical area tested. Links with other IVHS programs in the Midwest and nationwide will be established, with the goal of applying the IVHS simulator to the study of traffic in other geographical areas, as well as studying the problems associated with the linkage of different IVHS systems serving two or more geographical areas.

Technical Progress and Results: During FY 1994 the IVHS System Simulator architecture has been defined and the high level architecture has been implemented on a distributed computing SUN network. This architecture will also be implemented on the ANL SP-1 parallel computer by the end of FY 1994. The architecture defines a computer code system

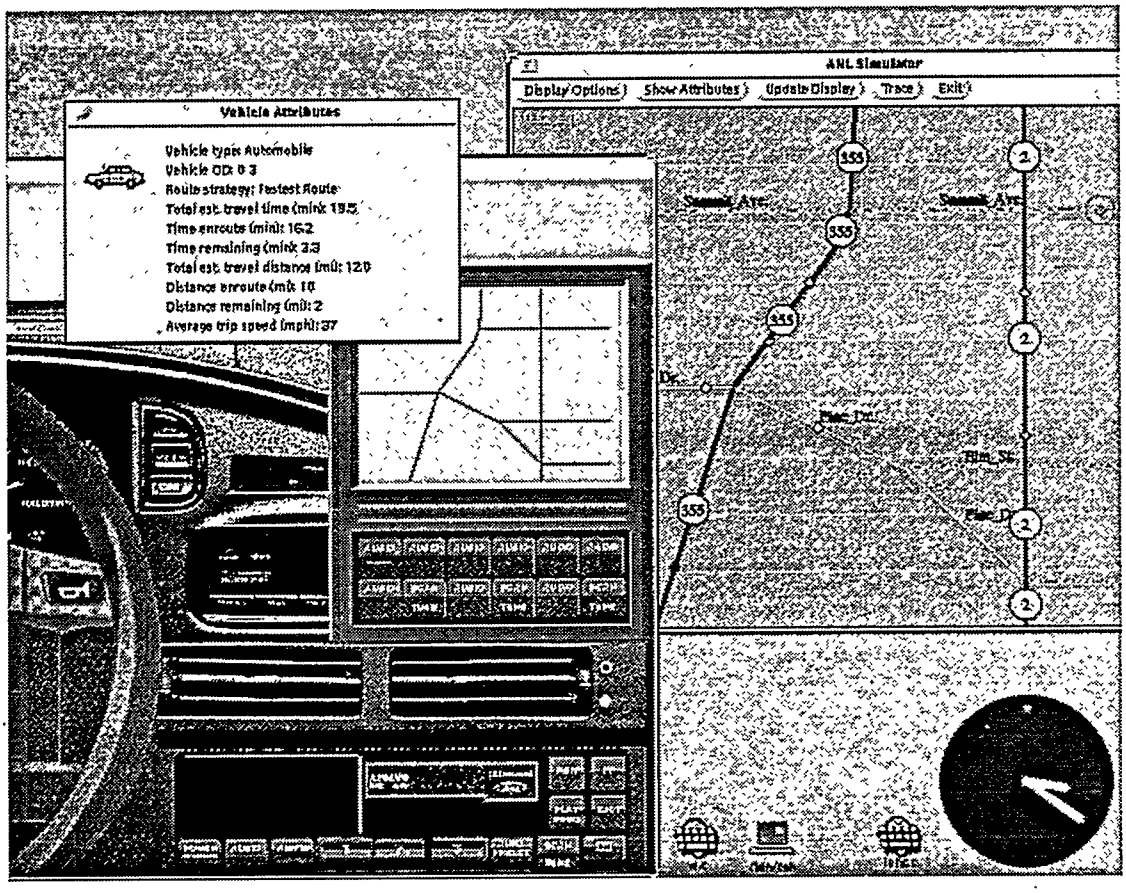
designed for a large-scale, detailed, scalable simulation of an IVHS, capable of running on massively parallel computers and distributed computer systems.

The prototype includes instrumented "smart" vehicles with in-vehicle navigation units capable of optimal route planning and an Advanced Traffic Management System (ATMS). The ATMS currently has only vehicle tracking capabilities, but will later provide 2-way interaction with traffic. Both the in-vehicle navigation module and the ATMS feature detailed graphical user interfaces to support human-factors studies.

A parallel effort was centered on obtaining and becoming familiar with an established traffic simulation code. A literature survey was conducted and a decision was made to use the TRAF/NETSIM code developed for DOT/FHWA, which is widely accepted in the traffic management and simulation community. A copy of the TRAF/NETSIM has been installed at ANL and a simulation of the ANL traffic at peak-demand hours has been developed. Steps have been taken to obtain the TRAF/NETSIM source, which is now available at ANL, and an effort to expand the NETSIM capabilities by taking advantage of parallel computing capabilities available at ANL has been initiated.

A copy of the Chicago area street map data base has been obtained from Navigation Technologies Inc. and work has been initiated to develop software tools which will allow the use of this data base in preparing the input for the IVHS Simulator.

Specific Accomplishments: The IVHS Simulation effort has been one of the central elements of the Intelligent Transportation Program at ANL, one of the major Laboratory initiatives. A description of the IVHS Simulator capabilities was prepared and presented to Laboratory management. Contacts have been established at IDOT, MNDOT, and other state and federal transportation organizations which have expressed an interest in the ANL IVHS Simulation capabilities. Contacts have also been established with other research organizations active in the IVHS Simulation area, such as Oak Ridge National Laboratory, The University of Illinois at Chicago, and Northwestern University.


ANL Simulator
Display Options
Show Attributes
Update Display
Trace
Exit
Vehicle Attributes
Vehicle type: Automobile
Vehicle ID: 0 3
Route strategy: Fastest Route
Total est. travel time (min): 19.5
Time enroute (min): 16.2
Time remaining (min): 3.3
Total est. travel distance (mi): 12.0
Distance enroute (mi): 10
Distance remaining (mi): 2
Average trip speed (mph): 37
355
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1995 LDRD PROJECT SUMMARY

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-001N	1995/$600K 1996/$600K 1997/$600K	Yanglai Cho	**Rapidly Cycling Synchrotron Performance Optimization** Pursue R&D lines identified by prior studies on accelerator systems performed in the U.S. and Europe. This project has three parts: 1) To carry out physics R&D to optimize the performance of a rapidly cycling synchrotron accelerator. 2) To initiate "bench-testing" of the key components critical to a fast cycling synchrotron, possibly in collaboration with TRIUMF personnel or other institutions. 3) To integrate and summarize the results of prior studies and compare with the results of studies performed by other institutions which include BNL, LANL, and ESS.
95-003N	1995/$100K 1996/$150K 1997/$150K	Richard Rosenberg John Noonan George Goeppner William Farrell	**High Power X-ray Induced Modification of Materials** Investigate the feasibility of using high powered X-ray synchrotron radiation for materials modification. The investigators approach will be to utilize an insertion device beamline at an existing synchrotron radiation facility (SSRL or NSLS) with the anticipation of continuing the project at the APS. Distinct avenues of research to be pursued: Understanding the mechanisms responsible for X-ray-induced defect formation in accelerator materials subjected to high-powered beams; Exploring the feasibility of using high-power X-rays to alter surface structure by causing crystalline to amorphous transitions; Exploring the feasibility of employing high-power X-ray beams for welding.
95-006N	1995/$220K 1996/$180K 1997/$0	G. S. Knapp C. L. Wiley	**Development of Cryogenically Cooled Monochromator Crystals for an APS Undulator-A Beamline** Develop monochromator crystals capable of handling the extremely high heat loads generated by the standard APS undulator, Undulator-A. A cryogenically cooled thin-crystal-silicon approach will be pursued.
95-007N	1995/$200K 1996/$0 1997/$0	M. Ramanathan M. A. Beno G. S. Knapp	**Development of a Monochromator System for the BESSRC X-Ray Beamlines at the APS** Develop a new monochromator system which will provide energy scanning capabilities and allow high vacuum operations for use at the BESSRC beamlines at the Advanced Photon Source.
95-008N	1995/$200K 1996/$230K 1997/$230K	B. S. Brown J. M. Carpenter	**Target Station Studies for the Intense Pulsed Neutron Source Upgrade** Computer studies will be performed on the target/moderators/reflectors system using existing codes and computer hardware. The results of these studies will be incorporated in the target station design. An R&D plan will be defined that will yield the metallurgical information required for the selection of materials and configuration. A slow booster target concept will be investigated.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-010N	1995/$180K 1996/$200K 1997/$0	T. Disz B. Nickless R. Stevens	**CAVE Virtual Environment Technology Development** Develop new technology for 3D immersive virtual environmental displays and apply this technology in the ANL CAVE. The technology that will be developed will improve the ability to use the CAVE virtual environment as a high-performance peripheral to the IBM SP parallel computer. The project will focus on a number of improvements to the basic CAVE capability including improvements in display technology, recording and playback of virtual experiences, improved texture mapping, new methods for navigation and control, and new tracking methods.
95-011N	1995/$140K 1996/$0 1997/$0	J. R. Norris L. X. Chen D. M. Tiede M. C. Thurnauer	**Time Domain Molecular Structure Determination for Metastable Reaction Intermediates in Photochemical Processes using X-Ray Absorption** Determine molecular structures of metastable intermediates in photochemical processes with time-domain x-ray techniques using synchrotron radiation. Based on our structural determinations for long-lived metastable states using currently available steady-state XAS, the feasibility and utility of studying structural intermediates has been established. This study will enter a new phase by extending the technique to intermediate species with lifetimes between microseconds and milliseconds. Several model systems relevant to solar energy conversion and information storage are proposed for this time domain investigation. The study is preparatory for determining molecular structures of excited states using x-ray techniques for APS.
95-012N	1995/$130K 1996/$150K 1997/$0	M. A. Beno P. Lee G. Jennings	**New Synchrotron Anomalous Scattering Techniques** Develop new techniques for anomalous scattering diffraction experiments. Anomalous scattering is an atom selective scattering technique which has been employed extensively in both single crystal and powder diffraction experiments. For powder diffraction studies, this technique can be used to derive site occupancy information for complicated materials with much greater accuracy than is possible from any other method. The data collection procedures presently employed for anomalous scattering from powder samples are extremely slow. Since the analysis of this type of data employs differences in scattering at two or more energies, highly accurate diffraction data is required.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-013N	1995/$80K 1996/$0 1997/$0	Mark R. Antonio	**Optical Luminescence X-Ray Absorption Fine Structure: A New Method to Probe the Coordination and Valence of f-Elements in Amorphous Materials** The UV-visible luminescence response of lanthanide and actinide ions is finding increased use in such diverse areas as x-ray detectors and optical fibers. Whereas the luminescent properties of these ions are well documented in crystalline materials, there is no predictive understanding of their behavior in amorphous materials. This dearth of information is the result of the extensive optical line broadening that often occurs in amorphous samples, which in part arises from the multi-site location of the f-ion. Even if single sites can be isolated optically, no correlation can be made between their optical response and their structural environment. The purpose of this project is to bridge the gap between the optical and structural studies of amorphous materials. This will be done with the development of a unique capability for the detection of x-ray absorption fine structure (XAFS) through optical luminescence. This scheme combines the well-known element-specificity afforded by conventional XAFS with the added capability for site selectivity. This selectivity can be achieved through luminescence wavelength and lifetime filtering in the frequency and time domains. In addition, the enhancement of XAFS detection over conventional methods now employed will provide a new method for studying the coordination and oxidation states of f-ions at trace-level real samples, such as those of interest in nuclear-waste problems.
95-020N	1995/$200K 1996/$200K 1997/$200K	Keng Leong Don Henley	**Development of Laser Technology for the Decontamination of Surfaces** Develop the necessary tools to use high power laser beams to decontaminate surfaces. The beam delivery will use fiber optics because of its flexibility and low loss over 100 m lengths. A processing head will be designed to interface with the fiber to obtain the necessary beam shape and intensity for optimal ablation of contaminated surfaces. The processing head will consist of transmissive optics for collimation and shaping of the high power beam exiting the fibers. The effluent capture system will be essentially a suction system that contains the particles using a HEPA filter. A special shroud will be designed to ensure optimal capture of the aerosol released during ablation. Performance tests of the ablation system will be carried out using the 1.6 kW pulsed, Nd:YAG laser. Data on ablation rate, contaminant removal, and effluent capture will be obtained.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-027N	1995/$225K 1996/$250K 1997/$0	J. D. B. Lambert P. G. Pahl R. V. Strain R. L. Parks	**Use of Spent Experimental EBR-II Fuels to Address Potential Materials Problems under Dry Storage Conditions** The Radioactive Scrap and Waste Facility (RSWF) at ANL-W is one of a very few places in the DOE complex where spent nuclear fuel (SNF) has been held under conditions approximating those required in a monitored retrievable storage (MRS) facility. A variety of high-enrichment SNF forms discharged from the EBR-II have been stored below grade for up to 25 years in inerted containers located in steel liners. The condition of these SNF after this extended dry storage is possibly a unique source of information of direct application to containment criteria for the MRS and the national repository. For many of the stored SNFs in the RSWF, archival data obtained during initial post-irradiation examination (PIE) are also available. The results of judicious reexamination of SNF from the RSWF will therefore be compared with original PIE data of as-discharged sibling elements to establish the extent of any deterioration in the RSWF. Little deterioration is anticipated so that quantitative methods will have to be used. Following completion of an inventory of the spent nuclear fuel in the RSWF for which original PIE data are available, selected elements from the RSWF will be subject to quantitative PIE to establish the mode and extent of deterioration during dry storage.
95-030N	1995/$200K 1996/$200K 1997/$0	S. M. Frank J. R. Krsul T. P. Zahn	**Development of Analytical Methods to Perform Waste Characterization of Activated Metals** Develop indirect methods to estimate the activity of difficult to analyze long-lived radionuclides in activated metal. This indirect method will be validated with actual analytical chemistry measurements. The ultimate goal is to indirectly characterize activated metal waste rapidly, accurately, and cost effectively. The development of indirect analytical methods will eliminate the need for complex, labor intensive, lengthy, and expensive separation techniques presently required for waste characterization of activated metal. Indirect methods based on valid correlations with actual measurements will contribute significantly to the cost effective disposal of activated metal waste optimizing the segregation of waste into the proper waste classification.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-037N	1995/$40K 1996/$0 1997/$0	Raymond T. Klann	**Investigation of Fast Neutron Radiography** Characterize the MF Physics A-711 Neutron Generator source and perform neutron transport calculations to scope the radiographic parameters such as exposure time, source strength, film and foil types, and L/D ratio. We will investigate the various foil and converter screen options and provide insight into the optimum foil and converter screen arrangements. We will then design the foil and cassette holders, develop the radiographic process, and obtain the necessary foils, converter screens, and film. All of the engineering design work will be performed. We will perform fast neutron radiography, iterate on the radiographic method, and demonstrate the benefits of fast neutron radiography through a comparative study with thermal neutron radiography and X-radiography. The comparative study will include performing radiography of all three types (X-ray, thermal neutron, and fast neutron) on identical configurations of objects.
95-040N	1995/$160K 1996/$200K 1997/$0	Humberto E. Garcia Azim Houshyar	**Optimization of Fuel Handling and Processing at ANL-West** New fuel handling and processing activities are to be conducted at ANL-W in support of new initiatives. Investigators will use discrete event simulation techniques to plan, supervise, and perform the fuel handling and processing tasks in a way that will guarantee improvements in safety, productivity, cost reduction, and strategic advantages. The central idea is to characterize this fuel task as composed of a collection of interconnected cells, and then apply operation research techniques to identify appropriate planning schedules for assumed scenarios. In addition, a supervisory system will be integrated into the fuel handling and processing system (FHPS) to provide ANL personnel with on-line information on the progress of specified fueling tasks and to suggest courses of action for decision-making in the event of changes in predicted operational conditions.
95-041N	1995/$240K 1996/$0 1997/$0	P. J. Collins G. R. Imel	**Utilization of Waste Hardware** Disposal of reactor hardware (e.g., stainless steel) creates a large volume of waste that is occupying valuable storage space in near-surface storage sites. This is a problem in present nuclear reactors and is a main concern in future fusion reactor designs. This investigation will consist of a calculational effort to characterize the waste hardware in terms of the best quantitative values for isotopic composition and a metallurgical effort to determine the recycling potential of the waste hardware. The calculational effort will provide the tools to separate the waste stream such that ground disposal, when necessary, can be performed in the most efficient manner, and it will provide the best estimate of the waste stream composition to determine the feasibility of recycling via a chemical metallurgical process.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-049N	1995/$300K 1996/$279K 1997/$0	C. C. McPheeters	**Hydroclones for Removal of Suspended Material from Fused Salts** Develop devices incorporating cyclonic flow for the removal of suspended droplets or solids from liquid salt streams involved in pyrochemical processes. Pyrochemical process streams that are to be transferred from one vessel to another often contain entrained material. In some cases, the entrained material may be the desired product that must be recovered, e.g., recovery of the product of a continuous process. In other cases, the entrained material may be a waste stream to be discarded or material to be recycled to a process step. Cyclone separators are commonly used to remove particulates from a process gas stream. Hydroclones, which apply the same principles for a liquid stream, have been investigated for some applications. This study will investigate their application to removing suspended materials from liquid salt streams.
95-050N	1995/$200K 1996/$150K 1997/$0	Shiu-Wing Tam James C. Cunnane	**Development of Performance Assessment Capability for Waste Disposal** Develop performance assessment capability at Argonne to support waste management disposal. The focus is on development of capability for performance assessment of radioactive waste materials. This capability will then be combined with the modeling capabilities needed to perform complete performance assessments of waste disposal systems. By "complete," it is meant that the performance assessment capability would cover the fate of radionuclides from source terms to downstream biological uptakes. It includes pre-source term issues such as fuel conditioning. The objective is to bring to bear, on source-term and pre-source term issues, state-of-the-art materials simulation methodology, which has evolved recently to the point where materials properties and behavior (both static and dynamic) can be simulated in a realistic manner.
95-051N	1995/$200K 1996/$305K 1997/$0	S. M. McDeavitt D. D. Keiser	**Evaluation of TRU-Bearing Disposal Alloys** Pyrochemical conditioning of spent nuclear fuel results in removal of long lived and hazardous transuranic (TRU) constituents from the fuel and allows disposal of a stable waste with very little long-term radiation hazard. The casting methodology for TRU-bearing alloys will be developed in this investigation. Induction, arc, and resistance furnaces in an inert atmosphere are available. Methods for mitigating the problems associated with the volatility of the actinides (notably americium) will also be developed. Metallographic examination on the alloy castings will be conducted to monitor and guide process development and to determine the microstructural distribution of the actinides. In addition, alloy slugs will be fabricated into test coupons for corrosion testing and evaluation. The alloy must also be stable against corrosion according to standard evaluation techniques. The basic metallurgical information will be related to the corrosion properties and processing conditions to determine the optimal alloy composition.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-054N	1995/$295K 1996/$60K 1997/$0	C. C. McPheeters	**Removal of Lithium Oxide and Lithium from Lithium Chloride-Based Process Salts** Develop techniques and devices for the removal of residual lithium oxide and lithium from reduction salts used in pyrochemical processes. Determine the reaction kinetics and characteristics of the reaction products for the reaction of lithium oxide and lithium dissolved in molten lithium chloride with aluminum. Determine the design parameters for packed beds and packed centrifugal filters for removing lithium oxide and lithium from molten salt.
95-062N	1995/$175K 1996/$0 1997/$0	R. F. Kulak J. L. Binder J. M. Kramer J. J. Sienicki	**Development and Testing of a Simulation System to Assess and Predict the Structural Properties of Welds** The work will be accomplished through four tasks: (1) develop a welding simulation environment on parallel and parallel-distributed computing platforms to simulate the welding process from a multidisciplinary perspective, (2) develop a welding test and visualization laboratory which will be able to provide data for the validation of the simulation code, (3) investigate the potential for the current flash X-ray cinematography system to provide time dependent radiographic visualizations of weld metal transport, and (4) determine high-temperature material properties for steel weldments to provide material property input data for the computer code.
95-063N	1995/$190K 1996/$0 1997/$0	David Y. Pan E. J. Plaskacz R. A. Uras	**Modeling and Applications of Composite Structures** Extend the current ANL structural modeling capability into the forefront of composite structural simulation. Investigate innovative ways of using composites. The project will start by incorporating conventional constitutive models for composite materials into ANL structural codes. The activity will give ANL the capability to simulate a variety of composite structures. The project will then take a step further to include neural networks to characterize and predict composite behavior. This new approach has the potential ability to capture causality and trends in the input data as well as being less costly.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-070N	1995/$200K 1996/$180K 1997/$120K	Ting Chen Kenny C. Gross Tom Ewing	**A Human-Computer Expert System for Automated Highway System** Conduct research in human factors to ensure the success of the man-machine relationship in an Automated Highway System for the Intelligent Vehicle Highway System Program. This research aims to develop a human-computer expert system for multiple tasks throughout all three (analysis, demonstration, and operational evaluation) phases of the Automated Highway System Program. The proposed human-computer expert system performs (1) integrating knowledge from human experts, such as operators, through interviews with them; (2) identifying uncertainties that human beings frequently make in their ambiguous statements; (3) formulating reasonings that are capable of managing these uncertainties; and (4) making intelligent decisions for the multiple tasks in the Automated Highway System Program such as local and global traffic pattern analysis, lateral and longitudinal control, vehicle operation analysis, safety-critical and mission-critical real-time surveillance, diagnosis, testing, etc.
95-071N	1995/$180K 1996/$180K 1997/$180K	R. N. Hill G. Palmiotti J. Roglans	**Risk Evaluation of Nuclear Waste — Uncertainty and Sensitivity Analyses** Develop a methodology for evaluating the uncertainty of the radiological risk associated with waste forms resulting from the nu clear fuel cycle and adapt existing repository performance models to evaluate alternative waste forms. The impact of a wide variety of data uncertainties will be evaluated using time-dependent sensitivity techniques. The sensitivity and uncertainty analyses will be performed for a variety of potential fuel cycle and waste form scenarios.
95-072N	1995/$172K 1996/$0 1997/$0	Jaques Reifman Javier E. Vitela Thomas Y. C. Wei	**Recurrent Artificial Neural Networks for Modeling of Nonlinear Systems** Perform feasibility studies in the application of recurrent artificial neural networks for modeling nonlinear systems. Plant data of a chemical process from an industrial partner or the Argonne Fuel Cycle Facility will be used to test the capability of the developed recurrent neural network architecture and learning algorithm for system modeling and identification. Establishing expertise in recurrent networks, that can be used as general purpose modeling tools for complex nonlinear systems, can become a valuable asset for the Laboratory.
95-075N	1995/$250K 1996/$250K 1997/$0	Kenny C. Gross Joseph C. Braun David W. Green	**New Technology for Removal of Heavy Noble Gases from Argon and from Air** Evaluate and select optimal performance parameters for an oil-based apparatus for continuous removal and isolation of radioactive noble gases from the Argonne Fuel Cycle Facility. This apparatus may replace costly and complex cryogenic charcoal technology for removal of fission gases from the Fuel Cycle Facility. A second use of the apparatus is for recovery of very expensive tag gas in the Fuel Manufacturing Facility. Finally, the apparatus can provide low-cost removal of radon from DOE hot cell and glove box facilities and removal of radon from homes, schools, office buildings, and mines.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-095N	1995/$150K 1996/$150K 1997/$150K	D. C. Wade J. J. Laidler	**Beneficial Uses for Nuclear Waste** Investigate novel beneficial applications arising from nuclear waste conditioning and/or waste forms production. Identify potential beneficial uses on the basis of technical plausibility and commercial need. Prioritize the list so generated and establish technical feasibility for the top several options.
95-159N†	1995/$75K	James V. Beitz	**Ultrapurification of Tungsten Hexafluoride for Semiconductor Use** The purpose of this program is to demonstrate, at the proof of principle level, the removal of alpha-emitting impurities in tungsten hexafluoride gas by a photochemical purification process. Tungsten hexafluoride is used in the fabrication of integrated circuits, and alpha-particle induced failures are the leading contributors to soft failures in such circuits. A vacuum ultraviolet concentric tube photoreactor assembly will be designed, fabricated, and tested, and mixtures of tungsten hexafluoride and uranium hexafluoride gases will be prepared as part of the tests.
95-160N†	1995/$75K	Mark B. Knickelbein John Harkness	**Plasma Synthesis of Novel Catalysts** Transition metal-containing aggregates will be synthesized by plasma dissociation of appropriate volatile organometallic precursors in a laboratory scale 2.45 GHz microwave discharge apparatus in a fast flow configuration. Emphasis will be on the production of aggregates containing transition metals known to be catalytically active in highly dispersed form, such as nickel, platinum, and palladium. The collected aggregates will be examined by electron microscopy and x-ray photoelectron spectroscopy in order to assess the dispersion and segregation of the metal particles. Aggregates produced by the plasma dissociation of the platinum and palladium HFAA complexes will be compared with those produced in laser photolysis study. In addition, other suitable gas phase precursors containing catalytically active metals will be identified. An important advantage of this approach is the ability to synthesize particles containing two or more metals (i.e., bimetallic catalysts) by using mixtures of the appropriate precursors. Testing of the collected aggregates for catalytic activity will involve simple model reactions.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-162N†	1995/$75K	Michael R. Wasielewski	**Ion-Specific Sensors Based on Conductive Organic Polymers** New monomers for the production of modified poly (phenylvinylene) will be developed. These monomers will make use of the fact that the phenyl group incorporated into the polymer can be modified at two ring positions without influencing the remaining ring sites at which the polymerization takes place. The phenyl monomer will be functionalized with crown ether and aza-macrocyclic derivatives. These monomers will be tested for selective metal ion binding. The monomers that successfully bind metal ions will be polymerized to produce the processible precursor polymer. Thin films of the precursor polymer on both conductive and insulating substrates will be produced, followed by final processing into the modified poly(phenylvinylene) using fluoboric acid. The nature of these thin films will be characterized by a variety of electrochemical, optical, and surface analysis techniques.
95-163N†	1995/$75K	Michael J. Pellin Lennox E. Iton	**Use of Self-Assembled Monolayers as Templates for Growth of Novel Microporous Molecular Sieve Films** A new approach to the growth of microporous molecular sieve materials will be explored. Self-assembled monolayers, consisting of thiols functionalized with amino groups and bound on gold substrates, will be employed as template arrays for the crystallization of novel microporous silicate and aluminosilicate framework structures. It is intended that the alkyl substituents of the amino functionality would be incorporated into the developing micropore structure. Growth of materials having either unidimensional or intersecting two-dimensional pore structures can be envisioned, including novel structures. Control can be exercised by varying the structure of the self-assembled monolayer. This approach to the growth of molecular sieve materials will also develop thin films that might be suitable for sensor and optoelectronic applications.
95-164N†	1995/$75K	Terry Gaasterland	**Reconstructing Metabolic Function from Genome Sequence Data** The genome sequence for an organism dictates which proteins can be synthesized in that organism. Hence, the process of interpreting genome sequence data can be considered to produce a partial "parts list" of components that are present in an organism's metabolic structure. Such a parts list, however, does not provide information about how these components fit together. An environment that can automatically reconstruct a metabolic structure for an organism from a partial "parts list" of the component proteins will be developed. The reconstructed metabolic structure will provide essential feedback that will focus the search for coding sequences (genes) in new DNA sequence, and it will enable large-scale sequence interpretation to proceed with metabolic accuracy.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-167N†	1995/$70K	Jorge More Zhijun Wu	**Optimization Methods for Macromolecular Conformation on High-Performance Architectures** Develop an environment for the solution of macromolecular conformation problems on massively parallel architectures. This project requires the synergy of a new continuation algorithm for global optimization, expertise in large-scale optimization, and Argonne's High-Performance Computing Research Facility. The goal of this project is to solve problems of biological interest; for example, mellitin (26 residues), rubredoxin (52 residues), and bovine pancreatic trypsin inhibitor (58 residues). The global solution of the last problem, in particular, would represent a major computational achievement.
95-170N†	1995/$59K	Craig D. Roberts	**Nucleon Amplitudes in QCD** The investigator will employ the nonperturbative Dyson-Schwinger equation approach to solving quantum field theory, analogous to using the Euler-Lagrange equations in classical field theory. The primary aim is to obtain a numerical solution of the covariant Faddeev equation for the three-quark bound state.
95-171N†	1995/$75K	T. W. LeBrun	**Development of a Fast Spectrometer for Studying X-Ray Induced Processes** A new spectrometer will be developed for studying X-ray induced processes that, when combined with other detectors, will allow coincidence measurements of the emitted particles. This would substantially enrich understanding of these processes because the bulk of the available information is not accessible to most current experiments which only measure the energy spectra of individual particles, effectively integrating over all other degrees of freedom. Specifically, the investigator will show that the measurement of electron energies by time-of-flight spectrometry possesses advantages that are well suited to coincidence measurements, and he will outline the development of a new instrument uniquely adapted for this purpose.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-176N†	1995/$75K	P. Thiyagarajan	**Solution Structures of GroEL and GroES Complexes with Proteins** In living organisms what makes proteins fold into their native structures has been a question biochemists and biophysicists have been trying to answer for the past four decades. It was shown that proteins contain within their amino acid (subunit) sequences the information necessary for protein folding. However, the recent identification of a class of proteins that interacts with a wide array of polypeptides from the time of synthesis until the final folded state implicates them in the process of protein folding "in vivo". These proteins, popularly referred to as molecular chaperons, were studied for many years in another context as heat shock proteins, universally synthesized by cells in response to stresses such as increases in temperature which will denature the proteins. GroEL and GroES belong to the family of chaperons, and protein crystallographers are in the process of solving their crystal structures. However, what would be more interesting is the information regarding how these two interact among themselves and then interact with other denatured proteins. This is not possible by protein crystallography and hence has to be answered with other scattering techniques. The major goal of this project is to delineate the solution structures of these proteins and their complexes by small angle neutron scattering.
95-178N†	1995/$75K	W. K. Kwok G. W. Crabtree V. M. Vinokur B. G. Glagola	**High Critical Currents and Patterning by Splayed and Columnar Defects in Superconductors** Since the advent of high temperature superconductors, a new magnetic flux structure, the "vortex liquid," has been recognized as the principle barrier to the development of technological applications. This vortex liquid state encompasses a large portion of the magnetic phase diagram in the high temperature-high field region. The absence of a shear modulus in the vortex liquid prevents effective flux pinning and the development of high superconducting critical currents for applications. This research will initiate the use of columnar defects produced by Argonne's ATLAS heavy ion accelerator to control and understand pinning in the vortex liquid state. The purpose of this research is twofold. First, to significantly enhance the critical current in high temperature superconductors in the regime just below their superconducting transition temperature, thus enabling their technological use at these high temperatures. This will be achieved using a novel technique of irradiating the superconductor with heavy ions in a bidirectional "splayed" geometry using ATLAS. Second, to use a novel submicron slit device to create customized patterns of columnar defects induced by heavy ion irradiation.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-182N†	1995/$75K	Jeffrey A. Eastman	**Synthesis and Characterization of Nanocrystalline Barium Titanate** Polycrystalline ferroelectric materials such as $BaTiO_3$ are used in a number of important technological applications of current interest to DOE and other federal agencies. Grain size is known to have a strong effect on the dielectric properties of these ferroelectric materials. The research will synthesize ultrafine-grained (nanocrystalline) $BaTiO_3$ with average grain sizes an order of magnitude smaller than previously produced and will do so using an inherently clean synthesis technique. Characterization studies will focus on establishing a scientific grounding of the expected changes in properties that will accompany the reduction of grain size.
95-183N†	1995/$75K	Marianne Schiffer Priscilla Wilkins Stevens	**Structure-Function Characterizations of Protein Regulators of Programmed Cell Death** Molecules which regulate cellular pathways of differentiation and cell death have only recently been identified and constitute a new structural and functional class of proteins. Two protein inhibitors of cell death, BCL-2 and BHRF-1, were sequenced in the mid-1980s, but in the past 14 months, six additional distinct proteins in this family have been described. Since these molecular regulators are just beginning to be isolated and their cellular functions defined, it is an appropriate time to begin characterizing the biophysical properties of these proteins and providing the detailed molecular structures required for understanding, modifying, and modulating their intracellular activities using protein engineering and rational drug design techniques. We propose to express the genes for these proteins in *E. coli*, purify the proteins, characterize their biophysical properties, and ultimately attempt crystallization to determine their three-dimensional structures. Since the roles of *BCL-2*, *BCL-*X_L, and *BCL-*X_S within the cell have been defined largely in phenomenological terms, there is a great need for structural information to provide significant information about molecular mechanisms of action, provide a basis for making mutant forms of the proteins, and facilitate rational design of cell-death modulators to alter the proteins' actions in the diseased cells of tumors, lymphomas, AIDS, or other human diseases. In addition, the structures of *BCL-2* and *BCL-X* will define a new structural class of proteins and serve as prototypes for generating structural models for other proteins within this class.
95-184N†	1995/$75K	Thomas D. Kaun Mark C. Hash	**Exploratory Development of Sulfide Fiber Glass Mat** Develop new fibrous ceramic materials that have application as components in next-generation batteries and fuel cells. A resilient separator membrane using sulfide fiber promises to double operation life and aid in further advances in power output. These corrosion-resistant sulfide fibers are also of interest for use as high-strength composite ceramics and as a filtration medium for extremely corrosive environments, such as molten-salt nuclear waste processing.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-191N†	1995/$75K	P. M. Dehmer S. T. Pratt E. F. McCormack	**Near-Field Scanning Optical Microscopy** Establish a new research activity in near-field scanning optical microscopy (NSOM). This new form of optical microscopy achieves a resolution far better than those of traditional far-field microscopies, which are constrained by the diffraction limit. NSOM removes this limitation by imaging a sample through an aperture much smaller than the wavelength (lambda) of the illuminating radiation, by placing the sample at a distance less than [lambda] from the aperture (i.e., in the near field), and by scanning the aperture with respect to the sample. We will use pulsed laser technology and gas-phase molecular photophysics to contribute to the development of NSOM by developing new contrast mechanisms using variable wavelength, pulsed excitation and by contributing to interpreting the resulting images in terms of the molecular photophysics and tip-sample interactions.
95-196N†	1995/$75K	Dileep Singh	**Feasibility Studies in Application of Phosphate Based Composites for Light Weight Construction Materials** Investigate processing parameters of novel phosphate composite based construction materials. Specifically, processing of particle board and pumpable insulating materials using phosphate binders will be investigated. The relevant properties of the resulting materials will be evaluated to establish their applicability as light-weight, fire-resistant, environment-friendly construction materials for energy conservation.
95-217N†	1995/$75K	Scott E. Carpenter	**Feasibility Study for the Development of a Miniature Rapid-Scan Passive Remote Fourier Transform Infrared Sensor** Determine the feasibility of developing a new type of interferometer which could be used to create a miniature Fourier transform infrared (FTIR) sensor. This sensor would be passive and used for remote detection. The term "passive" is used to indicate that the sensor, unlike a conventional infrared (IR) spectrometer, does not contain an internal IR radiation source. Instead, the sensor would be equipped with a special set of input optics which collect ambient IR energy. The term "remote" is used to indicate that gas-phase samples to be measured are located some distance from the instrument. If construction of the new interferometer is feasible, the resulting sensor would be approximately 17.8 x 12.7 x 10.2 cm (7 x 5 x 4 in.) and would be light weight and portable. This noninvasive sensor could be used in both domestic and military scenarios for detecting chemical vapors and could be utilized from stationary or moving platforms.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-221N†	1995/$67K	J. McWhirter R. King	**Alkali Metal Laser Doppler Velocimetry** Each Alkali metal is considered transparent to electromagnetic radiation below its particular ultraviolet "cutoff frequency." This research will investigate the feasibility of employing and, if possible, demonstrate Laser Doppler Velocimetry techniques in alkali metals. Such a technique would be useful for obtaining unprecedented accuracy in sodium system flowmeter calibrations, as well as for direct mapping of velocity fields in sodium-cooled reactor systems. The technique would also provide the first nonintrusive point velocity probe for liquid metals and could lead to breakthrough understanding of the phenomena of turbulence in the presence of a magnetic field. The central question is, "Is Laser Doppler Velocimetry feasible in alkali metal systems?"
95-229N†	1995/$75K	Jaques Reifman Javier E. Vitela Thomas Y. C. Wei	**Neural Network NO_x Emission Controller for Fossil Plants** Develop computational capabilities for controlling dynamic systems with artificial neural networks. With the established computational capabilities in place, we will then engage either Commonwealth Edison Company or Illinois Power to collaborate with ANL and provide plant data from one of their fossil units. The plant data will allow us to tailor the neural network controller for real-time on-line control of NO_x emissions. The controller will provide plant operators with the settings of the control variables that will achieve a given reference plant load and NO_x emission level. Developing these state-of-the-art general purpose modeling and control computational capabilities through artificial neural networks will allow ANL to contribute to the solution of current industrial problems such as emission control in fossil power plants.
95-241N†	1995/$75K	C. C. Chu J. J. Sienicki B. W. Spencer	**Improved Fuel Injector Spray Modeling for Internal Combustion Simulation** The automotive industry is engaged in intensive research to improve the performance of internal combustion engines to meet increasingly stringent environmental emission standards without unacceptable compromise of performance and efficiency. A major part of this effort involves the computational modeling of internal combustion engine designs. However, significant discrepancies between state-of-the-art three dimensional computer codes and actual engine behavior continue to exist. Some of these discrepancies are attributed to the overly simplified and inaccurate modeling of the liquid fuel sprays discharged from the fuel injectors. The purpose of this work is to achieve an advancement in the state-of-the-art of internal combustion engine modeling and a reduction in emissions into the atmosphere through the development of improved modeling of fuel injector sprays.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-247N†	1995/$75K	E. J. Plaskacz	**Artificial Intelligence Applied to Adaptive Mesh Refinement for Nonlinear Finite Element Analysis** Perform basic research in mesh adaptivity in nonlinear explicit transient finite element analysis and develop new methods to control the efficient allocation of computational resources using neural networks. The mesh topology will be adapted so as to capture the characteristic heterogeneity and critical localized conditions in large deformation behavior.
95-253N*	1995/$100K 1996/$150K 1997/$150K	Jeffrey A. Eastman Stephen U. Choi	**Applications of Nanoparticle Technology to the Development of a New Class of Energy-Efficient Industrial Heat Transfer Fluids** Demonstrate the feasibility of engineering an innovative new class of heat transfer fluids by suspending ultrafine metallic particles of nanometer dimensions in traditional heat transfer fluids. The resulting "nanofluids" are expected to demonstrate far higher thermal conductivities than those of current heat transfer fluids. This research effort to produce nanofluids and characterize their heat transfer behavior will consist of five main tasks: (1) Nanophase metal powders (copper initially) will be produced by the gas-condensation process in existing state-of-the-art gas-condensation preparation systems. (2) Technology for the production of nanoparticle suspensions will be developed. (3) The particle size and agglomeration behavior of nanophase powders in liquids will be studied by transmission electron microscopy and gas adsorption techniques while simultaneous studies of the flow characteristics of dilute and concentrated suspensions of nanoparticles are carried out. (4) A new apparatus for producing nanofluids by directly condensing nanophase powders from the vapor phase into a flowing low-vapor-pressure fluid will be developed. (5) Heat transfer tests will be conducted to characterize the energy efficiency of nanofluids.
95-260N*	1995/$100K 1996/$0 1997/$0	Dieter M. Gruen Alan R. Krauss Ali Erdemir George R. Fenske	**Development of Smooth Diamond Films for Cost-Effective Machining and Wear Applications** The main objective of this project is to demonstrate an efficient process for depositing smooth and adherent diamond films on ceramic substrates for cost-effective machining and wear applications. Furthermore, the investigators will characterize the microstructural, mechanical, and tribological properties of these smooth diamond films in order to demonstrate their technological potential for a wide range of demanding engineering applications. Investigators have developed a method for depositing nanocrystalline films of true diamond without introducing hydrogen, using an Ar-fullerene plasma. These films are exceptionally smooth and may be grown at a rate as high as or higher than those associated with conventional H_2/CH_4 plasmas.

Proposal Number*†	Authorized Funding**	Principal Investigators	Title
95-265N*	1995/$100K 1996/$200K 1997/$100K	S. A. Johnson V. A. Maroni V. J. Novick	**High-Sensitivity Infrared Chemical Sensor Development** Develop an ensemble of high-sensitivity chemical sensors by combining several state-of-the-art infrared spectroscopic techniques. The ultimate goal of the effort is economical, portable, research-quality instruments with field and factory floor utility that will detect a broad array of chemical effluents and provide high sensitivity for specific chemical functional groups on a near-real-time basis. The proposed sensors will combine established infrared spectroscopic methods with powerful sensitivity enhancement techniques and novel collection methods.
95-269N	1995/$105K 1996/$170K 1997/$175K	Paul Bash	**Computer Aided Drug Design using Virtual Reality** The goal of this project is to combine virtual reality computer graphics with protein molecular dynamics simulations in a real-time interactive environment in a usable form for biological chemists to interact in a "realistic" manner with biomolecular systems in order to facilitate both protein and drug design modeling. A proper implementation will require: (1) very fast molecular dynamics calculations on the order of 30 frames or steps per second, (2) interactive 3-D molecular graphics, (3) high bandwidth communications and proper coordination between dedicated graphics processors and high performance computers.
95-270N	1995/$125K 1996/$228K 1997/$240K	E. Huberman	**Lipogenin, A Potential Human "Hormone" that Acts as a General Inducer of Lipid Formation** Characterize a critical step in the molecular basis of obesity, a detrimental nutritional condition that afflicts many Americans. Although understanding of the cellular and molecular processes that underly obesity is limited, several studies have implicated specific "hormones" and receptors in the regulation of this nutritional condition. Investigators have recently found that a human tumor cell line used in differentiation studies releases into the culture medium a protein that at low concentrations causes the production of massive lipid droplets in different cell types. It was therefore conceivable that this protein, which we termined lipogenin, may represent a critical hormone involved in the regulation of obesity in humans. Immediate efforts are therefore directed towards purification of lipogenin in order to clone and sequence its cDNA and obtain appropriate antibodies. Long-term goals are to sequence the gene that codes for lipogenin, identify and characterize its receptor, and obtain appropriate DNA and immunological probes in order to establish the role this "hormone" and its receptor play in normal development and in the evolution of obesity and its related diseases.

*CCST Project
†DIIP Project
**Authorized funding for 1996 and 1997 is estimated.