Quarterly Technical Progress Report

August 1, 1996 - October 31, 1996

Submitted By

Los Alamos National Resource Center For Plutonium
Amarillo National Resource Center for Plutonium
A Higher Education Consortium of The Texas A&M University System, Texas Tech University, and The University of Texas System

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FORMAT: The format of this quarterly report, as in previous reports, follows the same order as the five major technical tasks established in the Cooperative Agreement. There are three main sections, the executive summaries, the detailed reports, and the DOE required forms. They can be found as follows:

- Executive Summaries for Tasks 1-5 (Tabs 1-5)
- Detailed Reports for Tasks 1-5 (Located behind Tabs 1-5)
- DOE Required Forms (Binder pockets)
  - DOE F 4600.3A, Milestone Log
  - DOE F 4600.5, Federal Assistance Management Summary Report
  - DOE F 1430.22, Notice of Energy RD&D Project
  - SF-269, Financial Status Report

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Executive Summary Of Research Activities

For more complete descriptions of these tasks and subtasks, please see the detailed reports at the back of this report.

The Electronic Resource Library task is managed within Communication, Education, and Training. Refer to the appended section for the Electronic Resource Library to see examples of the draft home pages which are still under construction.

During the reporting period, the document exchange laboratory of the Electronic Resource Library (ERL) was made available through the Amarillo College Lynn Library Learning Center. The newly hired staff were trained and the first document was scanned and exchanged to a portable document format (PDF) file, quality-assured, indexed, cataloged, and html code-written for home page display. Internet connections were established and the first page of the ERL was on-line for demonstration purposes in October.

A selection criteria policy for the archive section of the ERL - the section of full text/image documents - was written in collaboration with the Center. The final document established the following criteria: (a) scientific and technical documents about plutonium; (b) government documents in the public domain and copyrighted non-government documents; (c) documents from 1980 to present; (d) documents recorded in the English language; and (e) documents from the United States, Russia, Canada, France, Japan, England, Germany, Belgium, and Switzerland.

Once selected, documents on plutonium are considered to be scientific and technical (storage, use, disposition, environment, safety, health, and history). This allows a browsing-by-subject access to the archive collection and an alternative to the keyword searching access.

Because of their availability, documents in the DOE reading room at Amarillo College Lynn Library and documents in the technical library at the Center which met the selection criteria were scanned into the ERL first. Consequently, the deliverable of 100 titles by January, 1997 was met during this reporting period.
It has been found that electronic exchange (the act of converting a word processed file to a PDF file), indexing, and cataloging is a much faster process than scanning paper and applying quality-assurance methods before a document is converted to a PDF file. Further, linking to DOE sites and making information available through the ERL home pages is a cost savings.

Over 50 ERL web links provide access to collections of information on plutonium across the DOE complex. Links also provide access to electronic journals and electronic pre-prints. These links provide an efficient, effective, economical means of capitalizing on existing electronic resources.

The library catalog track of the ERL uses the Z39.50 (search engine) standard that provides keyword access to collections in libraries all over the world.

Under the electronic publishing button is access to special bibliographies, research reports, and reference services. The ERL currently offers:

- 900+ bibliography of titles in the DOE reading room at Amarillo College Lynn Library, and
- mixed-oxide fuel literature analysis with (a) over 600 titles, (b) an on-order list of over 100 titles featuring abstract highlights, and (c) reference lists of societies, associations, corporate sources, journal titles, and acronyms associated with mixed-oxide fuel. Refer to the appended section for the Electronic Resource Library for more information.

Special services of the ERL include:

- the Electronic Reserve Room, an access-controlled research support service consisting of copyright materials and access to the International Nuclear Information System CD-ROM database, and OCLC (national resource utility) scientific and technical databases, and
- electronic books once permission to scan the two companion books on Management and Disposition of Excess Weapons Plutonium is acquired from the National Academy of Sciences. Citations in the books will be made available through links to their full text/images.

During the reporting period, ERL personnel made three presentations and contributed a poster session on the ERL during the Panhandle Area Math and Science Teacher Conference.
A CONCISE REPORT ON THE
SENIOR TECHNICAL REVIEW GROUP ACTIVITIES
THROUGHOUT THE LAST YEAR WILL BE SUBMITTED
IN THE NEXT QUARTERLY REPORT.
EXECUTIVE SUMMARY:

During the period August 1, 1996 to October 31, 1996, the MAUA team continued to work on the plutonium disposition effort. In August, a meeting with Howard Canter, Pat Rhodes and Tom Edmunds was held at DOE headquarters to discuss future contributions of the team. A plan is in place to met DOE expectations and time requirements with regard to the issue of the MAUA documentation and analyses. The team’s primary activity during this period was assisting with the Technical Summary Report and a continued revisions of the MAUA data and analysis. The MAUA reports are set for tentative release to the public in December, providing the ROD is reached as scheduled.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

Collaborative/Support Status (UT Austin, Texas A&M):
This summary is a joint report by the universities collaborating in the ANRCP decisions analysis effort.

ROD Support:
The MAUA team has served as a consultant on the drafting of the Technical Summary Report

Other Technological Performance Responsibilities:
The MAUA team continues to analyze data from the cross-cutting teams and the DOE cognizant engineers for incorporation into the final draft MAUA report.

Baseline Or Scope Of Work Changes:
None

Risks/Issues/Problems:
None
WORK PLAN PROGRESS REPORT
Environment, Public Health, And Safety

Institution:
Program Manager:
Project Coordinator
Sub-Contract Number:

Executive Summary Of Research Activities

For a more complete description of these tasks and subtasks, please see the detailed reports at the back of this report.

GROUNDWATER TREATABILITY

Perched Aquifer And Tracer Testing, Water Treatment

Ken Rainwater (PI), Texas Tech University
Heyward Ramsey (Co-PI), Texas Tech University
David Thompson (Co-PI), Texas Tech University
Lloyd Urban (Co-PI), Texas Tech University
Tony Mollhagen (Co-PI), Texas Tech University
Rick Zartman (Co-PI), Texas Tech University
Graduate Students Sara Black and Denny Givens, Texas Tech University

EXECUTIVE SUMMARY:

During the past quarter, researchers at Texas Tech University were involved in three major subtasks in this project area. The first subtask involves the perched aquifer tracer test performed at the Zone 12 Treatability System (ZTTS). The second subtask includes field and modeling efforts for investigation of potential wetlands enhancement by discharging future treated effluent from the perched aquifer recovery systems to the ditch and playa system at the Pantex Plant. The third subtask consisted of equilibrium isotherm tests for sorption of HMX and RDX on core materials from the perched aquifer and its aquitard. Progress for each subtask is reported in the following paragraphs.

Perched Aquifer Tracer Test

The perched aquifer tracer test, originally proposed for commencement on June 1, 1996, officially began on July 15, 1996, and continued into this quarter. The TTU researchers appreciate the cooperation of engineering-environmental Management, Inc. (e²M), and the Battelle Environmental Restoration Group in allowing this project to occur. Observance of the movement of a conservative tracer in the perched aquifer flow system provides direct hydraulic representation of the affected flow regime. Differences in the migration of the injected tracer and the HE already in the perched aquifer can be interpreted as evidence of retardation of these compounds.
Under normal operation at the ZTTS, three extraction wells, EW-1, 2, and 3, pump continuously at approximately 10 gpm each, and the extracted water is passed through granular activated carbon treatment prior to injection at PTX06-1004. A few gpm also is provided from well PTX06-1014. For the purposes of the tracer test, the treated effluent was diverted for injection at passive vent well PV-4, in the center of the ZTTS well pattern. The injected water, free of dissolved high explosives (HE), was dosed with potassium bromide to cause an injected concentration of 100 mg/L of Br, serving as a conservative tracer. Samples were collected on a daily basis from the injection line and the three extraction wells. Samples were analyzed in the field for Br concentration (specific ion electrode) and combined RDX/HMX (DTECH kits). Water levels in wells PV-1, 2, 3, and 4 were monitored with pressure transducers and dataloggers.

As stated previously, the tracer test began on July 15, 1996. The ZTTS as modified ran continuously for 53 days, then was interrupted by several temporary power failures beginning on September 6, and the test was finally terminated on September 19. Complete raw data packages of the measured concentrations and water levels have been provided as they became available to the researchers at UT-Austin for related modeling. A complete report of the collected tracer test data was originally planned as a deliverable by the end of October, 1996. However, that date was based on a June 1 test commencement date. The data report should be available during December, 1996.

Investigation of Potential Wetlands Enhancement

The investigation of potential wetlands enhancement through the discharge of treated perched aquifer effluent into the ditch and playa system will allow evaluation of this concept as an alternative to direct injection through wells. The TTU research team has previous experience in field measurements of runoff flow and infiltration at the Pantex Plant and hydrologic modeling of playa storage under historical loadings. The current effort has three major components. First, during July, 1996, double-ring infiltrometer tests were performed at selected sites in Playas 2, 3, 4, and 5, and in the ditches that lead to all five playas on the Plant. During this quarter, the data from those tests were evaluated and interpreted for application in hydrologic modeling. Second, efforts began in this quarter to simulate the increase in inundated area in each playa that might be caused by introduction of up to 400 gpm in the ditch system leading to each playa. Those simulations will be completed in the next quarter. Those results will be used in the third quarter to evaluate the potential ecological modifications that would result from the increased flows to each playa. The report summarizing these findings will be produced in the next quarter.

Sorption Of HMX And RDX On Pantex Soils

The results of the HMX and RDX equilibrium sorption tests were reported by Rainwater et al. (1996) as listed in the following section. In these tests, core materials from within the perched aquifer and its aquitard were selected from wells PTX06-1012, 1013, 1014, and 1016. These materials had been previously characterized for grain-size distribution, Cr sorption, and TCLP chromium. In this subtask, the core materials were tested by the TCLP leaching test for HMX and RDX. Neither HE was found to be leachable from any of the eight samples. Next, equilibrium isotherm tests were performed, using 10 g of each soil sample exposed to initial 100-mL solutions with concentrations ranging from 0.1 to 5 mg/L of HMX or RDX. It was necessary to make the solutions from stock commercial HMX or RDX standards in acetone or acetonitrile solution dissolved in Pantex groundwater because the research team had not yet been able to obtain pure HE from commercial suppliers. Under these conditions, the sorption of HMX and RDX on the soils was measurable but small. This result is not surprising based on the significant distances of RDX migration seen at the Plant, and the sandy nature of the sediments. It is possible, however, that the organic solvents from which the HEs originated in these tests could have competed with the HEs for sorption on the core materials. It is recommended that these tests be repeated later when the HEs are available without the organic solvents.
Comibined Oxidation/Bioremediation Of High Explosives

Aydin Akgerman (PI), Chevron Professor, Chemical Engineering Department,
Texas A&M University, Experiment Station College Station, TX 77843-3122.

EXECUTIVE SUMMARY:

The project was initiated on 7/1/96 due to the delay in arrival of funding. This report covers the period 7/1/96 to 10/31/96.

During this period we have designed and constructed a reactor assembly to perform the catalytic oxidation reaction, identified a catalyst, developed two analysis techniques (HPLC and TOC) to determine reaction intermediates, completed reactor shakedown runs, and completed preliminary studies on catalytic oxidation of TNT/water solution in order to identify the optimum reaction conditions.

The reactor used in the study has 300 cc volume (Autoclave Engineers) capable of standing temperatures as high as 775°K and pressures of 300 atm and can be operated both in the batch and the flow modes. The heated and stirred autoclave batch reactor is equipped with all auxiliary attachments for feed introduction, sample removal, temperature control, pressure recording, and safety precautions (rupture disc) for pressure build-up. Agitation of the vessel is accomplished by a patented stirrer that sucks the gas phase and disperses it in the liquid phase through the hollow shaft and a specially designed impeller. An electric heater mounted on the reactor wall provides heat and a temperature controller was used to maintain a constant temperature throughout the reaction. The catalyst used is 4.5% Pt/TiO₂ which was used in our previous studies.

Total organic carbon (TOC) analysis was performed using an O. I. Analytical Corporation model 700 TOC analyzer. Separation of the reaction intermediates were performed by using a Dionex HPLC equipped with Ultracarb 5u ODS(20) column and following EPA draft method 8330.

In our shake down runs we studied the reactor at extreme temperatures and pressures expected in this study (523 K and 100 atm) and developed the sampling procedure, temperature control, emergency shut-down, etc. procedures.

To determine the optimum operating conditions and experiment reproducibility, several runs were made at different temperatures (150-200 C ± 1.5) and constant pressure (34 ± 0.6 atm) with the exception of the run at 160 C which was at 52.4 atm. The results showed no appreciable reduction in TOC when the temperature is below 180 C. When experiments are run at temperature higher than 180 C, more than 90% reduction of TOC occurred. However, HPLC analysis at all conditions indicated formation of basically four reaction intermediates.
EXECUTIVE SUMMARY:

This subtask began in FY 1996 with the following objectives:

- To characterize each bacterial isolate received from TAMU by its colonial and cellular morphology and staining reactions. Progress: All cultures received to date have been characterized.
- To determine carbon and nitrogen source utilization by isolates received from TAMU. Progress: All cultures received to date have been characterized.
- To determine the effect of C:N ratios on the growth of organisms received from TAMU. Progress: Complete for all cultures received to date.

In addition, since we had only a few organisms sent to us by TAMU, we proceeded with the following tasks listed below in order to move the project forward. These tasks allowed us to continue our research without waiting for the TAMU team and to support our current and future efforts in bioremediation of soil and groundwater.

Task 1: To develop a culture medium for screening soil and water samples for the presence of HE-degrading bacteria

**Justification** - There are several premises on which this culture medium's ingredients were chosen. First, microorganisms capable of degrading either or both RDX and HMX must remain viable in the presence of these compounds; that is, RDX and/or HMX should not be inherently toxic to any organism capable of degrading it. Second, the potential degraders must be able to not only remain viable in the presence of HMX and RDX, but must be able to withstand the levels (concentrations) at which the HEs are found in the soil or water samples tested. Third, they must remain metabolically active in the presence of HMX and RDX. Fourth, it is desirable (but not essential) that the organisms be able to use HMX and RDX as sole sources of nitrogen for growth to ensure that the HEs will be metabolized and not ignored in favor of more readily useable (preferred) nitrogen compounds. If the HEs are not used as sole N sources, they may be able to be cotransformed with other nutrients.

Because HMX and RDX contain nitrite (-NO₂) groups on the ring, and due to the lack of availability of HMX and RDX for testing purposes, inorganic nitrites were substituted for the HEs in the culture medium. The premise was that organisms capable of growing on potassium or sodium nitrite as the sole source of nitrogen would most likely be the ones able to survive in the presence of, and metabolize, HEs. Whether the organisms isolated on this nitrite-containing medium grow in the presence of and metabolize HMX and RDX can readily be tested when these compounds become available to us.

**Progress** - A screening medium for isolation of nitrite-utilizing bacteria from the soil was tested using soils taken from the Zone 12 burning grounds at Pantex. Ten distinctive forms of bacteria...
which grew on this medium were subcultured onto the same medium to make sure they could be cultivated in the laboratory. We verified that they remained viable on subculture. Work is in progress to characterize them morphologically and by their biochemical characteristics and to determine whether they also can grow on tryptic soy agar (TSA).

Task 2: To determine whether the bacteria isolated on the nitrite-utilizer culture medium described in Task #1 are obligate or facultative chemolithotrophs.

Justification - Very few strictly heterotrophic bacteria have been isolated that are substantially able to degrade HMX or RDX. In part this may be because heterotrophs are the wrong physiologic type of organism for degrading these nitrite-containing compounds. Nitrite utilization is rare among heterotrophic bacteria but more common among chemolithotrophic forms. Indeed, the most common nitrite-utilizers are chemolithotrophs that oxidize nitrite to obtain energy for growth. Some of these chemolithotrophs use the same nitrogen compound for both an energy source and a nitrogen source. They are referred to as "nitrite utilizers" and belong to the genera Nitrobacter, Nitrococcus and Nitrospina. Chemoheterotrophic bacteria derive their energy by using organic compounds as electron donors; chemolithotrophs use inorganic compounds. The chemolithotrophs use reduced forms of inorganic compounds such as ammonia, hydrogen, ferrous iron, thiosulfate and nitrite as sources of electrons for energy production, and also serve to reduce carbon dioxide for incorporation into cellular carbon. These organisms grow either aerobically using O2 as the terminal electron acceptor during electron transport phosphorylation reactions, or anaerobically using nitrate, sulfate and carbonate as the final electron acceptor.

Nitrite utilizers are found commonly in fresh and salt waters, soils, compost piles, and sewage disposal plants and frequently form zooglaea (organisms stuck together in a biofilm). Although most grow autotrophically using only CO2 as a carbon source, some can also grow heterotrophically using acetate as a carbon source. Their ability to form natural biofilms, oxidize nitrite to nitrate and use either CO2 or acetate as a carbon source makes them much more attractive than other organisms for constructing biofilms to degrade HEs on GAC. Their unusual nutrient and energy requirements (compared to those of the more common heterotrophs which might colonize the biofilm as contaminants) should make overcolonization of the constructed biofilms less likely and thus easier to maintain.

Progress - Bacteria isolated from HE-contaminated soils on the nitrite-utilizer screening medium are being tested for their ability to maintain their viability and grow as chemolithotrophs. In addition, whether they maintain the ability to oxidize nitrites to nitrates is being tested. Further, these organisms are currently being tested for their ability to grow in the presence of analytical-grade RDX.

Task 3: To determine the optimum C:N:P ratios for growth of organisms isolated from the nitrite-containing screening medium

Justification - Bioremediation of any recalcitrant compound, including HMX and RDX, is effective if the metabolic capacity of microorganism that are able to degrade the desired compound can be increased. Increased metabolic rates are often realized when the suboptimal conditions that control the rate of growth, such as O2 and nutrient concentrations, are made optimal. One of the most significant conditions to be realized is the achievement of the proper C:N:P ratio for the degrading organism.

Progress - Experiments are now being designed to test whether the nitrogen concentrations of RDX and HMX will alter the amounts of carbon, nitrogen and phosphorus-containing compounds in the culture media needed to obtain optimum growth and HE degradation.
Bioremediation Of Soil And Groundwater (Subproject)

Tony Mollhagen, and Caryl Heintz (CO-PIs), Texas Tech University
Graduate Student Victoria Harkins, Texas Tech University

EXECUTIVE SUMMARY:

- Funding for this project was anticipated in January of 1996 but it was not received until June. Development and validation of the analytical method for determination of selected high explosives (HEs) in soil and groundwater is essentially complete.
- Another task is to screen candidate soils for consortia of microorganisms pre-adapted to rapid degradation of HEs. Such microorganisms are most likely to occur at sites where soils have had long-term contamination by HEs. Candidate soils for testing were collected from playas 2, 3, and 4, and from the ditch exiting Zone 12.
- Preliminary reactor experiments on feeding and aeration strategies, seeded with soil from Playa 2, have confirmed the potential of such an approach. HEs were degraded and microbial populations grew.
- Replicated reactors seeded with soils from the candidate sites were established at the same time to compare performance. Result from these experiments are anticipated in three weeks.
- An attempt to further acclimate the best-performing consortium will follow.

Treatabilities Studies For High Explosives Biodegradation

R.L. Autenrieth (Co-PI), Texas A&M University
J.S. Bonner (Co-PI), Texas A&M University

EXECUTIVE SUMMARY:

HMX Degradation Studies

Previous experiments have shown that the Alderson Playa culture which had successfully degraded RDX could not degrade HMX. Cultures derived from Pantex burn-site soil samples have been able to degrade HMX when supplemented with carbon and nitrogen. Figure 1 (see detailed reports) shows the degradation of HMX over time in single reactors where the initial HMX concentrations and supplemented ammonium-nitrate concentrations varied (0.75, 1.5, and 3.0 mg/l HMX and 60, 120, and 240 mg/l ammonium nitrate). Comparing reactors spiked with the same initial HMX concentrations revealed that at increasing ammonium nitrate levels, degradation rates improved. Growth data showed that ammonium-nitrate accumulated when combined with regular additions of 240 mg/l and became toxic to the culture. From this experiment, it was determined that an initial level of 240 mg/l ammonium-nitrate with additions of 120 mg/l every 48 hours eliminated the ammonium-nitrate toxicity while maintaining a high level of HMX degradation.

An on-going experiment is to evaluate the rate and extent of HMX biodegradation. The initial target concentrations are 0.25, 0.5, 1.0, 2.0, and 4.0 mg/l. The experiment has been run over 20 days with the first 8 days of data having been analyzed to date. After 8 days, HMX transformation ranged from 54.4% in the 0.25 mg/l reactors to 34.6% in the 4.0 mg/l reactors, verifying an inhibitory effect at higher HMX concentrations. The data plots of figures 2 and 3a-3e (see detailed reports) indicates degradation to be linear. This is contrary to RDX degradation where there was a
lag phase, a peak degradation period, and finally, a slow-down because of poor RDX availability. The linear HMX degradation response would result if HMX is being co-metabolized along with ammonium-nitrate (whereas RDX was the sole nitrogen source in RDX experiments). Another possibility is that the shift in RDX availability was extreme whereas HMX has a low availability level throughout the experiment because of its lower solubility. Determining which mechanism is controlling the biodegradative response is part of our future efforts.

**Metabolite Determination**

We are currently optimizing extraction and GC/MS techniques to get the necessary precision required for metabolite identification. Past extractions were performed using methylene chloride, but the amount of mineral salts extracted along with the metabolites created an interference. Literature indicates that ethyl acetate extractions may eliminate this problem. Figures 4 and 5 show overlaid chromatograms from the present experiment at 10 days and at 0 days. The presence of some late eluting metabolites is clear, and there may also be metabolites concealed by the nutrient peaks. The isolation and identification of these peaks is in progress.

**VADOSE ZONE REMEDIATION**

Vadose Zone Remediation

Ken Rainwater (PI), Texas Tech University
Graduate Student Amit Armstrong, Texas Tech University

**EXECUTIVE SUMMARY:**

In this task area, the TTU research team is responsible for the development of a two-dimensional computer model to allow simulation of the soil-vapor extraction process, allowing for placement of extraction and passive vent wells in an unsaturated porous medium with a known initial distribution of residual liquid volatile organic contaminants (VOCs). The Pantex Plant includes several sites with known or potential residual VOCs from fuel or solvent losses. This project builds on previous experience at TTU in large-scale experiments and radial-flow modeling of soil-vapor extraction. The finite difference modeling approach taken in this research is somewhat unique in that the model accounts for the changes in air permeability over time as the VOC liquids are evaporated and removed.

During this quarter, work continued on the connection of the air flow and vapor transport subroutines. These subroutines were previously composed and initially tested separately. The coupled model is almost complete for single component VOC liquid, and will be upgraded to multicomponent VOC mixtures in the next quarter. Also in the next quarter, work will begin on a Visual-Basic graphical user interface to make the model more user-friendly.
Permeability Studies

Dr. Daene C. McKinney (PI), University of Texas at Austin

EXECUTIVE SUMMARY:

The focus of work during Aug.-Oct. 1996 has been focused on two areas, permeability studies and proposed tracer experiments for the Pantex high explosives study.

The goal of this work was to gain insight towards the intrinsic permeability of sand types that will later be used in laboratory column experiments (F-35 and F-75 grade Ottawa sands). In particular, we were interested in determining the relationship between residual water saturation of the sands and the resulting intrinsic permeability to air.

In conducting these permeability studies one task that was accomplished was the development of a consistent method for packing column samples. The success of this task is demonstrated the reproducibility of the results (within acceptable variations) for column pack porosity and intrinsic permeability to air for a particular grade of sand.

A second task that was achieved, was the application of an experimental procedure for determining the intrinsic permeability of a column pack at a given residual water saturation. This procedure involved measurements of pressure drop at five different flow rates in order to reduce the skewing effect of inaccurate measurements. The consistent and expected trend of measurements at different water saturations support the reliability of this procedure.

In order, to make the permeability measurements, a procedure had to be applied for establishing the column pack residual water saturation. This procedure involved an initial water flooding of the column with air sparging and stripping used to create a desired saturation.

A final task accomplished through the permeability experiments, was the development of a general familiarity with the lab equipment that will subsequently be used to perform tracer experiments. Specifically, the permeability studies provided an opportunity to become familiar with equipment such as the bubble meter and flow controller, in addition to procedures such as, leak testing and column packing that will ultimately expedite future tracer experiments.

Multicomponent Adsorption Isotherms

Aydin Akgerman (PI), Chevron Professor, Chemical Engineering Department, Texas A&M University Experiment Station, College Station, TX 77843-3122.

EXECUTIVE SUMMARY:

During this quarter we studied the adsorption equilibria of binary mixtures of VOCs on dry soil. The isotherms were determined by using a dynamic response technique based on frontal analysis chromatography. The organic compounds used were n-hexane, toluene, methanol, and chlorobenzene. The adsorption isotherm of one organic compound was obtained at a fixed concentration of the second adsorbate. Different concentrations of the second compound was considered. The binary systems were hexane/toluene (non-polar, slightly-polar), methanol/toluene (polar, slightly-polar), and chlorobenzene/methanol (polar, polar). The polarity of the adsorbates is an important characteristic in relation to the extent of adsorption on soil. It is logical to expect
binary adsorption to be at least partly governed by the relative polarities of the adsorbates involved. Whereas many authors studied the adsorption phenomena of VOCs on soils, the desorption process was rarely investigated. The literature available on this subject is very limited. One advantage of our dynamic experimental method is that concentration profiles can be obtained as a function of time for both adsorption and desorption. The technique enables determination of binary desorption breakthrough profiles.

We have already developed a method to determine adsorption isotherms of single compounds on soil a-priori during the first phase of the project. Thus it is not necessary to determine the adsorption isotherm of each species separately. Given the nitrogen adsorption data (a routine experiment in many laboratories) on soil and the VOC of interest, we can determine the isotherm within ±10% of the actual values. The next stage in our work plan is to develop the ability to determine the mixture isotherms from pure component isotherms. Since most contaminants are present as mixtures. If we are successful in extending our methodology we will be able to determine, a-priority, mixture isotherms, needed to determine desorption rates.

**Chromium Remediation**

Chromium Remediation

Ken Rainwater (PI), Texas Tech University
Heyward Ramsey and Tony Mollhagen (CO-PIs), Texas Tech University
Graduate Student Denny Givens, Texas Tech University

**EXECUTIVE SUMMARY:**

Chromium contamination at levels of a few mg/L have long been noted, primarily in and near Zone 12, at the Pantex Plant. Work by TTU researchers in the previous quarters included a report on potential Cr-waste waters discharged by the former cooling tower in Zone 12 and equilibrium isotherm tests of Cr sorption on core materials from the perched aquifer and its aquitard. In this quarter, one-dimensional column tests were begun to observe Cr sorption under flow conditions. One-dimensional column tests for Cr sorption under flow conditions were originally planned under this subtask. These tests were delayed by the request from Dr. Randy Charbeneau to proceed with the HE sorption isotherms immediately after the Cr isotherms. During this quarter, 1-D column tests have commenced using columns 25 cm long and 2.5 cm in diameter. The column tests are being performed in the same manner as similar tests done with core material from well BEG-PTX-02 previously by TTU researchers. A low-flow, high-pressure pump is used to drive a flow of a few mL/min through the packed column. The injected solution is Pantex groundwater with added Br and Cr concentrations at 10 mg/L each. The effluent concentrations of Br and Cr are measured and used to calculate dispersion and retardation coefficients. These tests will be completed and reported in the next quarter.
EXECUTIVE SUMMARY:

The experimental approach used in this work plan is to investigate combinations of zero valent metals (zvm) and amended zvm as reductants for the types of contaminants found at the Pantex site. Perched aquifer material from the site and simulated ground water (water with major ions added to mimic Pantex perched aquifer conditions) are added to the mixture. The classes of contaminants to be investigated, chromium, chlorinated organics, and high explosives, will be studied individually, then in combination with the other contaminants and aquifer material. We focus on iron and iron with palladium plating as the zvm. Trichloroethylene (TCE) is used as the model chlorinated organic and dinitrotoluene (2,4-DNT) as a model explosive. The three tasks shown below were developed in the initial proposal.

Task 1: Develop slurry reactor techniques and analytical techniques

Task 2: Examine the effectiveness of two types of zvm (iron and amended iron) with the three contaminants, Cr(VI), TCE, and 2,4-DNT, individually

Task 3: Examine the effectiveness of two types of zvm for the degradation of mixtures of the 3 contaminants

In this quarterly report, progress between August and October 1996 is summarized. The progress and results reported relate to Tasks 1 and 2. A final or milestone report covering all three tasks is scheduled at the end of the project period. In the previous quarterly report (May through July, 1996), results from experiments on the degradation of TCE by iron and iron/palladium (Fe/Pd) in the presence of pure water and Pantex aquifer solids were reported.

After we developed reactor conditions and analysis techniques for the chromium experiment, we conducted a series of experiments in reduction of chromium(VI) by zero valent iron (Fe⁰) and amended zero valent iron (iron coated with 0.05% by weight palladium, Fe/Pd). The experiments were conducted with composite Pantex soils and simulated Pantex ground water with an initial concentration of 2.1 ppm chromium(VI). It was found that the chromium(VI) concentration was lowered to below the detection limit (approximately 20 ppb Cr) in two hours by zero valent iron (Fe⁰) at 3.84 weight percent of solids; and for the same amount of amended iron (Fe/Pd), the concentration of chromium(VI) was reduced below detection limit in 40 minutes. From these experiments, both zero valent iron and amended iron were found to be effective in reducing the chromium(VI) concentration in a short period of time. Figure 1 in the Detailed Reports section summarizes the results of reduction of chromium(VI) in slurry reactors with Pantex aquifer solids containing 3.84% Fe⁰ and 3.84% Fe/Pd.

The slurry reactor technique and analytical technique for 2,4-dinitrotoluene (2,4-DNT) have also been developed and 2,4-DNT degradation experiments will be conducted soon. The trichloroethylene (TCE) experiments with composite Pantex soils and artificial ground water will be conducted in next quarter. In addition we will be conducting a series of experiments to find the effectiveness of zero valent iron and amended iron with mixtures of all three contaminants: chromium(VI), TCE, and 2,4-DNT.
Chemical Models And Redox Chemistry Of Chromium

Bill Batchelor and Mark Schlautman (CO-PIs), Texas A&M University

EXECUTIVE SUMMARY:

Chromium has been found at concentrations above background levels in several wells in the perched aquifer below the Pantex Plant, particularly in those beneath Zone 12. In some wells, the concentrations of total chromium exceed levels used to define hazardous wastes by the toxicity characteristic and approach being two orders of magnitude higher than drinking water standards. A research program has been initiated under the Amarillo National Resource Center for Plutonium to obtain information to support the remediation of chromium at the Pantex Plant. It is being carried out by research teams at Texas A&M University (TAMU), Texas Tech University (TTU) and the University of Texas at Austin (UT). This is the report on activities of one of the research teams at TAMU during the time period between August 1, 1996 through October 31, 1996. The research program for this team at TAMU includes two research tasks:

1. Develop chemical models for chromium in the vadose zone and perched aquifer
2. Evaluate redox chemistry of chromium

Chemical models for kinetics of chromium reduction in the presence of Pantex aquifer material and for conditions of chemical equilibrium have been developed during previous portions of the research. No additional development was conducted during the past quarter, although the equilibrium model continues to be used to evaluate experimental results and help design experiments.

Two aspects of chromium redox chemistry are being evaluated: reduction and oxidation of chromate. Evaluation of chromium reduction by ferrous iron in the presence of Pantex aquifer material continued during the past quarter. Additional data was collected to further refine kinetics reported in the milestone report submitted during the third quarter. This data is represented in Figure 1, in the section of this report titled “Detailed Report”. The additional data does not change the conclusions reported in the milestone report on chromium reduction kinetics. However, we have noted that there is evidence that some external oxidant, probably oxygen, could have entered the reactors in significant quantities during the experiments. This would result in loss of effective reducing power of the Fe(II) that was added. Substantially more Fe(II) was needed in experiments conducted with Pantex aquifer material than was needed in reduction experiments that were conducted without the presence of aquifer material and were completed within a few hours of introducing the Fe(II). The requirement for higher Fe(II) doses was attributed to reaction of Fe(II) with aquifer material. However, if substantial amounts of an external oxidant entered the reactor and caused the excess consumption of Fe(II), then lower Fe(II) doses could be used to effect treatment. The potential for external sources of oxidant entering the reactors is currently being evaluated and alternative experimental procedures will be developed if it is found to be a problem.

An experiment to evaluate the potential for reoxidation of chromate in Pantex soils was initiated during the past quarter and a milestone report was submitted on October 30, 1996. The potential for chromium reoxidation is important if in-situ chromium reduction is chosen as a remedial option. This remedial strategy seeks to reduce the toxicity and mobility of chromium by reducing it to the Cr(III) state, thereby reducing the risk to human health and the environment. Research on reduction of Cr(VI) by Fe(II) has shown that this remedial option offers promise both as an in-situ and ex-situ treatment process. However, the possibility exists that Cr(III) that has been reduced in-situ could be reoxidized to the more mobile and more toxic Cr(VI) form by introduction of
oxygen. If such a reaction cannot be shown to be highly unlikely, prudence might dictate that in-situ reduction not be used, because its long-term effectiveness could not be assured.

The chromium reoxidation experiment conducted during this quarter used slurry reactors containing Pantex aquifer material that had been spiked with Cr(VI) and to which Fe(II) was added as a reductant. Slurries with 1% aquifer material and 0, 9.7, 16.1 and 22.5 mg/L Fe(II); and slurries with 10% aquifer material and 0 and 19.3 mg/L Fe(II) were used. The reactor systems were the same that had been used to conduct chromium reduction experiments. After the reduction experiments were concluded, the reactors were oxygenated and the concentration of chromium in the solution monitored over time. Results of these experiments are shown in Figure 2, in the “Detailed Report” section.

The milestone report (“Reoxidation Potential of Chromium in Pantex Soils”) concludes that there was no evidence of reoxidation in the experiments conducted. None of the experiments showed a statistically significant change in chromium concentration with time at the 5% level. In fact, those experiments that had the closest approach to this level of significance were those that showed a slight decrease in chromium concentration. This decrease was interpreted as reduction or sorption of chromium that continued even when oxygenated conditions were established. The conclusion that chromium was not resolubilized is limited by the time period over which the data was obtained (30 days) and the fact that the oxidation state of aquifer material could have been altered by drying and storage. It is possible that chromium could be oxidized and thereby solubilized after longer periods of time. Time periods much longer than 30 days would be important in evaluating the long-term effectiveness of chromium remediation by reduction. Additional data is being gathered to extend the time period of the experiment. Drying of the aquifer material may have resulted in reduction of manganese oxides in the material. These oxides have been reported as being important potential oxidants for Cr(III) in soils. The potential exists that drying the aquifer material removed its ability to oxidize Cr(III).

**PHYTOACCUMULATION OF HEAVY METALS IN PLANTS**

**Phytoaccumulation Of Selected Heavy Metals, Uranium, And Plutonium In Plant Systems**

L.R. Hossner (PI), Soil and Crop Sciences Department, Texas A&M University, College Station, TX 77843

**EXECUTIVE SUMMARY:**

Research activities during this period have been allocated to the three primary objective areas: 1) Screening for Cr and U uptake and translocation by selected plant species under controlled conditions. 2) Basic studies on the mechanisms of Cr uptake and translocation by selected plants, and 3) Establishment of field trials on the High Plains of Texas that will determine the ability of common agricultural crops in the region to absorb and translocate Cr.

Plant growth, plant uptake and effect of chelating agents on Cr and U uptake and translocation were studied in soil media in controlled experiments. Twenty plant species were evaluated with two rates of Cr, three sources of Cr (CrO_4^{2-}, Cr^{3+}, and Cr^{3+} with EDTA chelate), and one source and rate of U, UO_2^{2+} at 100 mg U kg^{-1} soil. The tolerance and accumulation of Cr by plant species was dependent on the form of Cr in the soil. Chromium (VI) was the form of Cr that most adversely affected plant growth and was accumulated more than Cr^{3+} in all plant species.
Chromium(VI) applied at a rate of 500 mg kg\(^{-1}\) killed most of the plants. Chromium (III) application at a rate of 500 mg kg\(^{-1}\) had little effect on the growth of most plants. Uranium had no adverse effect on plant growth at 100 mg U kg\(^{-1}\) soil. Most plants that were screened with the CrO\(_4^{2-}\) source accumulated more than 2000 µg Cr g\(^{-1}\) in both shoots and roots at the 500 mg Cr kg\(^{-1}\) soil application rate. Sunflower (Helianthus annus) was the only plant species that accumulated more than 500 µg U g\(^{-1}\) plant material. Chromium as Cr\(^{3+}\) and U as UO\(_2^{2+}\) were accumulated mainly in (or on) the roots of the plants. The uptake of Cr(III) was significantly enhanced by the application of EDTA to the soil.

The success of phytoremediation depends on the total metal harvest (metal concentration of the plant tissue x plant biomass). Vetiver grass (Vetiveria zizanioides) is a promising candidate for phytoremediation as it has high dry matter production and relatively high concentrations of Cr and U in the above ground biomass. Sunflower and Indian mustard (Brassica juncea) accumulated more Cr and U than the other species. Sunflower is a multimetal accumulator, as it accumulated both Cr and U. Coastal bermudagrass (Cynodon dactylon) and switchgrass (Panicum virgatum) were the most Cr tolerant plant species. In hydroponic solution, soybean seedling height growth was less affected by Cr than was that of sunflower. Growth of sunflower was less in the presence of either Cr\(^{3+}\) or Cr\(^{6+}\) than was that of soybean. We hypothesize that sunflower accumulates more Cr than soybean. An alternate hypothesis is that soybean can sequester its Cr, and therefore can tolerate higher concentrations. We are in the process of testing this hypothesis by measuring the Cr content in the organs of each species. Canola appears to have a similar tolerance to that of soybean. In general, dicotyledonous plants accumulated more Cr and U than monocotyledonous plants.

Studies to evaluate the uptake and transport of Cr to the above ground plant parts were conducted in controlled experiments in hydroponic solution. Cucumis sativum (cv. lemon cucumber) exhibited enhanced ferric chelate reductase (FCR) activity when subjected to Fe stress and 1 µM Cr. However, higher Cr concentrations suppressed the FCR activity in Fe-stressed plants. Chromium had no significant effect on FCR activity in Fe-sufficient plants. A small scale FCR assay system for small whole plant roots was developed to allow rapid screening of plants for high FCR activity, which may be important in plant/heavy metal relations. Chromium (III) supplied as the chloride salt at alkaline pH had no significant effect on the growth of cucumber even in nutrients solutions saturated with Cr\(^{3+}\). The results of these experiments suggest that this cultivar of cucumber is not sensitive to Cr\(^{3+}\) under the conditions studied, and likely avoids toxification by an exclusionary mechanism. Clover grown under both Fe sufficient and Fe deficient conditions transported Cr to the above ground plant parts in the following order: CrO\(_4^{2-}\) > Cr\(^{3+}\) > Cr-DTPA. The concentration of Cr-DTPA was also very low in the plant roots indicating that this form of Cr is not readily absorbed by the plant. These results differ somewhat from the studies of Cr uptake in soils, in which Cr content of the leaves and shoots was slightly greater with Cr-EDTA compared to Cr\(^{3+}\). Visual observations of the roots of plants treated with CrCl\(_3\) in hydroponic culture indicated the probable presence of a Cr (OH)\(_3\) precipitate at the root surface. Thermodynamic evaluation indicated that at the pH of the soil or hydroponic solution, Cr\(^{3+}\) would be readily precipitated as Cr(OH)\(_3\), resulting in low equilibrium concentrations of solution phase Cr. The slightly higher uptake of Cr from Cr-EDTA compared to the Cr\(^{3+}\) source in soil culture probably reflects the higher concentration of dissolved Cr in the former system. There is no evidence that Cr is absorbed readily in either the Cr-EDTA or Cr-DTPA forms.

Electron paramagnetic resonance (EPR) spectroscopy was used to evaluate Cr form and complication in the roots and above ground plant parts. The precipitation of Cr on or in the root was confirmed by EPR. Also, a high spin Cr complex as observed in both the roots and shoots. Efforts are currently underway to identify this complex using EPR, high performance liquid chromatography (HPLC), and mass spectrometry. Identification of this complex is important, since it gives important clues to the biochemical and genetic control of Cr accumulation.
Roots of CrCl₃ treated plants were examined by environmental scanning electron microscopy (ESEM) and scanning electron microscopy (SEM). Spherical particles (=0.5 μm diameter) of chromium hydroxide or chromium phosphate were observed at the root surface. There was no evidence of precipitated Cr within the root or in the individual cells. Chromium transport to the shoots and leaves was significantly enhanced under Fe-deficiency stress conditions. One of the Fe-deficiency stress response reactions of dicots is an enhanced root plasma membrane H⁺ pump. This reaction also results in a concomitant production of the conjugate bases of organic acids, i.e., oxalate, malate and citrate. The second major hydroponic plant experiment has been completed, though analysis of the samples is still in progress. The experiment is designed to evaluate Cr oxalate, Cr malate and Cr citrate as sources of Cr for plant uptake, and to evaluate the uptake of Cr by several pea mutants that have exhibited accelerated uptake and accumulation of Fe. The formation and stability of the complexes have been evaluated as a function of pH. The kinetics of formation in regions of stability is very slow, as is the breaking of the complex in regions of instability. These factors negatively influence the mobilization and possibly the uptake of inorganic Cr³⁺, but positively influence the compartmentalization of complexed Cr within the plant.

Greenhouse and field experiments have been initiated on the Texas High Plains on two soils, a loamy sand and a clay loam, to determine the influence of soil type and plant type (monocots and dicots) on Cr (rates of 0, 10, and 100 mg Cr³⁺ kg⁻¹) utilization by cool and warm season crops. Agricultural crops common to the Texas High Plains have been selected for this study. Warm season species include sorghum, sunflower, bermudagrass and soybean. Cool season crops include winter wheat, canola, bromegrass, red clover, alfalfa, and rye. The crops will be rotated to simulate a continuous cropping system using combinations of warm and cool season crops.
Executive Summary

For more complete descriptions of these tasks and subtasks, please see the detailed reports at the back of this report.

Communication, Education, and Training (CET) is divided into Center programs, awards, and grant-funded projects. The size of the CET Center staff is projected to reach ten by the end of FY 1997; it is currently six plus one graduate assistant - an increase of one over the previous quarter.

For the reporting period, graduate assistant Alcantar worked with the TexPREP grant-funded project at Amarillo and Lubbock, and assisted the Center's Education Program Coordinator in the Center.

Program Management has been engaged in the following:

- Performing human resource needs analysis within CET in order to fill the positions of Information Resource Specialist, Training Program Coordinator, Science Information and Resource Center Project Coordinator, and Community Liaison;
- Strategic planning;
- Conveying education and outreach needs of the Center, analyzing Letters of Intent (refer to appended section for CET to see Selection Criteria & Weights for FY 1997 LOI Selection) and proposals in accordance with program needs and planning for FY 1997;
- Revising communication and education program plans in preparation for Peer Review held 9/19/96;
- Guiding the Electronic Resource Library project (Refer to Task 1) and leading a collaborative effort between Amarillo College and technical researchers across the Center (in nuclear, environmental, and education groups);
- Guiding the Science Information and Resource Center project and leading a collaborative effort with the Don Harrington Regional Discovery Center;
- Guiding the Graduate Education project which includes researching video conferencing resources, capabilities, and opportunities; and conducting trial conferences;
- Guiding the co-development of an Agriculture Communication and Education Plan with representatives from the Texas panhandle agriculture community;
• Drafting the Center’s publication policy; and
• Furthering education and outreach collaborations with DOE, and the Los Alamos and Sandia National Laboratories.

During this quarter, communication program personnel delivered:
• eight speeches including
  9/24/96 Pantex Plant Citizens Advisory Board
  9/25/96 Defense Programs in Washington, D.C.
  10/1/96 The Pantex Plant
• materials including nuclear primer (copy available upon request) for Mixed-Oxide for Texas Regulators meeting in Austin, TX on 8/29 and 8/30/96;
• mixed-oxide fuel information panels for the Center’s exhibit at the Amarillo Tri-State Fair, 9/14-9/21/96 and Panhandle Area Mathematics and Science Conference, 9/28/96;
• issue V of the Center’s newsletter with a distribution of 4,500 which included 3,000 to Pantex personnel (refer to appended section for CET to see the issue);
• news releases on business briefs, Chemistry Road Show, and Senior Technical Review Group (STRG) to Amarillo Globe News (refer to appended section for CET to see an example); and
• guest editorial by Dr. Randall Charbeneau to Amarillo Globe News and Austin American-Statesman, 9/8/96 (refer to appended section for CET to see the editorial).

The communication program personnel have been developing the Communication Program Plan, designing a flyer on mixed-oxide fuel, revising the Center’s information brochure, and designing the Center’s world wide web site.

The entire K-16 Education Program which includes the Center’s program, awards, and grant-supported projects was peer reviewed on 9/19 and 9/20/96 by colleagues from Fermi Laboratory, the University of Ohio, and NOVA Southeastern University in Florida. Their overall rating of the program was 4- on a scale of 1 to 5 with 5 being excellent. Refer to the appended section for CET to see instructions on how to use the Peer Review of Program Report Form. This form was used to evaluate the Center’s education program plan and associated plans. A similar form was used to evaluate the education proposals.

During this reporting period, education personnel appeared on KVII-TV to announce the Panhandle Area Mathematics and Science Teacher Conference held on 9/28/96 at West Texas A&M University. The conference was sponsored in part by an award from the Center. In addition to the keynote session, about 150 presentations were made. Approximately 730 teachers, speakers, students, and exhibitors registered for the day-long event. K through grade 12 teachers from more than 70 school districts in the Texas panhandle and south plains attended. Pre-service teachers at West Texas A&M University, Texas Tech University, Lubbock Christian University, and Wayland Baptist University participated. Four speakers were participants in Department of Energy funded projects in Nevada. Two speakers were Presidential Award Winning teachers. Evaluations of the conference were positive.

Education program personnel
• continued to work with Amarillo Independent School District (AISD) on the Caprock Cluster Tech Lab project (refer to the appended section for CET to see a progress report from AISD dated 11/14/96); and
• scheduled the Texas A&M University Chemistry Road Show at four Amarillo middle schools, at rural schools in three area communities, in Amarillo’s downtown mini-park, and at the
Panhandle Area Mathematics and Science Teacher Conference during 9/24 - 9/28/96 (refer to the appended section for CET for testimonial letters and newspaper coverage).

Training program personnel for CET have not been hired.
Implementation Of Grant Funded Projects

Follow up activities for the K-16 education project funded for FY 1996 are in place. Teacher observations and interviews should be complete in December and a final report should be complete in January, 1997.

During the reporting period, two new projects for CET were approved for FY 1997 funding:

- **Environmental Project: Integrative Studies in Science and Mathematics**
  Based on Integrative Learning Theory for Classroom Curricula and as a result of an in-depth field experience, twenty K through grade 12 teachers of science and mathematics in the Texas panhandle will be able to instruct and develop curricula that are grounded in concepts related to environment and sustainability. Teachers will be able to move away from fact-centered, textbook-driven classroom instruction toward instruction that integrates environment into mathematics and science; and that is theme-based, experiential, and problem-centered.

- **Building Foundations for Mathematics and Science Success**
  Approximately 800 elementary students will receive instruction that is capable of supporting students through advanced mathematics and science courses, and nurturing their critical thinking and problem solving skills. These students and their families will be engaged in focused and deliberate career research. Thirteen intern teachers will receive different and additional classroom experience and under the mentorship of master teachers; an experience otherwise not provided in the typical teacher education program.

**High School Computer-Assisted Physics**

A 10-day teacher workshop conducted 7/29 - 8/9/96 provided area high school physics teachers with

- information, instruction, and guidance in (a) instructional design of physics lessons using computer simulations, (b) use of physics simulation software to enhance instruction and effective methods of presenting physics concepts with computers, and (c) use of physics related resources on the Internet; and

- training in authoring computer-based tutorials and tests.

Teachers are developing simulations and lessons; they presented examples of their work at the Panhandle Mathematics and Science Teachers Conference, 9/28/96. The project managers are developing software, web pages, simulations, and tutorials. This project was funded for continuation in FY 1997.

**Middle School Science Resource Manual**

Activities for Teaching Fundamental Concepts of Nuclear Energy and Related Topics was developed during the summer of 1996 by a team of seven secondary school science teachers and printed in September. The manual contains 63 activities that are correlated to the national Standards for Science Education. During the reporting period, two workshops featuring the manual were conducted at the Panhandle Regional Mathematics and Science Conference. Teacher comments included:
"These activities are the kind that will help students understand some of the abstract concepts related to nuclear energy and radioactivity. I plan to use some of them immediately."

Eighty-nine teachers from across Texas received manuals. Follow-up will include a use and satisfaction survey during Spring 1997. This project was funded for continuation in FY 1997.

**Texas Prefreshman Engineering Program (TexPREP)**

TexPREP 1996 was conducted on the Amarillo College campus and in Lubbock on the Texas Tech University Campus for eight weeks from June 3 to July 26, 1996. The primary purpose of this program is to introduce high achieving middle school and high school students to the field of engineering by reinforcing college preparation in mathematics.

According to the final reports, 174 students completed the program: 106 in Amarillo; 68 in Lubbock. Of the total number, 36% were Hispanic, 30% were White, 21% were Asian, 11% were Black, and 2% were Native American. Follow up survey results revealed that 80% of college eligible students who completed TexPREP Amarillo and Lubbock in FY 1995 and FY 1996 are in college. One $2,500, one $1,000, and two $250 scholarships were presented to the top four students at each site. This project was funded for FY 1997.

**Public Outreach**

Public outreach is the grant-funded correlate of the Center’s communication program.
- Revisions to the informational video on the Center were completed (copy available upon request).

**Science Information and Resource Center**

For the reporting period, the review of literature and a conceptual design program document for a science center were completed. Final designs are due in January 1997.

Project personnel have been implementing the exhibit plan for the Plutonium Transportable Exhibit which is the partnership exhibit between the Center and Pantex (Mason & Hanger). All of the electronic components (CPUs, monitors, televisions, video disc players, video disc control units, amplifiers, speakers, and printer), wiring, and jacks are labeled. Detailed photographs were taken, diagrams were drawn, the unit was insured. The display schedule is:

- **Tri-State Fair (134,000 attendance)**: September 14 - 21
- **Panhandle Area Math and Science Conference**: September 28
- **Amarillo Airport**: October - December (confirmed)
- **Amarillo Farm and Ranch Show**: December 3 - 5
- **Don Harrington Discovery Center**: December - April, 1997

The Science Information and Resource Center project was funded for FY 1997. Project personnel will design and develop two exhibits that will inform and educate viewers on environmental and nuclear research of the Center. Exhibits will rotate through the Don Harrington Regional Discovery Center in Amarillo.
Executive Summaries Of Research Activities

For more complete descriptions of these tasks and subtasks, please see the detailed reports at the back of this report.

EXECUTIVE SUMMARY:

During the current reporting period (1 August 1996-31 October 1996), coordination and technical information support activities have consisted of the following:

- Fifteen New Technical Library Acquisitions
- Expansion of the Centralized Information Web Site
- Update and Dissemination of the Calendar of Conferences (formerly Technical Calendar)
- Attendance at two DOE Informational Meetings or Workshops
- Eight Internal Technical Working Documents (ITWDs)
Evaluation Of Fast Reactors

EVALUATION OF FAST REACTORS

W. D. Reece (PI), Department of Nuclear Engineering, Texas A&M University

During this quarter, the funds for transferring the safety codes developed for and used at FFTF (Fast Flux Test Facility) to the Russians have finally been approved. The efforts here to facilitate in the capture of the experience at FFTF seems to have been successful. Because the DOE funding levels are small, the FFTF staff have requested that their efforts start in January and extend for five months, with no analyses on Russian reactors to be done this year. We have been queried if we could help convert some of the codes from large mainframe formats to run on SPARC workstations, but thus far we have no students identified and no faculty time available.

Modular High Temp Gas Cooled Reactors

This task has been redirected. Please refer to the subproject entitled, “Water Reactor Options for Disposition of Weapons-grade Plutonium.”

Accelerator Based Transmutation

TRITIUM PRODUCTION USING ACCELERATOR-DRIVEN TECHNOLOGY

Theodore A. Parish (Co-PI), Department of Nuclear Engineering, Texas A&M University

EXECUTIVE SUMMARY:

Work on this task concludes this quarter due to its exclusion by the Joint Steering Committee from the US/Russian Joint Studies work. During the current reporting period, a final report entitled, “Accelerator Driven Production of Tritium: Target and Blanket Design” was completed and has been submitted for publication as a Nuclear Group Internal Technical Working Document. (information on this document series appears under “Coordination and Technical Information Support for Nuclear Group Activities” above.)
EXECUTIVE SUMMARY:

The task of supporting the US/Russia joint study team on water reactors continued to move forward. Drs. Adams and Peddicord visited IPPE and INPE in Obninsk, attending a workshop on plutonium disposition. Some information was gained about the Russian plutonium complex, about the capabilities of various institutes in Russia, and about the possibility of further collaborations with Russian researchers on the use of MOX in VVER-1000 reactors. Dr. Adams also attended a meeting at ORNL in September, at which US and French researchers discussed their respective collaborations with Russian researchers.

Since the Joint Steering Committee meeting in St. Petersburg in July, Dr. Klein has been in constant contact with the different Russian Institutes and US National Laboratories involved in the future Experimental Test Programs. Subsequently to the Joint Steering Committee meeting, a second set of subcontracts was drafted in order to include appropriate milestones. Two of these subcontracts have been signed during the present reporting period.

Dr. Igor Carron visited the Moscow Engineering Physics Institute on October 17-18. The trip was sponsored by a linkage grant of NATO Scientific Affairs Division (Disarmament Technologies). The discussion of relevance to the Russian activities of the Amarillo National Resource Center for Plutonium included an informal review of some of the results obtained by MEPhI researchers on research performed for the Center. The deliverables of this activity include a final report which was not available at the time. This deliverable is due in November. More specific discussion included interaction between MEPhI and the Center on one item of the MEPhI subcontract dealing with the establishment of a Master of Science program (Dr. David Boyle is monitoring this activity for the Center). The primary aim of this visit was to improve the working framework between the MEPhI research group working on plutonium bearing fuels with uncertain irradiation history and the group of Dr. Naeem Abdurrahman (University of Texas) who is the Center's monitor for this project. A visit to Texas of MEPhI researchers was arranged for the beginning of next year.
For information on coordination with DOE laboratories, please see also item I.G, “Storage Programmatic Coordination,” under the above subproject entitled, “Coordination and Technical Information Support of Nuclear Group Activities.”

POST EXPLOSION TRANSPORT (PET) STUDY

Dr. Dale Klein (PI), The University of Texas System
Steven Manson, Department of Mechanical Engineering, The University of Texas

EXECUTIVE SUMMARY:

This research has been undertaken to augment the computational models currently used to perform safety analyses of the PANTEX cell facilities. In the event of an accidental chemical explosive transient during disassembly activities, there is some concern that a release of plutonium aerosols may result. The computational modeling of some accident scenarios has been limited by the one dimensional approach of the MELCOR code. This effort uses multidimensional techniques to analyze the natural convection which drives the flow of particulates within the cell room in the aftermath of an explosion event.

The accident scenarios considered in this research are limited to those in which the roof of the cell room remains intact. The cells are designed such that a detonation of sufficient magnitude will destroy the roof, causing an over-burden of sand and gravel to fall in and contain the explosion. This containment feature will also act to filter dangerous aerosols out of the escaping gases. If, however, the inventory of chemical explosive present in the cell facility is insufficient to cause the failure of the roof, unfiltered gases may escape to the environment carrying some inventory of weapons plutonium in particulate form.

Past studies of these contained explosions have been limited to numerical consideration of the flow paths as one-dimensional channels with pressure driven flow. This approach may be adequate in narrow rampways and through leakage sites, but the flow in the cell room itself is clearly multidimensional. Multidimensional flow in the cell controls the mixing of particulates and the air, and hence is crucial to modeling aerosol transport. Furthermore, depressurization of the cell room is accomplished over relatively long times (>10 seconds), by both the leakage of air to the environment, and the cooling of hot gases through natural convection to the cell walls. This natural convection heat transfer is also multidimensional in character. Thus, this research effort will apply modern multidimensional computational techniques to post-explosion transient flow in cell facilities.
EXECUTIVE SUMMARY:

The following tasks were performed during the past quarter:

**Activities at Texas A&M University**

- A stability tool for a generic manipulator/gripper is under development. Work this quarter involved embedding a stability-testing algorithm into TELEGRIP software package which is used for graphical animation.

- An animation tool capable of animating the static and dynamic motions of a generic manipulator/gripper is under development. A motion generation algorithm is being embedded into TELEGRIP.

- The Integration of TELEGRIP with InterAgent was carried out during the past quarter. The system is undergoing testing and will be in use shortly.

- The design of a Modularized Simulation Construction set has been started.

- The underlying models required for bi-directional tele-operation between Texas A&M University and Texas Tech University have been built, and TAMU has supplied underlying code necessary for operation. On time completion of this task expected.

- An initial demonstration of a Virtual Reality-based inspection system using the flock of birds 6 DOF sensors has been developed. Tests have been carried out to ascertain the working environment required for successful use of the FOB.

- A voice recognition card has been installed and integrated into the Texas A&M simulation test-bed.
Activities at Texas Tech University

- Construction and testing of the Teleoperations Graphical User Interface (TGUI) with the Automated Weigh and Leak Test (AWALT) simulation has been completed.
- Progress in the safety and reliability task has been good. A Ph.D. program is well underway based on the project. The Ph.D. defense of the topic is expected in the spring of 1997. Papers are in review.
- The self-assessment of reliability model has made good progress. A Ph.D. proposal is forthcoming and a paper has been submitted for review.
- The bi-directional link between TTU and TAMU robotics testbeds is nearing completion. It is expected that the work will be complete in two to four weeks. Internal to TTU work is progressing to connect the Mechanical Engineering robot and the IE robot using the same protocol. This work lags behind the TTU to TAMU link but is expected to be completed this quarter.
- Work on the high-fidelity manipulator modeling tool is progressing well. Three papers have been submitted for journal review. Progress on the implementation of the models into Telegrip has been delayed until the bi-directional testbed is fully functional.

Activities at The University of Texas at Arlington

- At UT Arlington, we continued our work toward performance modeling and measurement. During this period, we have had to address significant problems associated with upgrade of the basic communications software that supports our distributed robotics/remote operations work environment and, specifically, the resolution of compatibility with our custom performance measurement and monitoring software. This is an essential precursor to the execution of planned experimental work with other members of the robotics group. Work is nearing completion on the initial phase of our efforts to measure “motion quality”; a thesis will be presented on 11/26/96 detailing the findings of this work. In addition, we have continued to assemble our technical report on standards for distributed remote operations systems design to support performance measurements. Efforts to broaden the base of funding support for the performance modeling and measurement portion of the overall project have also been pursued via submission of a proposal (10/15/96) jointly with our Texas A&M colleagues, Hughes Training, Inc., and United Space Alliance (Rockwell, etc.) pertaining to teleoperations and remote operations.

Activities at the University of Texas at Austin

- The module modeling of wheeled vehicles is progressing as planned. Modular tools have been developed for machines that are comprised of serially connected holonomic sub-systems, a serial chain robot being an example of this arrangement. Work toward module models of nonholonomic systems is in progress.
AIR MONITORING FOR DETECTING RELEASES OF PLUTONIUM IN A FUTURE INTEGRATED STORAGE FACILITY

H. M. Liljestrand (PI), Department of Civil Engineering, The University of Texas
A. R. McFarland, Department of Mechanical Engineering, Texas A&M University
W. H. Marlow, Department of Nuclear Engineering, Texas A&M University
P. K. Dasgupta, Department of Chemistry, Texas Tech University
S. Liu, Department of Chemistry, Texas Tech University

EXECUTIVE SUMMARY:

This research effort is to develop an optimized system for detecting plutonium releases in the Integrated Storage Facility. The system will ultimately provide meaningful data for alarm purposes, for determining the exact source of leakage, and a quantitative basis for indoor and outdoor exposure to such releases. The research program is divided into four subprojects, which include (principal investigator(s) from each institution are noted in parentheses) (1) development of a method for detecting the occurrence and isolating the location of leakage from storage (H. M. Liljestrand and R.L. Corsi, The University of Texas at Austin), (2) development of a method for predicting the best sampling and monitoring locations (A. McFarland, Texas A&M University), (3) development of a methods for accurate detection of plutonium aerosols (P.K. Dasgupta, Texas Tech University) and (4) plutonium leak detection by conductivity methods and optical detection of plutonium aerosols (W. Marlow, Texas A&M University). Each subproject is on schedule, and the results are available through M.S. reports, journal article submissions, and conference proceedings.

SUBPROJECT 1: DEVELOPMENT OF A TRACER-BASED FINGERPRINTING SYSTEM TO IDENTIFY AND LOCATE PU STORAGE CONTAINER LEAKAGE

H. M. Liljestrand and R. L. Corsi, Civil Engineering, The University of Texas

EXECUTIVE SUMMARY:

The premise behind a tracer-based fingerprinting system is that small quantities of other inert tracers, e.g., perfluorocarbons, could be added to helium in a container headspace. The use of multiple tracers at varying concentrations would allow for container-specific fingerprints. For example, if three tracers were all detected simultaneously in a specific ratio it would be possible to immediately identify the specific container from which they were released. It would then be possible to rapidly isolate and remediate the specific failure on the target container.

This primary task consists of six major sub-tasks. These include (a) the identification of a list of potential tracers, (b) a rigorous literature review on the effects of alpha radiation on each of the tracers listed in (a) (future experiments will confirm this task), (c) selection of final "target" tracers, (d) design of a fingerprinting scheme, e.g., specific tracers, tracer combinations, and concentration variations to allow for container-specific identification, (e) selection and potential design of an appropriate on-line monitoring system to allow detection of target tracers with required sensitivity, (f) development of fingerprint feedback software to facilitate leakage notification and container identification, and (g) development and testing of a prototype detection/fingerprint system.
SUBPROJECT 2: DEVELOPMENT OF IMPROVED SAMPLING SYSTEMS FOR THE COLLECTION OF PLUTONIUM AEROSOLS

A. R. McFarland, Department of Mechanical Engineering, Texas A&M University

EXECUTIVE SUMMARY:

Numerical studies on modeling of flow mixing in stacks and ducts have been initiated. Experimental and numerical studies on aerosol losses in transport system components have been conducted.

SUBPROJECT TASK 3: COLLECTION OF PLUTONIUM AEROSOL PARTICLES THROUGH AN ELECTRICAL MEANS FOLLOWED BY AN AUTOMATED IC MEASUREMENT

P. K. Dasgupta, Department of Chemistry, Texas Tech University

EXECUTIVE SUMMARY:

Aerosol particles are naturally charged or can be deliberately made to be highly charged. When introduced to an electric field, these charged particles will deposit onto the oppositely charged electrode. The composition of the aerosol particles can be obtained through chemical or radiochemical analysis. To date, an automated annular tubular aerosol collection system using an electrical means has been developed and its performance has been found to be in excellent agreement with that experimentally predicted.

SUBPROJECT 4: PLUTONIUM LEAK DETECTION BY CONDUCTIVITY METHODS AND OPTICAL DETECTION OF PLUTONIUM AEROSOLS

William H. Marlow, Texas A&M University

EXECUTIVE SUMMARY:

Calculations of the electric current pulse due to the passage of a single alpha particle through either air or a noble gas in a weak electric field are in progress with initial results having been obtained. The purpose of this study is to provide the design basis for initial experimental work to develop a practical system for monitoring pit leakage in double-walled containers under study in the AL-2100 Program of DOE/DP at Sandia, Los Alamos, and Lawrence Livermore National Laboratories. A presentation of the proposed plan of research was given October 9 for the AL-2100 Program Meeting at Sandia National Laboratory, Albuquerque, and attended by participating DOE and National Laboratory personnel. This work will be fully reported in the January, 1997, Milestone/Deliverable for this project subtask as indicated earlier.

Laboratory studies are being conducted of the fractional removal of aerosol particles from airstreams flowing through reticulated vitreous carbon foam. These studies are intended to determine if modern low density microporous materials can be used as aerosol capture media which will provide size-related spacial separations of 0.5 to 10 micrometer plutonium particles arising from leakage or other dispersal processes. If successful, these materials may in the future be used to provide samples for ultraviolet fluorescence detection of ultrasmall quantities of airborne plutonium. Due to extended delays in delivery of the materials under study, as cited in the preceding Quarterly Report, we were unable to fulfill the Milestone/Deliverable commitment.
originally scheduled for September, 1996. Completion is now anticipated for January, 1997, and no subsequent work will be conducted.

DEVELOPMENT OF MONITORING SYSTEM FOR ACCIDENTAL PLUTONIUM EMERGENCE

Purnendue K. Dasgupta (PI), Texas Tech University

EXECUTIVE SUMMARY:
A new continuously operating aerosol particle collection system has been developed. The system operates on the principle of forced condensation of vapor on to the particles after vapor (steam) introduction. The current system operates without any extraordinary cooling or impaction requirements and is very light weight. Further, high volume sampling is possible, permitting very sensitive measurements. The system facilitates quantitative collection of aerosol particles across a broad size range and therefore measurements can be done without any particle size bias. A manuscript is under preparation for publication of this work in a scientific journal. Further information of the system has been included in the following detailed report.

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Radiation Damage and Microstructural Change

RADIATION DAMAGE AND MICROSTRUCTURAL CHANGES OF STAINLESS STEEL DUE TO LONG-TERM IRRADIATION BY ALPHA PARTICLES FROM PLUTONIUM.

Ron R. Hart (Co-PI), Department of Nuclear Engineering, Texas A&M University
Kenan Unlu (Co-PI), Department of Mechanical Engineering, The University of Texas

EXECUTIVE SUMMARY:
This project will further our understanding of material problems that may arise during the long-term storage of Pu pits by continuing to study the radiation damage and associated surface and microstructural changes produced in stainless steel covers by high fluence alpha particle irradiations from Pu.

The effects of alpha particles emitted from weapons grade Pu on 316-stainless steel are being investigated to determine the integrity of stainless steel covers for long-term storage of Pu pits. To simulate the problem, He-3 ions with various energies and fluences will be implanted into polished stainless steel samples. The He-3 behavior in the samples will be monitored using Neutron Depth Profiling (NDP). Neutron Depth Profiling is a unique, nondestructive nuclear technique which utilizes thermal-neutron-induced charged particle reactions to determine concentration depth profiles of certain isotopes in any substrate. Surface conditions will be monitored by scanning electron microscopy (SEM) for any changes (e.g. blisters, pits) due to implantation to various He-3 fluences. Microstructural changes and bubble formation will be observed using transmission electron microscopy (TEM).

Helium-3 ions with fluences varying from 1E15 to 1E16 ions/cm² have been implanted into polished 316-stainless-steel test samples. The incident implantation energy was 140 keV. The implantations were performed at room temperature. Surface conditions were monitored by NDP before and after implantation. Depth distribution profiles for test sample were obtained by NDP.
Test sample preparations for TEM study are currently underway. Microstructure of the sample at the end of the range of the helium-3 ions will be observed using TEM. Bubbles and voids are expected to be observed at the grain boundaries of the maximum-damage region. For each sample, a correlation will be made between the implantation energy and fluence, the concentration depth profile, and microstructural information obtained from TEM.

**Risk Assessment**

**AIRCRAFT ACCIDENT FORECASTING FOR AN INTEGRATED PLUTONIUM STORAGE FACILITY**

James C. Rock (Co-PI), Department of Nuclear Engineering, Texas A&M University
Michael T. McNerney (Co-PI), Aviation Research Center, The University of Texas

**EXECUTIVE SUMMARY:**

The final DOE standard 3014-96, "Accident Analysis for Aircraft Crash into Hazardous Facilities" is now projected for mid-November release. The Draft Pantex Site Wide Environmental Impact Assessment (SWEIS) was revised to incorporate our comments submitted during the previous reporting period. That document is working its way through DOE approval channels, and the projected publication data has slipped past Oct 1996. The SWEIS will be based on the July 96 version of DOE Standard 3014-96 on the basis that the changes in the standard do not change the SWEIS conclusions.

In August, Drs. McNerney and Rock participated in a very productive meeting hosted by Lamb Associates in Albuquerque, NM. Attendees from Sandia National Labs, the Albuquerque Operations Office of DOE, Pantex, TetraTech, Inc., and the USAF Safety Center all contributed to a lively dialogue about improvements needed in aircraft accident models for public risk assessment. We left drafts of our analyses and obtained the same from the Sandia participants. By the end of the meeting, it was clear to all that the best course of action would be to collaborate so that all parties can benefit from prior work and experience of the others. We modified our 1997 ANRCP proposal to reflect that goal. Dr. McNerney received valued feedback on his efforts to use features of the Pantex airspace and type-specific aircraft accident rates to further refine the DOE accident probabilities. Dr. Rock received valued feedback on his continuing efforts to create a better bound on the threat posed to Pantex facilities by skidding aircraft.

**A FEASIBILITY STUDY FOR THE STORAGE OF PLUTONIUM PITS IN NON-PARTITIONED WAREHOUSE FACILITIES**

Darryl James (PI), Department of Mechanical Engineering, Texas Tech University

**EXECUTIVE SUMMARY:**

Completed phase I modeling for the FD-LANL facility. The FD-LANL facility that is being investigated will contain some five thousand pits, each stored in an individual AT-400A container. The containers will be stored in racks that contain four and six containers, referred to as a four pack and a six pack, respectively. The four pack is stacked on top of the six pack, or vice versa, such that the combined rack holds ten AT-400As stacked five high. The racks are arranged in ten
rows; eight rows hold five hundred containers and two rows, the first and last row, hold 250 containers.

The computational domain used in phase I consists primarily of the walkspace between two rows with the additional space between each rack and the ceiling. The total height from the floor to the ceiling is 4.0 m. The total length (axial direction) of the domain is 32.5 m corresponding to 25 racks of AT-400A containers. The height of each rack is 3.14 m. The ceiling is 3.325 m wide by 32.5 m long. The floor is 1.625 m wide by 32.5 m long. The temperature distribution, the velocity profile, and the pressure profile for the computational domain described above was predicted.

GEOLOGIC DISPOSAL OF IMMOBILIZED PLUTONIUM

R. T. Johns (Co-PI), Department of Mechanical Engineering, The University of Texas
M. M. Sharma (Co-PI), Department of Mechanical Engineering, The University of Texas
S. V. Bodwadkar, Department of Mechanical Engineering, The University of Texas

EXECUTIVE SUMMARY:

Research activities in this quarter were mainly focused on the colloid mediated transport of radionuclides, model for plutonium ion transport through bentonitic materials, and development of a well testing solution that includes factors unique to pressure transient testing in low permeability fractured formations.

A report titled- Colloid Mediated Transport of Radionuclides and Metal Ions in Groundwater was submitted to ANRCP. This topical report identifies various parameters governing the transport, and summarizes various field, laboratory, and model studies.

The work on a plutonium ion transport model continued from the previous quarter. This model is based on electrokinetic equations and predicts the flow of ions through charged microcapillaries (model for bentonitic clays). The model has been tested for sodium ions for which the required data, e.g. hydrated radius of ion, are available in the literature. Such data for plutonium ions is being gathered for further analysis.

A paper entitled "Analytical Solution for Sequential Hydraulic Tests in Low Conductivity Fractured Formations" is being prepared that discusses the new well testing solution. A portion of the paper will be presented at the AGU meeting in San Francisco this December.
LWR MOX FUEL IRRADIATION EXPERIMENT

Please see “Water Reactor Options for Disposition of Weapons-grade Plutonium” below.

MIXED OXIDE USE EVALUATION

K. L. Peddicord (PI), Department of Nuclear Engineering, Texas A&M University
John Alvis, Department of Nuclear Engineering, Texas A&M University

EXECUTIVE SUMMARY:

The MOX fuel evaluation project focuses on the in-reactor thermal and mechanical behavior of mixed oxide fuel fabricated with weapons plutonium. The thermal performance of the fuel is examined along with other key factors such as fission gas release, fuel-clad mechanical interaction and effects of burnup. Fuel pins will be analyzed for conditions in both US and Russian light water reactors.

To carry out the work, a review has been made of available fuel performance codes which can carry out this analysis for mixed oxide fuel in light water reactors. The conclusion was that the most suitable program is the COMETHE code from Belgonucleaire (BN). BN has been the world leader in manufacturing and irradiating LWR MOX fuel. Much of the irradiation data has been incorporated into the COMETHE code. It is recognized as one of the premier LWR MOX fuel performance codes.

During August 1 to October 31, 1996, meetings were held with Oak Ridge National Laboratory to coordinate the activities which will take place under this project. A meeting took place with Belgonucleaire which has led to a draft memorandum of agreement to enable the technical scope of the project to proceed.

Water Reactor Options for Disposition of Pu

WATER-REACTOR OPTIONS FOR DISPOSITION OF WEAPONS-GRADE PLUTONIUM

N. Abdurrahman (Co-PI), Department of Mechanical Engineering, The University of Texas
M. Adams (Co-PI), Department of Nuclear Engineering, Texas A&M University
D. Anistratov, Department of Nuclear Engineering, Texas A&M University
F. Best, Department of Nuclear Engineering, Texas A&M University
R. Hart, Department of Nuclear Engineering, Texas A&M University
Y. Hassan, Department of Nuclear Engineering, Texas A&M University
S. O'Kelly, Department of Nuclear Engineering, Texas A&M University
T. Parish, Department of Nuclear Engineering, Texas A&M University
C. Philip, Department of Chemical Engineering, Texas A&M University
W. Pitt, Department of Nuclear Engineering, Texas A&M University
W. D. Reece, Department of Nuclear Engineering, Texas A&M University
J. Rennie, Department of Nuclear Engineering, Texas A&M University
M. Roundhill, Department of Chemistry and Biochemistry, Texas Tech University
K. Unlu, Nuclear Engineering Teaching Laboratory, The University of Texas
EXECUTIVE SUMMARY:

Progress continued on research and development of practical dry methods for removal of gallium from weapons plutonium, which is a collaborative effort with researchers at LANL, LLNL, and PNNL. Recent experiments in quartz tube reactors at Texas A&M have shown that gallium trioxide can be readily volatilized from a matrix of cerium oxide (a surrogate for plutonium oxide) by reduction to the suboxide, using pure hydrogen at <1000 C. The gallium is then easily collected as a metal on copper wire or mesh. Significantly, the design of the apparatus (quartz tube reactor, gas flow path, and wire collector) protects the equipment from attack by gallium. Additional experiments using other reducing gases and lower temperatures are being planned. They will be instrumented so that removal rates can be determined.

Progress continued on beam-driven studies of the interaction of gallium with fuel cladding. Gallium was implanted into SS 316 to a fluence of 2x10^{17} ions/cm^2, and samples were examined by scanning electron microscope (SEM) as well as Rutherford backscattering analysis (RBA). In preparation for gallium implantation, Zircalloy samples were obtained, cut, and polished, and surface conditions were examined by SEM. A target-heating chamber was assembled for placement in the ion-implantation target chamber, to be used in upcoming studies of the effects of temperature on gallium-cladding interactions.

In collaboration with ORNL, progress was made toward finalizing the design of temperature-driven experiments to study gallium-cladding interactions. Much was accomplished toward the design of the liquid-metal system that will remove heat from the experiment while maintaining the desired temperature on the outer surface of the pellet. Further progress must await word from ORNL on pellet dimensions and manufacturability.

A CASMO-SIMULATE model of Westinghouse's Vogtle plant was completed. This model will be used by several tasks in the water-reactor project. It is the starting point for the study of multipurpose reactors and for the design of MOX cores that may reduce DOE's cost of plutonium disposition. The model will also be used in the task that studies the accuracy of existing reactor-analysis codes given MOX assemblies that contain burnable absorbers (discrete as well as integral).

The task of supporting the US/Russia joint study team on water reactors continued to move forward. Drs. Adams and Peddicord visited IPPE and INPE in Obninsk, attending a workshop on plutonium disposition. Some information was gained about the Russian plutonium complex, about the capabilities of various institutes in Russia, and about the possibility of further collaborations with Russian researchers on the use of MOX in VVER-1000 reactors. Dr. Adams also attended a meeting at ORNL in September, at which US and French researchers discussed their respective collaborations with Russian researchers.

The calculation of MOX benchmark problems continued with both MCNP and WIMS/DIF3D. An improved version of the WIMS-D4m code, with an expanded ENDF/B-V cross-section library, was obtained from ANL. The new version and library, coupled with the DIF3D and DANTSYS codes, is being used to calculate the SAXTON and WPPR critical experiments. In addition, 10 different SAXTON configurations have been calculated using MCNP-4A with continues energy ENDF/B-VI cross sections. For these configurations, MCNP underestimates k-effective by a few tenths of a percent (0.9941-0.9977). Measured relative-power values are within the 95% confidence intervals predicted by MCNP.

Efforts on the Mixed-Oxide Data Repository (MOXDAR) focused on collection of data for the repository and on obtaining the appropriate hardware for scanning documents. A high-resolution scanner is in place, and Adobe Acrobat publishing products have been selected for the job.
student, Edward Reott, spent several days at the ORNL central library and engaged in lengthy discussions with ORNL staff, resulting in a significant catalog of data to include.

Can-in-Canister Plutonium Immobilization

THERMAL/MECHANICAL MODELING OF THE "CAN-IN-CANISTER" PLUTONIUM IMMOBILIZATION PROCESS

Kenneth S. Ball (PI), Department of Mechanical Engineering, The University of Texas
Eric M. Taleff, Department of Aerospace Engineering and Engineering Mechanics, The University of Texas
Theodore L. Bergman, Department of Mechanical Engineering, The University of Connecticut
Edward E. Anderson, Department of Mechanical Engineering, Texas Tech University
Jaime F. Cardenas-Garcia, Department of Mechanical Engineering, Texas Tech University
Javad Hashemi, Department of Mechanical Engineering, Texas Tech University

EXECUTIVE SUMMARY:

Research activities during May-July 1996 have focused on:

- Experimental studies of the spectral absorption coefficient of surrogate DWPF and plutonium glasses are completed, and the Rosseland and Planck mean absorption coefficients have been determined as functions of temperature for these two glasses.
- The global models used to determine the heat transfer from the molten glass jet used to fill the DWPF canisters have been extended to include radial temperature gradients and semi-transparent, wave-length dependent radiation heat transfer.
- The cooling rates and axial and radial temperature variations of the poured glass stream were calculated using the measured optical properties of the surrogate DWPF glass.
- System level studies of the heat transfer in the glass pool that forms at the bottom of the DWPF canister as it is filled have been completed based upon a one-dimensional model. These studies have been conducted to obtain order of magnitude temperatures for the glass process.
- The results of the system level studies have been shared with the robotics group. They are using these models to build a system control model for this process.
- The development of a more realistic three dimensional model of the heat transfer in the glass pool, based upon a finite element approach, has been initiated. This model will also serve as the basis for calculating the thermal stresses induced within the glass cast as it cools.
- The high temperature experimental facility (glass melter or furnace, melting crucibles, and pouring apparatus) has been completed and the first sets of experiments with molten glass jets have been performed.
- The preliminary molten glass pours qualitatively match the low-temperature results using analogous fluids as well as the numerical results. Voids and cracking are observed in the solidified glass pours.
A new phenomenon known as "bird's nesting" has been identified and is associated with a periodic thinning of the molten glass jet. The parameters affecting this phenomenon are being studied, as well as its significance to the can-in-canister process.

A series of low temperature experiments were performed with room temperature corn syrup for different pour rates.

Heat transfer has been added to the detailed computational model of the molten glass jet, using the commercial CFD code FIDAP, to predict the axial and radial temperature variation within the jet. This is a necessary prelude to the incorporation of a temperature-dependent viscosity in the model. With the introduction of heat transfer, numerical stability problems have been encountered with FIDAP. We have been working with FIDAP to resolve these stability problems, but have had limited success so far.

Three dimensional isothermal simulations using FIDAP, corresponding to the low-temperature experiments, have been initiated.

A grant for $9000 of CPU time on the University of Texas Cray J90 supercomputer was awarded to us, which will be used to facilitate the three dimensional studies using FIDAP.

Performed a simplified one dimensional thermal stress analysis of the support rack using a finite element method.

Performed a one dimensional finite element - sequentially coupled thermal stress analysis of the solidified glass structure.

Performed a two dimensional finite element - sequentially coupled thermal stress analysis of the solidified glass structure.

A brief summary of each of these areas of activity is provided in the Description of Research Activities section below.

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**Immobilization Studies**

**IMMOBILIZATION OF PLUTONIUM IN CERAMIC MEDIA**

Abraham Clearfield (PI), Department of Chemistry, Texas A&M University

**EXECUTIVE SUMMARY:**

During the third quarter of 1996 the synthesis, via sol-gel methods, of cerium-doped zirconolite and the continued Rietveld analysis of the cerium-doped barium zirconate have been carried out. Samples of barium zirconate were prepared, by sol-gel methods, with calculated cerium substitution of 10, 20, 30, 40, 50, and 60 mole percent. All compounds were calcined at 1200°C to improve crystallinity for structure solution. The 50 and 60% substituted phases showed the presence of an impurity phase which was subsequently identified as cerium oxide. The samples show a progressive increase in cell parameters (all form the simple perovskite structure) from 4.193 Å in pure barium zirconate to 4.275(8) Å in both the 50 and 60% substituted samples. Rietveld whole pattern refinement of the X-ray diffractograms indicates a maximal substitution of 48 mole % cerium in the barium zirconate. Excess cerium fell out as cerium oxide. No barium cerate was found in the products.
A series of zirconolite samples was prepared into which 5 to 35 mole percent Ce was admixed as a replacement for Zr. Excess Ce at the mole percent level was detected by X-ray analysis. However, Rietveld analysis of the X-ray patterns was not possible because of the low-crystallinity of the products. Longer firing times and higher temperatures of calcination are under examination to access their affect on crystallinity.

A number of inorganic ion exchangers that have a very high affinity for cesium, strontium, chromium and lead in groundwater and strong electrolyte solutions have been synthesized. Their use in remediation of groundwater and/or providing a co-additive to the Pu containing ceramic to provide a radioactive shield is under investigation.

CROSS-CUTTING ISSUES

Non-destructive Assay

DEVELOPMENT OF NONDESTRUCTIVE ASSAY METHODS FOR WEAPONS PLUTONIUM AND MIXED OXIDE FUEL SAFEGUARDS

N. M. Abdurrahman (Co-PI), Department of Mechanical Engineering, The University of Texas
B. W. Wehring (Co-PI), Department of Mechanical Engineering, The University of Texas

EXECUTIVE SUMMARY:

We have revised our research plan to investigate in addition to the original lead slowing down time spectrometer (LSDTS) a graphite slowing down time spectrometer (GSDTS). The GSDTS has certain desirable features and complements the LSDTS as an assay device. It has different neutron source requirements in terms of the source pulsing rate and the pulse duration, and may have some advantages over the LSDTS when high accuracy of isotopic discrimination is not required. We extended our computational program to do neutronics calculations on the GSDTS to investigate its various performing parameters.

We have been offered a neutron generator with state-of-the-art pulsing system as a gift from The University of Michigan. We have completed all the paperwork required to transfer the generator to The University of Texas at Austin. Transferring, setting up, and testing the new generator replaces our original task of restoring and modifying the UT neutron generator to a pulsing device. The neutron generator is now in the process of being transferred to UT. We have continued our work researching other neutron sources suitable for SDT devices. We have recently identified a very attractive neutron source that is laser-based which has recently been developed in Russia by a group from Moscow State Engineering Physics Institute. The intensity and pulsing parameters of this source are ideal for our proposed LSDTS and GSDTS devices.

We continued our effort to coordinate with Los Alamos National Laboratory, the lead lab in the area of safeguards and nonproliferation technology. During a recent visit to LANL, we have agreed with various groups on specific collaborative activities in safeguards research. These include collaborating on development of intense neutron source, on instrumentation and data acquisition system for the LSDTS and GSDTS, on neutron computed tomography, and on curriculum development in safeguards and nondestructive assay measurements. We believe that our coordination with LANL provides definition, direction, and specific technical assistance to our project.
TRANSPORTATION ANALYSIS OF MIXED OXIDE FUELS

Hani S. Mahmassani (PI), Department of Civil Engineering, The University of Texas

**TASK 1: MODELING FOR SAFE ROUTING**

H. Mahmassani, The University of Texas  
P. Nelson, Texas A&M University

**EXECUTIVE SUMMARY:**

*Activities at The University of Texas*

The general objectives of the Transportation Analysis effort under the Nuclear Project is the identification and study of transportation-related issues that arrive in conjunction with the disposal of spent plutonium. These issues are integrally related to the identification and quantification of the various sources and types of risks that accompany the movement of radioactive materials. These include risks that arise from the behavior of the materials transported, and that of the storage containers used, as well as the interaction of these with external risk sources associated with vehicular reliability, traffic conditions and possible external threats. Several components of this overall project are addressing the source of these risks, but not all. The second major element of the transportation analysis is the development of strategic and related algorithmic procedures to incorporate these risks in decision-making regarding route selection before the shipment is sent, as well as regarding route modification in real-time as the conditions that affect these risks and their consequences change, to the extent that information becomes available. A third and equally important element pertains to the manner in which associated risks associated with a particular shipment are framed, communicated to and perceived by the population likely to be involved in the process of route selection and/or consequence management.

The present study aspires to be comprehensive in its outlook and scope, but has had to limit its focus to specific risk elements, and to the development and adaptation of modeling methodologies with specific application to the transport of spent plutonium. A major aspect of this effort is to identify and characterize the vast and complex regulatory framework applicable to the transport of radioactive substances, and incorporate these considerations in any mathematical or algorithmic set of decision support procedures. In addition, the project has along sought to complement the existing set of tools developed by DOE and its laboratories, such as TRANSNET and RADTRAN, by expanding the rule-set underlying route selection and evaluation to recognize different types and/or levels of risks, as well as the dynamic nature of these risks.
TASK 2: APPLICATION OF EXISTING CODES AND TECHNIQUES

R. Radha, Prairie View A&M University
Z. Huque, Prairie View AM University

EXECUTIVE SUMMARY:
Faculty members and students involved in the project are progressively developing expertise using the TRANSNET software. The different routes (shortest, quickest and commercial) between the pairs of origination points and destination points were generated using a minimum impedance algorithm. Minimization of vulnerability is being taken into account when generating routes. Practical routes will be compared with risk free routes for transportation of radioactive MOX fuels. Development has started on a new model to achieve safe transportation of MOX fuels and radioactive materials.

TASK 3: DEVELOPMENT OF SOURCE TERM COMPONENTS FOR FORMULATION AND INITIAL RELEASE OF PLUTONIUM-CONTAINING AEROSOL FOR CONDITIONS AND EFFECTS NOT TREATED BY EXISTING MODELS FOR TRANSPORTATION INCIDENTS.

Yassin A. Hassan, Texas A&M University
William H. Marlow, Texas A&M University

EXECUTIVE SUMMARY:
Verification of the three-dimensional space averaged program was performed. This program can be used after the completion of particle-tracking routines to investigate the plutonium aerosol which is likely to be generated during fire in a transportation accident.

TASK 4: INVESTIGATION OF NEURAL AND FUZZY LOGIC ANALYSIS TECHNIQUES FOR SURETY ISSUES IN TRANSPORTATION OF NUCLEAR MATERIALS

Donald C. Wunsch, II, Texas Tech University

EXECUTIVE SUMMARY:
During the past quarter we have been working on assessing the risk associated with the transportation process of Nuclear Materials. We are using fuzzy risk assessment to overcome the difficulties faced when using probabilistic analysis, due to the vagueness nature and lack of information characterizing the problem.

We use a fuzzy fault tree to assess the risk of failure associated with transportation of nuclear material. The fault tree describes the sequence/combination of events that may lead to a failure. Such events may be due to human errors, weather problems, intelligence leaks, or other hypothetical problems. The top event of the tree is system failure, defined as not having the nuclear material reach the destination safely within a specified amount of time.

Each event in the fault tree has its own membership function in which the fuzzy variable is the probability that this event may occur. The membership grade is the degree of belief that this
probability may take on a certain value. PHASER (Probabilistic Hybrid Analytical System Evaluation Routine), implemented at Sandia National Laboratories, is used to calculate the membership function of the top event. The sequence of evolution of the fuzzy set describing a particular basic event is derived in order to assess the risk of failure after a certain number of trips. A decision can then be taken as when to change one of the transportation parameters, such as: route, time, maintenance schedule or destination.

NEW POLYMERS AND EXTRACTANTS FOR PLUTONIUM SEPARATIONS

Richard A. Bartsch (PI), Department of Chemistry, Texas Tech University

EXECUTIVE SUMMARY:

For the recovery of contaminating plutonium, the plutonium-containing material may be dissolved in concentrated nitric acid and the plutonium separated from other components of the solution by sorption on commercially available Reillex™ HPQ anion-exchange resin. Subsequently the sorbed plutonium can be recovered from the resin by stripping (washing) with dilute nitric acid.

In earlier work, we have demonstrated that experimental, bifunctional, anion-exchange resins prepared at Texas Tech University and evaluated at Los Alamos National Laboratory are markedly superior to the commercial anion-exchange resin both in terms of the rate and efficiency of plutonium(IV) sorption from concentrated nitric acid solution. Although these new polymeric resins were demonstrated to rapidly and efficiently sorb plutonium from 7M nitric acid solutions, they suffer from compaction due to their low level of crosslinking. To be suitable for practical application in the recovery of plutonium which would involve column separations, bifunctional anion-exchange resins with a higher level of crosslinking are required.

During the reporting period, two series of bifunctional anion-exchange resins have been prepared which have the same level of crosslinking in the base polymer as does the Reillex™ HPQ resin. Two series of bifunctional anion-exchange resins were prepared by reactions of macroporous, 33\% crosslinked, Reillex™ HP poly(4-vinylpyridine) with (5-bromopentyl)trimethylammonium bromide and with (5-chloropentyl)pyridinium chloride in methanol under pressure at 100 and 120 °C. The rate and efficiency of plutonium(IV) sorption from 1M and 7M nitric acid were evaluated as a function of the levels of alkylation of the base polymer which were achieved under the different conditions of reaction temperature, reaction time, and alkylating agent. One series of the new bifunctional anion-exchange resins shows a markedly enhanced ability to sorb plutonium(IV) from 7M nitric acid relative to Reillex™ HPQ resin, but only modest enhancement in the rate of plutonium(IV) sorption. These results indicate that a base polymer with a somewhat lower level of crosslinking is needed.
EXECUTIVE SUMMARY:

PART 1: DIAMOND GENERATION BY EXPLOSIVE COMPRESSION OF BUCKMINSTERFULLERENE

A fourth three dimensional explosive compaction test was performed on November 8, 1996. This iteration of the design consisted of a solid steel sphere as the workpiece. This design replaced the composite, copper sphere encased in a steel shell design that was used in the previous three experiments. The sample was introduced into the sphere by drilling and tapping a hole to the center of the sphere, loading the sample material, then closing the hole and compressing the sample with a threaded screw. The resulting workpiece was inserted into the spherical high explosive around which a brass shell was placed. The final assembly was buried in sand before detonation. The sand and brass shell structure was employed to reflect a portion of the expansion waves back toward the center of the workpiece. The dimensions were manipulated to insure destructive interference of the expansion waves that are reflected after compression of the steel sphere, thereby helping to maintain the integrity of the piece.

The result of the fourth shot was complete recovery of the workpiece. This result represents a major accomplishment toward the ultimate goal of this project. We now have a workpiece design which allows for the study of materials under extreme temperatures and pressures. The recovered workpiece is enroute to UT for analysis. The piece will be cut in half in order to examine the effects of the detonation and compared to the simulations run at Texas Tech. The sample material will be subjected to x-ray analysis, raman spectroscopy, and scanning electron microscopy to test for the presence of diamond and to fully characterize the detonation products. Concurrent with 3-D work, one dimensional experiments have been progressing. Namely, flyer dimensions and stand off distances have been investigated in order to maximize the pressure delivered to the sample while insuring complete recovery of the sample. Simulations were used to determine an initial design for the flyer and stand off distance while maintaining the same dimensions of the sample holder and impacting piece (see past reports). Detonation of this design proved that the impact of the flyer caused excessive damage to the sample holder and a portion of the product was thought to be lost. Closer, microscopic investigation of this piece showed that the sample holder had not failed and the sample was contained. However, the margin of error for this design was too small to reliably retain the sample after compression. In order to reduce the damage, an additional 1/2 inch thick piece of steel was bolted to the top of the sample holder. With this design, there was minimal damage to the sample holder. However, this buffer piece of steel absorbed too much of the impact, thereby reducing the pressure pulse experienced by the sample. Currently, experiments are being conducted with 1/4 inch and 1/8 inch buffer plates in order to optimize the pressure while assuring recovery.
PART 2: DEMONSTRATION BURN FOR ENERGY RECOVERY

On September 17, 1996, a meeting was held with representatives from NAWCWPNS, Pantex, and UT to determine program directions and to reset goals and assign task responsibilities. Specifications on the hydro-machining of the explosives were established and subsequent testing of binder materials was initiated. Numerous binders have been investigated at UT.
WORK PLAN PROGRESS REPORT
Electronic Resource Library

Institutions: Texas Tech University
Amarillo College

Program Manager: Dr. Elda D. Zounar

Project Coordinator: Phillip T. Nash, P. E.

Co-Principal Investigators: Dr. Dale Cluff
Mr. George Huffman

Researcher/Information Scientist: Dr. Karen Ruddy

Appended Supporting Documentation

1. The Electronic Resource Library Sample of Homepages Under Construction
2. MOX FUEL Literature Analysis
Amarillo National Resource Center for Plutonium
A Higher Education Consortium of The Texas A&M System, Texas Tech University, and The University of Texas System
Sponsoring . . . . . . . . . . . . . The Electronic Resource Library:

The Electronic Resource Library (ERL)

The Electronic Resource Library (ERL) is the first uniquely designed full-service electronic, subject-specific library on the Internet - collecting, scanning, processing, and electronically exchanging information on plutonium.

It is designed primarily to support the scientific and technical research projects of the researchers and scientists funded by The Amarillo National Resource Center for Plutonium, but many of its services and resources are of interest (and are accessible) to elected officials and policy-makers, K-16 math and science teachers and students, and the interested citizen.

In the ERL's "collections" are found: titles of books at many libraries, citations to the scholarly journal literature, subject-core analysis, reference tools, links to relevant sites on the Web, and hundreds of full text/imaged documents on the topic of plutonium.

The Electronic Resource Library (ERL) is accessed through the World Wide Web (WWW) and builds this plutonium-specific library by applying a Selection Criteria to all potential titles, focusing the collection on areas of scientific and technical research topics concerning: storage, use, disposition, transportation, environmental, safety, health, and history of - plutonium.

The Amarillo National Resource Center for Plutonium (The Center)

The Amarillo National Resource Center for Plutonium (The Center), established as the national resource for scientific and technical information on the topic of plutonium, uses The Electronic Resource Library (ERL) as an electronic full-service vehicle. Researchers and scientists studying the topic of plutonium can access historical, current, and reference information - electronically - saving them immeasurable hours of time in their literature review. These hours can then be devoted to reading, synthesizing, and discovering new knowledge.

DISCLAIMER
This Electronic Resource Library (ERL) was prepared with the support of the U.S. Department of Energy, Cooperative Agreement No. DE-FC04-95AL85832. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the Library and do not necessarily reflect the views of the U.S. Department of Energy. This work is conducted through the Amarillo National Resource Center for Plutonium. Other Disclaimers, Copyrights, and Endorsements.

The full-image documents on this web site are in Adobe® Acrobat® Portable Document Format. You must have the Adobe® Acrobat® Reader® to view these documents. To download a free version, click here.

1. Amarillo National Resource Center for Plutonium - Homepage
2. Frequently Asked Questions (FAQs) Homepage
3. Questions or Comments for the Electronic Resource Library Webmaster: webmaster@plutonium-erl.acctx.edu
Electronic Resource Library
Resource Homepage

- This Netscape server site is best viewed with Netscape Navigator 3.0

The ARCHIVE "BUTTON" provides access to the "archive" or "collection" of full text/imaged documents that are prepared for the Electronic Resource Library (ERL) in the Document Exchange Laboratory at Amarillo College Lynn Library Learning Center. Currently over 100 government reports and proceedings are available to all visitors of the website - with the projection of 800,000 pages online by the end of 1997.

The WEB LINKS "BUTTON" networks multiple links of important resources on the Web that deal with the topic of plutonium. While web search engines are becoming more robust, locating specific websites with a keyword search is still a time-consuming endeavor. The Electronic Resource Library (ERL) links provide easy access across the U.S. Department of Energy complex of laboratories, factories, and agencies containing electronic collections of information on the topic of plutonium. This WEB LINK button is another way The Electronic Resource Library (ERL) saves researchers time and helps to lower information-seeking frustration on the Web.

The LIBRARY CATALOG "BUTTON" brings up the Z39.50 search engine from the U.S. Library of Congress Homepage. Over the years, libraries developed online catalogs with no effort to standardize the procedure. With the Z39.50 interface, it is no longer necessary to spend exorbitant amounts of time learning each online system. The Z39.50 standard provides keyword access to collections in libraries all over the world, as Library Card Catalogs have done for traditional libraries.
The ELECTRONIC PUBLISHING "BUTTON" highlights Special Bibliographies and other research reports and reference services. For example:

- A 900+ list (bibliography) of document titles residing in the Amarillo College Lynn Library Department of Energy Reading Room.

- A MOX (Mixed Oxide) Fuel Literature Analysis with:
  - over 600 titles on the topic of "MOX Fuel".
  - a "MOX Fuel" on-order list of over 100 titles featuring "Abstract Highlights".
  - lists of societies, associations, corporate sources, journal titles, and acronyms associated with the "MOX Fuel" study lists help the researchers get a time-savings "scope" of this particular literature core.

The OTHER SERVICES "BUTTON" leads the information-seeker to the OCLC (national resource utility) First Search databases and the Electronic Reserve Room. Like the traditional academic Library Reserve Desk, the Electronic Reserve Room contains materials to support the research, curricula and academic programs of The Amarillo National Resource Center for Plutonium. The specialized databases, copyright materials, and the International Nuclear Information System (INIS) CD-ROM database can be accessed here.

1. Amarillo National Resource Center for Plutonium - Homepage
2. Frequently Asked Questions (FAQs) Homepage
3. Questions or Comments for the Electronic Resource Library Webmaster: webmaster@plutonium-erl.govx.edu
MOX FUEL Literature Analysis

M. K. Ruddy, Ph.D. (Electronic Resource Library, Amarillo College, Amarillo, Texas, U.S.A.); collaborator (Texas A&M University, College Station, TX. U.S.A.)

November, 1996

Funded by the Amarillo National Resource Center for Plutonium

MOX Fuel Cumulative Bibliography.
MOX Fuel On-Order List with Abstract Highlights
MOX Fuel Societies, Associations, Corporate Sources.
MOX Fuel Proceedings, Conferences, Annual Reports
MOX Fuel Journal Analysis
MOX Fuel Subject Codes in INIS and NTIS databases.
MOX Fuel Acronyms

The entries in this bibliography are from 1980 to the present, in the English language, unclassified, and from the geographic areas of the United States, Russia, Canada, France, Japan, England, Germany, Belgium, and Switzerland. They include scientific and technical information found in government documents, peer-reviewed and non peer-reviewed proceedings, reports, journal articles, books, committee meeting minutes, and pre-publications. The retrospective compilation of the bibliography is scheduled to be complete by January, 1997 and newly published titles will be added from that date forward.


MOX FUEL Literature Analysis

- On-order List


- A brief analysis (based on unclassified sources) identifies implications if the Soviets started to actively try to provide reprocessing and MOX fabrication services to the US and other countries.
- Given brief information on Soviet intentions, the report postulates that the Soviets would offer to reprocess spent LWR at competitive prices, fabricate the plutonium and re-enrich the uranium, and sell these products back to the customer.
- It is not known whether they would insist on returning the waste from reprocessing or be prepared to keep it.
- Brief comment on what the implications of either of these actions are included.


- Electricite de France has been studying a high-moderating-ratio (HMR) pressurized water reactor that could accept 100% mixed-oxide (MOX) reloads. Total plutonium content is 9% to ensure a discharge burnup of 60,000 MWd/tonne.
By replacing 36 fuel rods by water holds, a high-moderating ratio (2.5 instead of 2.0) is obtained.
The advantages of high moderation (better efficiency of soluble boron, control rods, etc.) and technological continuity are combined in this solution.
The core should contain 241 fuel assemblies for a total thermal output of 4, 250 MW(thermal).
Core control requires the use of sup1 sup0 B-enriched boron carbide for the control rods and sup1 sup0 B-enriched soluble boric acid for the primary system, thereby ensuring satisfactory core behavior under accident conditions such as control rod ejection and unexpected valve opening on the secondary side.
The advantages of this 100% MOX core compared with a 50% MOX core are discussed.
This concept is fully compatible with the future European pressurized reactor (EPR).
This 100% MOX HMR reactor could be the plutonium version of the EPR.

Abstract Highlights
- Compares the once-through “direct disposal” irradiated nuclear fuel management strategy with the spent fuel reprocessing and MOX fuel recycle option in terms of three key environmental factors:
  - volumes of waste arising
  - the radioactivity of those wastes and
  - their radiotoxicity.
- The concept of radiological toxic potential is introduced and explained.
MOX FUEL Literature Analysis

• Societies, Associations, Corporate Sources

(Entries will be expanded to include full addresses)

ABB/Combustion Engineering, Inc., Windsor CT (U.S.A.)

AECL Technologies, Inc., Rockville, MD (U.S.A.) (See Also: Atomic Energy of Canada Limited)

American Medical Association

American Nuclear Society

American Society of Mechanical Engineers, United Engineering Center, 345 East 47th Street, New York, NY 10029 (U.S.A.)

Argonne National Lab., IL (U.S.A.)

Atomic Energy of Canada Ltd., Chalk River (Ontario). Chalk River Nuclear Labs (designs licenses builds, and supports CANDU reactors) (See Also: AECL Technologies Inc.)

Atomic Energy Council, Taiwan

Atomic Energy Regulatory Board, Bombay, India

BELGONUCLEAIRE, Brussels, Belgium

BNFL (see British Nuclear Fuels plc)

BNFL Instruments Ltd., Calderbridge (United Kingdom

British Nuclear Fuels plc (BNFL), Risley, (England).

Brookhaven National Lab., Upton, NY (U.S.A.)

COGEMA, Inc. of Chatillon, (France)
MOX FUEL Literature Analysis
• Proceedings, Conferences, General Reports, and Annual Reports

1996


1995


Annual meeting on nuclear technology - joint meeting of Deutsches Atomforum e.V. (DAtF) and Kerntechnische Gesellschaft e.V. (KTG): Research and technology - our future. Nuremberg, (Germany). May 16-18, 1995.
MOX FUEL Literature Analysis
• Journal Analysis

American Scientist: published in the interest of scientific research
Began: 1913
Published: bi-monthly
Cost: $45
Sigma Xi, Scientific Research Society
Box 13975. 99 Alexander Dr.
Research Triangle Park, N.C.
Tele: 919-549-0097
FAX: 919-549-0090
ISSN: 0003-0996
CODEN: AMSCAC
INDEXED: INIS, INSPEC
Review status: Peer Reviewed X Non Peer Reviewed
Gov Doc status: Gov Doc X Non Gov Doc
Language: X English ___ Other
Scope: academic/scholarly publication
On Copyright Clearance List: X yes ___ no

Analytical Chemistry
Began: 1929.
Published: Semi-monthly
Cost: $415
American Chemical Society
1155 16th St. N. W.
Washington, DC 20036
Tele: 800-333-9511
FAX: 614-447-3671
ISSN: 0003-2700
CODEN: ANCHAM
INDEXED: INIS
Review Status: Peer Reviewed X Non Peer Reviewed
### MOX FUEL Literature Analysis

#### Acronyms in MOX Fuel Study

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<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AECL</td>
<td>Atomic Energy of Canada Limited</td>
</tr>
<tr>
<td>AECL</td>
<td>AECL Technologies, Inc. (U.S. subsidiary of AECL)</td>
</tr>
<tr>
<td>ANS</td>
<td>American Nuclear Society</td>
</tr>
<tr>
<td>BNFL</td>
<td>British Nuclear Fuels Limited</td>
</tr>
<tr>
<td>BNFP</td>
<td>Barnwell Nuclear Fuel Plant at Barnwell NC.</td>
</tr>
<tr>
<td>BWR</td>
<td>Boiling Water Reactors</td>
</tr>
<tr>
<td>CANDU</td>
<td>(Reactors in Canada)</td>
</tr>
<tr>
<td>CEC</td>
<td>Commission of the European Communities, Luxembourg</td>
</tr>
<tr>
<td>COGEMA</td>
<td>Compagnie Generale des Matieres Nucleaires. COGEMA Inc. Chatillon, (France)</td>
</tr>
<tr>
<td>DAF</td>
<td>Device Assembly Facility at the Nevada Test Site (NTS)</td>
</tr>
<tr>
<td>DISPIM</td>
<td>Decommissioning In-Situ Plutonium Inventory Monitor</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>DWPF</td>
<td>Defense Waste Processing Facility</td>
</tr>
<tr>
<td>ECN</td>
<td>Electricite de France</td>
</tr>
<tr>
<td>ENS</td>
<td>European Nuclear Society</td>
</tr>
<tr>
<td>EPR</td>
<td>European Pressurized Reactor</td>
</tr>
<tr>
<td>ERU</td>
<td>Enriched Reprocess at Uranium</td>
</tr>
<tr>
<td>EVST</td>
<td>Ex-vessel storage tank</td>
</tr>
<tr>
<td>FMDP</td>
<td>Fissile Materials Disposition Program (DOE’s)</td>
</tr>
<tr>
<td>FMEF</td>
<td>Fuels Material Examination Facility at Hanford</td>
</tr>
<tr>
<td>FPF</td>
<td>Fuel Processing Facility at Idaho National Engineering Laboratory (INEL)</td>
</tr>
<tr>
<td>HMR</td>
<td>High Moderating Ratio (pressurized water reactor)</td>
</tr>
<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency, Vienna (Austria)</td>
</tr>
<tr>
<td>INEL</td>
<td>Idaho National Engineering Laboratory</td>
</tr>
<tr>
<td>LWR</td>
<td>Light Water Reactor</td>
</tr>
<tr>
<td>KTG</td>
<td>Kerntechniache Gesellschaft (Bonn Germany)</td>
</tr>
<tr>
<td>MONJU</td>
<td>(Prototype fast breeder reactor in Japan)</td>
</tr>
<tr>
<td>MOX</td>
<td>Mixed Oxide</td>
</tr>
<tr>
<td>MOX FAs</td>
<td>Mixed Oxide Fuel Assemblies</td>
</tr>
<tr>
<td>MPCA</td>
<td>Material protection, control, and accountancy</td>
</tr>
<tr>
<td>NATO</td>
<td>North Atlantic Treaty Organization</td>
</tr>
<tr>
<td>NAS</td>
<td>National Academy of Science</td>
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Amarillo National Resource Center For Plutonium

Quarterly Progress Report
For The Period
1 August 1996 - 31 October 1996

Environmental Group Detailed Reports
Environment, Public Health, And Safety
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## BIOREMEDIATION OF CONTAMINATED SOIL AND GROUNDWATER

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<td>Zero Valent Metal Remediation Of Chromium, Chlortinated Organics And High Explosives At The Pantex Site</td>
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<td>Chemical Models And Redox Chemistry Of Chromium</td>
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## PHYTOACCUMULATION OF HEAVY METALS IN PLANTS

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<tr>
<td>Phytoaccumulation Of Selected Heavy Metals, Unranium, And Plutonium In Plant Systems</td>
<td>27</td>
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EXECUTIVE SUMMARY:

During the past quarter, researchers at Texas Tech University were involved in three major subtasks in this project area. The first subtask involves the perched aquifer tracer test performed at the Zone 12 Treatability System (ZTTS). The second subtask includes field and modeling efforts for investigation of potential wetlands enhancement by discharging future treated effluent from the perched aquifer recovery systems to the ditch and playa system at the Pantex Plant. The third subtask consisted of equilibrium isotherm tests for sorption of HMX and RDX on core materials from the perched aquifer and its aquitard. Progress for each subtask is reported in the following paragraphs.

**Perched Aquifer Tracer Test**

The perched aquifer tracer test, originally proposed for commencement on June 1, 1996, officially began on July 15, 1996, and continued into this quarter. The TTU researchers appreciate the cooperation of engineering-environmental Management, Inc. (e²M), and the Battelle Environmental Restoration Group in allowing this project to occur. Observance of the movement of a conservative tracer in the perched aquifer flow system provides direct hydraulic representation of the affected flow regime. Differences in the migration of the injected tracer and the HE already in the perched aquifer can be interpreted as evidence of retardation of these compounds.

Under normal operation at the ZTTS, three extraction wells, EW-1, 2, and 3, pump continuously at approximately 10 gpm each, and the extracted water is passed through granular activated carbon treatment prior to injection at PTX06-1004. A few gpm also is provided from well PTX06-1014. For the purposes of the tracer test, the treated effluent was diverted for injection at passive vent well PV-4, in the center of the ZTTS well pattern. The injected water, free of dissolved high explosives (HE), was dosed with potassium bromide to cause an injected concentration of 100 mg/L of Br, serving as a conservative tracer. Samples were collected on a daily basis from the injection line and the three extraction wells. Samples were analyzed in the field for Br concentration (specific ion electrode) and combined RDX/HMX (DTECH kits). Water levels in wells PV-1, 2, 3, and 4 were monitored with pressure transducers and dataloggers.

As stated previously, the tracer test began on July 15, 1996. The ZTTS as modified ran continuously for 53 days, then was interrupted by several temporary power failures beginning on September 6, and the test was finally terminated on September 19. Complete raw data packages of the measured concentrations and water levels have been provided as
they became available to the researchers at UT-Austin for related modeling. A complete report of the collected tracer test data was originally planned as a deliverable by the end of October, 1996. However, that date was based on a June 1 test commencement date. The data report should be available during December, 1996.

Investigation of Potential Wetlands Enhancement

The investigation of potential wetlands enhancement through the discharge of treated perched aquifer effluent into the ditch and playa system will allow evaluation of this concept as an alternative to direct injection through wells. The TTU research team has previous experience in field measurements of runoff flow and infiltration at the Pantex Plant and hydrologic modeling of playa storage under historical loadings. The current effort has three major components. First, during July, 1996, double-ring infiltrometer tests were performed at selected sites in Playas 2, 3, 4, and 5, and in the ditches that lead to all five playas on the Plant. During this quarter, the data from those tests were evaluated and interpreted for application in hydrologic modeling. Second, efforts began in this quarter to simulate the increase in inundated area in each playa that might be caused by introduction of up to 400 gpm in the ditch system leading to each playa. Those simulations will be completed in the next quarter. Those results will be used in the third quarter to evaluate the potential ecological modifications that would result from the increased flows to each playa. The report summarizing these findings will be produced in the next quarter.

Sorption Of HMX And RDX On Pantex Soils

The results of the HMX and RDX equilibrium sorption tests were reported by Rainwater et al. (1996) as listed in the following section. In these tests, core materials from within the perched aquifer and its aquitard were selected from wells PTX06-1012, 1013, 1014, and 1016. These materials had been previously characterized for grain-size distribution, Cr sorption, and TCLP chromium. In this subtask, the core materials were tested by the TCLP leaching test for HMX and RDX. Neither HE was found to be leachable from any of the eight samples. Next, equilibrium isotherm tests were performed, using 10 g of each soil sample exposed to initial 100-mL solutions with concentrations ranging from 0.1 to 5 mg/L of HMX or RDX. It was necessary to make the solutions from stock commercial HMX or RDX standards in acetone or acetonitrile solution dissolved in Pantex groundwater because the research team had not yet been able to obtain pure HE from commercial suppliers. Under these conditions, the sorption of HMX and RDX on the soils was measurable but small. This result is not surprising based on the significant distances of RDX migration seen at the Plant, and the sandy nature of the sediments. It is possible, however, that the organic solvents from which the HEs originated in these tests could have competed with the HEs for sorption on the core materials. It is recommended that these tests be repeated later when the HEs are available without the organic solvents.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

The report summarizing the data collected in the perched aquifer tracer test will be submitted in December, 1996. The report describing the work in potential wetlands enhancement will be submitted by January, 1997. The report summarizing the HE sorption data was submitted to Dr. Randy Charbeneau on September 18, 1996, with the following citation:

EXECUTIVE SUMMARY:

The project was initiated on 7/1/96 due to the delay in arrival of funding. This report covers the period 7/1/96 to 10/31/96.

During this period we have designed and constructed a reactor assembly to perform the catalytic oxidation reaction, identified a catalyst, developed two analysis techniques (HPLC and TOC) to determine reaction intermediates, completed reactor shakedown runs, and completed preliminary studies on catalytic oxidation of TNT/water solution in order to identify the optimum reaction conditions.

The reactor used in the study has 300 cc volume (Autoclave Engineers) capable of standing temperatures as high as 775°K and pressures of 300 atm and can be operated both in the batch and the flow modes. The heated and stirred autoclave batch reactor is equipped with all auxiliary attachments for feed introduction, sample removal, temperature control, pressure recording, and safety precautions (rupture disc) for pressure build-up. Agitation of the vessel is accomplished by a patented stirrer that sucks the gas phase and disperses it in the liquid phase through the hollow shaft and a specially designed impeller. An electric heater mounted on the reactor wall provides heat and a temperature controller was used to maintain a constant temperature throughout the reaction. The catalyst used is 4.5% Pt/TiO₂ which was used in our previous studies.

Total organic carbon (TOC) analysis was performed using an O. I. Analytical Corporation model 700 TOC analyzer. Separation of the reaction intermediates were performed by using a Dionex HPLC equipped with Ultracarb 5u ODS(20) column and following EPA draft method 8330.

In our shake down runs we studied the reactor at extreme temperatures and pressures expected in this study (523 K and 100 atm) and developed the sampling procedure, temperature control, emergency shut-down, etc. procedures.

To determine the optimum operating conditions and experiment reproducibility, several runs were made at different temperatures (150-200 C ± 1.5) and constant pressure (34 ± 0.6 atm) with the exception of the run at 160 C which was at 52.4 atm. The results showed no appreciable reduction in TOC when the temperature is below 180 C. When experiments are run at temperature higher than 180 C, more than 90% reduction of TOC occurred. However, HPLC analysis at all conditions indicated formation of basically four reaction intermediates.
DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

Biodegradation of high explosives (TNT) contaminated wastewater has shown that the first step in TNT biotransformation is either the amination of preferably the para position nitro group and possibly denitration beginning with the position depending on the consortium population. Ring cleavage is the slowest step, but once accomplished, the bioremediation rate increases significantly. Catalytic oxidation of aromatics contaminated wastewater has shown that the first ring cleavage step is the fastest. The purpose of this preliminary study is to investigate the feasibility of treating HE contaminated water by catalytic oxidation.

2,4,6-Trinitrotoluene (TNT) solution, 32 PPM, was obtained from Dr. Autenrieth's (Civil Engineering - Environmental Division) laboratories at Texas A&M university. The solution was made by dissolving 0.32 g TNT in deionized, distilled and autoclaved water. The 4.45% Pt/TiO₂ catalyst employed in this study was obtained from Aldrich with a particle diameter of less than 105 μm. The support has a nominal BET surface area of 100 m²/g.

The batch reactor is an insulated stainless steel cylinder (20 cm length × 5 cm ID) with a capacity of 300 cc mounted on a steal frame. To provide a good mixing, a special agitator connected to a variable speed electric motor was used. The agitator has a channel and holes cut into the shaft which provide excellent solution/air contact by injecting air from the top of the reactor into the liquid at the bottom. An electric heater mounted on the reactor wall provides heat and a temperature controller was used to maintain a constant temperature during the reaction. Sample ports, temperature and pressure indicators, and appropriate valves and relief devices complete the system.

Total organic carbon (TOC) analysis were performed using an O. I. Analytical Corporation model 700 TOC analyzer. Separation of the intermediates were performed by using a Dionex HPLC equipped with Ultracarb 5u ODS(20) column and following EPA draft method 8330.

Before each experiment the reactor and relevant tubing are cleaned with deionized water and a brush. Execution of each experiment started by charging the reactor with 150 cc TNT solution and 0.3 g catalyst and sealing. To reach thermal stability prior to initiating an experiment, nitrogen was bubbled through the solution from the air inlet valve to remove any oxygen from the system to prevent pre-mature oxidation during the heat-up period. Then the reactor was pressurized with nitrogen to about 7 atm. The agitator was set at about 800 rpm, and the temperature adjusted to the desired temperature, 150-200 °C. The system was allowed about three hours to stabilize and reach the desired temperature. To initiate an experiment, compressed air from an oil-free compressor was charged into the reactor. All experiments were performed at constant pressure, 34 atm with the exception of one run which was at 52.4 atm. All reactions were carried out for 30 minutes. Periodically, samples were withdrawn for analysis by TOC and HPLC. TOC analysis, although qualitative in nature, is fast and performed during the reaction. HPLC analysis, which was quantitative, was used for determination of reaction extent and separation of the products for identification. Prior to sample withdrawing, the sample line was wrapped with a wet cloth to serve as a cooling jacket to eliminate any possible flashing. Also, the sample line which has a total volume of 1.5 ml was thoroughly flushed by discharging about 3 ml of liquid through the line into a waste bottle. Then about 1.5 ml sample is withdrawn in a glass sample vial. A metal filter is located on the end of the sample line in the reactor to prevent catalyst particles from coming out with the liquid effluent.

To determine the optimum operating conditions, several runs were made at different temperature 150-200 °C ± 1.5 and constant pressure 34 atm with the exception of the run at 160 °C which was at 52.4 atm. Figure 1 shows TOC analysis comparison at four different
temperature settings. The results showed no appreciable reduction in TOC when the temperature was below 180 C. When experiments are run at temperature higher than 180 C, TOC reduction is over 90%.

Figure 2 shows HPLC analysis of the TNT stock solution where TNT has a retention time of 17.1 minutes and a concentration of 31 PPM. Figures 3 and 4 show HPLC analysis of the last captured samples of runs at the two extreme conditions of 150 C and 200 C. At 150 C only about 35% of TNT was degraded in 30 min into four intermediates which have not been identified yet plus complete oxidation products. But for the runs at temperature higher than 180 C, almost complete disappearance of TNT was observed. It is interesting to note that there were no other peaks detected which indicates that all the TNT was oxidized to inorganic carbon and presumably ammonia.

The above results indicate that the reaction rate is very temperature dependent and it is virtually pressure independent. The temperature data are useful in determining the reaction kinetics which is an important step in designing a reactor.

Please see the following attached figures.
Fig. 1: TOC analysis of temperature effects on TNT oxidation
Figure 2: HPLC analysis of TNT stock solution.

Figure 3: HPLC analysis of TNT oxidation experiment at 150°C.

Figure 4: HPLC analysis of TNT oxidation experiment at 180°C.
EXECUTIVE SUMMARY:

This subtask began in FY 1996 with the following objectives:

- To characterize each bacterial isolate received from TAMU by its colonial and cellular morphology and staining reactions. Progress: All cultures received to date have been characterized.
- To determine carbon and nitrogen source utilization by isolates received from TAMU. Progress: All cultures received to date have been characterized.
- To determine the effect of C:N ratios on the growth of organisms received from TAMU. Progress: Complete for all cultures received to date.

In addition, since we had only a few organisms sent to us by TAMU, we proceeded with the following tasks listed below in order to move the project forward. These tasks allowed us to continue our research without waiting for the TAMU team and to support our current and future efforts in bioremediation of soil and groundwater.

TASK 1: TO DEVELOP A CULTURE MEDIUM FOR SCREENING SOIL AND WATER SAMPLES FOR THE PRESENCE OF HIGH EXPLOSIVE-DEGRADING BACTERIA

Justification - There are several premises on which this culture medium's ingredients were chosen. First, microorganisms capable of degrading either or both RDX and HMX must remain viable in the presence of these compounds; that is, RDX and/or HMX should not be inherently toxic to any organism capable of degrading it. Second, the potential degraders must be able to not only remain viable in the presence of HMX and RDX, but must be able to withstand the levels (concentrations) at which the HEs are found in the soil or water samples tested. Third, they must remain metabolically active in the presence of HMX and RDX. Fourth, it is desirable (but not essential) that the organisms be able to use HMX and RDX as sole sources of nitrogen for growth to ensure that the HEs will be metabolized and not ignored in favor of more readily useable (preferred) nitrogen compounds. If the HEs are not used as sole N sources, they may be able to be co-metabolized with other nutrients.

Because HMX and RDX contain nitrite (-NO₂) groups on the ring, and due to the lack of availability of HMX and RDX for testing purposes, inorganic nitrates were substituted for the HEs in the culture medium. The premise was that organisms capable of growing on potassium or sodium nitrite as the sole source of nitrogen would most likely be the ones able to survive in the presence of, and metabolize, HEs. Whether the organisms isolated on this nitrite-containing medium grow in the presence of and metabolize HMX and RDX can readily be tested when these compounds become available to us.
A screening medium for isolation of nitrite-utilizing bacteria from the soil was tested using soils taken from the Zone 12 burning grounds at Pantex. Ten distinctive forms of bacteria which grew on this medium were subcultured onto the same medium to make sure they could be cultivated in the laboratory. We verified that they remained viable on subculture. Work is in progress to characterize them morphologically and by their biochemical characteristics and to determine whether they also can grow on tryptic soy agar (TSA).

**TASK 2: TO DETERMINE WHETHER THE BACTERIA ISOLATED ON THE NITRITE-UTILIZER CULTURE MEDIUM DESCRIBED IN TASK #1 ARE OBLIGATE OR FACULTATIVE CHEMOLITHOTROPHS.**

**Justification** - Very few strictly heterotrophic bacteria have been isolated that are substantially able to degrade HMX or RDX. In part this may be because heterotrophs are the wrong physiologic type of organism for degrading these nitrite-containing compounds. Nitrite utilization is rare among heterotrophic bacteria but more common among chemolithotrophic forms. Indeed, the most common nitrite-utilizers are chemolithotrophs that oxidize nitrite to obtain energy for growth. Some of these chemolithotrophs use the same nitrogen compound for both an energy source and a nitrogen source. They are referred to as "nitrite utilizers" and belong to the genera *Nitrobacter*, *Nitrococcus* and *Nitrospina*. Chemoheterotrophic bacteria derive their energy by using organic compounds as electron donors; chemolithotrophs use inorganic compounds. The chemolithotrophs use reduced forms of inorganic compounds such as ammonia, hydrogen, ferrous iron, thiosulfate and nitrite as sources of electrons for energy production, and also serve to reduce carbon dioxide for incorporation into cellular carbon. These organisms grow either aerobically using O₂ as the terminal electron acceptor during electron transport phosphorylation reactions, or anerobically using nitrate, sulfate and carbonate as the final electron acceptor.

Nitrite utilizers are found commonly in fresh and salt waters, soils, compost piles, and sewage disposal plants and frequently form zoogele (organisms stuck together in a biofilm). Although most grow autotrophically using only CO₂ as a carbon source, some can also grow heterotrophically using acetate as a carbon source. Their ability to form natural biofilms, oxidize nitrite to nitrate and use either CO₂ or acetate as a carbon source makes them much more attractive than other organisms for constructing biofilms to degrade HEs on GAC. Their unusual nutrient and energy requirements (compared to those of the more common heterotrophs which might colonize the biofilm as contaminants) should make overcolonization of the constructed biofilms less likely and thus easier to maintain.

**Progress** - Bacteria isolated from HE-contaminated soils on the nitrite-utilizer screening medium are being tested for their ability to maintain their viability and grow as chemolithotrophs. In addition, whether they maintain the ability to oxidize nitrates to nitrates is being tested. Further, these organisms are currently being tested for their ability to grow in the presence of analytical-grade RDX.
TASK 3: TO DETERMINE THE OPTIMUM C:N:P RATIOS FOR GROWTH OF ORGANISMS ISOLATED FROM THE NITRITE-CONTAINING SCREENING MEDIUM

Justification - Bioremediation of any recalcitrant compound, including HMX and RDX, is effective if the metabolic capacity of microorganism that are able to degrade the desired compound can be increased. Increased metabolic rates are often realized when the suboptimal conditions that control the rate of growth, such as O₂ and nutrient concentrations, are made optimal. One of the most significant conditions to be realized is the achievement of the proper C:N:P ratio for the degrading organism.

Progress - Experiments are now being designed to test whether the nitrogen concentrations of RDX and HMX will alter the amounts of carbon, nitrogen and phosphorus-containing compounds in the culture media needed to obtain optimum growth and HE degradation.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

Results of original three tasks for FY 1996 were reported directly to the TAMU task leader in the form of quarterly progress reports by the end of Spring 1996, well ahead of the deadlines since so few organisms were sent from TAMU. The data forwarded to TAMU was held awaiting more formal milestone reports. The two milestone reports were the following:


Bioremediation Of Soil And Groundwater (Subproject)

Tony Mollhagen, and Caryl Heintz (CO-PIs), Texas Tech University
Graduate Student Victoria Harkins, Texas Tech University

EXECUTIVE SUMMARY:

- Funding for this project was anticipated in January of 1996 but it was not received until June. Development and validation of the analytical method for determination of selected high explosives (HEs) in soil and groundwater is essentially complete.

- Another task is to screen candidate soils for consortia of microorganisms pre-adapted to rapid degradation of HEs. Such microorganisms are most likely to occur at sites where soils have had long-term contamination by HEs. Candidate soils for testing were collected from playas 2,3, and 4, and from the ditch exiting Zone 12.

- Preliminary reactor experiments on feeding and aeration strategies, seeded with soil from Playa 2, have confirmed the potential of such an approach. HEs were degraded and microbial populations grew.
Replicated reactors seeded with soils from the candidate sites were established at the same time to compare performance. Result from these experiments are anticipated in three weeks.

An attempt to further acclimate the best-performing consortium will follow.

DETAILED REPORTS:

- There were no reportable milestones for this subproject and there have been no reports or presentations.

**Treatabilities Studies For High Explosives Biodegradation**

R.L. Autenrieth, Texas A&M University  
J.S. Bonner, Texas A&M University

**EXECUTIVE SUMMARY:**

**HMX Degradation Studies**

Previous experiments have shown that the Alderson Playa culture which had successfully degraded RDX could not degrade HMX. Cultures derived from Pantex burn-site soil samples have been able to degrade HMX when supplemented with carbon and nitrogen. Figure 1 shows the degradation of HMX over time in single reactors where the initial HMX concentrations and supplemented ammonium-nitrate concentrations varied (0.75, 1.5, and 3.0 mg/l HMX and 60, 120, and 240 mg/l ammonium nitrate). Comparing reactors spiked with the same initial HMX concentrations revealed that at increasing ammonium nitrate levels, degradation rates improved. Growth data showed that ammonium-nitrate accumulated when combined with regular additions of 240 mg/l and became toxic to the culture. From this experiment, it was determined that an initial level of 240 mg/l ammonium-nitrate with additions of 120 mg/l every 48 hours eliminated the ammonium-nitrate toxicity while maintaining a high level of HMX degradation.

An on-going experiment is to evaluate the rate and extent of HMX biodegradation. The initial target concentrations are 0.25, 0.5, 1.0, 2.0, and 4.0 mg/l. The experiment has been run over 20 days with the first 8 days of data having been analyzed to date. After 8 days, HMX transformation ranged from 54.4% in the 0.25 mg/l reactors to 34.6% in the 4.0 mg/l reactors, verifying an inhibitory effect at higher HMX concentrations. The data plots of figures 2 and 3a-3e indicates degradation to be linear. This is
Figure 1: HMX degradation vs time with varying concentrations of HMX and ammonium nitrate. The first number in the legend represents the ammonium nitrate concentration in mg/l, and the second number is the initial HMX concentration in mg/l.

contrary to RDX degradation where there was a lag phase, a peak degradation period, and finally, a slow-down because of poor RDX availability. The linear HMX degradation response would result if HMX is being co-metabolized along with ammonium-nitrate (whereas RDX was the sole nitrogen source in RDX experiments). Another possibility is that the shift in RDX availability was extreme whereas HMX has a

Figure 2: HMX degradation vs time for various initial concentrations. Data points represent the average of duplicate reactors while lines represent linear regression curves determined by the data points.
low availability level throughout the experiment because of its lower solubility. Determining which mechanism is controlling the biodegradative response is part of our future efforts.

**Metabolite Determination**

We are currently optimizing extraction and GC/MS techniques to get the necessary precision required for metabolite identification. Past extractions were performed using methylene chloride, but the amount of mineral salts extracted along with the metabolites created an interference. Literature indicates that ethyl acetate extractions may eliminate this problem. Figures 4 and 5 show overlaid chromatograms from the present experiment at 10 days and at 0 days. The presence of some late eluting metabolites is clear, and there may also be metabolites concealed by the nutrient peaks. The isolation and identification of these peaks is in progress.

Please see the following attached figures.
Figure 4: Overlaid chromatograms from a reactor with initial HMX concentration of 0.5 mg/l at 0 days (slightly broken line) and 10 days (solid line). The slight difference in the retention time of HMX results from 10 days of heavy column use.

Figure 5: Overlaid chromatograms of a 4.0 mg/l reactor at 0 days (slightly broken line) and 10 days (solid line).
EXECUTIVE SUMMARY:

In this task area, the TTU research team is responsible for the development of a two-dimensional computer model to allow simulation of the soil-vapor extraction process, allowing for placement of extraction and passive vent wells in an unsaturated porous medium with a known initial distribution of residual liquid volatile organic contaminants (VOCs). The Pantex Plant includes several sites with known or potential residual VOCs from fuel or solvent losses. This project builds on previous experience at TTU in large-scale experiments and radial-flow modeling of soil-vapor extraction. The finite difference modeling approach taken in this research is somewhat unique in that the model accounts for the changes in air permeability over time as the VOC liquids are evaporated and removed.

During this quarter, work continued on the connection of the air flow and vapor transport subroutines. These subroutines were previously composed and initially tested separately. The coupled model is almost complete for single component VOC liquid, and will be upgraded to multicomponent VOC mixtures in the next quarter. Also in the next quarter, work will begin on a Visual-Basic graphical user interface to make the model more user-friendly.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

It should be noted that the planned deliverable for this project was the model and a user’s guide, which were originally planned to be delivered at the end December, 1996. The graduate student working on this project is Amit Armstrong, a doctoral candidate originally for December 1996 graduation. This summer, the chairman of the Department of Civil Engineering left TTU to become Dean of the College of Engineering at Ohio University. This loss led to a shortage of faculty and instructors for our undergraduate courses this fall. Amit was the only capable doctoral student that could be asked to take on two undergraduate courses, with a total of over eighty students, that he had not previously taught. Being a willing servant who is also interested in a future teaching position, Amit committed to help our department. As the semester has progressed, it is apparent that he will not be able to complete his dissertation as soon as planned. The status of the modeling effort will be reported on January 15, 1997, and the complete dissertation will be made available as soon as possible in the spring of 1997. This delay is proposed as a no-cost extension, and will not delay the efforts of any other researchers.
PERMEABILITY STUDIES

Dr. Daene C. McKinney (PI), University of Texas at Austin

EXECUTIVE SUMMARY:

The focus of work during Aug. - Oct. 1996 has been focused on two areas, permeability studies and proposed tracer experiments for the Pantex high explosives study.

The goal of this work was to gain insight towards the intrinsic permeability of sand types that will later be used in laboratory column experiments (F-35 and F-75 grade Ottawa sands). In particular, we were interested in determining the relationship between residual water saturation of the sands and the resulting intrinsic permeability to air.

In conducting these permeability studies one task that was accomplished was the development of a consistent method for packing column samples. The success of this task is demonstrated the reproducibility of the results (within acceptable variations) for column pack porosity and intrinsic permeability to air for a particular grade of sand.

A second task that was achieved, was the application of an experimental procedure for determining the intrinsic permeability of a column pack at a given residual water saturation. This procedure involved measurements of pressure drop at five different flow rates in order to reduce the skewing effect of inaccurate measurements. The consistent and expected trend of measurements at different water saturations support the reliability of this procedure.

In order, to make the permeability measurements, a procedure had to be applied for establishing the column pack residual water saturation. This procedure involved an initial water flooding of the column with air sparging and stripping used to create a desired saturation.

A final task accomplished through the permeability experiments, was the development of a general familiarity with the lab equipment that will subsequently be used to perform tracer experiments. Specifically, the permeability studies provided an opportunity to become familiar with equipment such as the bubble meter and flow controller, in addition to procedures such as, leak testing and column packing that will ultimately expedite future tracer experiments.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

The results of the intrinsic permeability measurements for different residual water saturations for both the F-35 and F-75 grade sand are presented in Figure 1 on the next page. The two most apparent conclusions that can be made from this data is 1) that the intrinsic permeability of the coarser F-35 grade sand is greater than the F-75 sand and 2) for residual water saturation greater than 5 percent, intrinsic permeability decreases with increasing water saturation. The lack of a clear trend for measurements with residual water saturation less than 5 percent was attributed to a combination of measurement error, experimental error, and non-uniform water saturation throughout the column.
Proposed Tracer Experiments for Pantex HE Study

The primary goals of this study are to determine if the presence of high explosives (HE) in a column affects the activity of either the water partitioning (difluoromethane CF₂H₂) or conservative tracer (sulfur hexafluoride SF₆); determine the residual water content of the column packs via the partitioning behavior of the tracers; and to determine if the same results apply to both Ottawa sands and field packed columns.

A set of five lab column experiments have been suggested in order to achieve the purpose of the study. By performing these experiments we should be able to determine the feasibility of performing a partitioning tracer field experiment in the presence of HE in order to determine residual water saturation.

In addition to the development of tracer experiments, a literature review has been conducted on the high explosives, RDX and HMX. The focus of this literature review has been on the chemical characteristics of the explosives and in particular, their interactions with other substances (such as water solubility).
EXECUTIVE SUMMARY:

During this quarter we studied the adsorption equilibria of binary mixtures of VOCs on dry soil. The isotherms were determined by using a dynamic response technique based on frontal analysis chromatography. The organic compounds used were n-hexane, toluene, methanol, and chlorobenzene. The adsorption isotherm of one organic compound was obtained at a fixed concentration of the second adsorbate. Different concentrations of the second compound was considered. The binary systems were hexane/toluene (non-polar, slightly-polar), methanol/toluene (polar, slightly-polar), and chlorobenzene/methanol (polar, polar). The polarity of the adsorbates is an important characteristic in relation to the extent of adsorption on soil. It is logical to expect binary adsorption to be at least partly governed by the relative polarities of the adsorbates involved. Whereas many authors studied the adsorption phenomena of VOCs on soils, the desorption process was rarely investigated. The literature available on this subject is very limited. One advantage of our dynamic experimental method is that concentration profiles can be obtained as a function of time for both adsorption and desorption. The technique enables determination of binary desorption breakthrough profiles.

We have already developed a method to determine adsorption isotherms of single compounds on soil a-priori during the first phase of the project. Thus it is not necessary to determine the adsorption isotherm of each species separately. Given the nitrogen adsorption data (a routine experiment in many laboratories) on soil and the VOC of interest, we can determine the isotherm within ±10% of the actual values. The next stage in our work plan is to develop the ability to determine the mixture isotherms from pure component isotherms, a requirement since most contaminants are present as mixtures. If we are successful in extending our methodology we will be able to determine, a-priority, mixture isotherms, needed to determine desorption rates.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

Figure 1 shows the adsorption breakthrough curves of binary VOC mixtures on soil. In this figure the dimensionless time is equivalent to number of empty column volumes of gas passing over the bed. Figure 1 was obtained for n-hexane and toluene which were simultaneously adsorbing on soil with nitrogen as a carrier gas. A different behavior was observed in all binary adsorption experiments. The effluent concentration for the weakly adsorbed species took on values greater than the inlet concentration. This type of behavior has been reported in the literature for experiments where competitive adsorption of two or more components occurs. It is usually referred to as the "roll-up" effect. This effect is due to the different affinities of two components to soil.

When two organics were simultaneously adsorbing, the front of one component (for example, toluene in Figure 1) traveled slower than the front of the other component (n-hexane). The slower one (toluene) displaced the faster one (n-hexane), leading to a rise in the effluent concentration of the faster one (n-hexane) above the inlet concentration. For binary system adsorption, the adsorption isotherm of one component was obtained over the
whole range of concentrations while the concentration of the second component was fixed. Different fixed concentrations of the second component were considered. Some of the experimental data are listed in Table I and II.

The adsorption isotherms obtained for toluene in the presence of n-hexane, toluene in the presence of methanol, and chlorobenzene in the presence of methanol are shown in Figures 2-4. In all cases, the presence of a co-adsorbate inhibits adsorption of the other. The BET type II shape observed for single compound adsorption was conserved for the adsorption isotherms of the binary system of toluene and n-hexane. For the binary systems of toluene and methanol, chlorobenzene and methanol, the shape of the isotherms changes from type II to type III when the concentration of methanol increased. The presence of methanol reduced the adsorption of toluene on soil much more drastically than the presence of n-hexane. This shows that highly polar methanol molecules can compete more effectively with slightly polar toluene molecules for adsorption sites than non-polar hexane molecules. However, it appears that polarity is not the only important phenomenon affecting competitive adsorption. Although chlorobenzene and methanol exhibit similar polarities (dipole moments are 1.6 and 1.7 debye, respectively), the reduction in chlorobenzene adsorption due to the presence of methanol is essentially identical to the reduction in toluene adsorption if the difference in methanol partial pressure is considered. In addition, from the Table II, it should also be noted that the presence of toluene affects only slightly the adsorption of methanol, same small effect was observed in the presence of chlorobenzene as well (Table I). In other words, slightly polar toluene molecules and polar chlorobenzene molecules exhibit comparable behavior in presence of methanol. In addition, percent reduction in the amount of methanol adsorbed in presence of toluene is higher at higher relative concentrations of methanol (Table II). This shows that toluene competes with methanol at high amounts of methanol adsorption but can not compete at low amounts of methanol adsorption. This could be due to the hydrogen bonding capacity of methanol that enables it to initially adsorb on sites inaccessible to toluene molecules which do not possess hydrogen bonding capability. As the adsorption of methanol increases (i.e. as its concentration increases), it adsorbs on “regular” sites also accessible to toluene molecules and competition can occur leading to an increased reduction of the methanol adsorption. It appears that the hydrogen bonding capability, in addition to polarity, influence the binary vapor phase adsorption of VOCs on soil. The hydrogen bonding parameters of chlorobenzene and methanol are 1.0 and 10.9, respectively.

The desorption profiles for toluene and hexane are shown in Figure 5. The soil was initially contaminated by toluene and hexane simultaneously. After equilibration at inlet concentrations of both toluene and hexane, the pure nitrogen was introduced to the soil bed and the effluent concentrations of two compounds were recorded. The plot of the effluent concentrations versus the time (or volume of nitrogen passed) then gave the desorption profile.

Figure 6 shows the desorption profiles obtained for toluene from soil after it adsorbed in the presence of methanol. The soil was contaminated by toluene and methanol. The initial vapor concentrations of toluene (when toluene is adsorbing on soil) are the same in all three experiments, P/P_{sat}=0.24, but the vapor concentrations of methanol are different. The initial soil loading of toluene of curve 1 was 33.6 mg/gsoil. The initial soil loadings of toluene were 14.9 mg/gsoil and 5.6 mg/gsoil of curves 2 and 3, respectively. The decrease in the adsorbed amount is due to the presence of methanol. The desorption profile of curve 3, in which methanol initial concentration is high, exhibits a very fast decrease in concentration, but the desorption profile of curve 1 in which methanol is not present exhibits a slow decrease. Figure 7 shows the evolution of percent removal of toluene as a function of the volume of nitrogen passed over the soil for the three experiments. With a high initial equilibrium concentration of methanol, almost 100% removal is achieved with a
$t/v$ (number of column volumes) of about 400, but with only pure toluene present, even passing over 2000 column volumes of gas over the bed achieves only 90% removal. This behavior could have been predicted by considering the adsorption isotherms of toluene in the presence of methanol (Figure 3). The "pure" isotherm of toluene on soil is favorable to adsorption and, thus, unfavorable to desorption; but as the methanol concentration increases, the isotherms become more favorable to desorption (BET type III). The similar behavior was also observed in the desorption profiles of chlorobenzene from soil after it was adsorbed in the presence of methanol.

Figure 8 shows the toluene desorption profiles obtained for the desorption of the soil contaminated by toluene and n-hexane. In all three experiments, the initial soil loadings of toluene are the same. The same adsorbed amount of toluene by soil is 24.6 mg/gsoil. The equity of initial loadings could be confirmed by the same area under three desorption profiles. The initial vapor concentrations of n-hexane are from zero to 0.25$C^\text{n-hexane}$ (n-hexane). It should be noted that the initial vapor concentrations of toluene of curves 2 and 3 which have n-hexane presence are larger than that of curve 1 which is the desorption of only pure toluene. But at the end of desorption (after dimensionless time of about 750), the three desorption profiles are similar and all curves tend to fall on the same line. This can be explained by that n-hexane desorbs very fast compared to toluene (as shown in Figure 5) and after $t/v$ of 750, all n-hexane is removed and only toluene exists on soil. Therefore, all the desorption profiles tend to approach the tail section of pure toluene desorption. Similar behavior was observed for the desorption of other pairs. It has been previously shown that organic desorption from soil occurred in two steps: desorption of the multilayers followed by the desorption of the monolayer and that the desorption of the monolayer is the limiting step. The present findings show that in desorption of binary mixtures, the controlling step is the desorption of the monolayer of the stronger adsorbed component (toluene in this case). Thus, in the soil venting process, the rate will be controlled by the removal rate of the component that adsorbs the strongest.

The ideal adsorbed solution (IAS) theory was applied for predictions of adsorption of binary systems. In the IAS theory, the mixed adsorbates are treated as an ideal solution in equilibrium with the gas phase:

\[
y_i P = p^0(\pi T)x_i
\]

where $x_i$ and $y_i$ is mole fraction of component $i$ in adsorbed phase and gas phase, respectively. Ideal behavior for the gaseous phase is assumed. The single component pressure value $p^0(\pi T)$ in equilibrium, at the same spreading pressure and temperature values as the mixture, is given by Gibbs isotherm:

\[
\frac{\pi A}{RT} = \int_0^{p^0} \frac{X_i}{P} dP
\]

where $X_i$ is the single component adsorption isotherm. In this study, the three-parameter BET equation (equation 2) was used for single component adsorption isotherm. Equations 3 and 4 can be used with the stoichiometric relation, $x_1 + x_2 = 1$, to calculate the binary adsorption. The adsorbed amount for each component may be calculated as follows:

\[
X_i = X_i x_i
\]

where
Figure 9 shows the result of comparison of the prediction with the experimental data. The prediction for toluene/hexane has a very good agreement with the experimental data. When methanol is present, the IAS theory under-predicted the adsorbed amount for both toluene and chlorobenzene. This is probably due to the failure of the ideal solution assumption when methanol is present. At present we are continuing our work in extension of the theory non-ideal systems.

**Table I. Measured data for chlorobenzene and methanol adsorption on soil.**

<table>
<thead>
<tr>
<th>$P/P^{\text{sat}}$</th>
<th>Chlorobenzene (mg/g)</th>
<th>Methanol (mg/g)</th>
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<tbody>
<tr>
<td>0.13</td>
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<td>0.28</td>
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<td>0.49</td>
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</table>

**Table II. Measured data for toluene and methanol adsorption on soil.**

<table>
<thead>
<tr>
<th>$P/P^{\text{sat}}$</th>
<th>Toluene (mg/g)</th>
<th>$P/P^{\text{sat}}$</th>
<th>Uptake with presence of toluene (mg/g)</th>
<th>Uptake with presence of pure$^{(a)}$ (mg/g)</th>
<th>Reduction$^{(b)}$</th>
</tr>
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$^{(a)}$ Uptake of single adsorption was calculated by using BET 3-parameter equation (Equation 2).

$^{(b)}$ Reduction = (Uptake of single adsorption - Uptake with presence of second compound)/ Uptake of single adsorption.
Figure 1. Adsorption breakthroughs for simultaneous adsorption of n-hexane and toluene.

Figure 2. Adsorption isotherms of toluene on dry soil in the presence of n-hexane at 24°C, $P_{sat}^{(toluene)}=0.04$ atm, $P_{sat}^{(hexane)}=0.20$ atm.
Figure 3. Adsorption isotherms of toluene on dry soil in the presence of methanol at 24°C, $P_{sat}(toluene)=0.04$ atm, $P_{sat}(methanol)=0.16$ atm.

Figure 4. Adsorption isotherms of chlorobenzene on dry soil in the presence of methanol at 24°C, $P_{sat}(chlorobenzene)=0.015$ atm, $P_{sat}(methanol)=0.16$ atm.
Figure 5. Breakthrough profiles for binary desorption of n-hexane and toluene.

Figure 6. Desorption breakthrough of toluene from soil in the presence of methanol at 24°C; The initial equilibrium vapor concentrations are the same.
Figure 7. Percent removal of toluene from soil in the presence of methanol at different concentrations.

Figure 8. Desorption profiles of toluene from soil in the presence of n-hexane at 24°C. The initial soil loadings of toluene are the same.
Figure 9. Parity plot for IAS theory prediction of binary adsorption.
EXECUTIVE SUMMARY:

Chromium contamination at levels of a few mg/L have long been noted, primarily in and near Zone 12, at the Pantex Plant. Work by TTU researchers in the previous quarters included a report on potential Cr-wastewaters discharged by the former cooling tower in Zone 12 and equilibrium isotherm tests of Cr sorption on core materials from the perched aquifer and its aquitard. In this quarter, one-dimensional column tests were begun to observe Cr sorption under flow conditions.

One-dimensional column tests for Cr sorption under flow conditions were originally planned under this subtask. These tests were delayed by the request from Dr. Randy Charbeneau to proceed with the HE sorption isotherms immediately after the Cr isotherms. During this quarter, 1-D column tests have commenced using columns 25 cm long and 2.5 cm in diameter. The column tests are being performed in the same manner as similar tests done with core material from well BEG-PTX-02 previously by TTU researchers. A low-flow, high-pressure pump is used to drive a flow of a few mL/min through the packed column. The injected solution is Pantex groundwater with added Br and Cr concentrations at 10 mg/L each. The effluent concentrations of Br and Cr are measured and used to calculate dispersion and retardation coefficients. These tests will be completed and reported in the next quarter.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

The report covering the one-dimensional column tests will be available on January 15, 1997.

ZERO VALENT METAL REMEDIATION OF CHROMIUM, CHLORINATED ORGANICS AND HIGH EXPLOSIVES AT THE PANTEX SITE

Elizabeth Carraway (PI), Texas A&M University

EXECUTIVE SUMMARY:

The experimental approach used in this work plan is to investigate combinations of zero valent metals (zvm) and amended zvm as reductants for the types of contaminants found at the Pantex site. Perched aquifer material from the site and simulated ground water (water with major ions added to mimic Pantex perched aquifer conditions) are added to the mixture. The classes of contaminants to be investigated, chromium, chlorinated organics,
and high explosives, will be studied individually, then in combination with the other contaminants and aquifer material. We focus on iron and iron with palladium plating as the zvm. Trichloroethylene (TCE) is used as the model chlorinated organic and dinitrotoluene (2,4-DNT) as a model explosive. The three tasks shown below were developed in the initial proposal.

Task 1: Develop slurry reactor techniques and analytical techniques

Task 2: Examine the effectiveness of two types of zvm (iron and amended iron) with the three contaminants, Cr(VI), TCE, and 2,4-DNT, individually

Task 3: Examine the effectiveness of two types of zvm for the degradation of mixtures of the 3 contaminants

In this quarterly report, progress between August and October 1996 is summarized. The progress and results reported relate to Tasks 1 and 2. A final or milestone report covering all three tasks is scheduled at the end of the project period. In the previous quarterly report (May through July, 1996), results from experiments on the degradation of TCE by iron and iron/palladium (Fe/Pd) in the presence of pure water and Pantex aquifer solids were reported.

After we developed reactor conditions and analysis techniques for the chromium experiment, we conducted a series of experiments in reduction of chromium(VI) by zero valent iron (Fe\textsuperscript{0}) and amended zero valent iron (iron coated with 0.05% by weight palladium, Fe/Pd). The experiments were conducted with composite Pantex soils and simulated Pantex ground water with an initial concentration of 2.1 ppm chromium(VI). It was found that the chromium(VI) concentration was lowered below the detection limit (approximately 20 ppb Cr) in two hours by zero valent iron (Fe\textsuperscript{0}) at 3.84 weight percent of solids; and for the same amount of amended iron (Fe/Pd), the concentration of chromium(VI) was reduced below detection limit in 40 minutes. From these experiments, both zero valent iron and amended iron were found to be effective in reducing the chromium(VI) concentration in a short period of time. Figure 1 in the Detailed Reports section summarizes the results of reduction of chromium(VI) in slurry reactors with Pantex aquifer solids containing 3.84% Fe\textsuperscript{0} and 3.84% Fe/Pd.

The slurry reactor technique and analytical technique for 2,4-dinitrotoluene (2,4-DNT) have also been developed and 2,4-DNT degradation experiments will be conducted soon. The trichloroethylene (TCE) experiments with composite Pantex soils and artificial ground water will be conducted in next quarter. In addition we will be conducting a series of experiments to find the effectiveness of zero valent iron and amended iron with mixtures of all three contaminants: chromium(VI), TCE, and 2,4-DNT.

**DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:**

**Experimental Methods:** The 100 mesh iron powder from Fisher Scientific, palladium(II) chloride (5% by weight solution in 10% by weight HCl) from Aldrich Chemical Company, Inc. and K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} from Alfa Aesar were used as received. A composite soil samples were prepared by mixing soil samples from zone 12 (PTX-06-1012) and zone 13 (PTX-06-1013) in order to make representative samples of the site rather than using soil samples from a particular zone and depth. The composite soil samples of size less than 2 mm were used in our experiment.
A 40 ml PTFE/silicone septa economical EPA vial from Fisher Scientific was used as reactor. Each reactor vial contained 25 ml of artificial ground water, 2.5 gram of composite Pantex soil (< 2 mm), a varying amount of Fe⁰ and Fe/Pd, and 2.1 ppm chromium (VI). The artificial ground water solution has alkalinity of 165 mg/l as CaCO₃. Ion concentrations of the artificial ground water are based on the equilibrium modeling and from analyses of water samples from well PTX06-1011. The amount of Fe⁰ and Fe/Pd correspond to 1.96, 3.84 weight percent of the solids in each vial. The control vial contents were identical except for the exclusion of ZVM. During the reaction period, the contents of the vial were continuously mixed on a shaker table at 100 rpm at the ambient temperature. Vials were analyzed at zero, 20, 40, 60, 80, 120 minutes. The pH of the reaction contents was 8.35 in the beginning of the reaction and the pH at the end of reaction was 8.37.

At each sampling time, chromium samples were taken from vials by filtering through syringe filter with 0.45 μm membrane. The filtrate was collected in a sample bottle and acidified with concentrated nitric acid to pH < 2. The analysis of chromium(VI) was done by colorimetric method using HP 8452A Diode Array Spectrophotometer. The absorbance was measured at 542 nm with light path of 1 cm. Diphenylcarbazide solution was used as chelating agent and 0.2 N H₂SO₄ as buffer. The detection limits for this method are approximately 20 ppb Cr.

Figure 1 summarizes the results of reduction of chromium(VI) by 3.84% Fe⁰ and Fe/Pd. Each time point is an average of analysis of two replicate vials. It is shown in the figure that chromium(VI) concentration was reduced to below detection limit in two hours by Fe⁰ whereas as it took only 40 minutes to reduced chromium(VI) concentration below detection limit by Fe/Pd. At 20 minutes time, only 14.3% of the initial concentration of chromium(VI) was reduced by Fe⁰, but 55.6% of chromium(VI) concentration was reduced by Fe/Pd with the correction of loss in control vial. This shows the amended iron (Fe/Pd) is about 4 times effective than zero valent iron (Fe⁰).

Both the zero valent iron and amended iron were found to be very effective in reducing chromium(VI) in a short period of time. Based on these experiment results, the remediation of chromium by ZVM seems promising.

Please see the following figure.
Figure 1: Reduction of Chromium (VI) by $F_o^+$ and $F_o/F_d$

![Graph showing reduction of Chromium (VI) by $F_o^+$ and $F_o/F_d$.](image)

- Control for Fe
- 3.84% Fe
- Control for Fe/Pd
- 3.84% Fe/Pd

Time (min)

23
CHEMICAL MODELS AND REDOX CHEMISTRY OF CHROMIUM

Bill Batchelor and Mark Schlautman (CO-PIs), Texas A&M University

EXECUTIVE SUMMARY:

Chromium has been found at concentrations above background levels in several wells in the perched aquifer below the Pantex Plant, particularly in those beneath Zone 12. In some wells, the concentrations of total chromium exceed levels used to define hazardous wastes by the toxicity characteristic and approach being two orders of magnitude higher than drinking water standards. A research program has been initiated under the Amarillo National Resource Center for Plutonium to obtain information to support the remediation of chromium at the Pantex Plant. It is being carried out by research teams at Texas A&M University (TAMU), Texas Tech University (TTU) and the University of Texas at Austin (UT). This is the report on activities of one of the research teams at TAMU during the time period between August 1, 1996 through October 31, 1996. The research program for this team at TAMU includes two research tasks:

1. Develop chemical models for chromium in the vadose zone and perched aquifer
2. Evaluate redox chemistry of chromium

Chemical models for kinetics of chromium reduction in the presence of Pantex aquifer material and for conditions of chemical equilibrium have been developed during previous portions of the research. No additional development was conducted during the past quarter, although the equilibrium model continues to be used to evaluate experimental results and help design experiments.

Two aspects of chromium redox chemistry are being evaluated: reduction and oxidation of chromate. Evaluation of chromium reduction by ferrous iron in the presence of Pantex aquifer material continued during the past quarter. Additional data was collected to further refine kinetics reported in the milestone report submitted during the third quarter. This data is represented in Figure 1, in the section of this report titled “Detailed Report”. The additional data does not change the conclusions reported in the milestone report on chromium reduction kinetics. However, we have noted that there is evidence that some external oxidant, probably oxygen, could have entered the reactors in significant quantities during the experiments. This would result in loss of effective reducing power of the Fe(II) that was added. Substantially more Fe(II) was needed in experiments conducted with Pantex aquifer material than was needed in reduction experiments that were conducted without the presence of aquifer material and were completed within a few hours of introducing the Fe(II). The requirement for higher Fe(II) doses was attributed to reaction of Fe(II) with aquifer material. However, if substantial amounts of an external oxidant entered the reactor and caused the excess consumption of Fe(II), then lower Fe(II) doses could be used to effect treatment. The potential for external sources of oxidant entering the reactors is currently being evaluated and alternative experimental procedures will be developed if it is found to be a problem.

An experiment to evaluate the potential for reoxidation of chromate in Pantex soils was initiated during the past quarter and a milestone report was submitted on October 30, 1996. The potential for chromium reoxidation is important if in-situ chromium reduction is chosen as a remedial option. This remedial strategy seeks to reduce the toxicity and mobility of chromium by reducing it to the Cr(III) state, thereby reducing the risk to human health and
the environment. Research on reduction of Cr(VI) by Fe(II) has shown that this remedial option offers promise both as an in-situ and ex-situ treatment process. However, the possibility exists that Cr(III) that has been reduced in-situ could be reoxidized to the more mobile and more toxic Cr(VI) form by introduction of oxygen. If such a reaction cannot be shown to be highly unlikely, prudence might dictate that in-situ reduction not be used, because its long-term effectiveness could not be assured.

The chromium reoxidation experiment conducted during this quarter used slurry reactors containing Pantex aquifer material that had been spiked with Cr(VI) and to which Fe(II) was added as a reductant. Slurries with 1% aquifer material and 0, 9.7, 16.1 and 22.5 mg/L Fe(II); and slurries with 10% aquifer material and 0 and 19.3 mg/L Fe(II) were used. The reactor systems were the same that had been used to conduct chromium reduction experiments. After the reduction experiments were concluded, the reactors were oxygentated and the concentration of chromium in the solution monitored over time. Results of these experiments are shown in Figure 2, in the "Detailed Report" section.

The milestone report ("Reoxidation Potential of Chromium in Pantex Soils") concludes that there was no evidence of reoxidation in the experiments conducted. None of the experiments showed a statistically significant change in chromium concentration with time at the 5% level. In fact, those experiments that had the closest approach to this level of significance were those that showed a slight decrease in chromium concentration. This decrease was interpreted as reduction or sorption of chromium that continued even when oxygenated conditions were established. The conclusion that chromium was not resolubilized is limited by the time period over which the data was obtained (30 days) and the fact that the oxidation state of aquifer material could have been altered by drying and storage. It is possible that chromium could be oxidized and thereby solubilized after longer periods of time. Time periods much longer than 30 days would be important in evaluating the long-term effectiveness of chromium remediation by reduction. Additional data is being gathered to extend the time period of the experiment. Drying of the aquifer material may have resulted in reduction of manganese oxides in the material. These oxides have been reported as being important potential oxidants for Cr(III) in soils. The potential exists that drying the aquifer material removed its ability to oxidize Cr(III).

**DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:**

Please see the following attached figures.
Figure 1. Changes in Chromium (VI) Concentration with Time in Reduction Experiments.

Figure 2. Changes in Chromium (VI) Concentration with Time in Re-oxidation Experiments.
Phytoaccumulation Of Selected Heavy Metals, Uranium, And Plutonium In Plant Systems

L.R. Hossner (PI), Soil and Crop Sciences Department, Texas A&M University, College Station, TX 77843

EXECUTIVE SUMMARY:

Research activities during this period have been allocated to the three primary objective areas: 1) Screening for Cr and U uptake and translocation by selected plant species under controlled conditions. 2) Basic studies on the mechanisms of Cr uptake and translocation by selected plants, and 3) Establishment of field trials on the High Plains of Texas that will determine the ability of common agricultural crops in the region to absorb and translocate Cr.

Plant growth, plant uptake and effect of chelating agents on Cr and U uptake and translocation were studied in soil media in controlled experiments. Twenty plant species were evaluated with two rates of Cr, three sources of Cr (CrO$_4^{2-}$, Cr$^{2+}$, and Cr$^{3+}$ with EDTA chelate), and one source and rate of U, UO$_2^{2+}$ at 100 mg U kg$^{-1}$ soil. The tolerance and accumulation of Cr by plant species was dependent on the form of Cr in the soil. Chromium (VI) was the form of Cr that most adversely affected plant growth and was accumulated more than Cr$^{3+}$ in all plant species. Chromium(VI) applied at a rate of 500 mg kg$^{-1}$ killed most of the plants. Chromium (III) application at a rate of 500 mg kg$^{-1}$ had little effect on the growth of most plants. Uranium had no adverse effect on plant growth at 100 mg U kg$^{-1}$ soil. Most plants that were screened with the CrO$_4^{2-}$ source accumulated more than 2000 µg Cr g$^{-1}$ in both shoots and roots at the 500 mg Cr kg$^{-1}$ soil application rate. Sunflower (Helianthus annus) was the only plant species that accumulated more than 500 µg U g$^{-1}$ plant material. Chromium as Cr$^{3+}$ and U as UO$_2^{2+}$ were accumulated mainly in (or on) the roots of the plants. The uptake of Cr(III) was significantly enhanced by the application of EDTA to the soil.

The success of phytoremediation depends on the total metal harvest (metal concentration of the plant tissue x plant biomass). Vetiver grass (Vetiveria zizanioides) is a promising candidate for phytoremediation as it has high dry matter production and relatively high concentrations of Cr and U in the above ground biomass. Sunflower and Indian mustard (Brassica juncea) accumulated more Cr and U than the other species. Sunflower is a multimetal accumulator, as it accumulated both Cr and U. Coastal bermudagrass (Cynodon dactylon) and switchgrass (Panicum virgatum) were the most Cr tolerant plant species. In hydroponic solution, soybean seedling height growth was less affected by Cr than was that of sunflower. Growth of sunflower was less in the presence of either Cr$^{3+}$ or Cr$^{6+}$ than was that of soybean. We hypothesize that sunflower accumulates more Cr than soybean. An alternate hypothesis is that soybean can sequester its Cr, and therefore can tolerate higher concentrations. We are in the process of testing this hypothesis by measuring the Cr content in the organs of each species. Canola appears to have a similar tolerance to that of soybean. In general, dicotyledonous plants accumulated more Cr and U than monocotyledonous plants.
Studies to evaluate the uptake and transport of Cr to the above ground plant parts were conducted in controlled experiments in hydroponic solution. *Cucumis sativium* (cv. lemon cucumber) exhibited enhanced ferric chelate reductase (FCR) activity when subjected to Fe stress and 1 μM Cr. However, higher Cr concentrations suppressed the FCR activity in Fe-stressed plants. Chromium had no significant effect on FCR activity in Fe-sufficient plants. A small scale FCR assay system for small whole plant roots was developed to allow rapid screening of plants for high FCR activity, which may be important in plant/heavy metal relations. Chromium (III) supplied as the chloride salt at alkaline pH had no significant effect on the growth of cucumber even in nutrients solutions saturated with Cr^{3+}. The results of these experiments suggest that this cultivar of cucumber is not sensitive to Cr complexation and likely avoids toxification by an exclusionary mechanism. Clove grown under both Fe sufficient and Fe deficient conditions transported Cr to the above ground plant parts in the following order: CrO_{4}^{2-} > Cr^{3+} > Cr-DTPA. The concentration of Cr-DTPA was also very low in the plant roots indicating that this form of Cr is not readily absorbed by the plant. These results differ somewhat from the studies of Cr uptake in soils, in which Cr content of the leaves and shoots was slightly greater with Cr-EDTA compared to Cr^{3+}. Visual observations of the roots of plants treated with CrCl_{3} in hydroponic culture indicated the probable presence of a Cr (OH)_{3} precipitate at the root surface. Thermodynamic evaluation indicated that at the pH of the soil or hydroponic solution, Cr^{3+} would be readily precipitated as Cr(OH)_{3}, resulting in low equilibrium concentrations of solution phase Cr. The slightly higher uptake of Cr from Cr-EDTA compared to the Cr^{3+} source in soil culture probably reflects the higher concentration of dissolved Cr in the former system. There is no evidence that Cr is absorbed readily in either the Cr-EDTA or Cr-DTPA forms.

Electron paramagnetic resonance (EPR) spectroscopy was used to evaluate Cr form and complexation in the roots and above ground plant parts. The precipitation of Cr on or in the root was confirmed by EPR. Also, a high spin Cr complex as observed in both the roots and shoots. Efforts are currently underway to identify this complex using EPR, high performance liquid chromatography (HPLC), and mass spectrometry. Identification of this complex is important, since it gives important clues to the biochemical and genetic control of Cr accumulation.

Roots of CrCl_{3} treated plants were examined by environmental scanning electron microscopy (ESEM) and scanning electron microscopy (SEM). Spherical particles (~0.5 μm diameter) of chromium hydroxide or chromium phosphate were observed at the root surface. There was no evidence of precipitated Cr within the root or in the individual cells. Chromium transport to the shoots and leaves was significantly enhanced under Fe-deficiency stress conditions. One of the Fe-deficiency stress response reactions of dicots is an enhanced root plasma membrane H^{+} pump. This reaction also results in a concomitant production of the conjugate bases of organic acids, i.e., oxalate, malate and citrate. The second major hydroponic plant experiment has been completed, though analysis of the samples is still in progress. The experiment is designed to evaluate Cr oxalate, Cr malate and Cr citrate as sources of Cr for plant uptake, and to evaluate the uptake of Cr by several pea mutants that have exhibited accelerated uptake and accumulation of Fe. The formation and stability of the complexes have been evaluated as a function of pH. The kinetics of formation in regions of stability is very slow, as is the breaking of the complex in regions of instability. These factors negatively influence the mobilization and possibly the uptake of inorganic Cr^{3+}, but positively influence the compartmentalization of complexed Cr within the plant.

Greenhouse and field experiments have been initiated on the Texas High Plains on two soils, a loamy sand and a clay loam, to determine the influence of soil type and plant type
(monocots and dicots) on Cr (rates of 0, 10, and 100 mg Cr²⁺ kg⁻¹) utilization by cool and warm season crops. Agricultural crops common to the Texas High Plains have been selected for this study. Warm season species include sorghum, sunflower, bermudagrass and soybean. Cool season crops include winter wheat, canola, bromegrass, red clover, alfalfa, and rye. The crops will be rotated to simulate a continuous cropping system using combinations of warm and cool season crops.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

Please see the following attached figures.
### attachment 1: list of plant species

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<th>Scientific Name</th>
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<td>USDA (Iowa)</td>
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<td><strong>Monocotyledonous Crops</strong></td>
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<td><strong>Cool and Warm Season Grasses</strong></td>
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<tr>
<td>Seashore Paspalum</td>
<td><em>Paspalum vaginatum</em></td>
<td>Texas</td>
</tr>
</tbody>
</table>
Attach. 2. Cr concentration in shoots or roots of plant species with 100 mg kg\(^{-1}\) Cr(III) or Cr(VI) applied to the soil.

Attach. 3. Cr concentration in roots of plant species with 500 mg kg\(^{-1}\) Cr(III) or Cr(VI) applied to the soil.
Attach. 4. Cr concentration in shoots of plant species with 500 mg kg\(^{-1}\) Cr(III) or Cr(VI) applied to the soil.

Attach. 5. U concentration in the shoots of plant species and their relationship to U concentration in the roots, at 100 mg kg\(^{-1}\) U applied to the soil.
Attach. 6. Comparison of U, and Cr concentrations in shoots and root of plant species with soil application of 100 mg kg⁻¹ U and Cr(III,VI) to the soil.
WORK PLAN PROGRESS REPORT
Communication, Education, and Training

Institution: Texas Tech University
Program Manager: Dr. Elda D. Zounar
Project Coordinator: Phillip T. Nash, P.E.
Sub-Contract Number: UTA 95-0206

Appended Supporting Documentation

1. Selection Criteria & Weights for FY 1997 LOI Selection
2. Issue V of the Center's newsletter
3. News Release: Amarillo National Resource Center for Plutonium Convenes Meeting of Top Plutonium Experts This Week in San Francisco
4. Opinion Editorial: Dr. Randall J. Charbeneau
5. Peer Review of Program Report Form FY 1997
7. Chemistry Road Show
SELECTION CRITERIA & WEIGHTS FOR FY 1997 LOI SELECTION

For any LOI to be considered (litmus test):

- It must involve at least two of the three institutions in the consortium.
- It must include institutional or other cost sharing amounting to at least ten percent of the funds requested from the Center.

I. Relevance of the project to the mission and goals of the Center [40 pts]

- Clearly stated objective and outcomes of the project (10)
- Likelihood that the project will contribute to the accomplishment of Center goals (15)
- Evidence of collaboration with DOE, National Labs, Pantex, local universities (15)

II. Intrinsic Merit [30]

- Soundness of the proposed approach (20)
- Likelihood that the research or activity will lead to new discoveries or fundamental advances within the field (10)
- Or for educational and outreach activities, adequacy of plans for evaluating progress and results of the project (10)

III. Plan and Budget [20]

- Realistic time schedule (5)
- Appropriateness of budget for the project (10)
- Percentage of effort to be expended in the Amarillo area (5)

IV. Performance competence [10]

- Capability of project personnel (5)
- Adequacy of institutional resources (5)
Local delegation visits Mixed Oxide fuel plants

From both security and environmental perspectives, the issue of disposition of plutonium must be addressed. Using plutonium in mixed oxide fuel is one disposition option that DOE is seriously considering.

Panex, as the nation's nuclear weapons disassembly site, has more than 22 tons of excess plutonium which could be used in mixed oxide fuel. The fuel has been used in Europe for more than 30 years and seven Amarillo citizens got an up-close look at mixed oxide fuel plants this past May when they traveled to Sellafield, England and Cadarache and La Hague, France to learn more about mixed oxide operations.

The trip was initiated in April when Panhandle 2000 leaders approached Amarillo Mayor Kel Seliger to suggest that Amarillo send a delegation of people to learn more about mixed oxide fuel operations, to visit with people who live near the plants, to learn about European experiences with mixed oxide and agriculture, and to determine from the European operations whether or not a mixed oxide fabrication plant could be compatible with our area's agricultural and environmental interests. That initial conversation led the Mayor, the Amarillo Economic Development Corporation, and Panhandle 2000 to put together a group of elected officials and representatives from agriculture, labor, and education.

The group consisted of Amarillo Economic Development Corporation Pantex Retention and Expansion Coordinator Bob Juba, Mayor Kel Seliger, City Commissioner Trent Sisemore, Pantex Metal Trades Council Safety Officer Ron Zerm, Amarillo College Biology Professor Dr. Robert Bauman, Amarillo Chamber of Commerce Agriculture Committee Chairman C.C. Burgess, and a representative of the governor's office, Roger Mulder. The Amarillo National Resource Center asked a number of questions about their experiences.

What is mixed oxide fuel?

JUBA: Mixed oxide is a blend of uranium dioxide and plutonium dioxide that produces a fuel for use in nuclear reactors to generate electrical power. Plutonium makes up about 5-7% of the fuel and the uranium is like the depleted uranium that is used in reactors in the U.S. today. The actual fission process and generation of power is the same whether a plant uses uranium fuel or mixed oxide fuel.

Why is the U.S. government considering using plutonium to generate electricity?

JUBA: The government has an important objective, that of keeping plutonium—not just ours, but the Russian's as well—away from any person, groups, or countries that might want to use it in nuclear weapons.

The recent dismantlement of nuclear weapons has led to what the government has labeled “excess” plutonium. Some 38 tons of “weapons grade” plutonium has to be dealt with in some way. In broad terms, the government is considering three options: deep borehole disposal, immobilization, and using the plutonium to generate electricity which is what we are talking about today—mixed oxide fuel.

The government is evaluating the disposition choices in a number of ways. They are looking at the environmental and safety aspects and they are looking at keeping the cost to taxpayers as low as possible. From a cost/benefit standpoint, deep borehole disposal and immobilization would both be costly for taxpayers. Mixed oxide fuel, on the other hand, would produce billions of dollars worth of electricity for our country which would help to defray the cost of this option. It appears that mixed oxide fuel may be one of the selected disposition alternatives.

The Russians have already indicated that they choose to treat their plutonium supplies as “resources.” They are firmly committed to using their plutonium to generate electricity in reactors. Whatever the U.S. does, we will need to keep our plutonium supplies at approximately the same level as the Russians. As a nation, we would not want either side to be perceived as having a “strategic advantage.”

Continued on page 2
Why would utility companies be interested in using plutonium in their reactors?

JUBA: Utility companies realize that there is tremendous energy potential in this material. I believe that the energy equivalency is one gram of plutonium is equal to one to two tons of oil. Oil, gas, and coal are, of course, finite resources and utility companies are interested in preserving those resources.

Utility companies also realize that the government may absorb some of the costs of the conversion of plutonium from a weapons form to a fuel, so they feel that use of mixed oxide fuel could be an advantage for their customers and stockholders.

What did you learn from your visit to these three mixed oxide plants?

JUBA: We discovered that the British and the French are ahead of the U.S. in some aspects of the nuclear industry. For instance, the British, who currently use very little mixed oxide fuel in their reactors are building a large mixed oxide fuel production facility because they can export the fuel to other countries. In France, the Cogema plants supply French reactors. These reactors supply about 76% of France’s electric needs and, by the year 2000, France expects 28 mixed oxide reactors. Both Britain and France produce mixed oxide as part of their efforts to reduce the amount of nuclear waste from their plants and to “recycle” their nuclear materials.

American anti-nuclear groups, on the other hand, oppose any peaceful use of plutonium because they fear that the existence of a market for plutonium encourages further production of the material, which could be used in nuclear weapons. The fact is, the “plutonium economy” already exists because many other countries are already manufacturing and selling mixed oxide fuel. Of course, this is all done under very strict international control to prevent the use of the plutonium in weapons.

SELIGER: One of the key things I learned is that in the U.S. we need to determine what value we are going to place on plutonium as a resource. As Bob was saying, in France mixed oxide fuel provides about 75% of their electricity needs and it currently provides about 20-30% in Great Britain. So, one of the questions this country needs to address is, “Is this plutonium going to be utilized and then disposed of, or simply disposed of?”

Were any of these plants located in agricultural areas and what kind of relationship did they have with the ag community? Did you discover any pollution problems?

BURGESS: The Sellafield plant we visited in Northern England and the Cogema plants in France were in agriculturally based communities. It appeared that the ag-communities and the mixed oxide plants’ management teams had congenial relationships. A large percentage of the employees at the mixed oxide plants came from these agricultural communities. We didn’t hear of any problems pertaining to contamination of water supplies.

ZERM: Most of Europe is agricultural and both processing and mixed oxide fuel plants are in ag areas and also in tourism destinations. The companies have realized that they must co-exist in these areas and that they must do nothing to upset the ecological balance.

The plants carefully monitor their facilities. Last year, for example, at the La Hague plant, they took 23,000 environmental samples and performed about 80,000 laboratory analyses. They found nothing out of the ordinary, there was no ground water pollution, no air pollution, and no soil pollution. They even contract with the French Navy and local fishermen to get samples. The Navy takes deep sea samples of both fish and sediment and the fishermen provide samples of fish. Again, they have observed no problems.

They also have an air monitoring system that is available to the public at different locations throughout the countryside. It’s an ongoing thing and is updated every minute to let the public know exactly what the current situation is.

Is converting plutonium from nuclear weapons different from the processing they are doing in Europe?

ZERM: Yes. In Europe they are reprocessing spent fuel—technically a “dirtier” job, although environmentally they have handled it in a very clean way. The process that is being considered by the DOE does not involve reprocessing.

How could all this affect Pantex?

JUBA: Pantex is facing a decline in the number of people needed to perform the assembly/disassembly functions that the plant has performed for many years. This could represent 1,600 lost jobs which will affect our area’s employment rate, our retail growth, our retail sector, our nonprofit organizations, and every other sector of our economy. We are interested in pursuing any new missions for Pantex that could be performed in a safe and environmentally responsible manner to offset the declines that will occur in assembly/disassembly. Mixed oxide fuel production could possibly be a new mission at Pantex that would represent new jobs. DOE estimates that total employment for mixed oxide production, pit conversion, and associated storage may total 1,450 to 2,175 jobs at Pantex.

The DOE is only considering sites for mixed oxide fuel production that have experience with storing and handling plutonium. Since downsizing has resulted in the closure of several DOE sites, there are only a few remaining sites that are suitable for a mixed oxide plant. Amarillo is one.

ZERM: Pantex could do the conversion process. We could convert the pits into an oxide, mix the oxide with uranium dioxide, and fabricate fuel pellets. These pellets would then be assembled into fuel rods which would be shipped out of Texas (Texas does not have a reactor that is converted to use mixed oxide fuel) to user utilities.

Does this mean Pantex would begin to do Plutonium reprocessing?

JUBA: No! These terms get very confusing, but “reprocessing” is something that is done to fuel rods that have been removed from nuclear plants. When a fuel rod is removed, it contains 96% of its original uranium, 1% plutonium, and 3% highly radioactive waste products. Reprocessing involves dissolving the fuel rods in acid and separating the uranium, plutonium, and waste products. Reprocessing is basically the “manufacture” of plutonium. The plutonium that is stored at Pantex came from uranium fuel rods.

Continued on page 5
TexPREP students learn that learning can be fun!

One goal of The Amarillo National Resource Center for Plutonium is to advance mathematics, science, engineering, and technology education through partnerships and collaborations with the education community, business, and industry. To meet this goal, the Center supports TexPREP (Texas Pre-Freshman Engineering Program) which is designed to prepare secondary students for a college engineering program. TexPREP is an all-day, eight-week summer program on the Amarillo College and Texas Tech University campuses for students, grades 6-12, who show an interest in engineering.

TexPREP courses have a number of focuses including helping students to develop problem solving skills by providing hands-on learning activities and helping students to develop an appreciation for engineering principles. Toward that end, TexPREP students took a field trip to Hoover Dam, Yucca Mountain Site, Palo Verde Nuclear Power Plant, and the Grand Canyon. Over the course of the summer, students participated in a number of cause and effect activities including an "egg drop" and a bridge building exercise.

TexPREP students step out of the classroom for real-world experiences

David Merritt of Las Vegas, Nevada, geologist and TexPREP instructor, leads students during their VIP tour of Hoover Dam.

Students gather for a photo op in front of the entry to the DOE Exploratory Studies Facility at the Yucca Mountain Project. In the background is the conveyor system for the tunnel boring machine.

TexPREP students dress up for a mock session on handling radioactive contaminated materials at the Palo Verde Nuclear Power Plant, near Phoenix.

David Merritt at the Grand Canyon, shows students how the earth reveals its history through geologic formations.

TexPREP students’ put their design skills to the test as engineers from Utility Engineering apply stress to the students’ bridges.
Environmental and nuclear researchers meet

The Amarillo National Resource Center held the Center’s semi-annual Environmental Meeting in June and the Quarterly Nuclear Meeting in July. The Environmental Meeting was in Panhandle and 25 researchers attended. The Nuclear Meeting was in Amarillo and approximately 40 researchers attended.

The meetings are designed to keep communications open between researchers, to update researchers about ongoing research, and to encourage the researchers to ask the challenging questions that yield better research. These meetings help to keep research relevant, stimulate new ideas, and create building blocks for future environmental solutions and improved use and disposition options.

Researchers view virtual reality demonstration

Center researchers from Texas Tech, Texas A&M, and The University of Texas performed a virtual reality remote monitoring demonstration at the July Nuclear Quarterly Meeting.

The researchers, who were in Amarillo, controlled a robot located at College Station, through the Internet. The Amarillo operator used virtual reality hardware to demonstrate how robots could perform long-distance monitoring and handling of special nuclear materials. This research has implications for substantially reducing radiation doses to workers and furthering nonproliferation goals through international remote inspection.

Researcher speaks to local civic group

Dr. David R. Boyle, Deputy Director for the Texas A&M Center for Space Power spoke to the Amarillo South Rotary Club while he was in Amarillo for the July 10-12 Nuclear Meetings.

The former Nuclear Weapons Stockpile Manager for the Joint Chiefs of Staff at the Pentagon, Dr. Boyle holds masters degrees in Nuclear Engineering and National Security and Strategic Studies from the Georgia Institute of Technology and the U.S. Naval War College, respectively, and a Ph.D. in Nuclear Engineering from MIT.

Off Center

KACV-TV, Amarillo’s PBS station, will once again air the KACV-produced Pantex documentary on Saturday, August 17 at 7 p.m. and on Sunday, August 18 at 5 p.m.

The Department of Energy (DOE) was scheduled to issue a “Record of Decision” on November 25 regarding which options for the disposition of plutonium will be used in the United States. The DOE has postponed the decision. The Center will report the new date in a future issue of this newsletter.

The Center has provided funding to West Texas A&M and Texas Tech Universities to develop science and math curriculum modules and host teacher workshops. The workshops will help teachers meet the requirements of the new national math and science standards. The standards call for increasing the level of teacher facilitation as students have more experiential activities.

Shirley Floyd, administrative assistant for Communication, Education, and Training, was recently appointed chairwoman of the Business and Professional Women’s (BPW) Texas Public Relations Committee. Shirley, who was the Amarillo BPW Public Relations Chairwoman in 1995-1996, won this year’s state competition. This is Amarillo’s second win in three years, both under Shirley’s leadership.

The Amarillo National Resource Center for Plutonium will provide programs for your civic clubs and organizations. To schedule, call Cathy Dixon at 376-5533.

The Panhandle’s TexPREP students develop problem-solving skills with hands-on learning activities. In this event, the students used engineering and physics skills to design protective devices for raw eggs that were dropped from 3-meter and 10-meter heights.

The Center is finishing work on an informational video that helps to explain what the Center is and the work we do. If you would like to receive or borrow a copy, please call Shirley Floyd at the Center.
Mixed Oxide Fuel, continued from pg. 2 that were reprocessed years ago in Washington state or South Carolina. 

ZERM: The work Pantex could do is a conversion process. We would not be engaged in a reprocessing activity. We are looking at what to do with the plutonium that already exists.

What would keep Pantex from becoming contaminated?
BAUMAN: Making mixed oxide fuel is not a liquid process. It is all dry, so there is no waste stream. There is no contamination in the air, there is no contamination of water, because it is a dry process. The only thing that has to be disposed of is the machinery.
JUBA: The nature of the work to be performed would be considerably different from the work done at any other site. In addition, the technology for environmental protection has improved a great deal in the nuclear industry, just as it has in other industries. With France’s 30+ years of mixed oxide fabrication experience, the U.S. would not have to “reinvent the wheel.”

Also, the modern environmental protection processes employed in current plants would provide continuous monitoring and keep environmental problems from ever escalating.

SELIGER: I think the answer to that is that we can manufacture mixed oxide fuel without reprocessing it and without the risks that accompany reprocessing. The fuel would come directly from pits.

What was your overall impression?
BAUMAN: I would say I was openminded but skeptical when we went. I wasn’t in favor of plutonium in anything—I wished it didn’t exist. But we have plutonium and we have to do something with it. I was open minded to see what could be done. I came away enthusiastically supporting a mixed oxide fuel plant for Amarillo. The safety factors I saw built in, the automation, the fact that the environmental controls have gotten so good that they now are well below the government mandated levels of radiation release all influenced my change in perspective.

I liked how clean it was and how it would basically have no impact on the environment, except in a positive way because we are talking about converting plutonium into a fuel, which is used to generate electricity.

BURGESS: My overall impression of the mixed oxide fuel plants was favorable. All the plants we visited were sensitive to employee safety standards. They were also maintaining a stable eco-system around the nuclear plants. After visiting with the local citizens in the various communities, it appeared that the nuclear plants and the communities had a normal and compatible relationship. Additionally, the local people felt that employee opportunities at the nuclear plants contributed to a stable work environment in the areas.

From an environmental perspective, were you comfortable that mixed oxide fuel production could be an acceptable new mission for Pantex?
BAUMAN: I am a biologist and I understand biological and ecological concerns even though my research was in cell biology. I came away enthusiastically convinced that we need to get rid of our plutonium using mixed oxide fuel. That’s what the country needs to do. As a citizen of Amarillo, I would like to see it done here—for the jobs, but also because it makes sense. The plutonium is already here. Building a plant at Pantex to convert this plutonium makes economic sense, ecological sense, and is logical.

ZERM: For me worker safety is paramount, and before the environment would be affected, employees would be. I would not compromise employee safety. I came away with a very good feeling toward the mixed oxide fuel process. I saw that it is being accomplished with a minimum of risk to workers and the environment and I saw that the plants went to great extremes to maintain high levels of safety. They took minimal risks.

Overall, I was very impressed and I see no reason that if the mixed oxide fuel mission were located at Pantex that the same level of safety could not be attained here. I believe it is a very viable process for us.

Resource Center Names Technical Director

The Center has named Dr. Richard S. Hartley as the Center’s Technical Director. In his new position Dr. Hartley is responsible for identifying technical research opportunities for the Center and addressing concerns of the State of Texas and the U.S. Department of Energy.

Dr. Hartley holds a Ph.D. in Nuclear Engineering from the University of Texas at Austin, a Master of Science in Nuclear Weapon Effects from the Air Force Institute of Technology, and a Bachelor of Science in Physics from Texas A&M University. He recently retired from the Air Force and brings the Center 19 years of technical experience in environmental and nuclear engineering. His experiences include coordinating with the Department of Energy, the White House Office of Science Technology and Policy, and the Nuclear Regulatory Commission.

Most recently Dr. Hartley has served as an Assistant Professor of Nuclear Engineering and the Environmental Engineering Curriculum Chair in the Department of Engineering Physics at the Air Force Institute of Technology (AFIT). In this role, Dr. Hartley supported the Air Force Environmental Management Program and developed an environmental engineering masters degree program.

Prior to AFIT, Dr. Hartley spent three years as a program manager for the Defense Nuclear Agency in Alexandria, Virginia. He directed 166 scientists from foreign countries, national laboratories, universities, government agencies, and private contractors in support of all Department of Defense nuclear winter and nuclear weapon fire research.

Additionally, Dr. Hartley has headed field operations for the Air Force Technical Application Center in Fairbanks, Alaska and has headed the Nuclear Analytical Laboratory in Sacramento.
Center working with Russians to determine best disposition options for excess plutonium

American and Russian scientists are collaborating on efforts to determine how best to utilize and/or dispose of plutonium following the end of the Cold War. Toward that end, the American and Russian scientists met in Washington D.C. from May 13-17 and again in St. Petersburg, Russia from July 15-19 at a steering committee meeting of the Joint U.S./Russian Plutonium Disposition Study Groups. The steering committee, which is made up of representatives from the national laboratories, the Executive Office of the President Office of Science and Technology Policy and the Department of Energy met with the American and Russian co-chairs of the technical working groups.

Working group chairs reported on their research in the areas of fast reactors, geologic disposal, immobilization, water reactors, storage, stabilization, non-proliferation, and economics. Additionally, the steering committee discussed proposals for further technical cooperation in plutonium disposition technologies and approved six new projects.

Dr. Dale Klein of The University of Texas, the Executive Director of the Center; Dr. Lee Peddicord of Texas A&M University, a member of the Center’s Governing Board; Dr. Rick Hartley, the Center’s Technical Director; and Dr. Igor Carron, the Center’s liaison from Texas A&M University provided support for the Washington meeting.

Drs. Klein and Peddicord attended the meetings in St. Petersburg.

Do you have a question?

A primary objective of the Amarillo National Resource Center for Plutonium is to answer Amarillo citizens’ technical questions about plutonium, its use and disposition options and, whenever possible, questions about plutonium, specifically in relation to Pantex.

Not all questions are answerable at this time. For instance, we don’t yet know which of the three disposition options (deep borehole, immobilization, and/or mixed oxide fuel) the government will choose—or do we know which site(s) will be designated the preferred locations. However, we do have scientists and engineers from three university systems, involving more than 20 campuses, and if you have questions, we would like to ask these questions of our researchers. The questions you address to the Center will help shape our communications to better address the interests of the community. Many of your questions will be answered in future newsletters, others will become a part of future presentations, and others will be addressed in future press releases.

If you have questions, please send them to Communications Coordinator, 600 S. Tyler, Suite 800, Amarillo, TX 79101. Please include your name and phone number in case we need clarification.
FOR IMMEDIATE RELEASE

AMARILLO NATIONAL RESOURCE CENTER FOR PLUTONIUM CONvenes MEETING OF TOP PLUTONIUM EXPERTS THIS WEEK IN SAN FRANCISCO

A group of scientists, industry leaders and policy experts is meeting in San Francisco at the request of the Amarillo National Resource Center for Plutonium this week to discuss options for disposition or use of the 38 metric tons of weapons plutonium left over from the disassembly of nuclear bombs.

Called the Senior Technical Review Group, this group advises the Center, a consortium of three Texas universities conducting research supporting the U.S. Department of Energy on plutonium issues. All nuclear weapons are disassembled at the Pantex Plant near Amarillo, and about 60 percent of the nation’s excess weapons plutonium is being stored temporarily at the plant until the DOE develops a plan to store, dispose of, or use the plutonium. The Center is conducting research into DOE’s disposition options and is providing research support and verification on environmental and nuclear issues facing the Pantex Plant.

Among the 17 members of the group is Dr. Glenn T. Seaborg of the Lawrence Berkeley National Laboratory, who discovered plutonium in a Berkeley laboratory in 1940 and received a Nobel Prize for his discovery. The group also includes Richard T. Kennedy, a retired U.S. ambassador; Myron Kratzer, former assistant secretary of state; Kenneth L. Woodfin, retired admiral and former NASA assistant administrator; and Dr. Wolfgang Panofsky, director emeritus of the Stanford Linear Accelerator Center. Six of the group are members of the National Academies of Science and Engineering.

The group will meet Oct. 23-24 to discuss several pressing issues, including joint Russian-U.S. programs on plutonium disposition, the conversion of weapons plutonium to mixed-oxide

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fuel for nuclear power plants, nuclear non-proliferation, and the DOE’s upcoming decision on the disposition of excess weapons plutonium.

In a September 1996 report, the group recommended that the DOE convert excess plutonium in metal form to a mixed-oxide fuel for nuclear electric generating plants. Other forms of plutonium, the group has said, should be encased in glass in a process known as “vitrification,” or encased in ceramic. These glass or ceramic packages would then be permanently stored deep underground.

The reactor fuel option is popular with Russia, which also holds a large quantity of excess weapons plutonium. When used as fuel, plutonium is rendered almost useless for nuclear weapons, and it can generate great amounts of electrical power. Excess plutonium is more vulnerable to terrorists in Russia, so the need to generate electricity from plutonium is greater there. Russians are opposed to the U.S. vitrifying all excess plutonium because they view vitrification as a storage method from which plutonium could be retrieved and potentially re-used in nuclear weapons.

Reactor fuel made from plutonium is called mixed-oxide fuel because it is a mix of plutonium oxide and uranium oxide. Several companies in Europe fabricate this type of fuel for use in European nuclear power plants. All nuclear reactors generate plutonium, and by the end of a reactor’s fuel cycle, about 45 percent of the electricity generated is coming from plutonium. No U.S. utilities currently use mixed-oxide fuel in reactors, although 17 U.S. and Canadian utilities have expressed interest in using mixed-oxide fuel made from weapons plutonium.

The Amarillo National Resource Center for Plutonium is conducting research on plutonium disposition options through its university consortium, which is made up of The Texas A&M University System, Texas Tech University, and The University of Texas System. In addition, the

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resource center is conducting research into environmental issues at the Pantex Plant. The resource center was established in early 1995 with the mission of conducting scientific and technical research, advising decision makers, and providing information on the use and disposition of materials from nuclear weapons disassembly while building academic excellence in science and technology.
AUSTIN — If you have ever watched a dramatic court case unfold, you know how difficult it can be to determine the truth. Most of us believe we know the appropriate result after the prosecution presents its case. But, after the defense presents its side, we aren’t so sure.

Amarillo isn’t facing a court case, but when it comes to discussing possible future missions for Pantex, the city is receiving a lot of highly technical information. As cases are presented, it’s easy to become confused. As in any court case, people want to know, “What can I believe?”

Starting last year, the Department of Energy provided funding to the State of Texas to establish the Amarillo National Resource Center for Plutonium. A primary purpose of the Center is to provide factual information and answers to the public regarding the use and disposition of plutonium. The Center is a consortium of The University of Texas System, The Texas A&M University System, and Texas Tech University. This arrangement ensures the autonomy and academic excellence of the work of the Center.

The core issues Amarillo citizens face are how to assess the risks associated with Pantex’s current missions, which provide thousands of high-paying jobs, and how to assess the risks of potential new missions. Because, as the job of dismantling the nation’s excess weapons winds down, so will Pantex’s employment. The plant is slated to lose 1,200-1,600 jobs by the year 2000. The good news is that the community might be able to obtain a new mission for Pantex that would replace some of those lost jobs with new ones.

The end of the Cold War and recent treaties that have resulted in fewer nuclear weapons ensure that any significant new missions at Pantex would revolve around use and disposition of the plutonium that Pantex has removed from bombs. It is clear that the plant will be significantly downsized unless it receives new missions.

In the Amarillo National Resource Center for Plutonium’s efforts to provide facts and information, the Center, through the three universities, is doing a great deal of research. We have more than 120 researchers studying these issues, which are of great interest to Amarillo. These researchers are nuclear physicists, nuclear engineers, agricultural scientists, mechanical engineers, environmental engineers, civil engineers, and more. They are researching and applying environmental protection methods and technology; and they are researching safe and secure methods for handling, disposition and use of excess weapons plutonium. One use currently being studied is to convert plutonium to mixed oxide fuel for nuclear power plants.

Though the DOE has outlined some specific options, the Resource Center’s research is not complete. From a scientific point of view, however, there are two things we do already know.

First, and I am speaking from an environmentalist’s point-of-view, is that Pantex is a remarkably clean site. If I were evaluating an industrial facility and saw the levels of contamination I see at Pantex, I would say, “They don’t have much of a problem.” I would also say, “Be more careful.” But I would say that to any facility.

Our environmental sampling analyses are, to date, always within the same range as Pantex’s, and we have never seen any unexpected contamination. The plant publishes all its environmental data every quarter, and all samples are made available to the public. From our vantage point, it appears that Pantex, environmentally, has gone to incredible lengths to be a good neighbor in recent times.

It is evident that environmental concerns are prominent in our nation’s policy, and Pantex is conducting a comprehensive environmental remediation program. It makes sense because, when the Plant was built in 1942, the nation’s objective was to build bombs quickly, and less emphasis was placed on the environmental concerns.

Today, however, environmental regulations are stringent. They call for many service stations and industrial sites—even farms and ranches that have old pieces of equipment rusting in the fields—to undergo environmental remediation. Pantex’s current environmental remediation projects will be complete by the year 2000. Landfill remediation will begin in 1998 and should be complete by the year 2000. The perched aquifer remediation is being tested and will be significantly expanded by 1999.

The second thing we know is that the Pantex Plant is careful in its operations. The plant changed its waste management practices drastically in the mid to late ’80s. Today, it is in compliance with the Resource Conservation Recovery Act of the Environmental Protection Agency (EPA), which is administered by the Texas Natural Resource Conservation Commission (TNRCC). All DOE complex sites are moving toward compliance, but Pantex has gone well beyond the minimum requirements.

This isn’t from the scientific perspective, but the Center also knows a third thing. We, the researchers who work for the consortium, will continue to watch the plant. We will continue to observe the DOE, we will continue to research, and we will communicate the results of that research. If things change, and particularly if we begin to have real concerns, we will say so.

The Amarillo National Resource Center for Plutonium isn’t the judge. We aren’t the jury. We aren’t pro-Pantex, but neither are we anti-Pantex. I like to think that the Amarillo National Resource Center for Plutonium is a group of unbiased expert witnesses. We are working with top-notch scientists in order to present you with the facts that will help you make up your own mind.

As you ponder about environmental questions, and as you wonder about appropriate new missions for the plant, I hope you will remember the Amarillo National Resource Center for Plutonium. The Center will provide speakers for your meetings, answers for your questions, and will call things like we see them. We won’t tell you what to think, but we will work to put the information in perspective so that you may draw your own conclusions.

Randall J. Charbeneau, Ph.D., is director of the Center for Research in Water Resources at the University of Texas at Austin. He serves as environmental program coordinator for the Amarillo National Resource Center for Plutonium.
Amarillo National Resource Center for Plutonium

Peer Review of Program Report Form

FY 1997

Instructions: This Peer Review of Program Report Form is to be used to record the review committee's evaluation of one of the Center's programs (nuclear, environmental, or education).

- In the case of each program, combine the evaluation data from all of the Peer Review of Proposal Report Forms, summarize and record the comments and recommendations of the committee on this form.
- In the case of the education program, include an assessment of the Center's education program plans for an evaluation of the overall education program.
- From the committee of reviewers, select a committee chair who will summarize the evaluation data of each reviewer, and record the comments and recommendations of the committee on this form.

Use the following criteria in the priority listed to evaluate the overall program.

1. Relevance of the program to the mission and goals of the Center.
   a. Clearly stated objective(s) and outcome(s) of the program.
   b. Likelihood that the program will contribute to the accomplishment of the Center's goals.
   c. Evidence of collaboration with the U. S. Department of Energy (DOE), national laboratories, the Pantex Plant, consortium universities, or other institutions involved with the Center.

2. Intrinsic merit.
   a. Soundness of the proposed approach.
   b. Likelihood that the program will lead to new discoveries or fundamental advances within the field.
   c. Adequacy of plans for evaluating progress and results of the program.

3. Plan and budget.
   a. Realistic schedule.
   b. Appropriateness of budget.
   c. Percentage of effort to be expended in the Amarillo area.
4. Performance competence.
   a. Capability of program personnel in relation to this program.
   b. Past performance of program personnel in relation to this program.
   c. Adequacy of institutional resources.

Use the following five-point scale to rate the program against the criteria.

5  Excellent  The program meets the criteria. It exceeds the expectations of the review committee.
4  Very Good  The program meets the criteria. If adopted, the recommendations of the review committee would make this an excellent program.
3  Good      The program meets the criteria. However, recommendations of the review committee should be strongly considered in order to make this a very good or excellent program.
2  Fair       The program does not meet the criteria. If adopted, recommendations of the review committee would make this a better program.
1  Poor      The program does not meet the criteria. A complete revision is required.

Additional Comments:

Date of Review: September 19 and 20, 1996

Title of the Program: Education

Program Point-of-Contact:  Dr. Elda D. Zounar
                          Effie J. Harle
                          Phillip T. Nash
Amarillo Independent School District

To: Elda Zounar
From: Lynn McGee
Subject: High School and Middle School Research Labs
Date: November 14, 1996

In regard to the joint project to establish a Tech Lab at Caprock High School and Fannin Middle School, we have accomplished the following task to date:

- We have set aside matching district funds to accomplish the project.
- We have traveled to Wichita Falls and Ft. Worth, Texas to examine tech lab facilities. These fact finding trips were of great interest to the staff and principal; however, we felt that these labs would be a duplication of existing labs in the Amarillo school system.
- Teachers have been given release time to search out and examine software packages that will equip the students with a process that will enable them to actually participate in an ongoing research project.
- With the help of Effie Harle, we were able to seek and acquire the help of Dr. Eric Taleff. Dr. Taleff has shown great interest in the project and has been very helpful with advice as to proper software that might be appropriate in the research labs.
- Principals and staff have attended the demonstration of the new electronic library and are excited about the possibility of working with and through this new system.
- We have made numerous contacts with various educational tech lab and software companies. In doing so we have discovered that there is little interest in developing a project of this nature at the secondary level.

This only encouraged us to continue an in-depth planning process that will enable us to establish parameters for our research lab that will break away from the traditional "Tech Lab" concept where students work with canned modules that limit the scope of study and will become outdated in a few years. The real live research concept is what we are looking for. We have students and teachers who are ready for this kind of project and we do not want to limit them to a narrowly focused idea that they will soon become bored with and lose interest. Many high school students are ready for this kind of study program and we would like to break new ground with a project of this nature in Amarillo.

Through the cooperative effort of community organizations, agencies, industry, and individuals; the secondary education environment will be able to embrace the change necessary to provide all students with high level skills in order to meet the needs of the global work force of the twenty-first century. Amarillo Independent School District is grateful to the Amarillo National Resource Center for Plutonium for your gracious financial gift; but, your willingness to serve as a catalyst in the development of partnerships with institutions of higher learning as well as area industry is equally if not more important. Thank you.
October 7, 1996

Amarillo National Resource Center for Plutonium
Education Program Coordinator
600 South Tyler, Suite 800
Mail Box 12098
Amarillo, Texas 79101

Dear Ms. Harle:

I would like to personally thank the Amarillo National Resource Center for Plutonium and you for underwriting the cost of bringing the quality presentation of the Texas A&M Chemistry Road Show to the students of Horace Mann Middle School.

Mr. Erik Walke’s performance was outstanding. He successfully motivated our students concerning the wonders and excitement of science. We continue to field questions from our students as to the why and how a certain reaction takes place. We are building upon the enthusiasm of the students and anticipate keeping the momentum going through the course of the school year.

We believe it is important for our students to experience dynamic performances that teach abstract concepts with concrete examples. The Texas A&M Chemistry Road Show is a phenomenal means to expose students with limited resources to the wonders of science and the applications that it has in their daily lives.

Again, thank you for allowing the Horace Mann students the opportunity to participate in the Texas A&M Chemistry Road Show. We hope to once again participate in the programs offered by the Amarillo National Resource Center for Plutonium and look forward to seeing you again.

Sincerely,

Gail Sanchez
Science Department Chair
November 5, 1996

Effie Harle, Education Program Coordinator
Amarillo National Resource Center for Plutonium
600 S. Tyler, Suite 800
Amarillo, Texas 79101

Dear Effie,

Many thanks for all your efforts in arranging the Chemistry Road Show for five of our middle schools. Student and staff response to the show has been overwhelmingly positive, and the ANRCP is to be commended for sponsoring such an educationally inspiring program.

Each principal of a school where the show took place called to tell me how delighted he or she was with the quality of the presentation. I know from their calls that students were enthralled and their interest in science rejuvenated by what they saw.

An added bonus for me was that for weeks after the Chemistry Road Show, when I saw students or teachers who had attended, they made it a point to tell me how wonderful it was.

Again, thank you, Effie, for arranging for all of the marvelous performances of the Chemistry Road Show and for accompanying Erik Walke as he visited our campuses. It is, as always, a pleasure and an honor to be associated with ANRCP.

Sincerely,

Laurie Cizon
By DAVID SMALL
Globe News Feature Writer

A chemist from Texas A&M University at College Station took his show on the road in September during a five-day stopover to demonstrate the wonders of science for students in the Texas Panhandle.

Erik Walke, a research associate in Texas A&M's department of chemistry, took the Texas A&M Chemistry Road Show to several spots in Amarillo and Panhandle to show students that science can be fascinating and fun.

Walke made stops at Horace Mann, William B. Travis, David Crockett, Sam Houston and James B. Bonham middle schools in Amarillo and Panhandle and Bushland middle schools to enlighten and entertain students with a variety of dynamic experiments.

Walke also hosted a special version of the show for adults during the Sept. 25 lunch hour in downtown Amarillo.

During Walke's stop in Bushland, he began his show with a burning book and finished with a bang—several bangs, to be exact.

Walke captured students attention at the outset of the show by unleashing a flurry of flames as he opened a specially rigged book.

"This (book) is a symbol of the difference between science and magic," Walke said.

He proceeded to conduct a series of chemical experiments that rivaled the visual mystery of a magic show, but Walke offered scientific explanations for each display.

Walke described the inner workings of his burning book, which contained a simple camping lantern's lighting device inside its hollowed core.

Walke then made a fully inflated balloon shrivel, without releasing its air, by immersing it in liquid nitrogen, which maintains a temperature about 400 degrees colder than room temperature, he said.

The balloon inflated on its own once Walke removed it from the nitrogen, demonstrating the way air compresses at lower temperatures and expands at higher temperatures.

Walke also entertained students by making a steel ball explode and creating a fountain of colorful foam using hydrogen peroxide, dish soap and a chemical catalyst.

Bushland students held their ears as Walke created a thundering finish for his show.

He ignited several balloons containing different combinations of oxygen and hydrogen to see which gas was more combustible.

A series of small explosions followed, rattling the boards on Bushland's gymnasium floor and making students scream with laughter.

Walke said the road show normally travels only in the College Station vicinity, but the school hopes to establish a similar road show to travel to schools across the Panhandle.

Walke helped train two West Texas A&M University graduate students to host the road show during an appearance at the school's science and math conference on Sept. 28.

He said the show's goal is to make science more appealing and less intimidating to students.

"We're trying to prevent a lot of the 'chemi-phobia' that exists in the classrooms," he said.

The Chemistry Road Show's local appearances were sponsored by The Amarillo National Resource Center for Plutonium, a research consortium of the Texas A&M University System, the Texas Tech University System and the University of Texas System.

The Amarillo National Resource Center's mission is to serve as a scientific, technical and informational resource for the citizens of the Texas Panhandle, the State of Texas and the U.S. Department of Energy on issues related to the storage, use and disposition of plutonium and other materials from weapons disassembly, according to a news release from the center.
Amarillo National Resource Center for Plutonium

Quarterly Progress Report
for the period
1 August 1996 - 31 October 1996

Nuclear Group Detailed Reports
Plutonium and Other Materials Studies
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GENERAL ABSTRACT FOR DETAILED REPORT

This document contains detailed Quarterly Progress Reports on currently funded activities of the Nuclear Group of the Amarillo National Center for Plutonium for the period 1 August 1996-31 October 1996. A separate compilation of the Executive Summaries is available for those who require more abbreviated information. The Executive Summaries have been left in place in the following detailed reports because, in many cases, they act as introductions and provide context for the rest of the discussion.
EXECUTIVE SUMMARY:

During the current reporting period (1 August 1996-31 October 1996), coordination and technical information support activities have consisted of the following:

- Fifteen New Technical Library Acquisitions
- Expansion of the Centralized Information Web Site
- Update and Dissemination of the Calendar of Conferences (formerly Technical Calendar)
- Attendance at two DOE Informational Meetings or Workshops
- Eight Internal Technical Working Documents (ITWDs)

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

I. Flow of Information to the Nuclear Group

A. Technical Library Acquisitions

The Nuclear Group Technical Library continues to be maintained at Center headquarters in Amarillo. The following documents were added to the library during the current reporting period:


- Physor 96 Breakthrough of Nuclear Energy by Reactor Physics proceedings, Vol 1-5, Mito, Ibaraki, Japan, September 16-20, 1996.
- Draft Nonproliferation and arms control assessment of weapons-usable fissile material storage and plutonium disposition alternatives, DOE, Office of arms control and nonproliferation, October 1, 1996.
- Summary of the Mixed Oxide Fuel meeting for Texas regulators, SECO-PTX-96-01.

B. Centralized Information Web Page

The centralized information web page (http://trinity.tamu.edu/~igor/hi.html) continues to provide Nuclear Group participants a rapid and efficient survey of documentation and news relevant to their subjects of investigation. The site allows rapid and direct access to the DOE and other organizations' libraries and databases. Dr. Carron and Ms. Alexander share responsibility for maintaining this web site.

C. Public Information Hearings

No formal public information hearings were attended this quarter.

D. Participation in DOE-MD Meetings

No DOE-MD meetings were attended this quarter. However, David Boyle participated in other meetings with various DOE offices (not MD).

E. Newsletter

Newsletter 5 is currently being compiled.

F. Technical Calendar (Calendar of Conferences)
The Technical Calendar has been converted to the Calendar of Conferences and is now readily available on the web (http://trinity.tamu.edu/~igor/hi.html). The calendar is updated every time a new conference relevant to the interests of the group is advertised, or when a currently-listed conference has transpired. The text of the calendar is sent to Nuclear Group participants by electronic mail on a monthly basis. The last such transmission occurred on October 4, 1996. Dr. Carron and Ms. Alexander share responsibility for maintaining this calendar.

G. Storage Programmatic Coordination

David Boyle performed the following activities during the current reporting period:

1. Participated in a teleconference concerning possible ANRCP work in conjunction with the DOD's Cooperative Threat Reduction (CTR) Office. Based on the results of this teleconference, he engaged the CTR program office responsible for Russian storage activities and began an ongoing dialog to investigate potential areas of joint or cooperative research on transparency issues.

2. Worked with the ANRCP Technical Director during his review of storage-related activities at Texas A&M in preparation for the formal peer review of FY 1997 nuclear group technical proposals.

3. Supported the peer review team for two days at Amarillo; providing information on and answering questions about the storage-related proposals. He also received the peer review team's formal feedback briefing on all nuclear group proposals.

4. Prepared quad-chart briefing materials on storage-related projects for use by ANRCP management during the Center's initial briefing to HQ DOE-DP officials.

5. Drafted proposed letter from the ANRCP to the Governor's office (and other state officials) commenting on pending DOE preferred alternative for long-term storage. Advanced word on this preferred alternative is that Pantex will be chosen as the site for storage of all (excess and strategic reserve) pits. The proposed letter explains advisability and impacts of this preferred alternative and answers typical questions expected to be raised by the public and the press. This draft letter will be circulated for comments to appropriate ANRCP managers and PIs prior to formal distribution.

II. Flow of Information from the Nuclear Group.

A. Organization of Quarterly Meeting for the Nuclear Group

No meeting was held during the current reporting period. The next meeting of the Nuclear Group is scheduled for November 20-21, 1996, in Amarillo.

B. Prepare Quarterly Progress Report Describing Activities of the Nuclear Group.

A Quarterly Progress Report was submitted to the Center on August 12. The fifth of these Quarterly Progress Reports consists of the present document.

C. Technical Report Series

In September 1996, the Nuclear Group initiated an Internal Technical Working Document (ITWD) series. Eight reports have been produced and disseminated.

D. Annual Report

No discussion ensued on this item during the current reporting period.
E. Public Outreach/Education

David Boyle evaluated DOE's Draft Nonproliferation and Arms Control Assessment of Weapons-Useable Fissile Material Storage and Plutonium Disposition Alternatives and participated in a teleconference discussing this draft report. Based on the teleconference results, he composed formal comments to be passed from ANRCP to DOE-NN at a public hearing to review this document in Amarillo (4 November 96).

Dr. Carron was also involved in the comments of the Center to the draft of the nonproliferation and arms control assessment of weapons-usable fissile material storage and plutonium disposition alternatives.

David Boyle also corresponded via e-mail with Prof. Khromov at MEPhI, providing assessment of and questions about his proposed MS program on nuclear materials management.

Dr. Carron helped the Center in the preparation of the presentation on Mixed Oxide Fuel to the regulators of the state of Texas. This presentation was held in Austin on August 29 and 30, 1996.

III. Global Information Flow

A. Workshops Devoted to Specific Technical Issues of Interest to the Center and DOE-MD

David Boyle traveled to LANL and met separately with personnel from the Los Alamos Critical Experiments Facility and from the LANL Nonproliferation and International Security Division. Discussions centered on developing potential course materials and training concepts for Prof. Khromov's proposed MS program and on potential joint research in the general area of transparency quantification.

David Boyle also traveled to Washington, DC and met with DOE-NN personnel in charge of DOE's support for the Khromov MS program. The purpose of the meeting was to coordinate our activities to ensure efficiency and eliminate duplication of effort during this joint ANRCPEexas A&M/DOE-NN endeavor.

B. National and International Conferences on Broad Topics of Interest to the Center and DOE-MD

David Boyle attended PSA-96 (Probabilistic Safety Assessment) Conference, Sept. 29- Oct. 3. He collected current research results and information germane to safe storage of weapons-useable plutonium, aircraft crash analysis tools, and quantification of transparency and other subjective security measures.

David Boyle also reported attending the Institute of Nuclear Materials Management annual meeting in the last quarterly report. During this quarter, he distributed abstracts of that meeting's technical papers to key ANRCP PIs and composed an article for the Nuclear Group Newsletter which summarized the meeting.
EVALUATION OF FAST REACTORS

W. D. Reece (PI), Department of Nuclear Engineering, Texas A&M University

During this quarter, the funds for transferring the safety codes developed for and used at FFTF (Fast Flux Test Facility) to the Russians have finally been approved. The efforts here to facilitate in the capture of the experience at FFTF seems to have been successful. Because the DOE funding levels are small, the FFTF staff have requested that their efforts start in January and extend for five months, with no analyses on Russian reactors to be done this year. We have been queried if we could help convert some of the codes from large mainframe formats to run on SPARC workstations, but thus far we have no students identified and no faculty time available.

Modular High Temp Gas Cooled Reactors

This task has been redirected. Please refer to the subproject entitled, "Water Reactor Options for Disposition of Weapons-grade Plutonium."

TRITIUM PRODUCTION USING ACCELERATOR-DRIVEN TECHNOLOGY

Theodore A. Parish (Co-PI), Department of Nuclear Engineering, Texas A&M University

EXECUTIVE SUMMARY:

Work on this task concludes this quarter due to its exclusion by the Joint Steering Committee from the US/Russian Joint Studies work. During the current reporting period, a final report entitled, "Accelerator Driven Production of Tritium: Target and Blanket Design" was completed and has been submitted for publication as a Nuclear Group Internal Technical Working Document. (information on this document series appears under "Coordination and Technical Information Support for Nuclear Group Activities" above.)
EXECUTIVE SUMMARY:

The task of supporting the US/Russia joint study team on water reactors continued to move forward. Drs. Adams and Peddicord visited IPPE and INPE in Obninsk, attending a workshop on plutonium disposition. Some information was gained about the Russian plutonium complex, about the capabilities of various institutes in Russia, and about the possibility of further collaborations with Russian researchers on the use of MOX in VVER-1000 reactors. Dr. Adams also attended a meeting at ORNL in September, at which US and French researchers discussed their respective collaborations with Russian researchers.

Since the Joint Steering Committee meeting in St. Petersburg in July, Dr. Klein has been in constant contact with the different Russian Institutes and US National Laboratories involved in the future Experimental Test Programs. Subsequently to the Joint Steering Committee meeting, a second set of subcontracts was drafted in order to include appropriate milestones. Two of these subcontracts have been signed during the present reporting period.

Dr. Igor Carron visited the Moscow Engineering Physics Institute on October 17-18. The trip was sponsored by a linkage grant of NATO Scientific Affairs Division (Disarmament Technologies). The discussion of relevance to the Russian activities of the Amarillo National Resource Center for Plutonium included an informal review of some of the results obtained by MEPPhI researchers on research performed for the Center. The deliverables of this activity include a final report which was not available at the time. This deliverable is due in November. More specific discussion included interaction between MEPPhI and the Center on one item of the MEPPhI subcontract dealing with the establishment of a Master of Science program (Dr. David Boyle is monitoring this activity for the Center). The primary aim of this visit was to improve the working framework between the MEPPhI research group working on plutonium bearing fuels with uncertain irradiation history and the group of Dr. Naeem Abdurrahman (University of Texas) who is the Center's monitor for this project. A visit to Texas of MEPPhI researchers was arranged for the beginning of next year.
For information on coordination with DOE laboratories, please see also item I.G, “Storage Programmatic Coordination,” under the above subproject entitled, “Coordination and Technical Information Support of Nuclear Group Activities.”

POST EXPLOSION TRANSPORT (PET) STUDY

Dr. Dale Klein (PI), The University of Texas System

Steven Manson, Department of Mechanical Engineering, The University of Texas

EXECUTIVE SUMMARY:

This research has been undertaken to augment the computational models currently used to perform safety analyses of the PANTEX cell facilities. In the event of an accidental chemical explosive transient during disassembly activities, there is some concern that a release of plutonium aerosols may result. The computational modeling of some accident scenarios has been limited by the one-dimensional approach of the MELCOR code. This effort uses multidimensional techniques to analyze the natural convection which drives the flow of particulates within the cell room in the aftermath of an explosion event.

The accident scenarios considered in this research are limited to those in which the roof of the cell room remains intact. The cells are designed such that a detonation of sufficient magnitude will destroy the roof, causing an over-burden of sand and gravel to fall in and contain the explosion. This containment feature will also act to filter dangerous aerosols out of the escaping gases. If, however, the inventory of chemical explosive present in the cell facility is insufficient to cause the failure of the roof, unfiltered gases may escape to the environment carrying some inventory of weapons plutonium in particulate form.

Past studies of these contained explosions have been limited to numerical consideration of the flow paths as one-dimensional channels with pressure driven flow. This approach may be adequate in narrow rampways and through leakage sites, but the flow in the cell room itself is clearly multidimensional. Multidimensional flow in the cell controls the mixing of particulates and the air, and hence is crucial to modeling aerosol transport. Furthermore, depressurization of the cell room is accomplished over relatively long times (>10 seconds), by both the leakage of air to the environment, and the cooling of hot gases through natural convection to the cell walls. This natural convection heat transfer is also multidimensional in character. Thus, this research effort will apply modern multidimensional computational techniques to post-explosion transient flow in cell facilities.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

In the past quarter, research efforts have centered on the completion of the Post Explosion Transport (PET) code. This code is now capable of solving transient thermal hydraulics problems in geometries sufficiently representative of the cell rooms. Previous versions of this code provided modeling capabilities in two-dimensional Cartesian space for flows well-represented by the Boussinesq approximation. Because of the temperature gradients involved and the actual geometry of the cell rooms, these constraints have been eliminated. The main tasks completed in the past
quarter involved adding compressibility and axi-symmetry modeling capabilities to the PET code. Verification and validation of the completed PET code is in progress, and is scheduled for completion in December, 1996.

The PET code uses a stream-function vorticity method to simulate transient compressible flow within enclosed cylindrical cavities. Development of this code has proceeded since 11/95, when a simpler research code was modified to allow basic modeling of post explosion transients. This code has been continually expanded to include the physics and geometry required to accurately model the problem. In the summer of 1996, verification and validation efforts revealed that that the algorithm for enforcing mass conservation over the Cartesian domain led to violations of the first law of thermodynamics. A new algorithm was implemented and debugged in August, and found to perform satisfactorily in subsequent verification efforts continuing into September. The remainder of the quarter was devoted to the development and implementation of cylindrical geometric parameters, which allow the PET code to model the cylindrical PANTEx cell facilities accurately. Verification and validation of the final form of the code is underway, and PET code results will be available in January, 1997.

A Basic demonstration of a typical transient solution of a PET code problem (compressible flow, low heat load, Cartesian geometry) is viewable on the world wide web at:
http://uts.cc.utexas.edu/~boyce/tanim.html

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Robotics

**ROBOTICS, AUTOMATION, AND TELE-OPERATION PROGRAM FOR SAFE HANDLING AND LONG-TERM STORAGE OF NUCLEAR COMPONENTS**

Alan A. Barhorst (Co-PI), Department of Mechanical Engineering, Texas Tech University
Richard A. Volz (Co-PI), Department of Computer Science, Texas A&M University
George V. Kondraske (Co-PI), Human Performance Institute, The University of Texas—Arlington
Mica Endsley, Department of Industrial Engineering, Texas Tech University
Louis Everett, Department of Mechanical Engineering, Texas A&M University
William Kolarik, Department of Industrial Engineering, Texas Tech University
Hua Li, Department of Computer Science, Texas Tech University
José Macedo, Department of Industrial Engineering, Texas Tech University
Michael Parten, Department of Electrical Engineering, Texas Tech University
John W. Poston, Sr., Department of Nuclear Engineering, Texas A&M University
S. V. Sreenivasan, Department of Mechanical Engineering, The University of Texas
Jeffrey C. Trinkle, Department of Computer Science, Texas A&M University
Jeffrey Wolstad, Department of Mechanical Engineering, Texas Tech University

**EXECUTIVE SUMMARY:**

The following tasks were performed during the past quarter:

**Activities at Texas A&M University**

- A stability tool for a generic manipulator/gripper is under development. Work this quarter involved embedding a stability-testing algorithm into TELEGRIP software package which is used for graphical animation.
- An animation tool capable of animating the static and dynamic motions of a generic manipulator/gripper is under development. A motion generation algorithm is being embedded into TELEGRIP.
• The Integration of TELEGRIP with InterAgent was carried out during the past quarter. The system is undergoing testing and will be in use shortly.
• The design of a Modularized Simulation Construction set has been started.
• The underlying models required for bi-directional tele-operation between Texas A&M University and Texas Tech University have been built, and TAMU has supplied underlying code necessary for operation. On time completion of this task expected.
• An initial demonstration of a Virtual Reality-based inspection system using the flock of birds 6 DOF sensors has been developed. Tests have been carried out to ascertain the working environment required for successful use of the FOB.
• A voice recognition card has been installed and integrated into the Texas A&M simulation test-bed.

Activities at Texas Tech University

• Construction and testing of the Teleoperations Graphical User Interface (TGUI) with the Automated Weigh and Leak Test (AWALT) simulation has been completed.
• Progress in the safety and reliability task has been good. A Ph.D. program is well underway based on the project. The Ph.D. defense of the topic is expected in the spring of 1997. Papers are in review.
• The self-assessment of reliability model has made good progress. A Ph.D. proposal is forthcoming and a paper has been submitted for review.
• The bi-directional link between TTU and TAMU robotics testbeds is nearing completion. It is expected that the work will be complete in two to four weeks. Internal to TTU work is progressing to connect the Mechanical Engineering robot and the IE robot using the same protocol. This work lags behind the TTU to TAMU link but is expected to be completed this quarter.
• Work on the high-fidelity manipulator modeling tool is progressing well. Three papers have been submitted for journal review. Progress on the implementation of the models into Telegrip has been delayed until the bi-directional testbed is fully functional.

Activities at The University of Texas at Arlington

• At UT Arlington, we continued our work toward performance modeling and measurement. During this period, we have had to address significant problems associated with upgrade of the basic communications software that supports our distributed robotics/remote operations work environment and, specifically, the resolution of compatibility with our custom performance measurement and monitoring software. This is an essential precursor to the execution of planned experimental work with other members of the robotics group. Work is nearing completion on the initial phase of our efforts to measure “motion quality”; a thesis will be presented on 11/26/96 detailing the findings of this work. In addition, we have continued to assemble our technical report on standards for distributed remote operations systems design to support performance measurements. Efforts to broaden the base of funding support for the performance modeling and measurement portion of the overall project have also been pursued via submission of a proposal (10/15/96) jointly with our Texas A&M colleagues, Hughes Training, Inc., and United Space Alliance (Rockwell, etc.) pertaining to teleoperations and remote operations.
Activities at the University of Texas at Austin

- The module modeling of wheeled vehicles is progressing as planned. Modular tools have been developed for machines that are comprised of serially connected holonomic sub-systems, a serial chain robot being an example of this arrangement. Work toward module models of nonholonomic systems is in progress.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

The following activities were carried out during the past quarter:

**Stability Tool Implementation**

The implementation has continued for a stability-testing tool for situations in which a nominally rigid object (e.g., a pit) is in contact with a fixture (e.g., a containment vessel) or robot gripper, or other objects in its surroundings. Since the last quarterly report, code has been developed that determines contact points and contact normals more efficiently than TELEGRIP. This success furthers progress in the implementation of the tool. Implementation of this tool is expected to be on time.

Application of the test involves locating the points of contact and the surface normal vectors at the contacts. The test is then formulated as a linear program which is solved efficiently using a canned routine available in the IMSL library. Note that the friction cone is approximated as a polyhedral cone so that the friction constraints are linear. The polyhedral cone that is used is inscribed in the quadratic cone, so that the stability test is conservative.

The frictionless test can be modified easily to determine if kinematic restraint is complete, which implies that the object cannot be moved by any externally applied force.

**Animation Tool Design**

The animation tool design is progressing well. It will be based on two types of multi-rigid-body contact models - one quasi-static and the other dynamic. It will be possible to simulate and animate the motions of all types of bodies (e.g., robots, wheeled vehicles, containment vessels, etc.). It will be assumed that bodies are rigid with Coulomb Friction acting at the contact points. The user will have the ability to choose from several different models (dynamic or quasi-static, and with or without friction), to allow the use of the one best suited for task analysis.

**Storage Facility Simulation**

It is of paramount importance to fully test the design of a storage facility, to make sure it will fit all the barrels or racks or robots that it is designed for. The price of building such a facility without a careful design is obvious. Therefore, there's a great need to simulate the storage and check the design thoroughly. On the other hand, building a detailed simulation is no easy task. Making the geometric models can be very time consuming. In fact, it can not meet the need of rapid prototyping for a on-going design. A method to construct the simulation rapidly is needed.

The idea is to modularize the simulation, each module being a self-contained simulation unit which can also interact with the outside. The module is also generic; in other words, it is not unique to a particular storage facility, rather, it is common for a storage in general. For instance, a barrel or a robot is a generic module. The modules can be made regardless of a particular storage, and they can be composed to form a simulation specially for a storage facility. This modularized design is carried out following the methodology of the Object Oriented analysis and design.
The difficulty in obtaining the current CSF report has hindered this effort.

Integration of TELEGRIP with InterAgent: TELEGRIP is a 3-D simulation tool widely used in DOE facilities. Adding to it the capability of communicating with InterAgent, which is the network protocol used in the existing Telerobotics simulation test-bed, allows the collaboration among other members of the team. The following have been completed in the past quarter:

- The geometric models of the parts of the Merlin Robot is converted from SSM format to Deneb format. The coordinate systems of the parts were redefined in TELEGRIP’ CAD world. The parts were then joined together to form a 6 DOF device in the Device world of TELEGRIP.
- Inverse Kinematics was assigned to the Merlin Robot in TELEGRIP, T-jog (a way to check the correctness of the inverse kinematics) was performed.
- TELEGRIP’s LLTI (Low Level Telerobotics Interface) feature was explored and was used to communicate between InterAgent and TELEGRIP. LLTI is a set of well defined C routines for setting up a binary socket connection to TELEGRIP and commanding the device to move. A C Program (lilt_interAgent) was then written to listen to a predefined InterAgent Object which has the position of the real Merlin Robot. It sends the positions of the real merlin robot to TELEGRIP through LLTI socket upon receiving an InterAgent Object.
- The RCCL_REMOTE running on the Lynx machine was modified to send out additional InterAgent Object for lilt_interAgent.
- A wireframe rendered Merlin Robot was also made in TELEGRIP to display the operator's desired position.

Achievement of Bi-directional Tele-operation

Remote operational capabilities are essential to the study of robotic teleoperation. Thus, by establishing bi-directional network control of their robots, both Texas A&M University and Texas Tech University can implement and test their research plans in a very realistic manner. To further capabilities on both ends, Texas A&M and Texas Tech have proposed to establish bi-directional tele-operation between their two labs. The one-way connection from Texas Tech to Texas A&M has been completed. Thus, the link from Texas A&M to Texas Tech is the current focus. For this task, Texas A&M assumes a support role while Texas Tech develops connections and control to their side of the bi-directional system. The graphics models and control code used by A&M were transferred to Texas Tech for use as a guide and template. A&M also provided support by answering questions, partitioning the task, and directing the effort. To establish bi-directional control, it is necessary for Texas Tech to create a system similar to that already established at Texas A&M. First, a graphic model of Texas Tech's Staubli robot was created. Next, a control tree for this model is currently being established and linked to the network via our communications package IAgent. Thus, IAgent listens for commands coming from Texas A&M. When a command is received, the Staubli control code will calculate the new requested position of the robot, check to see if the new position is valid, and if so, move the robot to the new position and update the graphic model and control tree to reflect the new position.

Completion of Virtual Reality-based inspection on the flock of birds 6 DOF sensors:

- Remote inspection of objects/devices in hazardous locations can be safely and effectively carried out via cameras mounted on mobile, robotic platforms. The motion of these cameras can be tied to the motion of the operator's head and the video images sent to a head-mounted helmet display, thus providing a three-dimensional image of the remote location just as if the operator were present in the hazardous environment. To establish a
system such as this, accurate and reliable position/orientation tracking in 6 DOF is essential. Such tracking devices are available and Texas A&M is currently using 4 Flock of Birds (FOB) 6 DOF sensors to this end.

- To determine the FOB sensor accuracy and reliability, extensive testing was completed. Since the sensors are based upon electro-magnetic fields, it is possible that certain items can interfere with them. Results of the tests were found to be better than expected. While such items do interfere with the sensors, these effects can be minimized in a controlled fashion to allow a high degree of sensing accuracy and reliability.

- The FOB sensors depend upon sensing their position and orientation with respect to a static electro-magnetic field. Since items such as large metal objects and computer monitors can distort this field, errors can be introduced into the readings. Thus, it is important to characterize the effects of such items. Extensive testing has been completed, and it has been discovered that careful preparation of the operating environment can eliminate or reduce the errors to acceptable levels. For example, computer monitor sync cables can be utilized to force the FOB sensors to read the field only between pulses of the monitors, thus eliminating the error. The effects of large metal objects can be reduced by maintaining a minimum distance from such objects. Small metal objects have been found to have an insignificant effect upon the sensors. Thus, an operator environment can be restricted in certain ways to guarantee acceptable accuracy and reliability. A typical restriction would be to not allow the sensors to return values within several feet of the walls, floor or ceiling.

A voice recognition card has been installed and integrated into the Texas A&M simulation test-bed:

- Some systems require the operator to wear a head-mounted display helmet. While such systems can be very realistic and provide a very intuitive interface, they can be difficult to interact with since the operator cannot see outside the helmet to use typical control devices such as keyboards, joysticks, etc. Thus, alternative methods of control such as voice and gesture recognition are needed. Luckily, these alternative methods also provide very realistic and intuitive interfaces to the system. An operator can execute an action simply by speaking the words. Similarly, an operator can move an object simply by moving his hand.

- To this end, a voice recognition card has been installed and integrated into well with a data glove which provides hand and finger motion and position sensing. Plans are underway to order a data glove and integrate it into the test-bed.

Construction and testing of the Teleoperations Graphical User Interface (TGUI) with the Automated Weigh and Leak Test (AWALT) simulation has been completed.

- To investigate the effects of LOA (Levels of Automation) on teleoperators in nuclear material handling, an experiment was designed on a Silicon Graphics computer. The aim of this experiment is to measure the performance, situation awareness (SA) and accuracy of teleoperators under five different LOA. Operator workload, physical demand, mental demand, and fatigue was also measured in different levels.

- The software for this experiment was written in C and X-Motif. Telegrip package and Graphics Simulation Language (GSL) by Deneb software was used for simulations. Hardware included a Silicon Graphics Indigo2 Maximum Impact computer with 196 MB of RAM and 250 MHZ R4400 CPU and a 21" color monitor.

- Ten subjects were recruited for this experiment. Each subject participated for a total of 15 hours in five consecutive days. Five levels of automation were tested in five days. During experiment sessions, subjects were given SAGAT queries and asked to respond
to NASA-TLX workload rankings in order to observe the effects of LOA. Levels of Automation and related training vs. test period lengths are given below:

<table>
<thead>
<tr>
<th>Level of Automation Training Period Testing Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Action Support</td>
</tr>
<tr>
<td>Batch Processing</td>
</tr>
<tr>
<td>Blended Decision Making</td>
</tr>
<tr>
<td>Supervisory Control</td>
</tr>
<tr>
<td>Full Automation</td>
</tr>
</tbody>
</table>

With 10 subjects total training and testing time was 150 hours. The data that has been collected is being analyzed.

Safety and Reliability

Progress dealing with the development and refinement of theory, with regard to the intelligent control model is complete. The process identification module and the control module have each been tested separately. This quarter both were tested together as a unit. Both performed well individually and together as a unit. Evidence of these tests is described in two technical reports which are being submitted separately for publication as Nuclear Group Internal Technical Working Documents (please see the detailed report, “Coordination and Technical Information Support for Nuclear Group Activities” for more information on this report series). Work to date appears promising for Ms. Patro to defend her research in the form of a Ph.D. dissertation sometime in the spring of 1997.

An interface was established with the Thermal/Mechanical Modeling of the Can-in-Canister Plutonium Immobilization Process Project. The purpose of this interface was to determine the nature of the glass pouring process they were modeling and to tentatively assess the potential of the intelligent control model for this type of application. A tentative evaluation was performed as to the nature of this process; our conclusion was that our intelligent control model is capable of working with this process. However, this work is not included in the scope of our current project.

The self-assessment of reliability model has progressed in theoretical development, nearing a Ph.D. research proposal phase for Mr. H. Lu. The theoretical work is nearly complete. Attachment three describes some of the work completed on this model during the last quarter. A physical prototype, capable of demonstrating the theory in a physical setting has progressed. Currently, we are in the process of interfacing our theory with a LabView data monitoring package. Near-term plans call for a single physical input - single failure mode demonstration in the first half of 1997.

One conference/proceedings paper was accepted and two additional conference/proceedings papers were submitted:

- Accepted:
  Patro, S. and W. Kolarik, “Neural Networks and Evolutionary Computation for Real-time Quality Control of Complex Processes,” accepted by the 1997 Reliability and Maintainability Symposium and Proceedings (see attachment one).
Submitted:


Human/System Performance Modeling and Measurement

Remote Operations Studies - 1997 Experiments: Data collection has been temporarily delayed. An upgrade of basic distributed operations networking software (InterAgent) across sites rendered our custom data collection software inoperable in that only a partial subset of the required data is accessed and saved for off-line study. This has resulted in the unplanned need to readdress software subsystems that have long been viewed as "complete and stable", which has stressed our limited project resources. Progress has been made and it is anticipated that this issue will be resolved within the next quarter.

Motion Quality Measurement: Experimental data (using human-generated end-effector motion trajectories) and analyzed to test the concept that a multiplicative combination of certain lower level parameterizations yielded the best agreement with human subjective judgements of motion quality. This hypothesis was supported, which we believe will be viewed as a major breakthrough in many fields in which motion quality is of interest. Details will be presented in a thesis during the Fall 96 semester by graduate student Carl Fischer. Mr. Fischer recently received a 2nd place award for this work in the First Annual Graduate Research Symposium at UT Arlington.

Technical Report - Standard for Remote Operations Systems Design: This report will focus on issues that telerobotic system designers (and automated system designers in general) need to take into account in order to realize a system that will support real-time performance measurement (associated with any or all subsystems) and monitoring (i.e., during operations) from remote location. During this period, several subsections of this report have been addressed and rough working drafts produced. This specifically includes sections on overall system performance metrics and real-time software design issues for distributed modules (e.g., in robot controllers, operations workstations, etc.).

Mobile Platform Modeling

This research has investigated the development of modular numerical tools that will allow dynamic analysis and control law synthesis for mobile robots. Modular numerical tools have been developed for modeling and control of serial chain robots and multiple robots. A good example of this work is that of Robert Anderson of Sandia National Laboratories who has reported the development of SMART (Sequential Modular Architecture for Robotics and Telerobotics) [Anderson, 1995].

For a given level of granularity in a dynamic model, modularity allows the replacement of a sub-system (module) of the machine with another module, provided the two modules have essentially the same functionality. This modularity leads to significant ease in comparing the performances of design alternatives for the sub-systems of the machine. The modules that have been considered include two-wheeled and three-wheeled carts, and two different articulating mechanisms for inter-connecting carts. Detailed dynamic modeling of a three-wheeled module has been performed using Newton-Euler, Lagrangian and Kane's methods to identify the most efficient technique for developing equations of motions of the module [Choi and Sreenivasan, 1996].
The rolling and/or slipping conditions at the wheel-ground contact locations of a mobile robot lead to nonholonomic constraints. The presence of such "nonholonomic modules" leads to an important numerical issue associated with the "forward dynamics" problem. ("Forward dynamics" of a dynamic system involves using the equations of motion to numerically compute the accelerations and reaction forces/torques at the module interfaces, at a given instant of time, knowing the current system states and control inputs.) Lumped-parameter models of most machine systems lead to forward dynamics problems that involves solving linear equations. For instance, the systems considered by Anderson during the development of SMART are holonomic and their forward dynamics problem is linear. Therefore, the computational complexity and reliability issues associated with nonholonomic systems do not apply to these systems. A nonholonomic module leads to additional nonlinear kinematic constraints that have to be included in the forward dynamics problem in order to solve for extra kinematic variables that appear in the equations of motion. In general this nonlinearity propagates through the entire forward dynamics problem requiring the solution of a system of nonlinear equations. A numerical tool that can solve this nonlinear problem (which typically includes bifurcation) with very high reliability is required, since a typical 100 second simulation of the machine system may require the solution of this problem several thousand times. The tool also has to be efficient to allow the development of software that can provide useful design/control/navigation information in a reasonable period of time.

This research work has investigated "pre-processing" using symbolic algebra techniques to simplify the nonlinear systems resulting from a machine that has a small number of nonholonomic sub-systems. It has also investigated homotopy continuation techniques to numerically track the solutions of these nonlinear systems and handle bifurcations. A computer software that incorporates special symbolic and continuation techniques that is particularly suited for the practical mobile robot systems is being developed. An object oriented software architecture (using C++ programming language) that is specifically suited for the modular software development effort is being used and the software development is being performed on an available Silicon Graphics Workstation.

References


Generic Manipulator Tools

This quarter this work has progressed on the theoretical side. Six papers describing the tool that is used to provide the high fidelity models have been submitted for review. This papers will also be included in the Nuclear Group technical document series. The papers are listed below.

AIR MONITORING FOR DETECTING RELEASES OF PLUTONIUM IN A FUTURE INTEGRATED STORAGE FACILITY

H. M. Liljestrand (PI), Department of Civil Engineering, The University of Texas
A. R. McFarland, Department of Mechanical Engineering, Texas A&M University
W. H. Marlow, Department of Nuclear Engineering, Texas A&M University
P. K. Dasgupta, Department of Chemistry, Texas Tech University
S. Liu, Department of Chemistry, Texas Tech University

EXECUTIVE SUMMARY:

This research effort is to develop an optimized system for detecting plutonium releases in the Integrated Storage Facility. The system will ultimately provide meaningful data for alarm purposes, for determining the exact source of leakage, and a quantitative basis for indoor and outdoor exposure to such releases. The research program is divided into four subprojects, which include (principal investigator(s) from each institution are noted in parentheses) (1) development of a method for detecting the occurrence and isolating the location of leakage from storage (H. M. Liljestrand and R.L. Corsi, The University of Texas at Austin), (2) development of a method for predicting the best sampling and monitoring locations (A. McFarland, Texas A&M University), (3) development of a method for accurate detection of plutonium aerosols (P.K. Dasgupta, Texas Tech University) and (4) plutonium leak detection by conductivity methods and optical detection of plutonium aerosols (W. Marlow, Texas A&M University). Each subproject is on schedule, and the results are available through M.S. reports, journal article submissions, and conference proceedings.

Subproject 1 Development of a Tracer-Based Fingerprinting System to Identify and Locate Pu Storage Container Leakage
H. M. Liljestrand and R. L. Corsi, Civil Engineering, The University of Texas

EXECUTIVE SUMMARY:

The premise behind a tracer-based fingerprinting system is that small quantities of other inert tracers, e.g., perfluorocarbons, could be added to helium in a container headspace. The use of multiple tracers at varying concentrations would allow for container-specific fingerprints. For example, if three tracers were all detected simultaneously in a specific ratio it would be possible to immediately identify the specific container from which they were released. It would then be possible to rapidly isolate and remediate the specific failure on the target container.

This primary task consists of six major sub-tasks. These include (a) the identification of a list of potential tracers, (b) a rigorous literature review on the effects of alpha radiation on each of the tracers listed in (a) (future experiments will confirm this task), (c) selection of final "target" tracers, (d) design of a fingerprinting scheme, e.g., specific tracers, tracer combinations, and concentration variations to allow for container-specific identification, (e) selection and potential design of an appropriate on-line monitoring system to allow detection of target tracers with required sensitivity, (f) development of fingerprint feedback software to facilitate leakage notification and container identification, and (g) development and testing of a prototype detection/fingerprint system.
Subproject 2: Development of Improved Sampling Systems for the Collection of Plutonium Aerosols

A. R. McFarland, Department of Mechanical Engineering, Texas A&M University

EXECUTIVE SUMMARY:

Numerical studies on modeling of flow mixing in stacks and ducts have been initiated. Experimental and numerical studies on aerosol losses in transport system components have been conducted.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

Two categories of studies on the sampling of simulated Pu aerosols have been conducted. First, there are basic data that are lacking in the technology of air sampling system design, including characteristics of acceptable bends in transport lines. Studies are currently underway to develop such design criteria. Second, the trend in continuous emission monitoring (CEM) in the nuclear industry is to use single point sampling in accordance with the Alternate Reference Methodology (ARM) that was approved by EPA in November, 1994 for use at all DOE facilities. To comply with the requirements of the ARM, samples for CEM must be withdrawn from a location in the stack or duct where the flow is well mixed. Although mixing criteria are specified in the ARM, there is no a priori means for determining if a sampling location is suitable. During the current year, numerical modeling of flows in ducts has been improved via Large Eddy Simulation (LES) techniques using sub-grid modeling.

With respect to research into aerosol transport components, the effects of curvature ratio and tube flattening on losses in bends are being investigated. The methodology for design of air sampling systems for the nuclear industry is provided by ANSI N13.1-1969, "Guide to Sampling Airborne Radioactive Material in Nuclear Facilities." In that standard, it states the curvature ratio of bends shall be at least five, where the curvature ratio is the radius of curvature of the bend divided by the tube diameter. There does not appear to be a well-founded basis for this criterion, so tests have been conducted to either verify the criterion, or to offer a new value. It would be helpful to designers if value were less than five. Currently, there are no criteria for acceptable flattening of tube cross-section in bends.

Subproject Task 3: Collection of Plutonium Aerosol Particles Through an Electrical Means Followed by an Automated IC Measurement

P. K. Dasgupta, Department of Chemistry, Texas Tech University

EXECUTIVE SUMMARY:

Aerosol particles are naturally charged or can be deliberately made to be highly charged. When introduced to an electric field, these charged particles will deposit onto the oppositely charged electrode. The composition of the aerosol particles can be obtained through chemical or radiochemical analysis. To date, an automated annular tubular aerosol collection system using an electrical means has been developed and its performance has been found to be in excellent agreement with that experimentally predicted.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

An experimental system has been developed consisting of three major parts; an aerosol generation system, and aerosol collection interface, and an ion chromatographic measurement system.
Experimental results for 0.8-2.1 micrometer particles have shown high collection efficiency (about 90%). Research is progressing on schedule.

Subproject 4: Plutonium Leak Detection by Conductivity Methods and Optical Detection of Plutonium Aerosols
William H. Marlow, Texas A&M University

EXECUTIVE SUMMARY:
Calculations of the electric current pulse due to the passage of a single alpha particle through either air or a noble gas in a weak electric field are in progress with initial results having been obtained. The purpose of this study is to provide the design basis for initial experimental work to develop a practical system for monitoring pit leakage in double-walled containers under study in the AL-2100 Program of DOE/DP at Sandia, Los Alamos, and Lawrence Livermore National Laboratories. A presentation of the proposed plan of research was given October 9 for the AL-2100 Program Meeting at Sandia National Laboratory, Albuquerque, and attended by participating DOE and National Laboratory personnel. This work will be fully reported in the January, 1997, Milestone/Deliverable for this project subtask as indicated earlier.

Laboratory studies are being conducted of the fractional removal of aerosol particles from airstreams flowing through reticulated vitreous carbon foam. These studies are intended to determine if modern low density microporous materials can be used as aerosol capture media which will provide size-related spacial separations of 0.5 to 10 micrometer plutonium particles arising from leakage or other dispersal processes. If successful, these materials may in the future be used to provide samples for ultraviolet fluorescence detection of ultrasmall quantities of airborne plutonium. Due to extended delays in delivery of the materials under study, as cited in the preceding Quarterly Report, we were unable to fulfill the Milestone/Deliverable commitment originally scheduled for September, 1996. Completion is now anticipated for January, 1997, and no subsequent work will be conducted.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:
Calculations are in progress of the current pulse due to the ionization of a single alpha particle in a canister filled with air or rare gas. We model the systems of interest without considering the wall of the canister and the pit inside the canister. In other words, we study the transport of electrons or ions under a constant externally imposed electric field in air or rare gas without boundaries.

We have established the most general equation for this system, including ion or electron depletion during their transport. Using Green’s-function method, we have solved the equation in terms of a source, which in the present context is the initial electron or ion density created by the alpha track. Once the source is given, the time- and location-dependent electron or ion densities can be obtained through analytic or numerical integration. The current at any given location and time can be obtained as the surface integral of the current flux. Since the range of the alpha track in air or rare gas is only about 2 cm and the canister size is about 40 cm in diameter. If the alpha track is not very close to the surface of the pit or the wall of the canister, our modeling should be accurate. If the electrons or ions are collected far from the location of the alpha track, we may view the alpha track as a point source of charge. As a first step of this study, we treat the initial electron or ion density created by the alpha track as a delta-function-like source. Specifically, the canister fill-gas is chosen to be helium. The purposes of choosing this specific gas are three-fold: First we want to show that the amplitude of the current pulse due to either electrons or ions is measurable (i.e., no less than a picoampere) so that the proposed method can indeed be used to detect the leakage of Plutonium. Second the profile of the current pulse due to electrons is typical for any rare filled gas. For example, the current amplitude at a location 20 cm from the alpha track is on the order of a nanoampere, and the characteristic time is on the order of 10 milliseconds. Finally, the current
profile due to ions should characteristically resemble that when the fill-gas is air. In the later case, one should not detect the pulse due to electrons since they will quickly attach to air molecules to form negative ions. One can detect only the current pulse due to ions. Our study show that the amplitude of the current pulse is on the order 10 picoamperes with the characteristic time of 10 milliseconds. Since the two kinds of current profiles are very different, we can employ each of them for a proper filled gas to detect if there is a leakage of plutonium in the canister. In our calculations, we choose the location of collecting the electrons or ions at 20 cm from the alpha track, the constant electric field \( E = 76 \, \text{V/cm} \). The diffusion coefficients are \( D = 540 \, \text{cm}^2 /\text{sec} \) for electrons, \( D = 0.27 \, \text{cm}^2 /\text{sec} \) for He\(^+\), in He gas. The corresponding drift velocities are \( v = 2.7 \times 10^3 \, \text{cm/sec} \) and \( v = 790 \, \text{cm/sec} \), respectively. With these, the amplitude of the current pulse due to electrons is \( 3.5 \times 10^{-9} \, \text{A} \) and the peak occurs at time \( 7.5 \times 10^5 \, \text{sec} \). For He\(^+\), the current amplitude is \( 2.5 \times 10^{-11} \, \text{A} \) and the peak time is 0.025 sec.

These calculations indicate clear separations in arrival time and temporal spread of ionic and electron pulses, both of which are well within the capabilities of detections by readily available methods. Due to these characteristics of the two pulses, the operational hypothesis of this subproject is amply fulfilled and gives clear indication of how initial experimental work should be set up if this work will be supported for FY 1997.

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**Development of Monitoring System For Accidental Plutonium Emergence**

Purnendue K. Dasgupta (PI), Texas Tech University

**EXECUTIVE SUMMARY:**

A new continuously operating aerosol particle collection system has been developed. The system operates on the principle of forced condensation of vapor on to the particles after vapor (steam) introduction. The current system operates without any extraordinary cooling or impaction requirements and is very light weight. Further, high volume sampling is possible, permitting very sensitive measurements. The system facilitates quantitative collection of aerosol particles across a broad size range and therefore measurements can be done without any particle size bias. A manuscript is under preparation for publication of this work in a scientific journal. Further information of the system has been included in the following detailed report.

**DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:**

1. **Past accomplishments:**

   Two different systems have been developed in the past in this project for the collection of aerosol particles. These are (a) Electrostatic micro-collection interface, and (b) Corona -free electrostatic collection interface. These two systems have been shown to give reliable particle collection for continuous particle analysis and have already been published in reputed peer-reviewed scientific journals (1) Talanta 43 (1996) 1681-1688. (2) Analytical Chemistry 68 (1996) 3638-3644.). See also ANRCP-NG-ITWD-96-05. However, these systems permit only low sampling rates, and may have difficulty measuring low concentration of target analytes. We therefore developed another high volume sampling system in order to make sensitive measurements.

2. **Recent accomplishments:**

   Our previous work had established that easy particle collection will be facilitated by any approach that will initially increase the size of particles to be collected. We had also established that vapor introduction is a simple way of achieving particle growth. A packed column impactor was
proposed for downstream collection of particles, thus grown, in a large volume sampling scenario. Experiments were done by packing a 10.5 cm long 8 mm dia acrylic tube with 1mm dia glass beads. Initial results indicated quantitative collection of aerosol particles (99.6 ± 1.1%) at a flow rate of 5 SLPM. The flow resistance of the packed column was high, however.

During the process, we had also evaluated the cooling and impaction requirements. Now we have found that quantitative particle collection can be achieved with relatively simple cooling and impaction conditions. The packed column is replaced with a small length of flattened glass tube bent in a zigzag shape. The air draft from a 80 cfm fan provides sufficient cooling. This simple system is represented in Figure 1. Steam is mixed in to the aerosol sample flow and the mixture is led to a mixing chamber that provides sufficient residence time for particle growth, and is then led to the small glass coil impactor. The effluent from that is introduced in to an inertial air liquid separator. The collected liquid is aspirated out and send to a down stream analyzer. The whole system is placed in a 12 cm dia acrylic tube with a fan at the bottom end. Air flow from the fan provides the cooling.

The system has been evaluated for particle collection efficiency with house generated sodium sulfate aerosol in the size range of 0.1-2 μm. Quantitative collection is obtained at all the flow rates tested. (100 ± 1.9 % at 6 SLPM). The system is expected to give quantitative particle collection at even higher flow rates.

3. Plutonium Measurement Scheme:

Plutonium determination in the collected aerosol will be developed and tested, initially using Cerium as a surrogate. Spectrofluorometric determination of Cerium which has similar chemical properties is being tested. In order to improve sensitivity, Ce(III) is being concentrated on a 45 mm x 4 mm i.d column containing Amberlite CG-50 (200-400 mesh) weakly acidic cation exchange resin. It is eluted later with an acid plug. Early results indicate very good sensitivity for the method (less than 10^-15 mole of analyte).

The analytical system will be further evaluated for the performance. Later, the analytical component and the collection device will be combined and the performance will be tested with house generated Ce aerosol.
EXECUTIVE SUMMARY:

This project will further our understanding of material problems that may arise during the long-term storage of Pu pits by continuing to study the radiation damage and associated surface and microstructural changes produced in stainless steel covers by high fluence alpha particle irradiations from Pu.

The effects of alpha particles emitted from weapons grade Pu on 316-stainless steel are being investigated to determine the integrity of stainless steel covers for long-term storage of Pu pits. To simulate the problem, He-3 ions with various energies and fluences will be implanted into polished stainless steel samples. The He-3 behavior in the samples will be monitored using Neutron Depth Profiling (NDP). Neutron Depth Profiling is a unique, nondestructive nuclear technique which utilizes thermal-neutron-induced charged particle reactions to determine concentration depth profiles of certain isotopes in any substrate. Surface conditions will be monitored by scanning electron microscopy (SEM) for any changes (e.g. blisters, pits) due to implantation to various He-3 fluences. Microstructural changes and bubble formation will be observed using transmission electron microscopy (TEM).

Helium-3 ions with fluences varying from 1E15 to 1E16 ions/cm² have been implanted into polished 316-stainless-steel test samples. The incident implantation energy was 140 keV. The implantations were performed at room temperature. Surface conditions were monitored by SEM before and after implantation. Depth distribution profiles for test sample were obtained by NDP. Test sample preparations for TEM study are currently underway. Microstructure of the sample at the end of the range of the helium-3 ions will be observed using TEM. Bubbles and voids are expected to be observed at the grain boundaries of the maximum-damage region. For each sample, a correlation will be made between the implantation energy and fluence, the concentration depth profile, and microstructural information obtained from TEM.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

During The period of 8/1/96 to 10/31/96, the following were accomplished.

- Neutron Depth Profiling measurements of test samples were obtained.
- Surface conditions of test samples were checked with SEM after implantation.
- Test Samples for TEM measurements were prepared. TEM measurements for test samples are underway.
- Dr. Hart and Dr. Ünlü visited Los Alamos National Laboratory on August 26-27, 1996. They held meetings with Joe Martz of the Nuclear Materials Technology Division and Carl Maggiore of the Center for Materials Science.
- Graduate Students Mehmet Saglam (UT) and John D. Shipp (TAMU) made presentations at the Third Annual Student Research Conference at West Texas A&M University, Canyon,
Texas. This Conference was sponsored partially by ANRCP. Mr. Saglam's presentation, entitled "Alpha Radiation Effects on Stainless Steel," was awarded second place in special sessions on Nuclear Energy Issues category. Mr. Shipp's presentation was entitled "Lattice Disorder in Fe Due to He Irradiation."

The most tangible accomplishments of the project during this report period were:

- Neutron Depth Profiling measurements of test samples were done.
- Programmatic integration with DOE personnel was accomplished by visiting LANL and having beneficial discussions with Joe Martz and Carl Maggiore.

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**Risk Assessment**

**AIRCRAFT ACCIDENT FORECASTING FOR AN INTEGRATED PLUTONIUM STORAGE FACILITY**

James C. Rock (Co-PI), Department of Nuclear Engineering, Texas A&M University
Michael T. McNerney (Co-PI), Aviation Research Center, The University of Texas

**EXECUTIVE SUMMARY:**

The final DOE standard 3014-96, "Accident Analysis for Aircraft Crash into Hazardous Facilities" is now projected for mid-November release. The Draft Pantex Site Wide Environmental Impact Assessment (SWEIS) was revised to incorporate our comments submitted during the previous reporting period. That document is working its way through DOE approval channels, and the projected publication data has slipped past Oct 1996. The SWEIS will be based on the July 96 version of DOE Standard 3014-96 on the basis that the changes in the standard do not change the SWEIS conclusions.

In August, Drs. McNerney and Rock participated in a very productive meeting hosted by Lamb Associates in Albuquerque, NM. Attendees from Sandia National Labs, the Albuquerque Operations Office of DOE, Pantex, TetraTech, Inc., and the USAF Safety Center all contributed to a lively dialogue about improvements needed in aircraft accident models for public risk assessment. We left drafts of our analyses and obtained the same from the Sandia participants. By the end of the meeting, it was clear to all that the best course of action would be to collaborate so that all parties can benefit from prior work and experience of the others. We modified our 1997 ANRCP proposal to reflect that goal. Dr. McNerney received valued feedback on his efforts to use features of the Pantex airspace and type-specific aircraft accident rates to further refine the DOE accident probabilities. Dr. Rock received valued feedback on his continuing efforts to create a better bound on the threat posed to Pantex facilities by skidding aircraft.

Technical reports are progressing.

**DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:**

- Coordinated with USAF Safety Center on assumptions used to collect and report accident statistics.
- Used Mathematica version 2.2, a powerful simulation language, to solve non-linear differential equations of aircraft skid models. Manuscript is in preparation for publication.
- Collected information from USAF about future mix of military aircraft in the Pantex airspace.
Conducting sensitivity analysis of assumptions that control aircraft hit probabilities for critical Pantex facilities. Where the effect is significant, the plan is to recommend an improved final tier to the DOE aircraft accident risk assessment model.

A FEASIBILITY STUDY FOR THE STORAGE OF PLUTONIUM PITS IN NON-PARTITIONED WAREHOUSE FACILITIES

Darryl James (PI), Department of Mechanical Engineering, Texas Tech University

EXECUTIVE SUMMARY:

Completed phase I modeling for the FD-LANL facility. The FD-LANL facility that is being investigated will contain some five thousand pits, each stored in an individual AT-400A container. The containers will be stored in racks that contain four and six containers, referred to as a four pack and a six pack, respectively. The four pack is stacked on top of the six pack, or vice versa, such that the combined rack holds ten AT-400As stacked five high. The racks are arranged in ten rows; eight rows hold five hundred containers and two rows, the first and last row, hold 250 containers.

The computational domain used in phase I consists primarily of the walkspace between two rows with the additional space between each rack and the ceiling. The total height from the floor to the ceiling is 4.0 m. The total length (axial direction) of the domain is 32.5 m corresponding to 25 racks of AT-400A containers. The height of each rack is 3.14 m. The ceiling is 3.325 m wide by 32.5 m long. The floor is 1.625 m wide by 32.5 m long. The temperature distribution, the velocity profile, and the pressure profile for the computational domain described above was predicted.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

This is a progress report for phase I modeling of the feasibility study for the storage of plutonium pits in a non-partitioned warehouse facility referred to as the Fluor Daniel -- Los Alamos (FD-LANL). In this facility, the pits will be stored in their shipping/storage containers, the AT-400A. The FD-LANL facility that is being investigated will contain some five thousand pits, each stored in an individual AT-400A container. The containers will be stored in racks that contain four and six containers, referred to as a four pack and a six pack, respectively. The four pack is stacked on top of the six pack, or vice versa, such that the combined rack holds ten AT-400As stacked five high. The racks are arranged in ten rows; eight rows hold five hundred containers and two rows, the first and last row, hold 250 containers.

The modeling efforts for this proposal were divided into four phases. Phase one of the modeling began in August so that preliminary results of the fluid flow and temperature distribution of the air in the FD-LANL facility could be presented to Los Alamos National Laboratory (LANL). Several simplifying assumptions were made. A standard k-epsilon turbulent model was utilized to determine the air flow and temperature distribution in the warehouse. This numerical turbulent code currently models only forced air flow. Only a subsection of the warehouse was modeled for phase one. The subsection consisted of one half a row (250 containers), the walk space between the rows, and half of another row (250 containers). The rows of AT-400A containers were assumed impermeable to fluid flow resulting in air movement only in the walk space between rows and in the space above each row for the computational domain. The energy generated by the decay of plutonium in the pit was assumed to be 15 W per pit. The total energy generated was 3.75 kW for each half row for a total generation of 7.5 kW of energy entering the flow. The energy generated was assumed as a uniform heat flux entering the flow via two surfaces, 3.42 kW from the front and 0.38 kW from the top surface of each row. Cool air entered uniformly through the ceiling with
a velocity of 1 m/s (total mass flow rate equaled 108.1 meters cubed per second) and exited through the floor of the warehouse at the same mass flow rate.

The boundary conditions used for phase I modeling were chosen for convenience to demonstrate the capabilities of the code. The inlet temperature was assigned a value of 1 degree C with a uniform inlet velocity of 1 m/s. The subsequent volume flow rate entering the domain corresponds a value between 1 and 2 cubic feet per minute (cfm) (Note that in many industrial settings, the amount of cool air required is between 1 to 2 cfm per square foot of floor area.). Because the inlet mass flow rate was assumed to be uniform over the entire ceiling area, the velocity profile, the temperature profile, and the pressure profiles are exactly the same at any axial location. When specifically sized inlet diffuser locations and return air locations are specified, the above mentioned profiles will then change in the axial direction.

The temperature distribution, the velocity profile, and the pressure profile for the computational domain described above was predicted. For the conditions specified, the temperature rise is confined in the boundary layer along the front surfaces of the walkspace. The bulk of the flow is close to 2 m/s in the walkspace area. This increase in velocity is attributable to the choice of boundary conditions; the walls that make up the walkspace were assume non-permeable and since that area is smaller than the ceiling area, the velocity had to increase. Note the maximum static pressure predicted was 5 psig vacuum and this was also a result of the non-permeable boundary conditions used for this phase of the study.

GEOLOGIC DISPOSAL OF IMMobilIZED PLUTONIUM

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S. V. Bodwadkar, Department of Mechanical Engineering, The University of Texas

EXECUTIVE SUMMARY:

Research activities in this quarter were mainly focused on the colloid mediated transport of radionuclides, model for plutonium ion transport through bentonitic materials, and development of a well testing solution that includes factors unique to pressure transient testing in low permeability fractured formations.

A report titled- Colloid Mediated Transport of Radionuclides and Metal Ions in Groundwater was submitted to ANRCPR. This topical report identifies various parameters governing the transport, and summarizes various field, laboratory, and model studies.

The work on a plutonium ion transport model continued from the previous quarter. This model is based on electrokinetic equations and predicts the flow of ions through charged microcapillaries (model for bentonitic clays). The model has been tested for sodium ions for which the required data, e.g. hydrated radius of ion, are available in the literature. Such data for plutonium ions is being gathered for further analysis.
A paper entitled "Analytical Solution for Sequential Hydraulic Tests in Low Conductivity Fractured Formations" is being prepared that discusses the new well testing solution. A portion of the paper will be presented at the AGU meeting in San Francisco this December.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

Colloid Transport

A detailed survey of available literature on colloid mediated transport of contaminant was conducted. Various aspects of colloidal transport such as adsorption of radionuclides and factors affecting mobility of colloids were studied. The report provides a summary of field and laboratory observations, and also reviews past modeling efforts. The major conclusions from this study are:

1. Geochemistry of groundwater and soils, ionic strength, pH, valence of cations present in the ground water and, size, composition, and molecular weight of the colloids are the primary parameters controlling the adsorption and mobility of contaminants and colloids. Of these only the effects of ionic strength, pH, and size of colloids have been understood to some extent. More theoretical and experimental work is needed to understand the role of other parameters.

2. Most of the field studies have been directed towards gathering evidence that shows the presence or absence of colloid-assisted transport. Even though these studies characterize the natural colloids and their environment extensively, they provide limited information about the mechanisms of contaminant adsorption and transport. A great deal of laboratory work has been done to understand the role of water and colloidal properties but very few studies have been aimed at understanding contaminant-colloid interactions. Nonetheless these experiments provide valuable insight into the distribution of contaminants and the effects of organic materials on adsorption. Because of the inherent complexity of natural colloidal systems, studies available to date offer a very limited understanding of the role each parameter plays in the sorption and transport of metal ions and radionuclides.

3. The various approaches that have been proposed to incorporate colloid mediated transport of contaminants differ mainly in the way contaminant transport is coupled with groundwater flow.

4. Additional research is needed in the following areas:
   - The reversibility or irreversibility of radionuclide and metal ion adsorption on clays, humic substances, and other naturally occurring colloids.
   - The release/detachment of groundwater colloids by changes in groundwater chemistry and flow rates.
   - The retention and transport of colloids in fractures and other high permeability pathways.
   - The formation and chemistry of precipitates that incorporate radionuclides.

Pu ion Transport Model

The plutonium ion transport model is based on three governing equations: Nernst-Planck Equation, Navier-Stoke's Equation, and Poisson-Boltzmann Equation. The flow of ions through charged capillaries depends on the size of ions. Ions have a layer of water molecules surrounding them. The effective size or hydrated radius of an ion depends on the valance of the ion. Plutonium ions can coexist at various oxidation states- III, IV, V, and VI. The relative abundance of these states at equilibrium is a complex function of various aqueous and solid phase parameters. For simplicity we plan to use the most stable form of plutonium ion (Pu-IV) in our calculations. The current focus of our efforts is to obtain data related to the aqueous chemistry of plutonium.
Geosphere Characterization

A new analytical solution and methodology has been developed that accounts for many factors unique to well testing in low-permeability formations. Such factors include: 1) formation hydraulic parameters and flow model; 2) wellbore storage, skin and tool compliance effects; 3) variable pre-test pressures; 4) wellbore temperature changes; and 5) complex test-sequence design. Currently, numerical methods are often used to simulate such complex conditions, obtain a match to the observed pressures, and predict the formation parameters of interest. Although simulators can be useful, they are often affected by numerical problems such as added dispersion and singularities near the wellbore, and are not easily adaptable if a new flow model grid is required.

The developed methodology and solution can account for these complexities and can be easily modified for new flow models. The solution technique treats a sequence of pre-test pressures and multiple test events (thus far only slugs and pulses have been included) as one test sequence, thereby accounting for the influence of one test event upon another. The solution is derived so that only a kernel function (i.e. pumping test solution) is input as required for new flow models. Furthermore, the solution is developed for any flow dimension allowing for interpretation in fractured formations where linear, radial, and fractional flow may exist. The proper flow model and formation parameters is obtained by inversely matching the simulated pressures to the actual formation pressures.

Future development of the analytical solution will consist of adding the ability to model sequential constant-rate tests and constant pressure tests. We will also examine the effect of nonlinear terms in the pressure continuity equation on the pressure response in low-permeability formations. In addition, we will develop a faster and more robust program for calculating pressures from the analytical solution.

LWR MOX FUEL IRRADIATION EXPERIMENT

Please see “Water Reactor Options for Disposition of Weapons-grade Plutonium” below.

MIXED OXIDE USE EVALUATION

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John Alvis, Department of Nuclear Engineering, Texas A&M University

EXECUTIVE SUMMARY:

The MOX fuel evaluation project focuses on the in-reactor thermal and mechanical behavior of mixed oxide fuel fabricated with weapons plutonium. The thermal performance of the fuel is examined along with other key factors such as fission gas release, fuel-clad mechanical interaction and effects of burnup. Fuel pins will be analyzed for conditions in both US and Russian light water reactors.

To carry out the work, a review has been made of available fuel performance codes which can carry out this analysis for mixed oxide fuel in light water reactors. The conclusion was that the most suitable program is the COMETHE code from Belgonucleaire (BN). BN has been the world leader in manufacturing and irradiating LWR MOX fuel. Much of the irradiation data has been incorporated into the COMETHE code. It is recognized as one of the premier LWR MOX fuel performance codes.

During August 1 to October 31, 1996, meetings were held with Oak Ridge National Laboratory to coordinate the activities which will take place under this project. A meeting took place with
Belgonucleaire which has led to a draft memorandum of agreement to enable the technical scope of the project to proceed.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

During the reporting period, meetings were held with staff of the weapons MOX fuel project of the Oak Ridge National Laboratory on August 23, 1996, in Oak Ridge, Tennessee. The purpose of the meeting was to coordinate activity in the area of fuel thermal and mechanical performance modeling between ANRCP and ORNL. The participants from Oak Ridge were Trent Primm, Brian Cowell, and Don Spellman. Agreement was reached on the scope of the activities and the overall approach. ORNL has a strong interest in the fuel performance results which would come out of the analysis to support the fuel development efforts for the plutonium disposition program.

Subsequently, a meeting was held with Didier Haas of Belgonucleaire on October 3, 1996, in Washington, DC. The purpose of the meeting was to discuss the terms of a memorandum of agreement between TAMU/TEES and Belgonucleaire which would result in collaboration on fuel performance modeling. Under the agreement, ANRCP through Texas A&M would participate in model development of thermal conductivity and fission gas release for uranium dioxide fuel and mixed uranium-plutonium dioxide fuel at high burnups typical of U.S. light water conditions. The models would be based on extensive irradiation data for UO₂ and (U,Pu)O₂ in the possession of Belgonucleaire. In exchange, TAMU would have the use of the COMETHE code to analyze the performance of weapons MOX fuel. This will be a valuable asset in establishing the technology base for MOX fuel as part of the plutonium disposition plutonium. As a result of the meeting, a draft of a memorandum of agreement has been prepared to be reviewed by both organizations.

FUTURE ACTIVITIES

A meeting is planned with the technical staff of Belgonucleaire to define the modeling activity. This is anticipated to take place in December. This will lead to a signed memorandum of agreement outlining the collaboration on the project. Following this, John Alvis from Texas A&M will travel to Brussels to spend a year at Belgonucleaire working with the staff there to develop the thermal conductivity model and fission gas release model based on BN data.

DOE LABORATORY INTEGRATION

Trent Primm and Brian Cowell of Oak Ridge National Laboratory serve as DOE points of contact for this task.
EXECUTIVE SUMMARY:

Progress continued on research and development of practical dry methods for removal of gallium from weapons plutonium, which is a collaborative effort with researchers at LANL, LLNL, and PNNL. Recent experiments in quartz tube reactors at Texas A&M have shown that gallium trioxide can be readily volatilized from a matrix of cerium oxide (a surrogate for plutonium oxide) by reduction to the suboxide, using pure hydrogen at <1000 C. The gallium is then easily collected as a metal on copper wire or mesh. Significantly, the design of the apparatus (quartz tube reactor, gas flow path, and wire collector) protects the equipment from attack by gallium. Additional experiments using other reducing gases and lower temperatures are being planned. They will be instrumented so that removal rates can be determined.

Progress continued on beam-driven studies of the interaction of gallium with fuel cladding. Gallium was implanted into SS 316 to a fluence of 2x10^{17} ions/cm^2, and samples were examined by scanning electron microscope (SEM) as well as Rutherford backscattering analysis (RBA). In preparation for gallium implantation, Zircalloy samples were obtained, cut, and polished, and surface conditions were examined by SEM. A target-heating chamber was assembled for placement in the ion-implantation target chamber, to be used in upcoming studies of the effects of temperature on gallium-cladding interactions.

In collaboration with ORNL, progress was made toward finalizing the design of temperature-driven experiments to study gallium-cladding interactions. Much was accomplished toward the design of the liquid-metal system that will remove heat from the experiment while maintaining the desired temperature on the outer surface of the pellet. Further progress must await word from ORNL on pellet dimensions and manufacturability.

A CASMO-SIMULATE model of Westinghouse’s Vogtle plant was completed. This model will be used by several tasks in the water-reactor project. It is the starting point for the study of multipurpose reactors and for the design of MOX cores that may reduce DOE’s cost of plutonium disposition. The model will also be used in the task that studies the accuracy of existing reactor-analysis codes given MOX assemblies that contain burnable absorbers (discrete as well as integral).
The task of supporting the US/Russia joint study team on water reactors continued to move forward. Drs. Adams and Peddicord visited IPPE and INPE in Obninsk, attending a workshop on plutonium disposition. Some information was gained about the Russian plutonium complex, about the capabilities of various institutes in Russia, and about the possibility of further collaborations with Russian researchers on the use of MOX in VVER-1000 reactors. Dr. Adams also attended a meeting at ORNL in September, at which US and French researchers discussed their respective collaborations with Russian researchers.

The calculation of MOX benchmark problems continued with both MCNP and WIMSD/3D. An improved version of the WIMS-D4m code, with an expanded ENDF/B-V cross-section library, was obtained from ANL. The new version and library, coupled with the DIF3D and DANTSYS codes, is being used to calculate the SAXTON and WPPR critical experiments. In addition, 10 different SAXTON configurations have been calculated using MCNP-4A with continues energy ENDF/B-VI cross sections. For these configurations, MCNP underestimates k-effective by a few tenths of a percent (0.9941-0.9977). Measured relative-power values are within the 95% confidence intervals predicted by MCNP.

Efforts on the Mixed-Oxide Data Repository (MOXDAR) focused on collection of data for the repository and on obtaining the appropriate hardware for scanning documents. A high-resolution scanner is in place, and Adobe Acrobat publishing products have been selected for the job. A student, Edward Reott, spent several days at the ORNL central library and engaged in lengthy discussions with ORNL staff, resulting in a significant catalog of data to include.

**DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:**

The previous sections some important research progress this quarter. What follows is a very brief, more detailed, but incomplete list of activities.

- Drs. Abdurrahman, Adams, Anistratov, Best, Carron, Hart, Parish, Pitt participated in a telecon with ORNL personnel S. Greene, G. Copeland, D. Spellman, and R. T. Primm, to discuss and refine the water-reactor project’s task plans for FY97. 8/28/96.
- Initial implantations of 100 keV Ga into SS 316 were completed, up to a fluence of 2x10^17/cm^2, at room temperature. Rutherford Backscattering Analyses using 300-keV alpha particles were performed. SEM micrographs showed significant surface roughening.
- Drs. Hart and Unlu contacted six US and European vendors to obtained Zircalloy samples. Several samples of Zircalloy-2 and Zircalloy-4 were finally obtained from Teledyne Wah Chang Corporation, 1600 N. E. Old Salem Road, P. O. Box 460, Albany, Oregon 97321.
- Fifty Zircalloy samples were cut, and eight of them were polished.
- Surface conditions of polished samples were checked by SEM.
- A target-heating unit was assembled. This will allow studies of Ga-Zirc interactions at prototypic reactor temperatures.
- Dr. Adams attended a two-day meeting at ORNL, with personnel from France, ORNL, LANL, LLNL, and DOE. Subject was collaborative efforts with Russia on Pu disposition. 9/25-26/96.
- Dr. Adams presented an overview of the ANRCP water-reactor project to professors at the Institute of Nuclear Power Engineering, Obninsk, Russia. 10/11/96.
Dr. Adams presented results from collaborative work with Westinghouse, "Using Weapons Plutonium in Westinghouse Reactors," at the Institute of Nuclear Power Engineering, Obninsk, Russia. 10/12/96.

A postdoc, Musa Yavuz, who is working with Dr. Abdurrahman, attended a course at ORNL on the SCALE code system, and discussed benchmark calculations with R. Trent Primm. 10/15-24/96.

Dr. Carlos Rios-Martinez was hired as a Post Doctoral Research Associate at the University of Texas.

A student, Edward J. Reott, spent several days at ORNL, gathering documents for MOXDAR from the Central Library and from ORNL staffers. 10/96.

Through his contacts at ANL, Dr. Parish obtained an improved version of WIMS-D4m with an expanded cross section library processed from ENDF/B/V. This code is much better suited for MOX calculations. In addition, Dr. Parish obtained an improved manual for WIMSD4m.

Dr. Parish and students began applying the new WIMS-D4m code to the calculation of the Saxton criticals and the WPPR calculational benchmarks for Pu fuel. The global calculations are being done with DIF3D (two-dimensional and three-dimensional diffusion models) and DANTSYS (two-dimensional transport) models.

Dr. Parish and students familiarized themselves with the requirements for reporting critical experiments in accordance with the formats specified in the International Handbook of Evaluated Criticality Safety Benchmark Experiments. Reporting according to these guidelines is considered by ORNL to be very important.

Can-in-Canister Plutonium Immobilization

THERMAL/MECHANICAL MODELING OF THE "CAN-IN-CANISTER" PLUTONIUM IMMobilIZATION PROCESS

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Eric M. Taleff, Department of Aerospace Engineering and Engineering Mechanics, The University of Texas
Theodore L. Bergman, Department of Mechanical Engineering, The University of Connecticut
Edward E. Anderson, Department of Mechanical Engineering, Texas Tech University
Jaime F. Cardenas-Garcia, Department of Mechanical Engineering, Texas Tech University
Javad Hashemi, Department of Mechanical Engineering, Texas Tech University

EXECUTIVE SUMMARY:

Research activities during May-July 1996 have focused on:

- Experimental studies of the spectral absorption coefficient of surrogate DWPF and plutonium glasses are completed, and the Rosseland and Planck mean absorption coefficients have been determined as functions of temperature for these two glasses.
- The global models used to determine the heat transfer from the molten glass jet used to fill the DWPF canisters have been extended to include radial temperature gradients and semi-transparent, wave-length dependent radiation heat transfer.
- The cooling rates and axial and radial temperature variations of the poured glass stream were calculated using the measured optical properties of the surrogate DWPF glass.
- System level studies of the heat transfer in the glass pool that forms at the bottom of the DWPF canister as it is filled have been completed based upon a one-dimensional model. These studies have been conducted to obtain order of magnitude temperatures for the glass process.

- The results of the system level studies have been shared with the robotics group. They are using these models to build a system control model for this process.

- The development of a more realistic three dimensional model of the heat transfer in the glass pool, based upon a finite element approach, has been initiated. This model will also serve as the basis for calculating the thermal stresses induced within the glass cast as it cools.

- The high temperature experimental facility (glass melter or furnace, melting crucibles, and pouring apparatus) has been completed and the first sets of experiments with molten glass jets have been performed.

- The preliminary molten glass pours qualitatively match the low-temperature results using analogous fluids as well as the numerical results. Voids and cracking are observed in the solidified glass pours.

- A new phenomenon known as "bird's nesting" has been identified and is associated with a periodic thinning of the molten glass jet. The parameters affecting this phenomenon are being studied, as well as its significance to the can-in-canister process.

- A series of low temperature experiments were performed with room temperature corn syrup for different pour rates.

- Heat transfer has been added to the detailed computational model of the molten glass jet, using the commercial CFD code FIDAP, to predict the axial and radial temperature variation within the jet. This is a necessary prelude to the incorporation of a temperature-dependent viscosity in the model. With the introduction of heat transfer, numerical stability problems have been encountered with FIDAP. We have been working with FIDAP to resolve these stability problems, but have had limited success so far.

- Three dimensional isothermal simulations using FIDAP, corresponding to the low-temperature experiments, have been initiated.

- A grant for $9000 of CPU time on the University of Texas Cray J90 supercomputer was awarded to us, which will be used to facilitate the three dimensional studies using FIDAP.

- Performed a simplified one dimensional thermal stress analysis of the support rack using a finite element method.

- Performed a one dimensional finite element - sequentially coupled thermal stress analysis of the solidified glass structure.

- Performed a two dimensional finite element - sequentially coupled thermal stress analysis of the solidified glass structure.

A brief summary of each of these areas of activity is provided in the Description of Research Activities section below.

**DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:**

**Global Models**

The thermal models for the molten glass jet, which account for the radial temperature gradient and semi-transparent nature of glass, have been incorporated within the global model developed earlier. The optical properties of the surrogate DWPF glass measured at Texas Tech University and The University of Texas at Austin were used to predict the temperature of the glass jet impinging on the glass pool at the bottom of the DWPF canister. Considering the unstable feed from the glass melter, the calculation was conducted for different pour rates, pour temperatures, and convection...
heat transfer coefficients. The details of the thermal models for the glass jet and glass pool, as well as the predicted results, will be provided separately as a report. The flow and heat transfer simulations for the glass pool are in progress.

**High Temperature Experiments**

Two preliminary pours have been accomplished using the completed crucible and pouring apparatus. The temperature during the first pour was continually increased from 800 deg. C to 1050 deg. C during the pour. The jet behavior is seen to have a very high dependence on temperature. Spiraling of the jet just above the impact area is observed at the lower temperatures. As the temperature increases the amplitude of the spiraling decreases and the pile-up and subsequent slumping of the glass pile starts to occur. Both the spiraling and slumping are observed in the low-temperature experiments. The second pour was performed at a constant 1050 deg. C. The jet spiraling and slumping was again observed. As the flow decreased the jet appeared to be discontinuous, but it is believed the jet necked down thin enough that it was difficult to observe. While the jet was "discontinuous" a "bird's nest" formed on the top of the glass pool. This bird's nest formation consists of glass fibers that protrude from the glass pool. This particular jet instability is not observed in the low temperature experiments. The solidified glass pools cracked and fragmented due to residual stresses. The fracture surfaces were examined and seen to have voids with cracks forming from within them. The next step is to measure void content and to isolate the different parameters effecting void formation, e.g. pour rate, pour temperature and pour height.

**Low Temperature Experiments**

Previous experimental results using low temperature analogous fluids (corn syrup or silicone oil) indicated a significant change in the flow behavior at different viscosities and temperatures. The size of the voids was found to be directly proportional to the viscosity. To obtain quantitative results, measurements of the void fraction were made at different mass flow rates, covering a range of about 50% above and below the currently used mass flow rate for the DWPF canister filling process. The conditions were isothermal (room temperature, 297 K), with the viscosity corresponding to that of glass at 1190 K. The measured values for void fraction were in the range of 0.6% to 0.8%. A conclusive correlation between void fraction and mass flow rate could not be deduced, but it seems that the void fraction decreases with increases in the mass flow rate. Further experiments should clarify this correlation. Other future plans include obtaining measurements at different temperatures (ranging from 283 to 313 K) and using different analogous fluids to cover a broader range of viscosities.

**Detailed Models**

We are continuing our efforts to resolve the stability problems caused by the addition of thermal effects to the detailed computational model using FIDAP. This effort is proceeding along two parallel approaches. One approach will be to look for the cause of the stability problems in the temperature solutions, by starting from a simplified model and gradually adding effects to determine the onset of instability. We suspect that the problems encountered are inherent with FIDAP and will require the assistance of the vendor to correct the problem. The other approach is to develop alternative solution strategies, possibly involving the use of other CFD codes, to obtain physically realistic temperature values. This will include the addition of temperature-dependent fluid properties. The three dimensional isothermal modeling efforts are unaffected by the current stability problems with FIDAP.

**Stress Analyses**
Preliminary work was done on a simplified one dimensional thermal stress analysis of the support rack and a one dimensional finite element - sequentially coupled thermal stress analysis of the solidified glass structure. The objective was to verify the capabilities of FIDAP, the pre- and post-processor, and of ABAQUS, the finite element computer code that we are using, and our ability to use them. The results showed that we could model these one dimensional structures to conform with the corresponding theoretical models. Additionally, work was completed on a two dimensional finite element - sequentially coupled thermal stress analysis of the solidified glass structure. This includes modeling of convection effects on the outside surfaces of the container, to promote heat transfer and cooling of the solidified glass structure. This has provided us with preliminary results related to the accumulation of thermal stress damage in the solidified glass structure. Further development of this model will continue through the next quarter.

COORDINATION WITH DOE OR DOE LABORATORY PERSONNEL:

Our group continues to have extensive interaction with personnel at Lawrence Livermore National Laboratory (LLNL) and Westinghouse Savannah River Company (WSRC). In addition, we have initiated contacts with Sandia National Laboratory (Steven Gianoulakis, Thermal Sciences Department), as well as West Valley Nuclear Services Co. (John Victor and Ronald Palmer), to explore areas of mutual interest in the broader area of vitrification and glass processing. Specific meetings during the last quarter are listed below.

Lawrence Livermore National Laboratory (LLNL):


West Valley Nuclear Services Co. (WV):

Dr. Theodore L. Bergman visited WV in August, meeting with John Victor and Ronald Palmer.

Sandia National Laboratory (SNL):

Drs. Kenneth S. Ball and Theodore L. Bergman met with Dr. Steven Gianoulakis in Houston at the National Heat Transfer Conference in August. Dr. Steven Gianoulakis also visited the University of Texas at Austin in October, touring our laboratory facilities and discussing glass processing interests.

FUTURE WORK

Several reports (Internal Technical Working Documents) are being prepared and will be submitted to the Center later this month, including:

1. A Model for Radiative and Convective Cooling of a Semitransparent Molten Glass Jet
2. Experimental Investigation of Void Formation During Glass Pours
3. Optical Properties of Surrogate DWPF and Pu Glass
IMMOBILIZATION OF PLUTONIUM IN CERAMIC MEDIA

Abraham Clearfield (PI), Department of Chemistry, Texas A&M University

EXECUTIVE SUMMARY:

During the third quarter of 1996 the synthesis, via sol-gel methods, of cerium-doped zirconolite and the continued Rietveld analysis of the cerium-doped barium zirconate have been carried out. Samples of barium zirconate were prepared, by sol-gel methods, with calculated cerium substitution of 10, 20, 30, 40, 50, and 60 mole percent. All compounds were calcined at 1200°C to improve crystallinity for structure solution. The 50 and 60% substituted phases showed the presence of an impurity phase which was subsequently identified as cerium oxide. The samples show a progressive increase in cell parameters (all form the simple perovskite structure) from 4.193 Å in pure barium zirconate to 4.275(8) Å in both the 50 and 60% substituted samples. Rietveld whole pattern refinement of the X-ray diffractograms indicates a maximal substitution of 48 mole % cerium in the barium zirconate. Excess cerium fell out as cerium oxide. No barium cerate was found in the products.

A series of zirconolite samples was prepared into which 5 to 35 mole percent Ce was admixed as a replacement for Zr. Excess Ce at the mole percent level was detected by X-ray analysis. However, Rietveld analysis of the X-ray patterns was not possible because of the low-crystallinity of the products. Longer firing times and higher temperatures of calcination are under examination to access their affect on crystallinity.

A number of inorganic ion exchangers that have a very high affinity for cesium, strontium, chromium and lead in groundwater and strong electrolyte solutions have been synthesized. Their use in remediation of groundwater and/or providing a co-additive to the Pu containing ceramic to provide a radioactive shield is under investigation.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

Immobilization of CeO2 in Zirconolite.

Preparation of Samples

Zirconolite has an approximate composition CaZrTi2O7, although the same phase exists over a range of compositions from Zr0.85Ti2.15 to Zr1.3Ti1.7. A new series of zirconolites was prepared utilizing a solid-gel method. This method consisted of weighing out the required amounts of zirconium and titanium isopropoxides, M(OSiH2)x (M=Ti, Zr), adding an aqueous solution of Calcium nitrate, Ca(NO3)2, and homogenizing the resultant precipitant. The mixture was then rotary evaporated at 60-70°C to produce a fine thoroughly mixed powder. This powder was transferred completely to a crucible and heated slowly to 400°C to remove the nitrate and organic material. The mixture of oxides was then fired at 1100°C. An X-ray diffractogram of the fired powder is shown in Figure 1. Alternatively the samples were prepared from a solution of TiCl4, ZrOCl2•H2O and CaCl2. The hydrous oxides and Ca(OH)2 were precipitated with excess ammonia, stirred for 1 h and then filtered and dried at 100°C. This powder was then fired at 1100°C for 17 h to yield a zirconolite that gave an X-ray pattern similar to that shown in Figure 1. Samples were then prepared with 5, 10, 15, 25 and 35 mole percent Ce. The cerium was added to the initial mix as ammonium cerium nitrate, (NH4)2Ce(NO3)6 or CeO2. Since CeO2 substitutes for ZrO2 an equivalent amount of this
latter oxide is omitted from the mix. An X-ray pattern of a zirconolite sample containing mole % Ce is shown in Figure 2. In all our studies CeO₂ is used as a surrogate for PuO₂.

Reitveld and X-ray Analysis of the Samples

Rietveld analysis of X-ray powder patterns allows the determination of the amount of substitution of one element for another, provided the two elements differ in their X-ray scattering power (or atomic number) sufficiently. Zr, atomic number 40, and Ce, atomic number 58, meet the criterion. The X-ray scattering power is proportional to the square of the atomic number. In the Reitveld method a mathematical function needs to be developed that duplicates the observed pattern after subtracting the background. The pattern is then calculated from the structure of the phase giving rise to the pattern. The calculated pattern is then subtracted from the observed one to yield the error. This error is minimized by refinement procedures that normally involve shifts in positional and thermal parameters. In the present case the scattering factor of Ce is substituted for Zr in small increments until the error is a minimum. Additional refinement of positional and thermal factors yields the final result. Although this procedure has been successfully applied in the case of BaZrO₃ (next section), it could not be applied to zirconolite because the shapes of the X-ray peaks were irregular. This result is apparently due to firing the oxides at too low a temperature. Even long annealing at near 1200°C did not sufficiently improve this situation. This result was anticipated and a furnace, capable of temperatures of 1500°C, purchased. The samples will be reheated and annealed at elevated temperatures in the next quarter.

Immobilization of Ce in Barium Zirconate

As part of our search for new ceramic phases that can serve to immobilize plutonium we examined calcium titanate CaTiO₃, and calcium zirconate, CaZrO₃. These compounds are perovskite phases that are known to form from a variety of metals whose valence sums are six. For example CaCeO₃ is a perovskite. However, neither of the phases mentioned above incorporated any significant amounts of CeO₂. The result dramatically reversed with BaZrO₃. Samples were prepared by doping with 10, 20, 30, 40, 50, 60 mole percent CeO₂. The general method of preparation, provided as Scheme I, consisted of mixing zirconyl chloride, barium chloride and CeO₂ (insoluble) or ammonium cerium nitrate (soluble) together and adding a mixture of ammonium hydroxide NH₄OH and ammonium bicarbonate, NH₄HCO₃, to the first mixture. The combined mix was stirred for several hours, filtered washed twice with distilled, deionized water and dried overnight. The resultant powder was then heated to 1085°C and kept at this temperature for 24 h. X-ray powder patterns as a function of amount of CeO₂ added is shown in Figure 3. It is observed that as the amount of CeO₂ incorporated increases so does the peak width. Therefore, the samples were retreated at 1200°C for 24 h and now the peaks sharpened up to a very significant degree, Figure 4. These reheated samples were then subjected to Rietveld analysis. It was shown conclusively that the Ce⁴⁺ substitutes for Zr⁴⁺ up to a level of 48 mole percent. This result was in good agreement with the X-ray powder patterns that showed no excess CeO₂ up to 40% but did at the 50% level. This level of substitution amounts to 22.3% by weight of Ce⁴⁺, equivalent to 33 weight percent of plutonium. This is the largest extent of plutonium uptake for all phases reported so far in the literature.
Evidence that substitution of Ce$^{4+}$ for Zr$^{4+}$ is taking place is also available from determination of unit cell dimensions (Table I).

**Table I.** Increase in the Cubic Unit Cell Dimensions of BaCe$_x$Zr$_{1-x}$O$_3$ as a function of $x$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>UNIT CELL (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.193 (2)</td>
</tr>
<tr>
<td>0.1</td>
<td>4.205 (1)</td>
</tr>
<tr>
<td>0.2</td>
<td>4.235 (1)</td>
</tr>
<tr>
<td>0.3</td>
<td>4.255 (8)</td>
</tr>
<tr>
<td>0.4</td>
<td>4.275 (3)</td>
</tr>
</tbody>
</table>

The monotonic increase of the unit cell dimension is a reflection of the larger Ce$^{4+}$ ion ($r=0.82\,\text{Å}$) in comparison for Zr$^{4+}$($r=0.728\,\text{Å}$) in sixfold coordination.

We are arranging to have experiments carried out with Pu$^{4+}$ at Lawrence Livermore Laboratory or alternatively at ANSTO.

**Ion Exchange Materials and Environmental Considerations**

In the recent past we have developed an ion exchanger phase of composition Na$_4$Ti$_9$O$_{20}$ that is able to remove strontium ion, Sr$^{2+}$, from strongly alkaline radioactive waste systems. On heating to 600°C or higher the compound forms strontium titanate and TiO$_2$ (equation (1))

\[
\text{Sr}_2\text{Ti}_9\text{O}_{20} \xrightarrow{\Delta} 2\text{SrTiO}_3 + 7\text{TiO}_2
\]

The stable strontium titanate phase locks in radioactive $^{90}\text{Sr}^{2+}$ making it suitable for a radioactive shield. Furthermore, TiO$_2$ and strontium titanate are phases compatible with zirconolite or SYNROC.

The sodium titanate phase is being tested for strontium removal at PNNL, Savannah River and at British Nuclear Fuels, LTD. In preliminary tests at PNNL, it was found that not only was Sr$^{2+}$ exchanged but plutonium was also present in the sodium titanate exchanger. Since Pu was present in only trace amounts, it is significant that these small amounts were exchanged by the sodium titanate in the presence of 6M Na$^+$. Thus, this exchanger may have some role to play in Pu$^{4+}$ purification or separation in alkaline solution.

A second ion exchanger that has been synthesized is a sodium zirconium silicate of composition Na$_2$Z$_4$(Si)$_3$O$_9$H$_2$O. Its structure was determined from X-ray powder data and shown to have two types of cavities as seen in Figure 5. This compound exhibits a high affinity for Cs$^+$. In a ground water simulant the silicate exchanger exhibited a Kd value of 400,000 ml/g or 99.8% removal for 12 equilibrations. The sodium zirconium silicate is one member of a family of such compounds in which Ti, Ce, Sn, Pb and Nb can replace all or much of the zirconium.
EXECUTIVE SUMMARY:

We have revised our research plan to investigate in addition to the original lead slowing down time spectrometer (LSDTS) a graphite slowing down time spectrometer (GSDTS). The GSDTS has certain desirable features and complements the LSDTS as an assay device. It has different neutron source requirements in terms of the source pulsing rate and the pulse duration, and may have some advantages over the LSDTS when high accuracy of isotopic discrimination is not required. We extended our computational program to do neutronics calculations on the GSDTS to investigate its various performing parameters.

We have been offered a neutron generator with state-of-the-art pulsing system as a gift from The University of Michigan. We have completed all the paperwork required to transfer the generator to The University of Texas at Austin. Transferring, setting up, and testing the new generator replaces our original task of restoring and modifying the UT neutron generator to a pulsing device. The neutron generator is now in the process of being transferred to UT. We have continued our work researching other neutron sources suitable for SDT devices. We have recently identified a very attractive neutron source that is laser-based which has recently been developed in Russia by a group from Moscow State Engineering Physics Institute. The intensity and pulsing parameters of this source are ideal for our proposed LSDTS and GSDTS devices.

We continued our effort to coordinate with Los Alamos National Laboratory, the lead lab in the area of safeguards and nonproliferation technology. During a recent visit to LANL, we have agreed with various groups on specific collaborative activities in safeguards research. These include collaborating on development of intense neutron source, on instrumentation and data acquisition system for the LSDTS and GSDTS, on neutron computed tomography, and on curriculum development in safeguards and nondestructive assay measurements. We believe that our coordination with LANL provides definition, direction, and specific technical assistance to our project.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

The research and other project related activities during this reporting period have focused on the following tasks:

- Expanding our neutronics analysis program to investigate the suitability of a graphite slowing down time spectrometer (GSDTS) as an assay device.
- Continuing the neutronics analysis program, but with more realistic geometries, to assess the viability of the lead slowing down time spectrometer (LSDTS) as an assay device.
- Expanding our investigation of practical options for the intense neutron source for the LSDTS and the GSDTS.
Completing the arrangements and paperwork to transfer a well-instrumented pulsed neutron source from the University of Michigan to the University of Texas.

Furthering our coordination and integration effort with Los Alamos National Laboratory (LANL) and other organizations.

Calculational Program

As a continuation to our previous neutronics calculations of the lead slowing down time spectrometer, we have extended our calculations to include a more realistic geometries. The following is a summary of some of the calculations:

- Cylindrical lead pile was investigated by looking at the signatures of fissile materials. These calculations were carried out for two distinct cases. The first was an idealized cylindrical lead spectrometer made of pure lead in which the fission neutrons count rates from $^{235}U$ and $^{239}Pu$ were tallied at different points inside the lead pile. In the second case, a simulated LWR fuel assembly was inserted inside the spectrometer. In the later case, the effect of self shielding on the neutron flux was also studied.

- The neutron energy distribution in the homogeneous lead at different slowing down times corresponding to 0.1 eV, 1 eV, 10 eV, 100 eV, and 1 keV average energies were fitted to a Gaussian. From the parameters of the Gaussian fit, we would be able to determine the resolution function and the time-energy correlation for the spectrometer.

Parallel to the lead calculations, we started similar calculations to look at assay signatures in graphite as a potential slowing down time spectrometer. The preliminary calculations were found to be encouraging that we are now focusing considerable part of our effort on the graphite concept. The following is a summary of some of the calculations carried out with idealized graphite spectrometer:

- Fission signatures of $^{235}U$ and $^{239}Pu$ in graphite sphere of radius 50 cm were calculated. A good isotopic discrimination was found at slowing down time of 100 microseconds.

- A detailed analysis of the evolution of the interrogating neutron pulse in the graphite was carried out and the neutron flux at different slowing down times was fitted by Gaussian functions as in the lead case. The resolution of the proposed graphite spectrometer was obtained and found to be adequate for certain applications in fissile assay.

We have just started modeling a cylindrical graphite spectrometer in which two cases are going to be investigated, a homogenized graphite pile and a graphite pile housing a fuel assembly. In these calculations we will be looking at the signatures (shapes) and flux (number of fission events) as monitored by simulated fission chambers and threshold fission detectors.

Pulsed Neutron Sources

We have recently received, as a gift from the University of Michigan (UM), another Texas Nuclear 14 MeV neutron generator similar to the one we currently have at the University of Texas. The Michigan generator is fitted with a pulsed beam capability. This new development made it unnecessary for us to continue our work on restoring and upgrading the University of Texas (UT) neutron generator. We are now in the process of transferring the new generator from UM to UT and it is scheduled to be at UT during the second week of November 1996.

This new generator is equipped with an elaborate pulsing system. A sweeper is used to form pulses of approximately 30 to 40 ns in length at a rate of 1 MHz from the steady state deuterium beam by sweeping the beam across a slit. A buncher of the klystron type is used to time-focus the
beam, compressing the length of the beam pulses from about 35 ns to about 1 ns. The dc beam is focused using a quadrupole doublet positioned near the exit of the accelerator, while the pulsed beam coming out of the buncher is focused using a quadrupole triplet to a spot 2.5 cm in diameter. The average beam intensity for this system was measured to be approximately $10^9$ n/s. The system also employs a mass analysis magnet that allows bending the beam in a certain direction, and helps eliminate the molecular component from the beam, and therefore prolongs the target life.

The ultra short pulsing capability of such a system will enable us to setup and investigate the GSDTS. Preliminary MCNP calculations are showing favorable results for the discrimination between the U$^{235}$ and Pu$^{239}$ signatures when a graphite moderator is used. Since neutrons thermalize much faster in graphite and have larger fractional energy decrements than in lead, ultra-short pulses become essential to prevent any further deterioration in the resolution that could result from a wider pulse.

Our research on evaluating other options for a pulsed neutron source is continuing. During our September visit to LANL, we agreed to collaborate with Mark Pickrell on his work on the development of an electrostatic inertial confinement (plasma) device.

We have also obtained information on a new laser-based neutron generator that has been developed by researchers at the Moscow State Engineering Physics Institute (MEPhI). We met with Professor Alexander S. Tsybin of MEPhI during the IRMMA conference (10/96). Professor Tsybin is going to send us additional information on their device. This device uses a new approach to increase the neutron yield of compact impulse neutron sources by using a laser to create plasma in the ion source and then accelerating the deuterons from the laser plasma. The MEPhI group claims that with this approach one can obtain in compact laboratory apparatus yields of $10^8$ to $10^{10}$ neutrons/pulse, pulse durations of $10^{-8}$ to $10^{-7}$ seconds, and pulse rate of 10 to $10^3$ Hz. These are ideal performance parameters for the LSDTS and GSDTS neutron source requirements.

Integration and Coordination

We have established good coordination and collaboration with the three Nonproliferation and International Security (NIS) groups within LANL that are of particular interest to this project. All three groups are involved with various aspects of nonproliferation and safeguards technology. These groups are NIS-5, NIS-6, and NIS-7. More information on our coordination and integration effort with LANL can be found in previous quarterly reports. The following gives the most recent development with the LANL groups.

A delegation from the Center that included Naeem Abdurrahman (PI), Bernard Wehring (CO-PI), Paul Nelson, and David Boyle, visited LANL on September 6, 1996 for a meeting with NIS-5, NIS-6, and NIS-7 to further discussions on collaborative and joint activities. It was agreed that we will collaborate with NIS-5 on the development of intense neutron source, with NIS-6 on the instrumentation and data acquisition system for the LSDTS, and with all three groups on education programs in the safeguards area.

As a result of several visits and continuous communication with the three NIS groups of LANL, we have developed a good understanding of the state of safeguards technology research at the national labs and established an extensive list of potential collaborators and contacts that are interested in one aspect or another of our research project. The following is a partial list of our contacts at the three groups:


3. NIS-7: Richard Strittmatter, group leader, (505) 667-7903; Bryan Fearey, (505) 665-2423; Chad Olinger, (505) 667-7626.

In summary, we believe we have achieved good coordination and have made considerable progress toward full integration with the three leading groups in the safeguards technology in the US. The three groups have demonstrated strong interest and enthusiasm to collaborate with us on this and other related activities of the Center.

Transportation Analysis

TRANSPORTATION ANALYSIS OF MIXED OXIDE FUELS

Hani S. Mahmassani (PI), Department of Civil Engineering, The University of Texas

Task 1: Modeling for Safe Routing

H. Mahmassani, The University of Texas
P. Nelson, Texas A&M University

Activities at The University of Texas

EXECUTIVE SUMMARY:

The general objectives of the Transportation Analysis effort under the Nuclear Project is the identification and study of transportation-related issues that arrive in conjunction with the disposal of spent plutonium. These issues are integrally related to the identification and quantification of the various sources and types of risks that accompany the movement of radioactive materials. These include risks that arise from the behavior of the materials transported, and that of the storage containers used, as well as the interaction of these with external risk sources associated with vehicular reliability, traffic conditions and possible external threats. Several components of this overall project are addressing the source of these risks, but not all. The second major element of the transportation analysis is the development of strategic and related algorithmic procedures to incorporate these risks in decision-making regarding route selection before the shipment is sent, as well as regarding route modification in real-time as the conditions that affect these risks and their consequences change, to the extent that information becomes available. A third and equally important element pertains to the manner in which associated risks associated with a particular shipment are framed, communicated to and perceived by the population likely to be involved in the process of route selection and/or consequence management.

The present study aspires to be comprehensive in its outlook and scope, but has had to limit its focus to specific risk elements, and to the development and adaptation of modeling methodologies with specific application to the transport of spent plutonium. A major aspect of this effort is to identify and characterize the vast and complex regulatory framework applicable to the transport of radioactive substances, and incorporate these considerations in any mathematical or algorithmic set of decision support procedures. In addition, the project has all along sought to complement the existing set of tools developed by DOE and its laboratories, such as TRANSNET and RADTRAN, by expanding the rule-set underlying route selection and evaluation to recognize different types and/or levels of risks, as well as the dynamic nature of these risks.
DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

During the period of August 1 to October 31, 1996, an internal document was produced to summarize routing criteria and models applicable to highway transportation of defense-owed fissile materials. This document builds upon previous research identifying both formal and informal Department of Energy routing practices. This information is to be used to ensure models under development capture both formal (or regulated) and informal (or practical) DOE routing objectives.

This internal document also reinforced prior conclusions about two key parameters that are not adequately modeled by a single DOE declassified routing model. In particular, routing risk has been found to be very sensitive to the varying spatial and temporal properties of population and travel time parameters. As a result of this finding, work has begun to develop a Geographic Information Systems interfaced with a time-dependent routing algorithm in order to determine if current DOE declassified routing models adequately capture this variance. This document is undergoing final editing prior to submission as a project deliverable for wider dissemination.

The research effort has also continued towards the development of an integrated framework and procedures for a priori routing strategies that recognize the time-varying, stochastic nature of risk and travel characteristics, both of which are inherent to this problem. Specifically, we have finished testing the algorithms for determining the least expected time path in stochastic, time-varying networks to be described in a technical paper under preparation titled "Least Expected Time-Paths in Stochastic, Time-Varying Networks," by Miller-Hooks and Mahmassani. In addition, work has continued on the extension of algorithms for determining minimum time paths in stochastic, time-varying networks to algorithms for determining minimum cost/risk paths and best paths with respect to multiple objectives in such networks.

To test these procedures, we have initiated the set-up of an example network of Texas using 1992 population statistics from the U.S. Bureau of the Census and actual distances to show results of the algorithms with respect to minimum time paths, minimum population paths and paths that are Pareto-optimal with respect to both objectives.

Ms. Elise Miller-Hooks, UT-Austin doctoral student and research assistant, helped organize a session titled "Cross Cutting Issues on the Disposition of Surplus Weapons Plutonium" for the Third Annual Student Research Conference at West Texas A&M (sponsored by Southwestern Bell Telephone Foundation and Amarillo National Resource Center for Plutonium) to be held on November 1, 1996.

Activities at Texas A&M University

An Internal Technical Working Document, "RADTRAN User Guide Supplement," has been written by Ms. Amy Caldwell in order to provide a project deliverable for the Transportation Analysis milestone to demonstrate familiarity with RADTRAN. RADTRAN is a code developed to assess the risks of transporting radioactive materials by various transport modes. The document is designed to describe the menu-driven features and functions of RADTRAN to a target audience of new users who will utilize the code to perform risk assessments involving the transport of radioactive materials. The document does not apply the code to actual data sets or detail the scientific aspects of performing such an analysis. The main objective of the document is to augment the existing user's manual by making the documentation congruent with the latest features of the software. The code and its accompanying documentation were developed and are maintained by Sandia National Laboratories.

Preliminary transportation risk analysis results have been completed. A hypothetical situation, consisting of two options, was explored. In the first scenario, the plutonium pits, removed from
nuclear weapons and in NRC Type B containers, were shipped in Safe Secure Trailers (SSTs) from the Pantex Plant near Amarillo, Texas, to the Savannah River Plant (SRS) near Aiken, South Carolina, where the pits would be used to manufacture MOX fuel, which would then be shipped to the Palo Verde Generating Station near Phoenix, Arizona. The second scenario consisted of MOX fuel from the Pantex Plant being shipped to the Palo Verde Generating Station in the event that the Pantex Plant converts the plutonium pits to MOX fuel on site. The overall risk was evaluated in terms of the workers’ and general public’s exposure (in person-rem) during incident-free shipments and shipments in which an accident occurs. Parameters for the risk analyses used data from the Storage and Disposition of Weapons-Usable Fissile Materials Draft Programmatic Environmental Impact Statement for shipment criteria and accident rates for SSTs utilized the default rates in RADTRAN. HIGHWAY, a routing component of the TRANSNET suite of codes, was used for route distances and population densities.

Task 2: Application of Existing Codes and Techniques
R. Radha, Prairie View A&M University
Z. Huque, Prairie View AM University

EXECUTIVE SUMMARY:
Faculty members and students involved in the project are progressively developing expertise using the TRANSNET software. The different routes (shortest, quickest and commercial) between the pairs of origination points and destination points were generated using a minimum impedance algorithm. Minimization of vulnerability is being taken into account when generating routes. Practical routes will be compared with risk free routes for transportation of radioactive MOX fuels. Development has started on a new model to achieve safe transportation of MOX fuels and radioactive materials.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:
The Prairie View team has started using the TRANSNET software, after completing successfully the earlier tasks of literature survey, information collection, developing familiarity with minimum impedance algorithm and study of the usefulness of RADTRAN component of the software. At present, efforts are made to impose different types of constraints during the computational analysis, calculate routes that maximize use of the Interstate Highway system and allow the user to predict routes that comply with DOT regulations.

At present, the study is addressing the following often raised question: whether routes that minimize the risk of accidents should be used in lieu of the routes that have the lowest operating costs. The commonly utilized minimum impedance objective function,

\[ L = \text{Min} \, S \, (aD + bT) \]

offers quickest route, shortest route and commercial route according to the appropriate values of the distance and time biases and their chosen combinations.

Our team realized the importance of minimizing risk in transportation of MOX fuels and radioactive materials. The concept of minimum risk in transportation will be dealt with mathematically by specifying a new objective function that minimizes the vulnerability along with the minimum impedance objective function referred to before. The new objective function to be considered is

\[ L = \text{Min} \, S \, (aD + bT) + \text{Min}(V) \]

where \( V \), the vulnerability is the product of \( R \) (accident rate), \( F \) (shipment frequency), \( P \) (population affected) and \( T \) (response time).
Task 3: Development of Source Term Components for Formulation and Initial Release of Plutonium-Containing Aerosol for Conditions and Effects Not Treated by Existing Models for Transportation Incidents.
Yassin A. Hassan, Texas A&M University
William H. Marlow, Texas A&M University

EXECUTIVE SUMMARY:

Verification of the three-dimensional space averaged program was performed. This program can be used after the completion of particle-tracking routines to investigate the plutonium aerosol which is likely to be generated during fire in a transportation accident.

Task 4: Investigation of Neural and Fuzzy Logic Analysis Techniques for Surety Issues in Transportation of Nuclear Materials
Donald C. Wunsch, II, Texas Tech University

EXECUTIVE SUMMARY:

During the past quarter we have been working on assessing the risk associated with the transportation process of Nuclear Materials. We are using fuzzy risk assessment to overcome the difficulties faced when using probabilistic analysis, due to the vagueness nature and lack of information characterizing the problem.

We use a fuzzy fault tree to assess the risk of failure associated with transportation of nuclear material. The fault tree describes the sequence/combination of events that may lead to a failure. Such events may be due to human errors, weather problems, intelligence leaks, or other hypothetical problems. The top event of the tree is system failure, defined as not having the nuclear material reach the destination safely within a specified amount of time.

Each event in the fault tree has its own membership function in which the fuzzy variable is the probability that this event may occur. The membership grade is the degree of belief that this probability may take on a certain value. PHASER (Probabilistic Hybrid Analytical System Evaluation Routine), implemented at Sandia National Laboratories, is used to calculate the membership function of the top event. The sequence of evolution of the fuzzy set describing a particular basic event is derived in order to assess the risk of failure after a certain number of trips. A decision can then be taken as when to change one of the transportation parameters, such as: route, time, maintenance schedule or destination.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

We have been using PHASER (Probabilistic Hybrid Analytical System Evaluation Routine) developed at Sandia National Laboratories and we are collaborating with the responsible personnel at Sandia for the use of this software. We have also developed algorithms that could be used along with PHASER for the calculation of fuzzy membership functions of repetitive events during a transportation process.
NEW POLYMERS AND EXTRACTANTS FOR PLUTONIUM SEPARATIONS

Richard A. Bartsch (PI), Department of Chemistry, Texas Tech University

EXECUTIVE SUMMARY:

For the recovery of contaminating plutonium, the plutonium-containing material may be dissolved in concentrated nitric acid and the plutonium separated from other components of the solution by sorption on commercially available Reillex™ HPQ anion-exchange resin. Subsequently the sorbed plutonium can be recovered from the resin by stripping (washing) with dilute nitric acid.

In earlier work, we have demonstrated that experimental, bifunctional, anion-exchange resins prepared at Texas Tech University and evaluated at Los Alamos National Laboratory are markedly superior to the commercial anion-exchange resin both in terms of the rate and efficiency of plutonium(IV) sorption from concentrated nitric acid solution. Although these new polymeric resins were demonstrated to rapidly and efficiently sorb plutonium from 7M nitric acid solutions, they suffer from compaction due to their low level of crosslinking. To be suitable for practical application in the recovery of plutonium which would involve column separations, bifunctional anion-exchange resins with a higher level of crosslinking are required.

During the reporting period, two series of bifunctional anion-exchange resins have been prepared which have the same level of crosslinking in the base polymer as does the Reillex™ HPQ resin. Two series of bifunctional anion-exchange resins were prepared by reactions of macroporous, 33 %-crosslinked, Reillex™ HP poly(4-vinylpyridine) with (5-bromopentyl)trimethylammonium bromide and with (5-chloropentyl)pyridinium chloride in methanol under pressure at 100 and 120 °C. The rate and efficiency of plutonium(IV) sorption from 1M and 7M nitric acid were evaluated as a function of the levels of alkylation of the base polymer which were achieved under the different conditions of reaction temperature, reaction time, and alkylating agent. One series of the new bifunctional anion-exchange resins shows a markedly enhanced ability to sorb plutonium(IV) from 7M nitric acid relative to Reillex™ HPQ resin, but only modest enhancement in the rate of plutonium(IV) sorption. These results indicate that a base polymer with a somewhat lower level of crosslinking is needed.

DETAILED DESCRIPTION OF RESEARCH ACTIVITIES:

At Los Alamos National Laboratory (LANL), the state-of-the-art method which has been developed for the recovery of contaminating plutonium from a variety of matrices is dissolution of the material in concentrated nitric acid followed by removal of the plutonium by sorption on a commercial anion-exchange resin, Reillex™ HPQ. Subsequently the sorbed plutonium(IV) can be recovered from the resin by stripping (washing) with dilute nitric acid. The Reillex™ HPQ resin, which was jointly developed by Reilly Industries in Indianapolis, Indiana, and Los Alamos National Laboratory, is a partially methylated poly(4-vinylpyridine). The structure of the Reillex™ HPQ resin is shown below.
The Kd (mL/g) values which were measured at LANL for sorption of plutonium(IV) from 1M and 7M nitric acid solution after contact for varying time periods are presented in Table 1.

Table 1. Plutonium(IV) Sorption from Nitric Acid Solutions\(^a\) by Reillex\textsuperscript{TM} HPQ Resin.

<table>
<thead>
<tr>
<th>Sorption Time (hr)</th>
<th>1M nitric acid</th>
<th>7M nitric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>6.7</td>
<td>490</td>
</tr>
<tr>
<td>2</td>
<td>7.1</td>
<td>850</td>
</tr>
<tr>
<td>6</td>
<td>6.8</td>
<td>680</td>
</tr>
</tbody>
</table>

\(^a\)Initial plutonium concentration of 3g/L

In earlier work, we demonstrated that experimental, bifunctional anion-exchange resins prepared at Texas Tech University (TTU) and evaluated at LANL are markedly superior to the commercial anion-exchange resin in terms of both the rate and efficiency of plutonium(IV) sorption from concentrated nitric acid solution. (1) Although these new polymeric resins were demonstrated to rapidly and efficiently sorb plutonium from 7M nitric acid solutions, they suffer from compaction due to their low level of crosslinking. To be suitable for practical application in the recovery of plutonium which would involve column separations, bifunctional anion-exchange resins with a higher level of crosslinking are required.

During the reporting period, two series of bifunctional anion-exchange resins TTU-1 and TTU-2 were prepared at Texas Tech University. For these experimental resins, the base polymer has the same 33 % crosslinking as does the Reillex\textsuperscript{TM} HPQ resin. For both series of bifunctional anion-exchange resins the base polymer was macroporous, 33 % crosslinked, Reillex\textsuperscript{TM} HP poly(4-vinylpyridine). Reaction of the Reillex\textsuperscript{TM} HP resin with (5-bromopentyl)trimethylammonium bromide under pressure in methanol at 100 and 120 °C gave the TTU-1 resins (Equation 1). Similarly the reaction of the base polymer with (5-chloropentyl)pyridinium chloride under...
pressure in methanol at 100 and 120 °C gave the TTU-2 resins. For both experimental resin series, there is a five-atom spacer between the pyridinium group from the base polymer and the second positively charged center. In earlier studies (1), it was established that five-atom spacers gave higher levels of plutonium(IV) sorption than when the spacer was shorter or longer.

For the preparation of the TTU-1 anion-exchange resins, the alkylation reactions (Equation 1) were performed at two different reaction temperatures and with different reaction times. The percent of alkylation was determined from the percent of bromine in the resin as determined by combustion analysis. As shown in Table 2, alkylation levels of 70-88 % were achieved. Results obtained at LANL for sorption of plutonium(IV) from 1M and 7M nitric acid solutions by the bifunctional anion-exchange resins TTU-1 are presented in Table 2. Comparison of the results in Tables 2 and 3 reveal that the sorption of plutonium(IV) from 7M nitric acid with a 30-minute contact time is slightly higher for the TTU-1 resins than was observed with Reillex™ HPQ resin. However the sorption levels obtained with the TTU-1 resins after contact times of 2 and 6 hours are several times higher than those noted for Reillex™ HPQ resin. These much higher levels of plutonium(IV) sorption are attributed to the bifunctional nature of the TTU-1 resins. If such high efficiency in plutonium(IV) sorption could be achieved with a 30-minute contact time, this would represent a major advance in the technology for the recovery of contaminating plutonium.

For the preparation of the TTU-2 anion-exchange resins, the alkylation reactions (Equation 2) were also performed at two different reaction temperatures and with different reaction times. The degree of alkylation was determined by combustion analysis for chlorine. As can be seen from the results given in Table 3, the levels of alkylation were found to be 23-77 % even though relatively long reaction times were involved. The lower level of alkylation is attributed to the poorer chlorine leaving group in the alkylation agent. Results obtained at LANL for sorption of plutonium(IV) from 1M and 7M nitric acid by the experimental TTU-2 resins are presented in Table 3.
Table 2. Plutonium(IV) Sorption from Nitric Acid Solutions by the Bifunctional Anion-exchange Resins TTU-1.

<table>
<thead>
<tr>
<th>Reaction Temp. (°C)</th>
<th>Reaction Time (Days)</th>
<th>Percent Alkylation (%)</th>
<th>Sorption Time (Hr.)</th>
<th>Kₐ Value For Pu(IV) Sorption from 1m Nitric Acid</th>
<th>Kₐ Value For Pu(IV) Sorption from 7m Nitric Acid</th>
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</table>

ND² = Not determined

Plutonium(IV) sorption behavior superior to that of Reillex™ HPQ was achieved with the TTU-2 resins only when the level of alkylation was >50%. Due to the extended alkylation reaction periods required for the preparation of the TTU-2 resins, they appear to be much less promising than the TTU-1 resins.

Attention will now be focused upon bifunctional anion-exchange resins to be prepared from 16% crosslinked macroporous poly(4-vinylpyridine). It is anticipated that less crosslinking in the base resin will lead to higher levels of plutonium sorption for the shorter contact times.
Table 3. Plutonium(IV) Sorption from Nitric Acid Solutions by the Bifunctional Anion-exchange Resins TTU-2.

<table>
<thead>
<tr>
<th>Reaction Temp. (°C)</th>
<th>Reaction Time (Days)</th>
<th>Percent Alkylation (%)</th>
<th>Sorption Time (Hr.)</th>
<th>K₃ Value for Pu(IV) Sorption from 1M Nitric Acid</th>
<th>K₃ Value for Pu(IV) Sorption from 7M Nitric Acid</th>
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Reference


EXECUTIVE SUMMARY:

Part 1:  *Diamond Generation by Explosive Compression of Buckminsterfullerene*

A fourth three dimensional explosive compaction test was performed on November 8, 1996. This iteration of the design consisted of a solid steel sphere as the workpiece. This design replaced the composite, copper sphere encased in a steel shell design that was used in the previous three experiments. The sample was introduced into the sphere by drilling and tapping a hole to the center of the sphere, loading the sample material, then closing the hole and compressing the sample with a threaded screw. The resulting workpiece was inserted into the spherical high explosive around which a brass shell was placed. The final assembly was buried in sand before detonation.
The sand and brass shell structure was employed to reflect a portion of the expansion waves back toward the center of the workpiece. The dimensions were manipulated to insure destructive interference of the expansion waves that are reflected after compression of the steel sphere, thereby helping to maintain the integrity of the piece.

The result of the fourth shot was complete recovery of the workpiece. This result represents a major accomplishment toward the ultimate goal of this project. We now have a workpiece design which allows for the study of materials under extreme temperatures and pressures. The recovered workpiece is enroute to UT for analysis. The piece will be cut in half in order to examine the effects of the detonation and compared to the simulations run at Texas Tech. The sample material will be subjected to x-ray analysis, raman spectroscopy, and scanning electron microscopy to test for the presence of diamond and to fully characterize the detonation products.

Concurrent with 3-D work, one dimensional experiments have been progressing. Namely, flyer dimensions and stand off distances have been investigated in order to maximize the pressure delivered to the sample while insuring complete recovery of the sample. Simulations were used to determine an initial design for the flyer and stand off distance while maintaining the same dimensions of the sample holder and impacting piece (see past reports). Detonation of this design proved that the impact of the flyer caused excessive damage to the sample holder and a portion of the product was thought to be lost. Closer, microscopic investigation of this piece showed that the sample holder had not failed and the sample was contained. However, the margin of error for this design was too small to reliably retain the sample after compression. In order to reduce the damage, an additional 1/2 inch thick piece of steel was bolted to the top of the sample holder. With this design, there was minimal damage to the sample holder. However, this buffer piece of steel absorbed too much of the impact, thereby reducing the pressure pulse experienced by the sample. Currently, experiments are being conducted with 1/4 inch and 1/8 inch buffer plates in order to optimize the pressure while assuring recovery.

Part 2: Demonstration Burn for Energy Recovery

On September 17, 1996, a meeting was held with representatives from NAWCWPNS, Pantex, and UT to determine program directions and to reset goals and assign task responsibilities. Specifications on the hydro-machining of the explosives were established and subsequent testing of binder materials was initiated. Numerous binders have been investigated at UT. The results of these screening studies are summarized below.

1. **EcoFoam**: A water soluble starch product used as a shock absorber for shipping purposes.
   - **BINDING MECHANISM**: Redissolve the polymer in an aqueous solution of the recyclable polymer/explosive (P/E) and then dry.
   - **ADVANTAGES**: Inexpensive, environmentally friendly, uses the water already present in our process, will burn cleanly.
   - **DISADVANTAGES**: EcoFoam is designed not to become “tacky” when wetted and thus does function as a good binder.
   - **OUTCOME**: Not a suitable option

2. **AlcoGum SL70**: A commercial polyacrylate solution made up of 30% solids in water primarily used as a thickener.
3. AlcoGum ARM II 135: A commercial polyacrylate solution made up of 13% solids in water primarily used as a thickener.

- **BINDING MECHANISM:** Disperse the P/E in the alcogum, add base, and the system forms a gel.
- **ADVANTAGES:** Instantaneous binder (forms gel immediately upon addition of base), wet process, less viscous than alcogum SL70, no health hazards.
- **DISADVANTAGES:** Does not form solid pellet (need container which can be disposed of as well), not easily dried (skin forms on top surface which bubbles up with additional heating), cost issue ($0.455/wet lb.), needs strong base.
- **OUTCOME:** Possible option

4. **Asphalt:** Received a sample, Coastal AC 20, from Civil Engineering Dept. at UT.

- **BINDING MECHANISM:** Disperse the P/E in heated (melted) asphalt and allow to cool.
- **ADVANTAGES:** Ease of process, cheap, forms a solid pellet which is non brittle, also a good source of energy when incinerated.
- **DISADVANTAGES:** Asphalt does not actually melt, rather becomes less viscous as the temperature is increased. In order to reduce the viscosity to a workable mixture, the temperature will need to be at least 110 °C which will be costly. Also, at this viscosity, there is a chance of a settling problem since it takes a long time for the asphalt to cool.
- **OUTCOME:** Coastal AC 20 does not appear feasible, however, other asphalts which melt at lower temperatures are still an option.

5. **Elotex Redispersible Powders:** Polymer powders made from aqueous emulsions formulated to improve the binding ability of inorganic binders.

- **BINDING MECHANISM:** Redissolve the powder in an aqueous solution of the P/E and then dry.
- **ADVANTAGES:** Uses the water already present in our system.
- **DISADVANTAGES:** Does not form a brick (water removal of an aqueous emulsion results in a powder), cost.
- **OUTCOME:** Not a suitable option
6. **Phenolic Resin**: One of many permutations consisting of a phenol, an aldehyde, and an initiator.

- **BINDING MECHANISM**: Mix phenol and aldehyde with P/E then initiate polymerization.
- **ADVANTAGES**: Results in solid pellet due to high degree of crosslinking, water present in system is not a problem, and no settling of explosives.
- **DISADVANTAGES**: Tried reaction with p-cresol and formaldehyde using an acid catalyst but was unsuccessful. The toxicity of starting materials is also a concern.
- **OUTCOME**: Not an option due to brittle pellet

7. **Furan Resin**: Polymer formed from the acid catalyzed polymerization of furfuryl alcohol

- **BINDING MECHANISM**: Wet the P/E with furfuryl alcohol and then add acid to polymerize.
- **ADVANTAGES**: Forms a very solid brick, polymerization occurs in only five minutes, no settling of the explosive.
- **DISADVANTAGES**: Health and handling hazard, polymerization is very exothermic and will heat the P/E to a significant degree, possible cost issue, requires strong acid, resulting brick becomes brittle after time.
- **OUTCOME**: Not an option as tried. However, commercial operations using similar technology exist, i.e., particle board, so it is certainly possible. More work needs to be done before discounting this option.

8. **Phenolic Urethane Resin**: Resin produced from polymerization of isocyanates and a diol.

- **BINDING MECHANISM**: Mix isocyanates and diol with P/E and initiate polymerization.
- **ADVANTAGES**: Fast polymerization which is only slightly exothermic, solid pellet which is non-brittle.
- **DISADVANTAGES**: Toxicity of starting materials, cost
- **OUTCOME**: Possible option

9. **Modified Bitumin**: Melt adhesive used in the roofing industry
• BINDING MECHANISM: Disperse P/E in a melted sample and cool.
• ADVANTAGES: Ease of process
• DISADVANTAGES: Cost is prohibitive for this project.
• OUTCOME: Not an option

10. Non-Solvent Induced Vitrification of Polymer Solution: Formation of pellet by vitrification of polymer solution in NMP.

• BINDING MECHANISM: Dissolve waste polymer in NMP to form a viscous dope. Mix in explosive and then submerge mixture in water which results in the formation of a rubbery solid.
• ADVANTAGES: Instantaneous formation of pellet, no settling of explosives, pellet is non-brittle.
• DISADVANTAGES: Waste polymer must be soluble in NMP, cost.
• OUTCOME: Possible option

Other Possible Options
Fly Ash
Xantham Gum
Roofing Tar
Wax
PVC dissolved in dioctalphtalate
Commercial Gelatins
Latex mixes