REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	August 14, 2000	Final Feb. 1, 2000 to July 31, 2000

4. TITLE AND SUBTITLE
Engineering Design Software for Military Incinerators

5. FUNDING NUMBERS
C DAAD19-00-C-0061

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REI 4218

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office Attn: AMSRL-RO-RI (Sylvia Hall)
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT (see Section 5.3b of this solicitation)
Approved for public release, distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
Report developed under SBIR contract for topic A99-027. The Phase I program was to provide proof of concept for an engineering design workbench (EDW) for military incinerators. There is a great need to develop computational tools capable of (1) assessing the health and environmental impact performance of these existing incinerators during both steady-state and transient (upset) conditions, and (2) evaluating potential opportunities to enhance online availability and to increase munitions throughput.

In Phase I, the focus was on developing component models for a selected subset of the incinerators and afterburners at the Tooele Chemical Agent Disposal facility (TOCDF).

The Phase I program demonstrated that there is sufficient data available to define the incinerator systems and operating conditions at the TOCDF. Our models predict complete destruction of the chemical agent when the incinerators and afterburners are operated as per standard operating conditions. The models also highlight that under severe upset conditions incomplete destruction could occur.

14. SUBJECT TERMS
Chemical weapons incinerators, reduced chemical mechanisms, destruction efficiency, reacting CFD, simulation, modeling

15. NUMBER OF PAGES 23

16. PRICE CODE

17. SECURITY CLASSIFICTION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	unlimited

REF C

Department of Defense

SBIR Phase I Final Report

Engineering Design Software for Military Incinerators

Principal Investigator: Dr. Michael P. Heap

Contract Number: DAAD19-00-C-0061

Program Official: Dr. Robert Shaw

Contract Start Date: February 1, 2000

August 14, 2000

REACTION ENGINEERING INTERNATIONAL

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Introduction

The United States has maintained a stockpile of highly toxic chemical agents and munitions for more than half a century. The manufacture of such agents and munitions and their subsequent stockpiling were undertaken in the belief that they were valuable as deterrents to similar materials being used against U.S. forces. That deterrence is no longer considered necessary. Consequently, the United States can no longer justify the continuing risk and expense of storage.

In the 1970s, the Army had commissioned studies of different disposal technologies and tested several of them. In 1982, incineration was selected as the method of disposing of agents and associated propellants and explosives and of thermally decontaminating metal parts. Incineration technology is embodied in today's baseline incineration system that is operating at two sites (Johnston Island in the Pacific Ocean; Tooele Army Depot, Tooele, Utah) and is under construction/installation at three sites (Anniston Army Depot, Anniston, AL; Pine Bluff Arsenal, Pine Bluff, AK; and Umatilla Depot, Umatilla, OR). A total of 79.6% of the nation's chemical agent is stored at these sites. Two sites, with 11.5% of the agent, are awaiting a technology decision.

Incineration processes raise concerns about potentially harmful emissions and many people living around these sites have remained resolutely opposed to the baseline incineration system. Further, the aging chemical weapons stockpile has created many challenges to the operational efficiency of the baseline system. These and other factors have resulted in major increases in the cost of the Chemical Stockpile Disposal Program (CSDP), from over $1B to $15B (a typical plant costs $200,000 per day to operate) and a thirteen (13) year increase in the disposal schedule (1994 to 2007). Since storage risk dominates overall risk, this has greatly increased the risk to those living near the storage sites. There is a great need to develop tools capable of (1) assessing the health and environmental impact performance of these existing incinerators during both steady-state and transient (upset) conditions, and (2) evaluating potential opportunities to enhance online availability and to increase munitions throughput.

In the following sections we present, in order, a summary of

- program goal,
- Phase I accomplishments ,
- programmatic approach,
- Task 1 – Program Definition,
- Task 2 – Pyrolysis and Flame Chemistry,
- Task 3 – Module Development,
- modeling a severe upset condition, and
- Phase I option.
- Conclusions

The answers to the research questions that were posed in the Phase I proposal are interspersed within the body of the report. The research questions are highlighted with bold print to facilitate their identification within the text of the report.

In addition, in our Phase I SBIR Proposal we outlined a Phase I Option, or extension of the Phase I work, in which REI would develop a time-dependent model for the heel of a canister and outline the software requirements for the EDW. The Phase I Option was not funded and therefore no work was performed on these items.

Program Goal

The overall goal of this program was to develop an Engineering Design Workbench (EDW) to provide an engineer the ability to optimize and evaluate the performance of military incinerator units under a variety of operating conditions.

The planned "workbench" was to:

- Contain tools to allow the rational engineering design of optimized, economical incinerators for military use.
- Define optimum operating conditions, destruction efficiency as a function of throughput, reactor configuration, product species and concentrations, and energy needs.
- Provide information about potential onset of reactor upsets and enable diagnosis of failures.
- Allow engineers to consider a wide range of "what if scenarios"
- Simulate both military and commercial sector incinerators

To achieve these requirements, the EDW tool was to be based on a combination of detailed CFD models and fast running process models. The CFD models were to include the detailed chemistry and physics required to meet the EDW objectives for analysis of the incinerator units. The process models provided the ability to include modeling the gross behavior of less complex equipment within the incineration plant, such as the Pollution Abatement System (PAS).

The proposed EDW would have provided the engineer with a tightly integrated problem-solving environment containing an array of "tools" that communicated in a seamless manner. The EDW was to be PC based, user friendly, and allow for a wide degree of customization to meet specific customer needs concerning incinerator configuration, materials to be treated and the output visualization. All of the tools required to setup, execute, and visualize simulations were to be contained within the EDW. To ensure that a commercially viable product would be available at the end of Phase II the EDW was to be built using models and software infrastructure that could be upgraded readily as advances are made in the relevant physics and chemistry.

The Phase I program was to provide proof of concept for the EDW. In Phase I, the focus was on developing component models for a selected subset of the incinerators and afterburners at the Tooele Chemical Agent Disposal facility (TOCDF). The focus of Phase II would be to use the component models developed in Phase I and include them in a user-friendly software environment to create the EDW. We have been informed that the Phase II project will not be funded.

We chose to use the incinerators at the TOCDF because the incinerators to be used at other Army incineration sites will use systems similar (some are identical) to those at the TOCDF. In addition, the TOCDF is located only a short drive from our offices in Salt Lake City, Utah. The Tooele Army Depot stores the largest and most diverse chemical weapons stockpile. It includes all three agents GB, VX and mustard, and the entire spectrum of munitions and storage containers. Consequently, the EDW developed for TOCDF will have applicability across the four baseline incineration system sites.

Phase I Accomplishments

We have achieved all of the Phase I objectives defined in our proposal. The Phase I program demonstrated that there is sufficient data available to define the incinerator systems and operating conditions at the TOCDF. Our models predict complete destruction of the chemical agent when the incinerators and afterburners are operated as per standard operating conditions. The models also highlight that under severe upset conditions incomplete destruction, and potentially no destruction, could occur.

In Phase I we have:

- Obtained a full chemical mechanism for the GB simulant DMMP.
- Used this full mechanism to calculate DMMP destruction along streamlines defined from CFD solutions of afterburners and furnaces
- Developed two reduced mechanisms that approximate the performance of the full mechanism for temperatures typical of chemical demilitarization incinerators.
- Applied a reduced mechanism to a CFD simulation of an afterburner.
- Constructed and exercised CFD models of a liquid incinerator, a metal parts furnace, a deactivation furnace and a representative afterburner.
- Demonstrated that these models are useful for exploring scenarios relevant to chemical demilitarization incinerator operation and closure.

Programmatic Approach

The goal of Phase I was to develop and demonstrate, as proof-of-concept, workbench computational fluid dynamics (CFD) modules for military incinerators. To achieve this goal, three (3) major tasks were identified.

Task 1 – Program Definition

The objective of this initial task was to ensure that the program plan as outline in the Phase I proposal, if executed successfully, would achieve the stated goal.

Task 2 – Pyrolysis and Flame Chemistry

The objective of this task was to identify the best available pyrolysis and flame chemistry suitable for toxic military materials containing phosphorous, sulfur and halogens.

Task 3 – Module Development and Testing

This task required the construction of process models for three incinerators (liquid incinerator, metal parts furnace, deactivation furnace system) and one afterburner at the Tooele Chemical Agent Disposal Facility (TOCDF), Tooele Utah, and the demonstration that these models operate in a stand-alone manner. The construction of these models required considerable design and operating information. We would like to acknowledge the considerable assistance and cooperation of Mr. Kevin Gildner (PMCD) in obtaining this information.

In addition, we proposed to perform two optional tasks at the completion of Phase I.

Phase I Option Task 1 - Transient Heel Removal Model Development

The objective of this task was to improve the munition projectile submodel used to predict the rate of agent vaporization rates from the projectiles in the Metal Parts Furnace. The temperature distribution in the wall of the projectile was to be handled by the transient conduction equations. Allowance was to be made for the three dimensional variation in temperature in the shell, including the temperature gradients across the shell thickness, around the perimeter, and along the axis.

Phase I Option Task 2 - Simulator Definition

The final task was to define the performance specs for the military incinerator simulator. The workbench was to include several modules such as input definitions, incinerator configuration, chemistry reduction, stream tube post-processor and a visualization tool.

These Phase I Option Tasks were not funded and therefore were not completed.

Task 1 - Program Definition

To ensure that the program plan as outlined in the Phase I work plan would be of value to the CSDP, a series of informal discussions and formal briefings were held with the Program Manager for Chemical Demilitarization (PMCD) personnel, senior management at the Tooele Chemical Agent Disposal Facility (TOCDF) and the Manager, Operations, Raytheon Demilitarization Company (systems contractor for three (3) of the baseline incineration system plants). These meetings proved to be extremely beneficial and encouraging. Participants endorsed the approach and work plan proposed by REI and, importantly, suggested numerous areas and software enhancements that would increase the Engineering Design Workbench (EDW) utility to the CSDP.

Task 2 - Pyrolysis and Flame Chemistry

In this task we sought to answer two questions:

1 How adequate is the information available on the pyrolysis and flame chemistry of the military materials of importance?

An adequate mechanism exists for the GB simulant DMMP. A full mechanism does not exist for VX and mustard agent but mechanisms could be constructed. We have identified an approach for developing mustard agent and VX chemistry in Phase II.

2 Must the process models treat the full chemistry or are reduced mechanisms adequate and if so under what conditions?

Global mechanisms based on partial equilibrium of radicals have been created but were found to be inadequate. A skeletal reduced mechanism has been created but is still too large to be incorporated into the CFD code. Reduced mechanisms for DMMP combustion with 15 and 21 species have been created using the automatic mechanism reduction software CARM (Chen, 1997). Both reduced mechanisms compare well to the full mechanism in simple reactor test cases. The smaller reduced mechanism has been implemented into the CFD post processing software.

Chemistry of Agent Destruction

It was never envisioned that this project would develop detailed chemical mechanisms for pyrolysis and flame chemistry that would be applicable to agent destruction in incinerators but rather to extract the best available mechanisms from the literature. Our primary thrust to date has been to focus on pyrolysis and flame chemistry for DMMP, a nerve agent simulant. This decision was taken, in large part because a detailed chemical kinetic mechanism is available for this material. Dr. Fred Gouldin (Cornell), a project team member, provided us with the DMMP mechanism of Werner and Cool (1999), with unpublished modifications by Babushok and Tsang. This represents the most up-to-date mechanism available. We are kept abreast by Prof. Fred Gouldin about new developments in the field of organophosphorus combustion kinetics. Korbeinichev et al. (2000) present kinetic mechanisms for combustion of DMMP and TMP. It is the opinion of Prof. Gouldin that the mechanism we are using, which was updated by Babushok (formerly of the Novosibirsk group) and Tsang of NIST includes the recent work of these Russian researchers. This mechanism contains 63 species and 436 reactions. In addition to pyrolytic decomposition, this mechanism accounts for the H and OH radical attack mechanisms that dominated under the low temperature ($T < 1500$ K), fuel-rich H_2-O_2 flame conditions studied by Werner & Cool (1999), as well as attack by O and methyl radicals encountered in significant concentrations in the fuel-lean hydrocarbon flames used in incineration equipment.

As expected, calculations with the DMMP mechanism show DMMP to be thermally unstable - that is, it quickly disintegrates at elevated temperatures. Figure 1 shows results of Plug Flow Reactor (PFR) calculations using the full DMMP mechanism. Even in the absence of other reactants, DMMP is easily destroyed (Figure 1a). In these calculations the DMMP was mixed with nitrogen so the initial destruction is due entirely to unimolecular decomposition. When DMMP is added to equilibrated rich methane air combustion products (Figure 1b) destruction occurs at lower temperatures. Agents are relatively unstable, ranking low on the hazardous organic compound incinerability index. For example, mustard agent ranked 132, just below 1,1 dichloroethane (Taylor et al., 1990). This can be compared with HCN that ranked first and benzene second on this index. The temperature requirement for 99 percent destruction (T_{99}) for HCN and benzene are >1150°C and ~ 1150°C, respectively. By contrast mustard gas has a T_{99} of less than 680°C (Taylor et al. 1990). Our calculations of T_{99} for DMMP give a value of 900 C. This value is probably too high, because our calculations are unable to account for wall reactions which are likely to be very significant in the small diameter reactor used by Taylor et al. (1990).

Although no detailed mechanism currently exists for the combustion of mustard agent, we have defined an approach by which mustard agent destruction kinetics can be approximated. This approach is detailed in Section 3.5.

Integration of Detailed Chemistry Along Streamlines

REI has a tool that allows information to be extracted from CFD simulation results giving information about the flow and reactions along a streamline. Given a starting location, this tool will tabulate the temperature, species concentrations, velocities, or any other quantity from the CFD simulation as a function of time along the path that would be experienced by an infinitesimal fluid element. This time and species history information can be input to a modified version of the SENKIN code that calculates

detailed chemical kinetics in a plug flow reactor (PFR). Thus, both temperature and major species (N_2, H_2, H_2O, CO, CO_2, O_2) concentrations can be interpolated from a CFD simulation along a streamline and specified as functions of time within the PFR calculation. This allows detailed chemical kinetics to be used for post-processing a CFD simulation, while incorporating effects of mixing and heat release from the CFD simulation. Before the reduced mechanism was available we used this approach with the full DMMP destruction mechanism with the four CFD modules described in this report. In all cases we demonstrated very rapid and complete destruction of the agent simulant. However, this streamline approach extracts only mean information from the CFD solution and thus neglects turbulent fluctuations. Consequently it is important that a reduced mechanism that replicates the results of the full mechanism over the conditions of interest is available and can be added to the CFD modules to account for the interaction of chemistry and turbulence.

Applicability of Reduced Mechanisms

The CARM software is able to create reduced mechanisms from the detailed mechanisms. The first step in this process is to create a "skeletal mechanism" by using sensitivity analysis to remove species and reaction steps that are unimportant at the conditions of interest. This resulted in a skeletal mechanism with 47 of the original 63 species and 149 of the original 436 reactions. From this skeletal mechanism, reduced mechanisms containing 15 and 21 species were created. Figure 2 compares DMMP destruction in a fixed-temperature perfectly stirred reactor (PSR) for stoichiometric methane/air with 1000 ppm of DMMP added. Both reduced mechanisms give reasonable results. These mechanisms were both optimized for conditions in the MPF afterburner, i.e. lean stoichiometry, T = 1200-1800 K. The reduced mechanisms cannot be expected to perform well outside this range of conditions. Reduced mechanisms can be created to model a broader range of conditions, but may require retaining more species.

The 15-species reduced mechanism includes the species N_2, H_2, O_2, H_2O, H, O, OH, CH_4, CH_3, CO, CO_2, PO_2, $HOPO_2$, $OP(OH)_3$, and DMMP. This mechanism has been implemented into REI's in-house CFD post-processing software. This code uses the temperature and velocity fields calculated using equilibrium chemistry as a background for calculations of chemical kinetic effects using the reduced mechanism. REI has previously successfully applied this technique to NOx reduction by injection of ammonia and urea reagents in the upper part of a coal fired utility boiler (Cremer et al., 2000). The reduced mechanism post-processing code has been applied to the MPF afterburner base case and upset case with one burner disabled assuming extraordinarily poor performance of the MPF in which 1000 ppm of agent simulant enters the afterburner. Extremely high destruction efficiency is predicted in both cases.

We investigated a second approach to reduce the detailed mechanism by creating a global mechanism for DMMP destruction. This global mechanism contains the most important DMMP destruction steps determined through sensitivity analysis. These are the reactions of DMMP with the radicals O, H, OH, and CH_3. The concentrations of these radicals are determined through partial equilibrium relations with the major species that are interpolated from the CFD simulation. This approach was unsatisfactory because the radical concentrations are underestimated by the partial equilibrium expressions, resulting in DMMP destruction rates that are slower than those given by the detailed kinetic mechanism. The reduced mechanisms that were created have been found to be vastly superior to the global approach.

Task 3 - Module Development and Testing

Task 3 of the Phase I program involved the construction of CFD models for four components of the TOCDF; these models were then used to simulate different operational scenarios in order to answer the following question:

What are the performance characteristics of the incineration system models and what improvements are required?

Models have been constructed and tested for 1) the Metal Parts Furnace (MPF) afterburner; 2) the Liquid Incinerator (LIC); 3) the MPF primary chamber, and 4) the Deactivation Furnace System (DFS) rotary

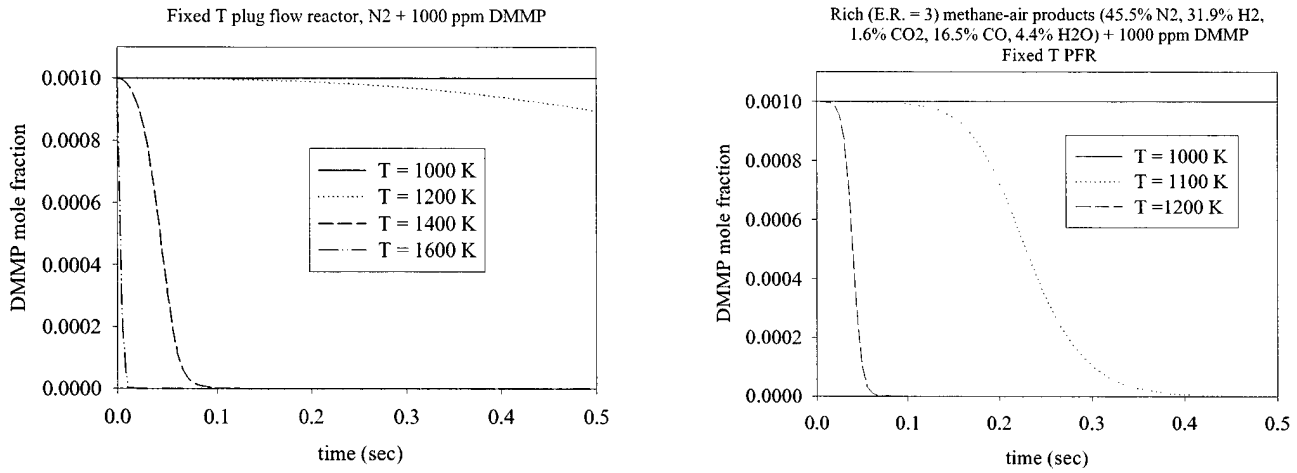

Figure 1. DMMP destruction. PFR calculations with full mechanism a) in nitrogen and b) in rich methane combustion products

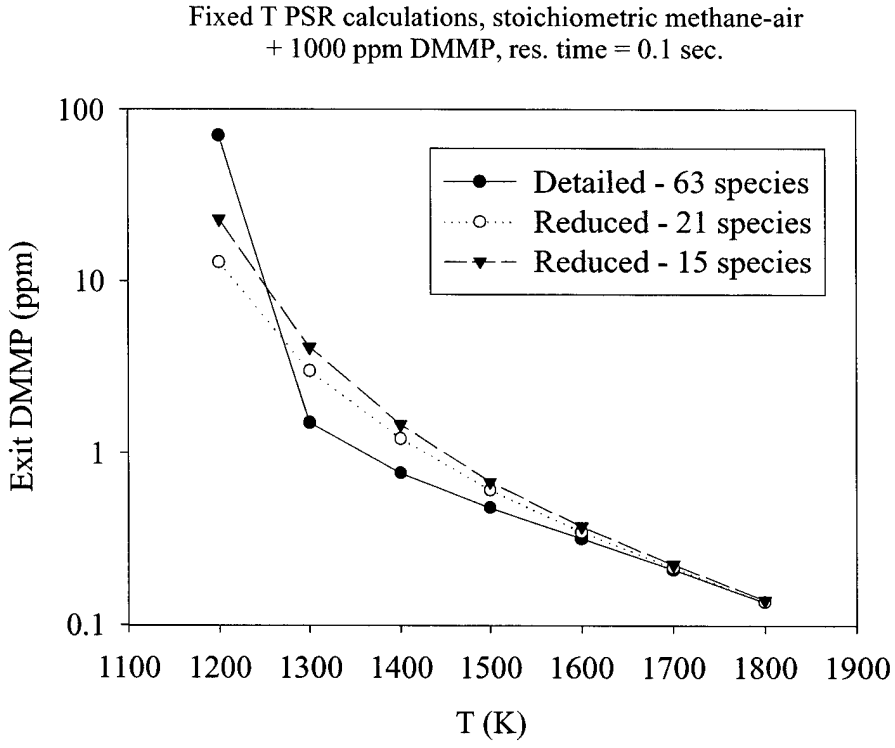

Figure 2. Comparison of full and reduced mechanisms

kiln. This subsection will present results for the following test cases to illustrate the value of these models to the CSDP:

- MPF Afterburner
  - Baseline
  - Upset condition, one auxiliary burner out of service.
  - Rapid, concentrated release of agent (puff) from the primary furnace
- LIC
  - Baseline
  - Nitrogen oxide formation during standard operation
  - Destruction of pulverized material from a carbon filter
- MPF
  - Baseline which had munitions bodies containing 5% agent
  - The same amount of agent as the baseline but in fewer, undrained munitions
  - Increased agent input
- DFS
  - Baseline

Incinerator-specific submodels such as a munitions/agent transient heat transfer model for the MPF and an energetics combustion model for the DFS kiln were developed as stand-alone computer programs, and are not coupled with the respective reacting CFD code. Coupling between these submodels and the main reacting CFD model needs implementation, as does the coupling between the primary chamber and the appropriate afterburner. Such coupling was never contemplated in this Phase I proof of concept demonstration.

Constructing CFD Modules for Incinerator Components

The technical approach used to produce the furnace module involved the following:

1. REI's reacting two-phase CFD code, *GLACIER*, predicted the temperature and flow fields using equilibrium chemistry with an assumed shape probability density function (PDF) to account for turbulence chemistry interactions.
2. To reduce the required memory, only a subset of the species contained in the detailed mechanism was used in the CFD calculations involving equilibrium chemistry. These species included major reactant and product species with relatively few intermediates. The species subset was selected to reproduce the adiabatic flame temperature obtained with the complete list of the species in the mechanism over a wide range of stoichiometries.
3. Finite rate kinetic calculations either by the streamline approach or the reduced mechanism were then applied as a post-process using the previously calculated temperature and flow fields.

It is important to gage the significance of flame suppression and understand under what conditions it occurs because the CFD models used in this project use an equilibrium chemistry approximation, which is unable to account for these effects. The approach we are adopting in developing incinerator models is to obtain the flow and temperature fields from CFD models assuming chemical equilibrium followed by detailed chemistry calculations as a post-process. Following an approach suggested by Dr. Gouldin at the project kick-off meeting, a study was performed to investigate the validity of equilibrium chemistry to obtain the overall heat release and resulting flow field. The study showed that the blowout residence time increases as more DMMP is added, demonstrating the well-known flame suppression characteristics of organo-phosphorus compounds. These studies suggest that inhibition only occurs at combustion intensities (very short residence times or high strain rates) much greater than are encountered in the incineration units.

The addition of phosphorus compounds to flames can also result in a significant increase in temperature due to the resulting enhancement of exothermic radical recombination reactions. Our calculations show that addition of up to a few thousand ppm of DMMP to a methane-air flame has a very small effect (<5K) on the equilibrium temperature, but can significantly increase the temperature (100-150 K) of an intermediate residence time (0.001 sec.) stirred reactor flame that lies between extinction and equilibrium conditions. Similar conclusions were reached by Glaude et al. (2000) from simulations of premixed flames to which DMMP was added. Twarowski (1995) suggested adding phosphorus to rocket

propellants to lessen dissociation losses and improve performance. Thus, for conditions under which extinction does not occur, the phosphorus compounds will speed the equilibration of the system, improving the validity of our CFD approach. These results suggest that organo-phosphorus flame suppression is not an important effect in the systems being modeled, justifying our modeling approach.

The information needed to construct the models was provided by PMCD including: process flow diagrams for TOCDF, Agent Trial Burn (ATB) reports for TOCDF (EG&G, 1997, 1998a, 1998b, 1999), additional Process Data Acquisition and Recording System (PDARS) data in spreadsheet form for LIC #1, heat and mass balance design conditions for the Umatilla, Oregon facility (Parsons Infrastructure and Technology Group, Inc., 1998), and a vaporization rate study for the MPF (Rinker, 1987). Also other information pertinent to the models has been obtained from the Utah State Department of Environmental Quality (DEQ), Demilitarization Section.

Flow rates required as model inputs were determined using the design conditions for the Umatilla Facility and then scaling values to correspond to the trial burn conditions for TOCDF. The resulting calculated furnace temperatures were verified to be within the permit limits for TOCDF. This provided confidence that reasonable operating conditions were used as inputs in the models. Additional PDARS data for the LIC have also been obtained. The flow rates scaled from the UMCDF data were within the range of this PDAR data.

The MPF Afterburner CFD Model

In addition to providing a proof-of-concept for a typical afterburner, the MPF afterburner model provided a test bed for the application of detailed chemistry for agent destruction. A base case was created in which the velocity, temperature, and concentrations at the outlet of the MPF primary chamber CFD simulation discussed below were mapped to the inlet of the afterburner. This demonstrates the capability to link the various modules into a unified whole which would be done for the Phase II workbench. Typical results are shown in Figure 3 for the base case. The MPF afterburner includes two rapid mix, natural gas fired tunnel burners directed along the length of the afterburner chamber. The high temperature gases produced by these burners are shown in red in Figures 3a and 3b. These figures show axial and radial temperature profiles respectively. Also shown in Figure 3b are representative streamlines entering the chamber. These are the mean paths of differential fluid elements calculated from the predicted flow field and they are colored by the local mean temperature. The tortuous path of some elements is because they are entrained in the backflow created by the afterburners. The streamline integrator described in the previous section was used with the full DMMP kinetic mechanism to calculate DMMP destruction. It was assumed that 5200 ppm of agent simulant DMMP enters the afterburner. This very high concentration assumes almost no destruction in the MPF primary chamber. As shown in Figure 3c, the DMMP very rapidly breaks down to levels that are far below the detection limit. It should be noted that the calculated mean residence time in the afterburner is 1.4 seconds, which is far longer than needed to completely destroy the simulant.

We have also run two upset conditions for the MPF afterburner. The first is a case with the lower burner disabled. The second upset condition makes the impossibly bad assumption that all of the agent released in the MPF enters the afterburner as a concentrated, unreacted "puff" of pure agent. To consider a worst-case scenario we have placed the puff to the side of the duct between the MPF and the afterburner to delay its interaction with the afterburner flames. Streamline calculations for these upset conditions show complete destruction of the agent within 0.25 seconds, whereas the residence time within the afterburner roughly 1.4 seconds.

We have successfully integrated our 15-species reduced mechanism into our *GLACIER* pstprocessor and run the two MPF afterburner cases (baseline and one burner out). In both cases the agent is destroyed in the duct connecting the furnace with the afterburner. The agent never reaches the auxiliary gas flames. This can be seen in Figure 4 which shows a surface corresponding to 10^{-8} ppm of DMMP which is five orders of magnitude below the detection limit.

The Liquid Incinerator CFD Model

The liquid injection furnace is used to dispose of chemical agent drained from storage tanks and munitions. It uses an air atomized drained agent spray and an auxiliary fuel (natural gas) vortex burner firing into a refractory lined chamber. Figure 5 shows the computational grid and the temperature field in

the horizontal vortex burner as it enters the vertical cylindrical LIC chamber. The LIC afterburner was not modeled.

It was necessary to model the vaporization of the GB simulant, DMMP. The vapor pressure data and gas thermodynamic data available for the simulant were used with the Clapeyron Equation to generate the thermodynamic data for the liquid phase. This was needed so that the existing model, which REI has previously used to model particle drying and water droplet vaporization, could be used for agent droplet vaporization. The droplet size distribution of the spray was determined from a correlation for air blast atomizers (Lefebvre, 1989). Conservation of momentum between the atomization air and liquid stream dictated the starting velocities of the droplets.

Figure 5 shows the predicted gas temperatures and droplet trajectories in the vortex chamber. Combustion is almost complete within the burner chamber. When the droplet trajectories terminate, the droplets have evaporated. At this point the agent has been completely released into the gas phase. The internal recirculation zone induced by the swirling air flow enhances the mixing resulting in chamber exit conditions that are well mixed with only a slight stratification in O_2 concentration. The exit O_2 was predicted at 5.4% wet (6.1% dry) consistent with complete combustion. The detailed DMMP chemistry was integrated along streamlines within the LIC for the streamlines shown in Figure 5. The results of these integrations are shown in Figure 6, showing the calculated DMMP mole fraction. This calculation assumes that pure agent (mole fraction = 1) exists at the beginning of each streamline. Temperature and major species (N_2, H_2, H_2O, CO, CO_2, O_2) concentrations were interpolated from the CFD simulation along a streamline and specified as functions of time within the kinetics integration. The mole fraction associated with the detection limit is shown in red. The line in purple represents the level at which the last molecule of agent is destroyed. The initial number of molecules is that number that enters the furnace over the residence time of streamline 1 (0.7 sec). The location along the streamlines where the last molecule of agent has been destroyed is roughly at the position of maximum temperature within the flame, which is just outside the vortex chamber.

GLACIER has the capability to predict NOx formation in combustion systems using reduced chemistry in a post-processing mode. It accounts for thermal, fuel and prompt NOx formation as well as destruction under fuel rich conditions. A NOx prediction was also performed on the baseline case for the LIC. Since there is no nitrogen in the agent or fuel, all of the NOx is formed from molecular nitrogen in the air, that is, thermal NOx. The regions of highest NOx formation are coincident with regions of highest temperature. The predicted NOx formation in the primary chamber is low (0.044 lb NOx per MBtu).

One challenge at facility closure is how to dispose of potentially contaminated material. One such example is the carbon filter material that is in the air filtration system. One possibility is to grind the material and burn it either dry or as a slurry. *GLACIER* has the capability to predict heterogeneous combustion; we have simulated a case in which the fine carbon particles were injected pneumatically into the LIC. The flow rate of the carbon and liquid agent was adjusted to provide 5% of the heat input from the carbon. The natural gas flow rate was unchanged. The total heat input was the same as the baseline case. Carrier air was used to inject the carbon particles such that the particle loading of the injection stream was 0.5 lb particles per lb air. The carbon particles were made up of three size fractions of 38, 50, and 79 microns, the whole having a Sauter mean diameter of 50 microns. Complete burnout was predicted for each of these sizes. Figure 7 shows the predicted gas temperature for the LIC primary chamber which also shows the droplet and carbon trajectories. When the particles are burned out they are no longer tracked. As seen in the figure, the carbon particles travel roughly half way across the chamber before they are consumed. There is also a slight downward motion of the particles due largely to the flow patterns in the furnace, but also partly due to gravity. Other cases were run with larger particle sizes. The maximum particle size for predicted complete carbon burnout was approximately 200 microns. This is smaller than the actual particle size in the carbon filters, which are millimeter sized particles (40% passing through U.S. mesh #12 (1.40 mm)). Therefore, a further grind would be required to ensure full burnout, which makes the LIC unattractive for carbon closure.

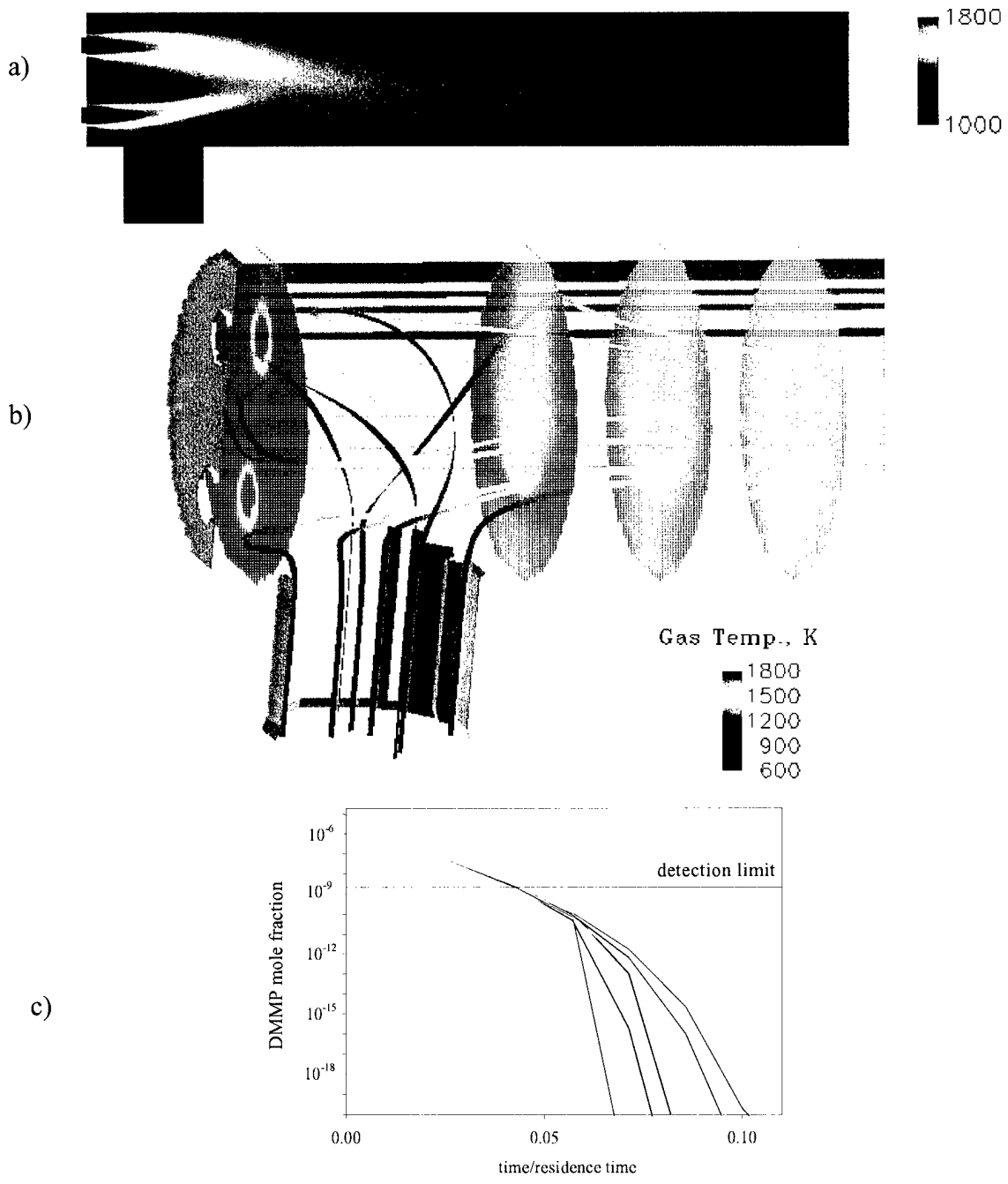

Figure 3. MPF Afterburner Simulation and DMMP destruction calculated along stream lines

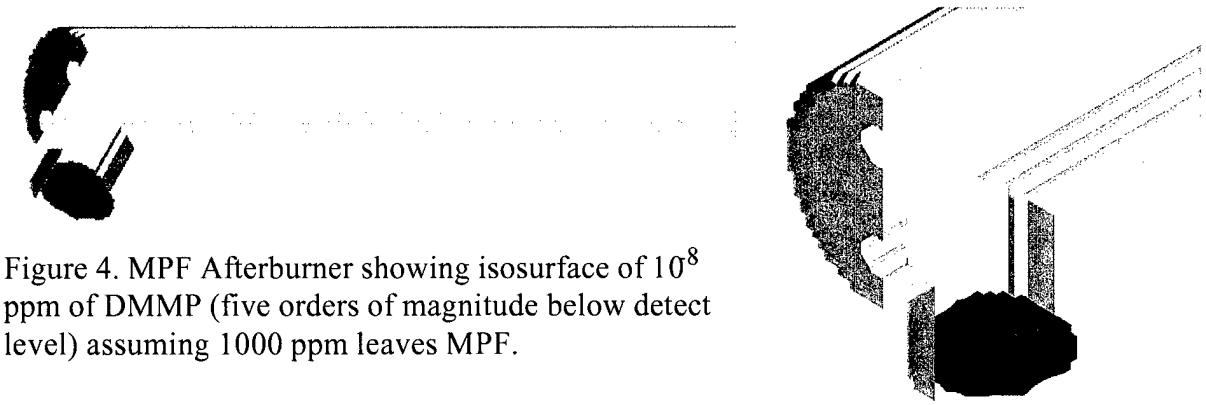

Figure 4. MPF Afterburner showing isosurface of 10^8 ppm of DMMP (five orders of magnitude below detect level) assuming 1000 ppm leaves MPF.

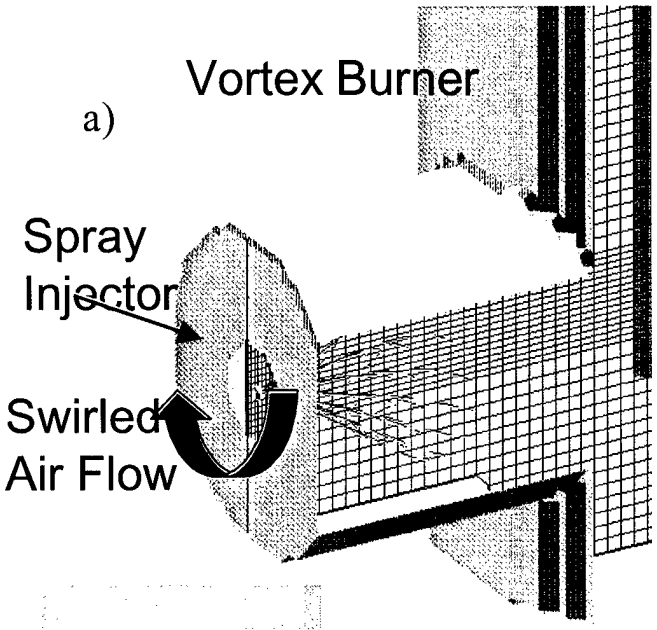

Figure 5a. LIC CFD model and temperature distribution in the vortex burner showing the reagent spray and typical stream lines

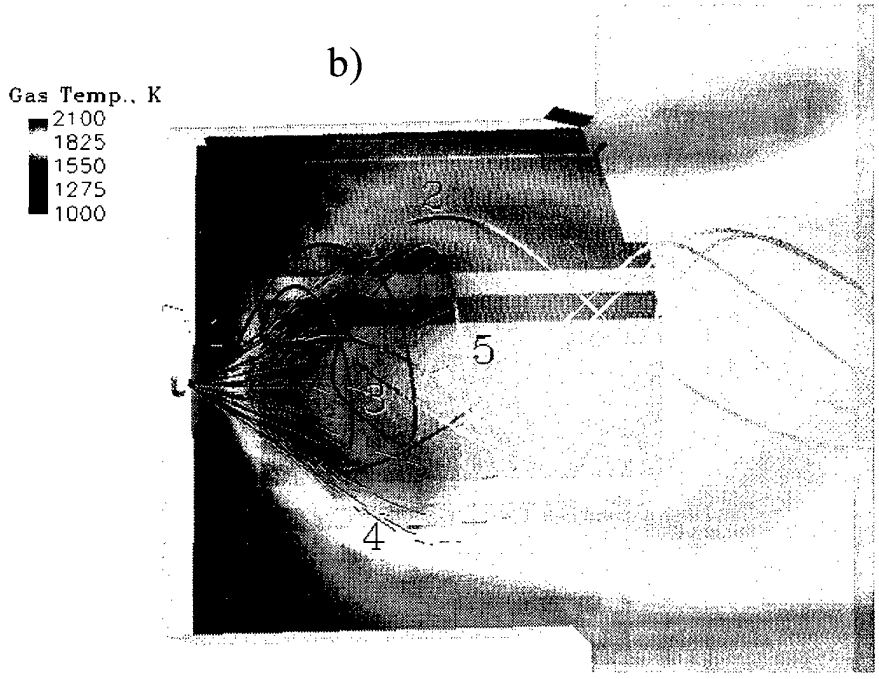

Figure 5b. Predicted gas temperatures and droplet trajectories in the LIC vortex chamber

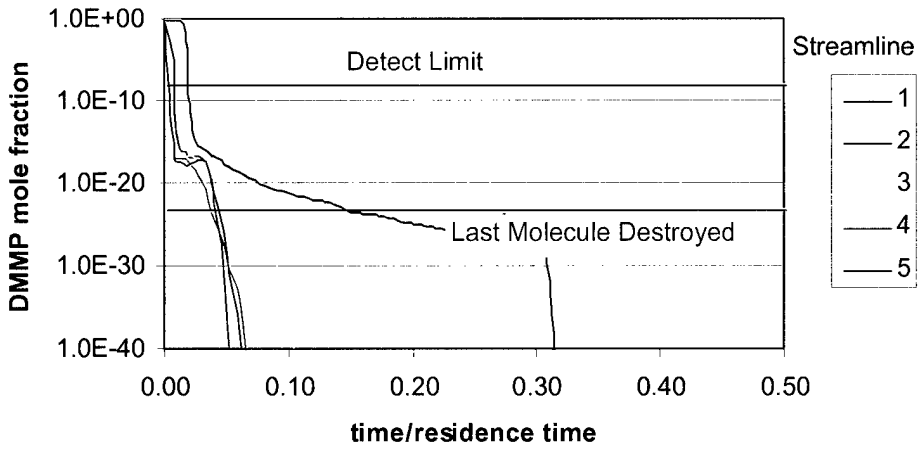

Figure 6. DMMP mole fraction calculated along streamlines fromLIC primary chamber.

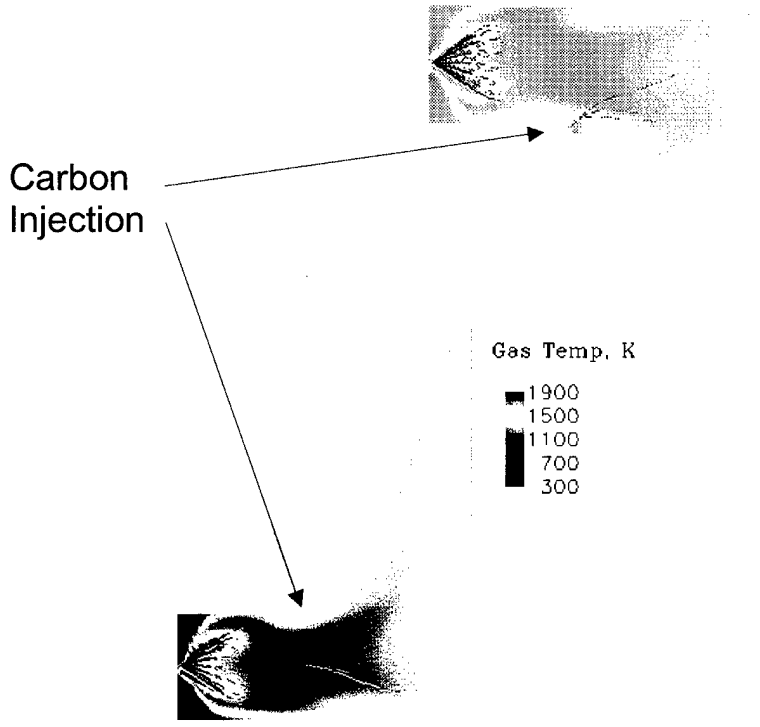

Figure 7. Predicted Gas Temperature and Spray Droplet and CarbonTrajectories of LIC

Metal Parts Furnace CFD Module

The three zone metal parts furnace is used for decontamination of relatively inert materials. Firing an auxiliary fuel with air provides high temperature combustion products. Metal parts pass intermittently through the furnace at a temperature of at least 540 °C and with a residence time of 15 minutes. During this time condensed agent decontamination is achieved through a combination of evaporation, decomposition and oxidation.

The MPF module consists of two parts: a transient projectile vaporization model and the combustion CFD model. A quasi-steady approach was used, as the CFD model is a steady state combustion model. This quasi-steady approach consisted of three steps:

1. The flow field and temperature fields were predicted with the CFD model using the heat sink of the feed and the expected maximum agent release rate.
2. A lumped two-node transient calculation of the projectile temperature and agent release rate was performed for each projectile on the tray using the heating rates predicted from the incident heat fluxes. These were obtained from the CFD solution.
3. The CFD solution was updated with the predicted agent release rate distribution and heat sinks at time of maximum agent release rate for the tray in zone 1. The agent release rate for the other two zones was zero. The temperature of the projectiles for the other two zones was taken from the projectile submodel prediction at the corresponding time for those zones.

A simple two-node projectile model was developed for the MPF model to predict the rate and distribution of agent release from 155mm projectiles containing GB simulant, DMMP. A simple one-node lumped model was first implemented. However, when the boiling point was reached, all of the heat transfer to the projectile went to vaporize the agent, which resulted in a predicted peak release rate three to four times the value from a study performed by Maumee Research and Engineering, Inc. (Rinker, 1987). By using a two-node model, one node for the metal and a second for the liquid agent, comparable rates were obtained. Nucleation boiling heat transfer between the projectile and liquid was included in the submodel. Figure 8 shows the total agent release rate as a function of time for three tray configurations. The 48 projectile configuration was used for the baseline simulation. Figure 9 shows the heat transfer to the individual projectiles on the three trays in the MPF. The heat flux to the first two trays is the highest because of the energy generated by the DMMP combustion. The projectiles in the interior of the tray receive less heat than those stacked on the sides. The interior projectiles are partially shielded from radiation from the furnace walls by the outer projectiles. Figure 10a shows the predicted gas temperature for the baseline case. The flame from the agent combustion can be seen above the front of the first tray where the majority of the agent is being released from the projectiles at this particular "snapshot" in time. Figure 10b shows the predicted gas temperature for a second case where two full projectiles are introduced into the furnace. Although the maximum release rate of the two full projectiles is less than the baseline (360 lb/hr versus 460 lb/hr), the gas temperatures above the projectiles are higher in the two full projectiles case. This is because only two projectiles are present on the tray providing a significantly smaller heat sink in the furnace. The same water quench rate was assumed in this prediction.

Detailed chemical kinetics calculations were performed along streamlines for the streamlines shown Figure 11, which originated at the tips of projectiles calculated to have large rates of agent release. The streamline kinetics calculations assume that the gas at the tip of the projectiles is 100% DMMP. Figure 12 shows the destruction histories of the gas originating in the projectiles. It can be seen that destruction takes place in the MPF within 0.1 seconds whereas residence times of these trajectories in the MPF approximately fall in the range 0.4-1.5 sec. It should be remembered that after the gases exit the MPF they are processed in the afterburner.

Deactivation Furnace System

The deactivation furnace System (DFS) is a gas-fired counterflow rotary kiln designed to treat energetics (fuses, boosters, bursters, and solid rocket propellant). Energetics are all contained in thin-walled metallic housings that must be punched or cut into pieces prior to burning; confined energetics would detonate in the kiln rather than burn.

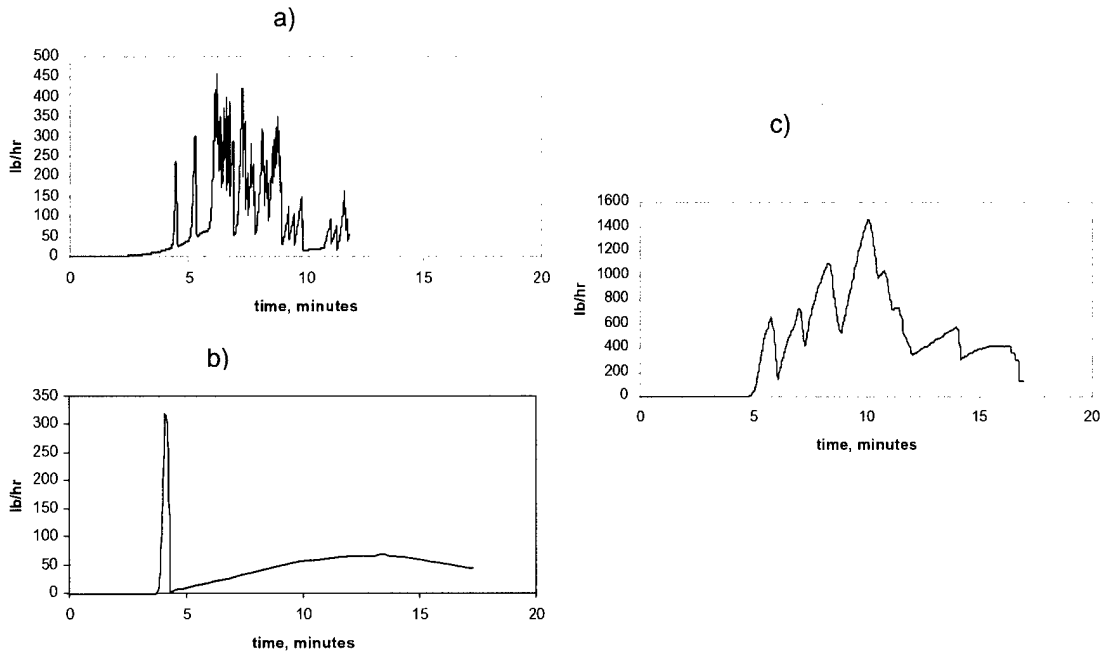

Figure 8. Total agent vaporization rate as a function of time for 155 mm projectiles. a) 48 projectiles with 5% residual agent. b) Two full shells. c) Twenty full shells.

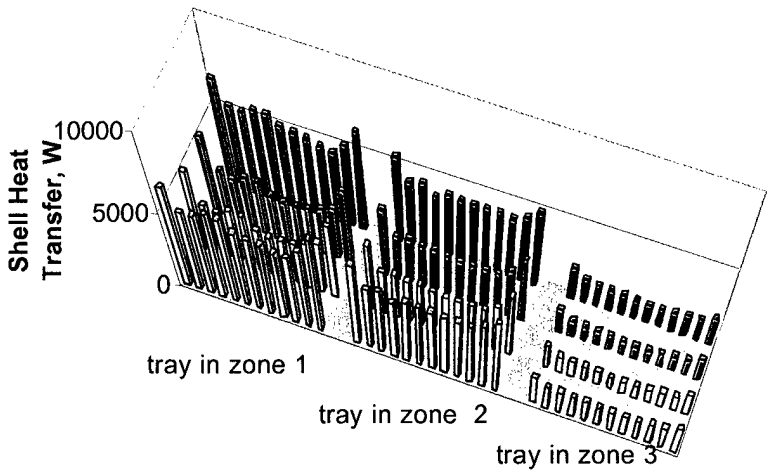

Figure 9. Net heat transfer rate to 155 mm projectiles.

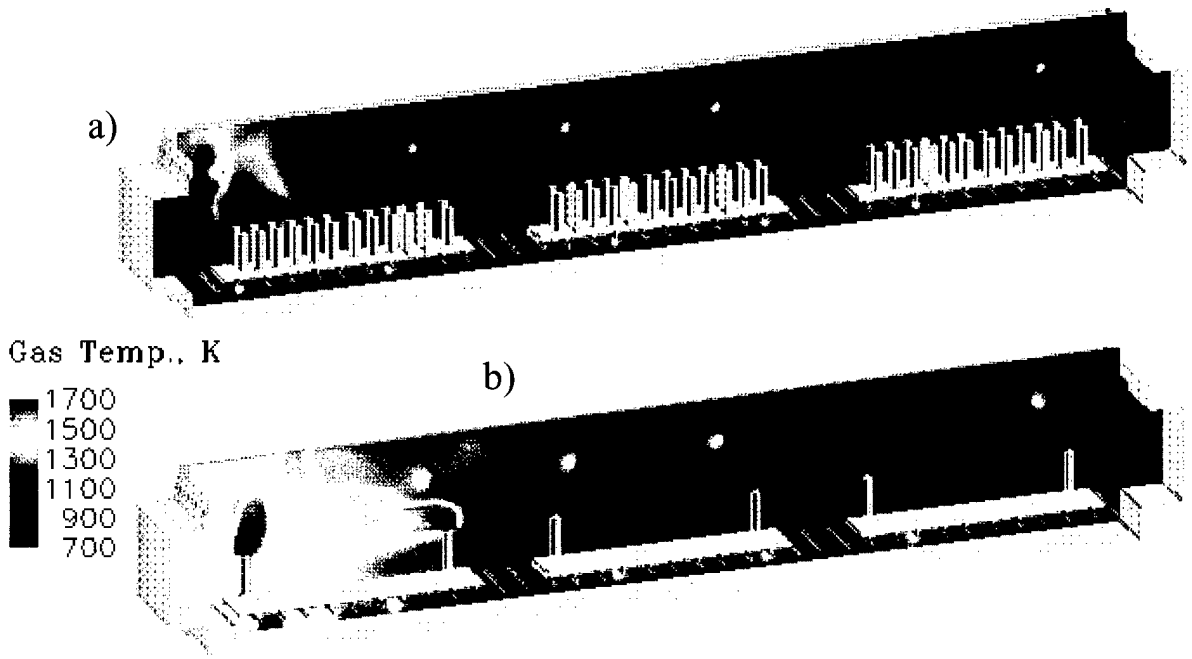

Figure 10. MPF primary chamber gas temperature. a) Baseline case – 48 projectiles with 5% residual agent. b) Two full projectiles.

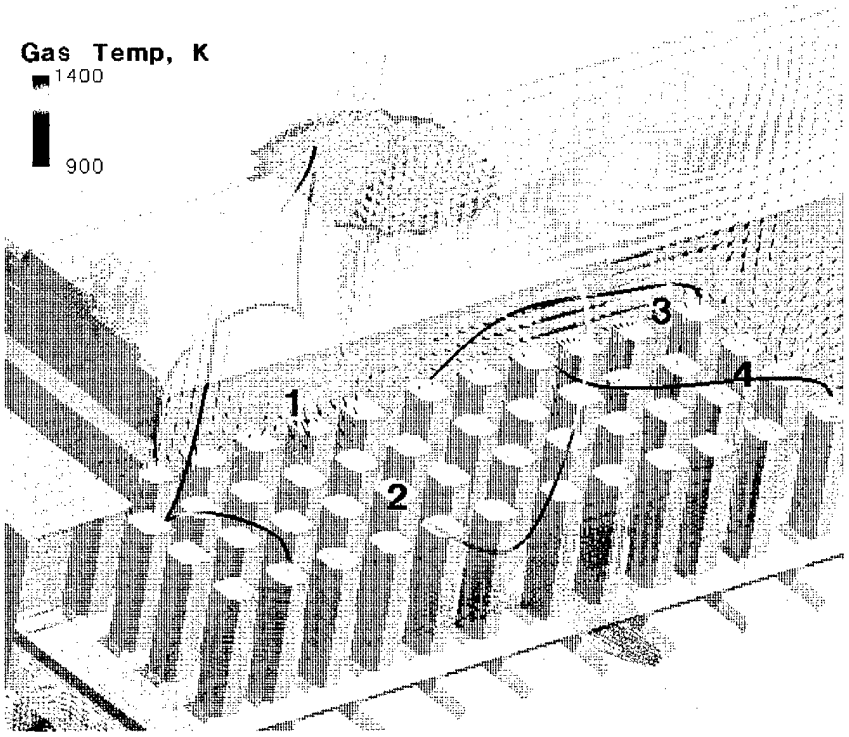

Figure 11. Streamlines originating at tips of projectiles in the Metal Parts Furnace. Projectiles with very high calculated agent release rates were selected.

The MPF module consists of two parts: an energetics/rocket piece combustion submodel and the gas phase combustion CFD model. A simple energetics combustion submodel was developed for the DFS kiln module, which consisted of tracking rocket pieces along the bottom of the kiln at a constant velocity corresponding to the rotational speed of the kiln (1.7 rpm) and the pitch of the spiral flights (30 inch pitch). The incident radiation field was used to calculate the rocket piece temperature and burn rate of the propellant as a function of time and axial position using an assumed propellant surface area. The source terms for the energetics and agent off-gas were calculated for use in the gas phase calculations. A propellant burn rate of 0.025 cm/s was estimated at the total pressure of the kiln. The most significant unknown in the energetics model is the propellant surface area of the sheared rocket pieces. The surface area of the propellant was assumed to be linearly proportional to the remaining propellant mass.

Figure 13 shows the predicted gas temperature and oxygen concentration in a vertical plane along the centerline-axis of the kiln. As seen in the figure, the propellant in the rocket pieces in this simulation started combusting at about one third the distance from the charge end of the kiln. The gas temperatures immediately around this region of maximum burn rate are about 2900 K. The oxygen is depleted around this region largely because of the equilibrium assumption used in this CFD calculation. The propellants contain their own oxidant so that the fuel and oxidant are already well mixed as energetics off-gas. Product species containing oxygen (CO_2, CO, and H_2O, $HOPO_2$) are in higher concentration in this region of high temperature.

Modeling Upset Condition

As an additional task beyond the original project plan, the MPF afterburner model was used to investigate agent destruction for an upset condition in which the burners in the afterburner and in the DFS kiln are inactive. *It should be emphasized that the upset condition modeled does not represent an actual event.*

The simulations were performed assuming only a short time had passed since the burners were extinquished, thus the refractory walls were assumed to still be hot. The purpose of the study was two-fold. First, to demonstrate how REI's CFD models could be used to study an upset condition. Second, to determine if hot walls alone would be sufficient to destroy small amounts of agent entering the afterburner after the burners are inactive.

All burners in the kiln and afterburner were assumed to be inactive. That is, there was no gas or airflow though the burners. A series of quasi-steady simulations were performed where the inlet airflow rate, air temperature, and wall temperature were varied. For each scenario, the steady-state heat-up of the inlet gas was determined. The assumed thermal capacity of the afterburner refractory was sufficient to maintain the wall temperatures constant during mean gas residence time. The cool down of the refractory walls was then calculated over a 15-minute time step using a simple heat transfer model. A CFD simulation was used to predict the flow field within the afterburner and agent destruction along streamlines was determined using the post-processor streamline integrator tool with detailed DMMP chemistry. An initial pocket of pure agent was used as an initial condition along each streamline

Table 1 summarizes the results of this study. It was found that the inlet airflow rate and temperature have a major impact on predicted level of agent destruction. The inlet flow rate and temperature alter the residence time and time-temperature history along the streamlines within the afterburner. The simulations demonstrate that for sufficiently high mass flow rates, or if the incoming air is sufficiently cool, that conditions can be encountered where **no** agent destruction is predicted to occur within the afterburner. Changes in afterburner wall temperature had little impact on predicted agent destruction. Hence, depending on the inlet airflow conditions, hot walls do not insure hot bulk gas temperature sufficient for agent destruction. For the cases studied, the bulk air temperature increased 350-550F (200-300 K) within the afterburner.

Our results show how state-of-the-art computer models can be used to understand potential upset scenarios. It should be emphasized that these simulations do not represent any actual event.

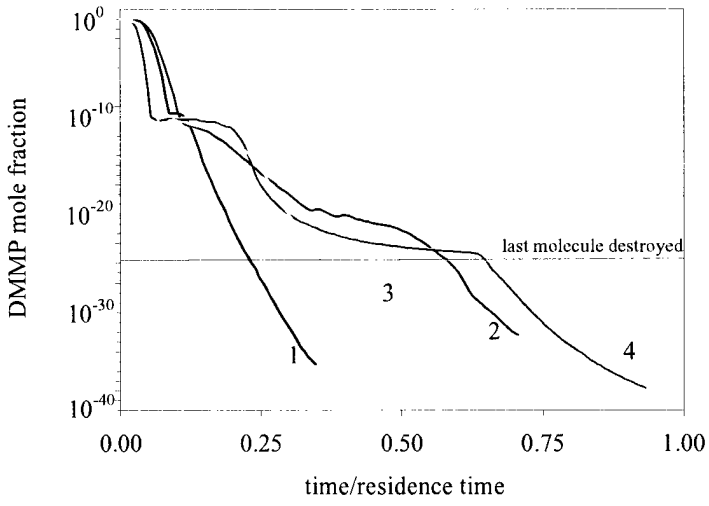

Figure 12. Calculated destruction of agent simulant DMMP along streamlines from MPF CDF simulation.

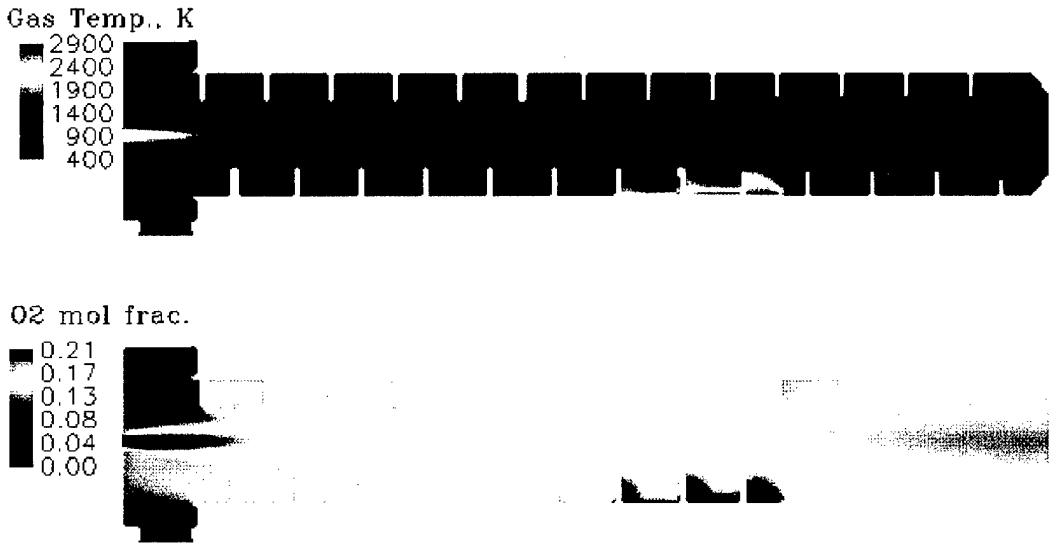

Figure 13. DFS - Gas Temperature and Oxygen Distributions.

Table 1. Summary of results of afterburner upset condition modeling.

Wall Temperature 2060 deg F (1400 K)

	inlet air temp, deg F (K)	
flow rate, lb/hr	440 (500)	1070 (850)
5400	below detect	N/A
Nominal flow → 10900	no destruction	below detect
21700	N/A	below detect

Wall Temperature 1700 deg F (1200 K)

	inlet air temp, deg F (K)	
flow rate, lb/hr	440 (500)	1070 (850)
10900	no destruction	below detect

Note: the nominal flow indicated in Table 1 is based on the airflow for standard operating conditions

Phase I Option – Transient Heel Removal Model Development and Simulator Definition

In the Phase I Option we planned to 1) improve the munition projectile submodel used to predict the rate of agent vaporization rates from the projectiles in the Metal Parts Furnace, and 2) to define the performance specs for the military incinerator simulator.

The Phase I Option was not funded. Hence, no work was performed on these tasks.

Conclusion

Phase I has demonstrated that CFD models of key components of chemical demilitarization incinerators can be constructed and provide very useful information on the physical processes that affect their performance in terms of destruction efficiency and operability. We have devised and demonstrated two methods by which detailed chemical kinetic mechanisms can be incorporated with these CFD models. Both methods involve compromise. The streamline integration approach does not account for the effects of turbulence on chemistry but it does allow the use of a full kinetic mechanism. Although the use of reduced mechanisms does allow calculation of the species concentration at all computational cells in the domain and includes the effect of turbulent mixing, the mechanism is specific to a well-defined range of

conditions and is probably not accurate if applied outside this range. The models have value to the CSDP because they can help address

- Operational questions that might improve throughput and reduce downtime.
- Closure
- Post closure litigation protection.

We have made formal presentations to the PMCD headquarters in Edgewood, Maryland and to senior personnel from EG&G Defense Materials, Inc, at Tooele, Utah. Both meetings were helpful in helping to further focus our efforts. We pointed out that the term "design" was a misnomer. Chemical demilitarization incinerators are already designed, installed and operating.

These meetings identified areas where the software tools to be developed in Phase II could greatly benefit the program. Specific examples cited include:

1. Demonstration that all the agent is destroyed in the incinerator
2. Analysis of transient (upset) events
3. Assessment of refractory erosion
4. Operations in an oxygen deficient environment
5. MPF two vs. three zone operation
6. Secondary waste treatment in the MPF
7. Mustard projectile operations
8. Evaluation of monitoring strategies during closure

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REPORT OF INVENTIONS AND SUBCONTRACTS

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Form Approved
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Expires Aug 31, 2001

PLEASE DO NOT RETURN YOUR COMPLETED FORM TO THIS ADDRESS. RETURN COMPLETED FORM TO THE CONTRACTING OFFICER.

1.a. NAME OF CONTRACTOR/SUBCONTRACTOR	c. CONTRACT NUMBER	2.a. NAME OF GOVERNMENTPRIME CONTRACTOR	c. CONTRACT NUMBER	3. TYPE OF REPORT *(X one)*
Reaction Engineering International	DAAD19-00-C-0061			a. INTERIM ☐ b. FINAL ☐

b. ADDRESS *(Include ZIP Code)*	d. AWARD DATE *(YYYYMMDD)*	b. ADDRESS *(Include ZIP Code)*	d. AWARD DATE *(YYYYMMDD)*	4. REPORTING PERIOD *(YYYYMMDD)*
77 West 200 South, Suite 210 Salt Lake City, UT 84101	2000/02/01			a. FROM Feb 1, 2000 b. TO July 31, 2000

SECTION I - SUBJECT INVENTIONS

5. "SUBJECTINVENTIONS"REQUIREDTO BE REPORTEDBY CONTRACTOR/SUBCONTRACTOR *(If "None," so state)*

NAME(S) OF INVENTOR(S) *(Last, First, Middle Initial)* a.	TITLE OF INVENTION(S) b.	DISCLOSURE NUMBER, PATENT APPLICATION SERIAL NUMBER OR PATENT NUMBER c.	ELECTION TO FILE PATENT APPLICATIONS *(X)* d.				CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER *(X)* e.	
			(1) UNITED STATES		(2) FOREIGN			
			(a) YES	(b) NO	(a) YES	(b) NO	(a) YES	(b) NO
	none	none						

f. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR		g. ELECTED FOREIGN COUNTRIES IN WHICH A PATENT APPLICATION WILL BE FILED	
(1) (a) NAME OF INVENTOR *(Last, First, Middle Initial)*	(2) (a) NAME OF INVENTOR *(Last, First, Middle Initial)*	(1) TITLE OF INVENTION	(2) FOREIGN COUNTRIES OF PATENT APPLICATION
(b) NAME OF EMPLOYER	(b) NAME OF EMPLOYER		
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			(1) CLAUSE NUMBER	(2) DATE *(YYYYMM)*		(1) AWARD	(2) ESTIMATED COMPLETION

SECTION III - CERTIFICATION

7. CERTIFICATIONOF REPORT BY CONTRACTOR/SUBCONTRACTOR *(Not required if: (X as appropriate))* ☐ **SMALL BUSINESSor** ☐ **NONPROFITORGANIZATION**

I certify that the reportingparty has proceduresfor promptidentification and timely disclosureof "Subject Inventions," that such procedureshave been followedand that all "Subject Inventions" have been reported.

a. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL *(Last. First. Middle Initial)*	b. TITLE	c. SIGNATURE	d. DATE SIGNED
Bockelie, Michael J.	Vice President Computational Technologies		