

Computational Modeling of a Chemical Liquid Incinerator Chamber

Martin K. Denison
Reaction Engineering International
77 West 200 South, Suite 210
Salt Lake City, UT 84093 USA

Brooke A. Sadler, Christopher J. Montgomery, Adel F. Sarofim, Michael J. Bockelie
Reaction Engineering International

Alfred G. Webster
Continental Research and Engineering
6825 East Tennessee Avenue, #101
Denver, CO 80224 USA

ABSTRACT

Incineration is being used or is planned as a destruction technology for stockpiles of chemical warfare agents (CWA) in the United States. This paper presents the development of models for analyzing a Liquid Incinerator Chamber (LIC) for destroying liquid chemical weapon agent (GB, HD, or VX) drained from munitions contained in the US Army chemical weapons stockpile. The models predict complete destruction of the chemical agent when the incinerators and afterburners are operated as per standard operating conditions. Under normal operating conditions the agent is destroyed within the primary furnace chamber.

INTRODUCTION

The United States has selected incineration as one of the methods for destroying the highly toxic chemical agents and munitions contained within the Chemical Weapons Stockpile. Incineration technology has been used at two sites, and is under construction/installation at three additional sites. As plans are made for weapons destruction, advanced computer modeling tools are playing an important role in reducing the time, cost and technical risk of using incineration methods to destroy the highly toxic chemical agents and munitions contained within the Chemical Weapons Stockpile.

To assist the demilitarization process, a simulation tool for analyzing chemical demilitarization incinerators is being developed [1,2,3]. Agent destruction within the furnaces and afterburners is analyzed through recently developed detailed chemical kinetics integrated with computational fluid dynamics (CFD). Both full CFD and streamline calculations for agent destruction have been performed. Models for the destruction of mustard (HD) in the Metal Parts Furnace (MPF) and Sarin (GB) in the Deactivation Furnace System (DFS) have been previously developed and demonstrated [4,5].

In this paper we present the development of models for analyzing the liquid incinerator chamber (LIC) for processing chemical agent (GB, HD, or VX) that has been drained from different munitions.

LIC DESCRIPTION

The liquid incinerator chamber (LIC) is used to dispose of chemical agent drained from storage tanks and munitions. The LIC consists of two natural-gas-fired combustion chambers. Air and natural gas are introduced into the primary chamber through a swirled low velocity burner, and liquid agent is injected at the burner through an air atomizer. Exhaust gas from the primary chamber passes through a duct to the secondary chamber where it encounters a high velocity natural gas burner. The purpose of this secondary chamber is to thermally treat any residual agent in the exhaust gas from the primary chamber. The burner in the secondary chamber is oriented offset from the chamber centerline, in a tangentially fired manner, in order to promote a swirling flow field within the secondary chamber. In addition, spent decontamination solution may be injected through an injection port in the roof of the chamber for incineration in the secondary chamber.

LIC MODELING APPROACH

The LIC operates in steady state where the natural gas flow rate is adjusted based on the agent and air flow rates (and the Decon flow rate in the secondary chamber) to achieve the set point temperature. A steady-state, zero-dimensional (0D) process model has been developed as a preprocessor to calculate the necessary fuel flow rates to each chamber for use in the CFD models. These flows are calculated using a chemical equilibrium approach with wall heat transfer. Inputs to the process model include the agent feed rate and the set point temperatures for the primary and secondary chambers. The spent decontamination solution flow rate into the secondary chamber is also an input. The model computes the natural gas flow rate needed to achieve the set point temperature at equilibrium and the equilibrium combustion gas composition at that temperature. The LIC CFD models use these inputs and calculated flow rates.

LIC Primary and Secondary Chamber CFD Models

The technical approach used in the furnace CFD model involves the following:

1. *GLACIER*, an in-house reacting CFD code of Reaction Engineering International (REI), is used to predict the temperature and flow fields using equilibrium chemistry with an assumed shape probability density function (PDF) to account for turbulence chemistry interactions. The code incorporates models for turbulent flow, radiation heat transfer, and chemistry turbulence interactions with both equilibrium and finite rate chemistry.
2. To reduce the required memory, only a subset of the species contained in the detailed mechanism is used in the CFD calculations involving equilibrium chemistry. These species include major reactant and product species with relatively few intermediates. The species subset is selected to reproduce the adiabatic flame temperature and stoichiometric ratio obtained with the complete list of the species in the mechanism over a wide range of stoichiometries.
3. Finite rate kinetic calculations are performed to predict the agent destruction as a post process to the combustion and flow calculation. Three approaches are available: (1) integrating the complete detailed kinetic mechanism along streamlines, (2) applying a reduced mechanism in the solution of conservation equations for each species, and (3) solving a conservation equation

for only the parent molecule of the agent by applying only the initial destruction paths in the detailed mechanism. Results of the first and third approach are presented in this paper.

A key submodel in the LIC CFD agent destruction model is the agent droplet vaporization and combustion model. The droplets are tracked in a Lagrangian reference frame and the trajectories are calculated from conservation of momentum. The vaporization rate of the droplets is also calculated along the trajectories where the agent mass sources are distributed to the gas phase. The combustion is then calculated in an Eulerian reference frame as outlined above. The agent droplet size was calculated using a correlation for an air-blast atomization spray nozzle given by Lefebvre [6].

Agent vapor pressure data were used to obtain the heat of vaporization as a function of temperature. Agent gas enthalpy, liquid heat capacity and heat of vaporization values were used to calculate liquid agent enthalpy. The calculated liquid enthalpy was fit to obtain the necessary thermodynamic parameters that were used in the droplet vaporization model.

For the streamline calculations, detailed chemical kinetics calculations were performed along streamlines originating along the agent droplet trajectories to match agent vaporization from which agent release is calculated. Destruction calculations along streamlines use pyrolysis, including local radical concentrations (e.g., O, H and OH), and temperature interpolated from the combustion flow field. The streamline kinetics calculations assume that the gas at the starting locations is 100% agent. If any agent survives the primary chamber, the kinetic calculations may continue as a post process calculation with the secondary chamber CFD model.

CWA Mechanism Development

Destruction of the chemical weapons agents GB, HD, and VX has been modeled in this study. Development of the detailed chemical mechanisms for HD and GB has been reviewed previously [4,5], and the detailed chemical kinetic mechanism for VX has been completed [7]. The new mechanism contains thermochemical information for 31 new species and kinetics for 137 new reactions. To complete the elementary description of pyrolysis and oxidation of VX and its products, the new reaction steps were added to phosphorus combustion chemistry from the mechanism of Glaude et al. [8], sulfur chemistry from Nimmo et al. [9] and from an HD mechanism recently completed [10], and nitrogen chemistry from Dean & Bozzelli [11].

Standard enthalpy of formation, $\Delta H_{f,298}^0$, entropy, S_{298}^0 , and heat capacities $C_p(T)$, were determined for stable molecules, intermediates, and transition states in oxidation of sulfur-containing hydrocarbons using density functional calculations with the B3LYP and the KM-LYP functionals. *Ab initio* calculations, using the CBS-Q composite method, were also used.

Enthalpies of formation ($\Delta H_{f,298}^0$) were determined using the Density Functional and CBSQ methods and working reaction analysis with isodesmic or group balance constraints. Entropy (S) and heat capacity ($C_p(T)$), values from vibrational, translational, and external rotational contributions were calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional studies. The contribution to S and $C_p(T)$ from analysis on the internal rotors was incorporated into the analysis instead of the more conventional use of torsion frequencies. This is an important consideration in the thermochemical and kinetic analysis because of the loss of internal rotors in

transition states. The dominant path for unimolecular dissociation of the VX molecule is a retro-ene reaction with an energy barrier of 41.64 kcal/mol.

Figure 1 compares computed VX destruction in a plug flow reactor with a 2-second residence time to destruction of agents HD and GB. The stability of VX relative to the other two agents is seen in the figure. The incinerability index of the chemical weapon agents, as determined from the kinetics developed in this study, along with the index of other hazardous compounds is given in Table I. The “T99(2)” designation refers to the temperature at which 99% of the agent is destroyed with a residence time of 2 seconds. The incinerability ranking of the chemical weapons agents is consistent with the trend seen in Figure 1.

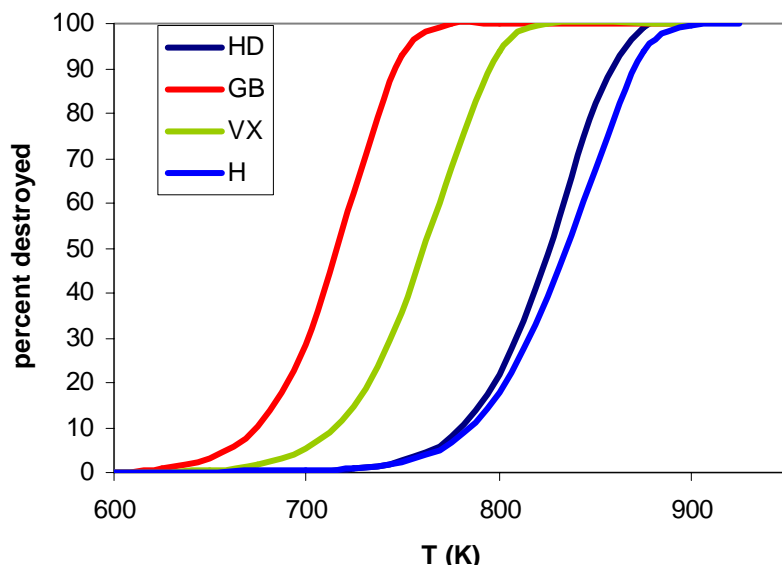


Figure 1. Calculated destruction of VX, GB, HD, and H in plug flow reactor with a 2-second residence time as functions of temperature.

Table I. Incinerability Rankings of Chemical Weapons Agents Compared to other Hazardous Compounds.

Compound	T99(2)	Class
Benzene	1150 C	1
Toluene	895 C	2
Vinyl Chloride	770 C	3
Trichloroethane	635 C	4
H	622 C	4
HD	602 C	4 (barely)
Chloroform	545 C	5
VX	541 C	5
Hexachloropropene	505 C	5
GB	491 C	5
Strychnine	320 C	6

RESULTS

Destruction of GB

The model was run using GB agent trial burn data from the Tooele Chemical Demilitarization Facility (TOCDF) in Utah. Natural gas and agent flow rates were taken from the data, and combustion air flow was calculated based on the exit O₂ measurement. Figure 2 shows the predicted gas temperature and droplet trajectories for the LIC primary chamber. Combustion takes place primarily within the burner cylinder just beyond where the droplet trajectories terminate or where the droplets have vaporized releasing gaseous agent.

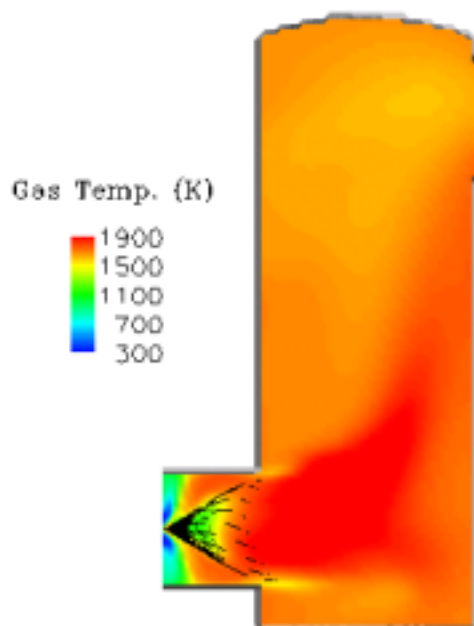


Figure 2. Predicted Gas Temperature and Spray Droplet Trajectories of LIC Primary Chamber for GB.

Destruction along streamlines using pyrolysis, including local radical concentrations (e.g., O, H and OH), and temperature interpolated from the combustion flow field is shown in Figure 3. Streamlines were placed in the burner cylinder along the GB droplet trajectories to match agent vaporization. In addition, one streamline was initialized farther into the chamber. The model predicts agent destruction below detection within a few milliseconds for all streamlines. Streamline four, which begins in a cold region of the burner cylinder, shows the slowest destruction; however, agent is destroyed along this streamline below detection within the burner cylinder.

The combustion flow field for LIC primary chamber was also modeled for processing HD, using flow rates from UMCDF mass and energy balance calculations. The resulting combustion flow field was similar to that of GB, yet cooler with the operating conditions used. Equilibrium calculations for HD combustion agree with the CFD model result.

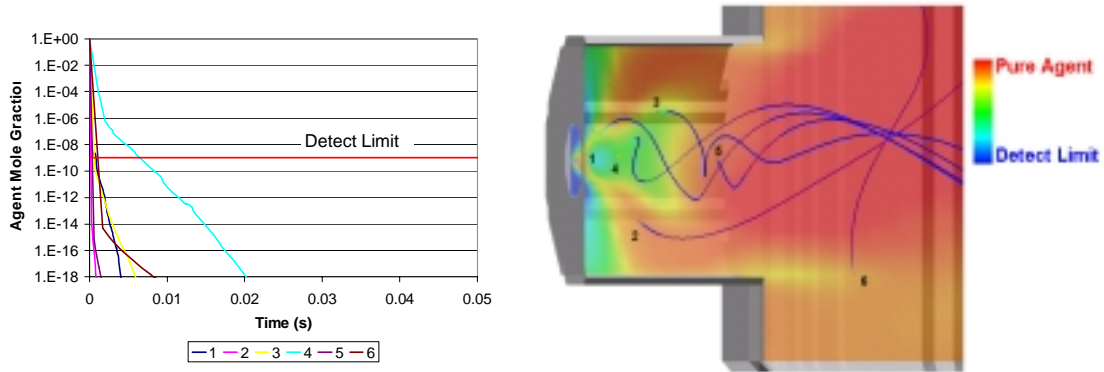


Figure 3. GB Destruction Calculated Along Streamlines for LIC Primary Chamber.

The CFD model of the secondary chamber was run using a natural gas flow rate determined from agent trial burn data. The combustion air flow rate was calculated to match the exit O₂ concentration, accounting for the gases entering from the primary chamber. The decontamination solution was modeled as water in a generic spray.

Predicted gas temperature and decontamination solution droplet trajectories for the LIC secondary chamber are illustrated in Figure 4. The flow of the primary chamber gases and the burner gases, both offset from the center of the chamber, combine and cause the decontamination solution spray to swirl.

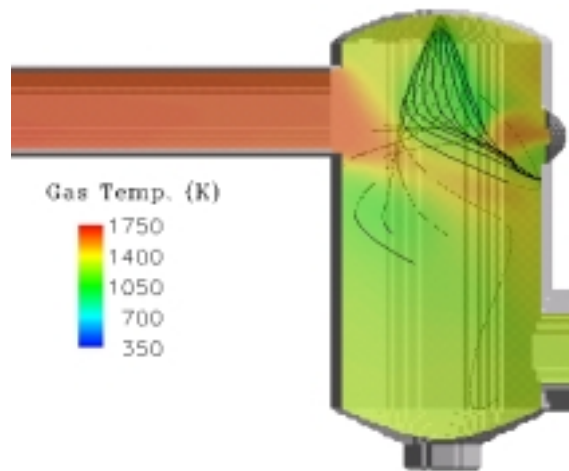


Figure 4. Predicted Gas Temperature and Decon Spray Droplet Trajectories of LIC Secondary Chamber for processing GB.

Agent destruction along streamlines in the secondary LIC chamber is shown in Figure 5. As in the primary chamber, streamlines were initialized with pure agent. The integration shows that if any agent could survive to the crossover duct, it would be destroyed within 2.5 milliseconds of entering the duct and thus would not survive to the end of the duct. Streamline five shows that any agent surviving within the secondary chamber will be destroyed as rapidly as agent found in the crossover duct.

The procedure for computing agent destruction along streamlines included the impact of radicals (e.g., O, H and OH) on the agent decomposition. Hence, the agent destruction calculations along streamlines shown in Figure 5 (and Figure 3) include the effects of pyrolysis, temperature and radicals from the local flow field.

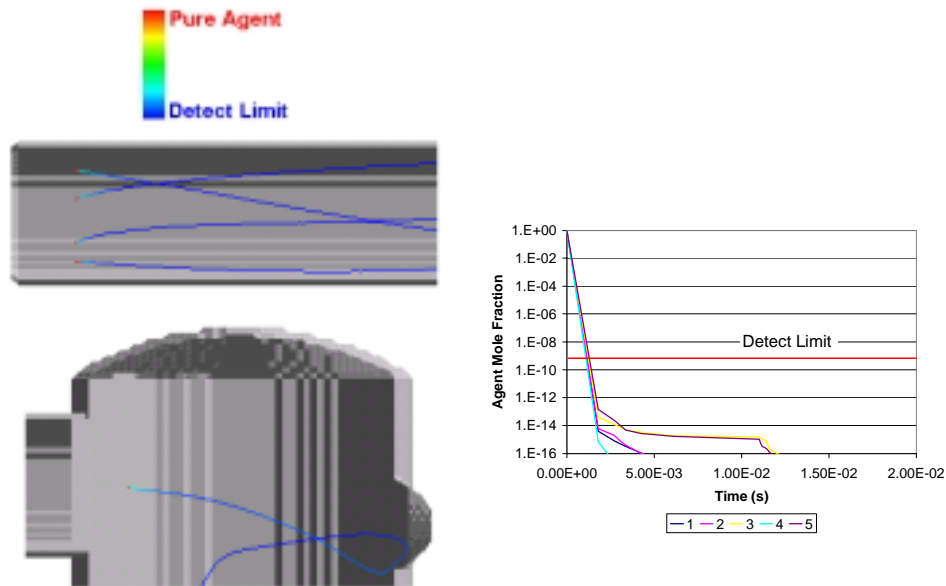


Figure 5. GB Destruction Calculated Along Streamlines for LIC Secondary Chamber.

Destruction of VX

VX combustion was also modeled in the LIC using flow rates from the Umatilla Chemical Disposal Facility (UMCDF) mass and energy balance calculations. Figure 6 shows the predicted gas temperature and droplet trajectories for the LIC primary and secondary chambers for VX. Similar to previous results with GB in the primary chamber, combustion takes place primarily within the burner cylinder and continues where the droplet trajectories terminate. In the secondary chamber, the burner is tangentially fired. Also, the product gas from the primary chamber is introduced into the secondary chamber via the cross-over duct which is offset to produce additional swirl. This swirled flow is apparent in the decontamination solution droplet trajectories shown in Figure 6. Note that the decontamination solution spray acts to cool the combustion gases.

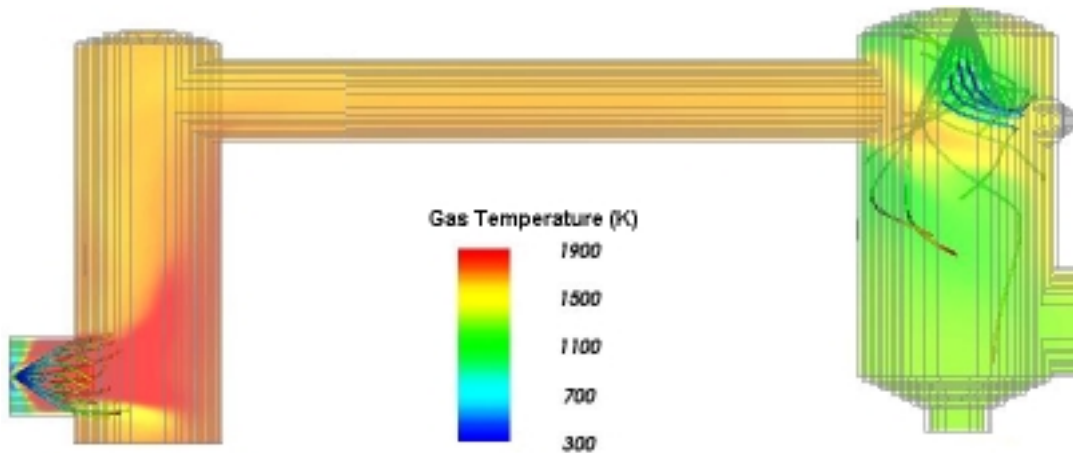


Figure 6. Predicted Gas Temperature (K) and Spray Droplet Trajectories of LIC Primary and Secondary Chambers for VX.

Two methods have been used to calculate agent destruction for VX. Agent destruction calculated using parent molecule kinetic rates is shown in Figure 7. In this model, only the initial reaction steps involving the parent molecule from the detailed mechanism are used and a single transport equation of the agent is solved. The dominant step is the unimolecular decomposition. Radical attack is also included. Since the radical concentrations are obtained from the equilibrium combustion solution, the resulting radical concentrations are conservatively low. Using this approach allows performing a very fast running CFD simulation to estimate destruction of the agent compound (i.e., from lethal to non-lethal), but does not provide information on intermediate or final products. Agent destruction using global rates predicts that VX is destroyed below 1 ppb early in the burner cylinder. Beyond this region, the calculations indicate that trace amounts of agent (below 1ppb) continue to be vaporized and breakdown. Note that the detect limit for VX is \sim 1ppb.

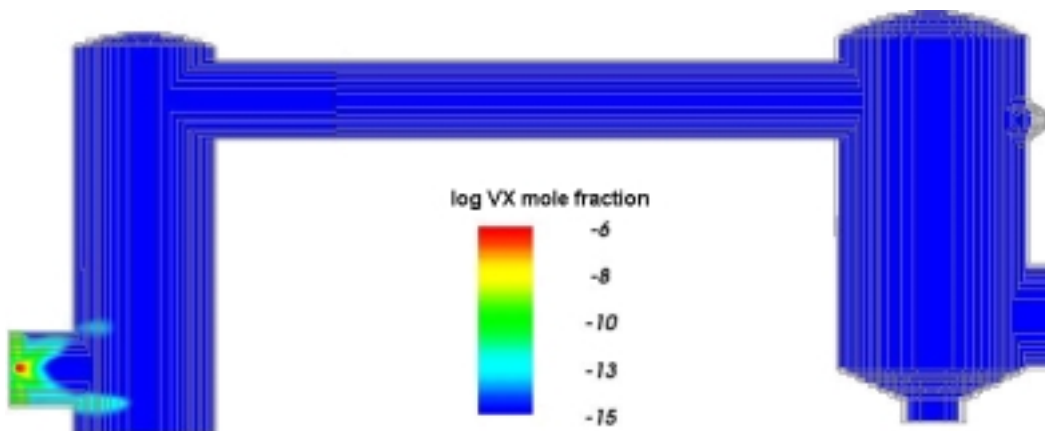


Figure 7. VX Destruction using parent molecule kinetic rates - LIC Primary and Secondary Chambers.

The second method for calculating agent destruction computes the destruction of agent along a streamline in the furnace and uses the complete detailed chemical mechanism for pyrolysis and oxidation, including the effects of local radical concentrations (e.g., O, H and OH) and temperature interpolated from the combustion flow field. Streamlines are initialized with pure agent. By performing the calculation with detailed chemistry, the intermediate and final products of agent destruction can be predicted. The streamline calculation results are shown in Figure 8. In this figure, the agent concentration scale was chosen to illustrate the progress of agent destruction. The background color in the figure represents gas temperature. Streamline color indicates VX concentration. Streamlines were placed in the burner cylinder along the VX droplet trajectories to match agent vaporization. Destruction was calculated along five streamlines, and the results for all streamlines predict that VX is destroyed below the detect limit in the LIC primary within a few milliseconds. Although the primary chamber calculations predict that all agent would be destroyed before reaching the secondary chamber, streamlines were also initialized in the secondary chamber. Should any agent survive the primary chamber, these calculations predict that it would be destroyed within the crossover duct. In addition, similar calculations have shown that any agent entering with the decontamination solution sprayed into the secondary chamber will also be quickly destroyed within the secondary chamber.

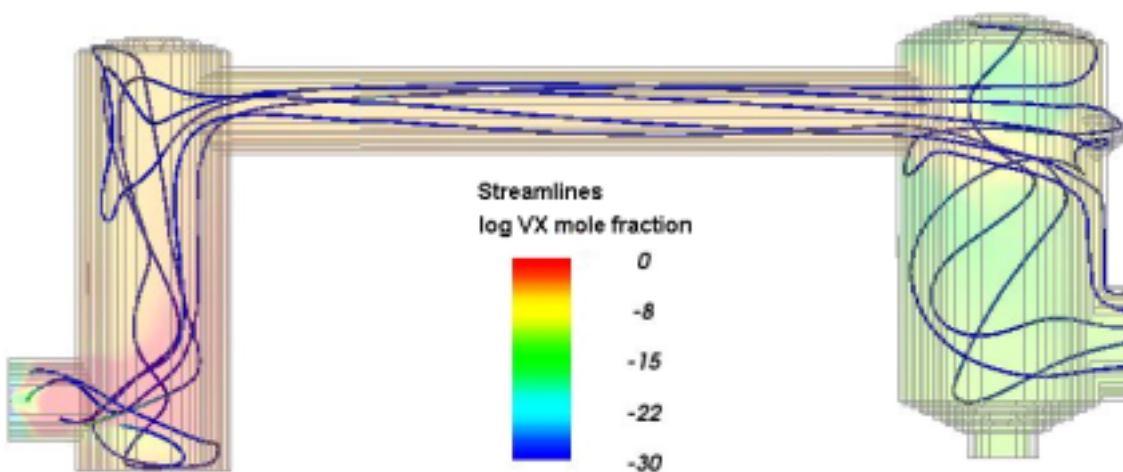


Figure 8. Streamline Agent Destruction - LIC Primary and Secondary Chambers.
Background color represents gas temperature. Streamline color indicates VX species.
Legend = Mole Fraction on a log scale (Pure Agent = 0, Detect Limit ~ -9).

CONCLUSION

This paper has demonstrated that zonal and CFD models of the Liquid Incinerator Chamber (LIC) can be constructed to provide useful information on the physical processes that affect furnace performance in terms of destruction efficiency and operability. The models have predicted complete destruction of the chemical agent when the incinerators and afterburners are operated as per standard operating conditions. Under normal operating conditions no agent survives beyond the primary chamber. The models can be used to simulate upset conditions and failures that could potentially lead to an agent release so that appropriate design and operational modifications can be made to mitigate such occurrences.

REFERENCES

1. Denison, M.K., Montgomery, C.J., Sarofim, A.F., Bockelie, M.J., Magee, R., Gouldin, F., McGill, G., "Detailed Computational Modeling of Military Incinerators," 20th International Conference On Incineration and Thermal Treatment Technologies, Philadelphia, PA, (May 2001).
2. Bockelie, M.J., Denison, M.K., Montgomery, C.J., Sarofim, A.F., Gouldin, F., and Bozzelli, J., Poster presentation: "Advanced Computer Simulations of Military Incinerators," Twenty-third Army Sciences Conference, Orlando, FL, (December 2002).
3. Bockelie, M.J., "Modeling of Metal Parts Furnace and Deactivation Furnace," NRC Stockpile Committee Meeting, Irvine, CA, (January 2003).
4. Denison, M.K., Montgomery, C.J., Sarofim, A.F., Bockelie, M.J., Webster, A.G., and Mellon, R.J., "Advanced Computational Modeling of Military Incinerators," 21st International Conference On Incineration and Thermal Treatment Technologies, New Orleans, LA, (May 2002).
5. Denison, M.K., Montgomery, C.J., Sarofim, A.F., Bockelie, M.J., and Webster, A.G., "Computational Modeling of a Chemical Demilitarization Deactivation Furnace System," 22nd International Conference On Incineration and Thermal Treatment Technologies, Orlando, FL, (May 2003).
6. Lefebvre, A.H., Atomization and Sprays, Hemisphere Publishing Corporation, New York, (1989).
7. Montgomery, C.J., Bockelie, M.J., Sarofim, A.F., Magee, R.S., Gouldin, F.C., Bozzelli, J.W., Westbrook, C.K., Chemical Agent Decomposition Rates at Temperatures Anticipated in the Discharge Airlock. Report by Reaction Engineering International Project No. 4440, (2003).
8. Glaude, P. A., Melius, C., Pitz, W. J., and Westbrook, C. K., "Detailed Chemical Kinetic Reaction Mechanism for Incineration of Organophosphorus and Fluoro-Organophosphorus Compounds," Proceedings of the Combustion Institute, Vol. 29, pp. 2469-2476, (2002).
9. Nimmo, W., Hampartsoumian, E., Hughes, K. J., and Tomlin, A. S., "Experimental and Kinetic Studies on the Effect of Sulfur-Nitrogen Interactions on NO formation in Flames," Twenty-Seventh Symposium (International) on Combustion, pp. 1419-1426, (1998).
10. Montgomery, C. J., Bockelie, M. J., Lee, J., and Bozzelli, J. W., "Thermochemical Properties, Reaction Paths and Kinetic Mechanism for Sulfur-Chloro Hydrocarbon Combustion: Part I: Thermochemistry and Pyrolysis of Chlorosulfides," The American Flame Research Committee International Symposium on Combustion, Livermore, CA, (Oct. 2003).
11. Dean, A.M., and Bozzelli, J.W., "Combustion Chemistry of Nitrogen," in Gas-Phase Combustion Chemistry, Gardiner, W.C., ed., Springer, pp. 125-341, (1999).

ACKNOWLEDGEMENT

Funding for this project was provided through a DoD-Army Phase II SBIR, "Engineering Design Software for Military Incinerators", contract number: DAAD19-01-C0050, Program Official: Dr. Robert Shaw (Army Research Office).

The authors would like to acknowledge the contributions of the SBIR project chemistry advisory panel members: Prof. Fred Gouldin (Cornell), Prof. Joseph Bozzelli (NJIT), Dr. Charlie Westbrook (LLNL), Dr. Wing Tsang (NIST), and Dr. Richard Magee (CARMAGEN).