

## ADVANCED COMPUTATIONAL MODELING OF MILITARY INCINERATORS

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### ABSTRACT

Incineration is being used or is planned as a primary destruction technology of stockpiles of chemical warfare agents (CWA) in the United States. Computer modeling tools may play an important role in reducing the time, cost and technical risk of using incineration. A simulation workbench is being developed to assist the chemical demilitarization community. The workbench will consist of models for a Liquid Incinerator (LIC), Metal Parts Furnace (MPF), a De-Activation Furnace System (DFS), and the afterburners and Pollution Abatement Systems (PAS) for these incinerators. In this paper we present recent development of the component models for the MPF for the incineration of mustard. Both a transient zonal model and CFD models are presented. Results of several practical cases are presented including comparison with experimental data. The models predict complete destruction of the chemical agent when the incinerators and afterburners are operated as per standard operating conditions.

### NOMENCLATURE

$f_i$	Mass fraction of $i^{\text{th}}$ stream
$h$	Enthalpy, J/kg
$\dot{m}$	Mass flow rate, kg/s
$Q_c$	Convective heat transfer, W
$Q_r$	Radiative heat transfer, W
$t$	Time, s
$V$	Volume, $\text{m}^3$
$\rho$	Density, $\text{kg}/\text{m}^3$

### NOTATION

CFD	Computational Fluid Dynamics
CRE-Denver	Continental Research and Engineering Denver
CWA	Chemical Warfare Agents
DFS	Deactivation Furnace System

DMMP	dimethyl methylphosphonate
GB	Sarin
HD	Mustard Agent
JACADS	Johnston Atoll Chemical Agent Disposal System
LIC	Liquid Incinerator Furnace
MPF	Metal Parts Furnace
REI	Reaction Engineering International
TOCDF	Tooele Chemical Agent Disposal Facility
UMCDF	Umatilla Chemical Agent Disposal Facility
VX	VX nerve gas

## INTRODUCTION

Advanced computer modeling tools could play an important role in reducing the time, cost and technical risk of using incineration methods to destroy the chemical weapons agents (CWA) and munitions contained within the Chemical Weapons Stockpile. Incineration technology is embodied in today's baseline incineration system that is operating at one site and is under construction/installation at three sites. Through funding from a DOD SBIR Phase II award, Reaction Engineering International (REI) is developing a simulation tool for analyzing chemical demilitarization incinerators. Within this project REI is collaborating with Continental Research and Engineering (CRE-Denver). This collaboration will ensure that the developed simulation tool will be of use to the chemical demilitarization community.

The workbench tool being developed within the SBIR project will include the ability to study the combustion process, agent destruction and product species and concentrations for nerve agents (GB and VX) and mustard (HD). The workbench will provide the flexibility to simulate a range of operating conditions and configurations for different munitions and storage containers. Altogether, the workbench will provide the engineer with the ability to study a wide range of "what if" scenarios. By design, the workbench will be user-friendly and execute on inexpensive, PC computers. These models are to help with: (1) assessing the health and environmental impact of the incinerators, (2) evaluating potential opportunities to enhance online availability and to increase munitions throughput, and (3) assessing problems with decommissioning and retroactive assessments of questions that may arise after closure.

The three incineration systems, their associated afterburners and pollution abatement systems (PAS) to be included in the workbench are:

- The Liquid Incinerator Furnace (LIC) used to incinerate the liquid CWA drained from the munitions;
- The Metals Parts Furnace (MPF) designed to decontaminate the drained shells, and
- The Deactivation Furnace (DFS) used to deactivate the energetic materials used as propellants and fuses in the munitions.

In Phase I of the project, reacting CFD models were developed for the MPF, LIC, DFS and MPF afterburner at the Tooele Chemical Agent Disposal Facility (TOCDF) [1]. The models include the full coupling of turbulent fluid mechanics, all modes of heat transfer (including radiation), incineration of agent droplets and equilibrium combustion chemistry. The destruction of chemical agent was predicted using non-equilibrium chemistry models that include full and reduced chemical kinetic mechanisms. In Phase I, we considered only the destruction of GB. Currently we are focusing on HD.

In this paper we focus on recent development of the component models for the MPF. The MPF has been identified as a key incinerator for potential increases in throughput. The baseline operation of the existing unit currently in operation at TOCDF and under construction at the Umatilla Chemical Disposal Facility (UMCDF) requires that the projectiles be drained to have only a 5% residual agent when introduced in the MPF. In this paper we only model the destruction of HD agent. The modeling approach for the MPF is discussed. The current status of development of destruction chemistry for the actual agent is reviewed and results for several demonstration cases are presented.

## **MPF DESCRIPTION**

The metal parts furnace is used for decontamination of relatively inert projectiles and containers. Firing an auxiliary fuel with air provides high temperature combustion products. The three-zone design is shown in Figure 1. Metal parts pass intermittently through the furnace at a set point gas temperature typically of 1600 °F and with a residence time sufficient to drive off and destroy the agent and bring the projectiles to at least 1000 °F for at least 10 minutes. A tray of projectiles is introduced from an airlock (not shown) into the first zone where the majority of agent is driven off and combusted or pyrolyzed. The tray then passes to the second zone where the projectile temperatures continue to rise destroying any remaining agent. The last zone is used to provide the required 1000+ °F for at least 10 minutes. An airlock on the otherside is used to ensure that there are no residual agent vapors. During operation every zone contains one tray of projectiles. The bursters are removed from the munitions before they are introduced into the MPF.

The MPF at the TOCDF (and other incineration sites under construction) is a three-zone design (Figure 1a), whereas an MPF proposed for the Pueblo, CO site will have four-zones (Figure 1b) designed to process full projectiles.

The MPF is equipped with an afterburner (Figure 2) to combust any remaining agent that may exit the primary furnace. The afterburner has two natural gas burners in a vertical arrangement. The crossover duct shown at the bottom of the afterburner in Figure 2 is connected into the outlet at the top of the MPF shown in Figure 1 for each furnace.

## **MPF MODELING APPROACH**

In the MPF, the periodic loading of trays with projectiles containing undrained agent combined with burner and quench spray control to maintain a furnace temperature set point results in an inherently time dependent operation that must be adequately captured in the MPF model. To model the MPF operation with a true transient CFD simulation would require excessive computing resources. To better represent the time dependent nature of the MPF in an efficient manner, we use a combination of a transient “zonal” model and a steady state CFD model. The transient zonal model captures the transient effect of sudden changes in agent release rate, burner turndown and quench flows on the furnace temperature and overall gas composition. A steady

state 3D CFD model is used to compute the local mixing and destruction efficiency for a prescribed instant in time. A key aspect is that the agent release rate, burner turndown and quench flows determined with the transient zonal model are used to define the boundary conditions, required by the CFD model. These boundary conditions are the munition metal temperatures, agent release rate, fuel and quench flow rates.

### Transient MPF Zonal Model

The transient zonal model consists of a gas phase zonal combustion submodel and a projectile agent vaporization submodel. The gas temperature and composition of each zone is assumed uniform. Ordinary differential equations (ODE's) are integrated over time representing the material and energy balances of the gas phase of each zone and the agent within each individual projectile. The following ODE governs the material balance in each zone:

$$\frac{df_i}{dt} = \frac{1}{\rho V} \left( -f_i V \frac{d\rho}{dt} - \dot{m}_{out} f_i + \sum_{in} \dot{m}_{in} f_{i,in} \right) \quad (1)$$

where  $f_i$  is the mass fraction of the  $i^{th}$  stream,  $V$  is the zone volume, and  $\rho$  is the gas density. The streams tracked are the fuel such as natural gas, agent, air, and quench water. Mass conservation for each zone is expressed as:

$$\dot{m}_{out} = \sum_{in} \dot{m}_{in} - V \frac{d\rho}{dt} \quad (2)$$

The following gas enthalpy equation for each zone is also integrated:

$$\frac{dh}{dt} = \frac{1}{\rho V} \left( -h V \frac{d\rho}{dt} - \dot{m}_{out} h + \sum_{in} \dot{m}_{in} h_{in} + Q_c + Q_r \right) \quad (3)$$

where  $Q_c$  and  $Q_r$  represents the convective and radiative heat transfer in the zone, respectively. Continuity, Equation (2), may be substituted into Equations (1) and (3) to simplify those expressions.

For each projectile, ODE's for the agent temperature, mass, and metal temperature are also integrated. Free convection heat transfer between the metal shell and agent is assumed until the agent bulk liquid temperature reaches the saturation or boiling temperature at which time either nucleation or film boiling takes over depending on whether the calculated nucleation heat flux is greater than the maximum flux for transition to film boiling.

The MPF model is advanced through time using a 4th order Runge-Kutta time stepping scheme with adaptive time step size control [2] to maintain prescribed accuracy tolerances. At each time step the zones are updated with upstream zones first. The zone containing the outlet duct to the afterburner is updated last. The inflows consist of outflows from adjacent upstream zones in addition to the agent vaporization and burner and water quench flows. At each time step a chemical equilibrium calculation is performed to obtain the zone furnace gas temperature and composition from the stream mass fractions and enthalpy. The model simulates proportional-integral-differential (PID) control of the burner fuel and quench flow rates maintain the furnace temperature between two set points. The lower set point controls the burner flow rate and the upper controls the quench flow rate. The radiation heat transfer calculation involves the view factors between different projectiles and between projectiles and walls. These view factors are

calculated based on the placement of projectiles on the trays. The Hottel cross-string method [3] is used to obtain the view factors accounting for blockage by other munitions and a correction factor is applied to account for the 3-D effect of the finite length of the munition cylinders. This correction factor was determined from full 3-D integrations. A polynomial fit was obtained for the correction factor as a function of distance between munitions for each projectile type.

Output from the transient model includes as a function of time the vaporization rate (i.e., flow rate of vaporized agent from the projectiles), fuel flow rate, quench flow rate, furnace gas temperature and gas composition. The vaporization rate and the burner, quench and air flow rates are used as inputs (boundary conditions) to the 3D CFD model of the MPF.

### **Metal Parts Furnace and Afterburner CFD Models**

Since the zonal model is incapable of resolving smaller scale mixing and destruction efficiency, the CFD furnace model is applied at the instant of time of interest. As many as  $10^6$  control volume cells are used in the CFD calculation. The technical approach used in the furnace CFD model involves the following:

1. REI's reacting CFD code, *BANFF*, predicts 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 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 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 are then applied as a post-process using the previously calculated temperature and flow fields.

Detailed chemical kinetics calculations are performed along streamlines originating at the tips of projectiles from which agent release is calculated. The streamline kinetics calculations assume that the gas at the tip of the projectiles is 100% HD. If any agent survives the primary furnace, the kinetic calculations may continue as a post process calculation with the afterburner CFD model. Figure 2 shows the typical gas temperature distribution as predicted by the MPF afterburner CFD model.

### **CWA Mechanism Development**

HD is believed to be more stable than GB, but less stable than dimethyl methylphosphonate (DMMP) a surrogate for GB. This surrogate was previously used in simulating destruction of GB [Denison et al., 2001]. Bozzelli [4], who serves on the project advisory panel, has provided several initial pathways for destruction of HD. One first step in the HD decomposition is the elimination of HCl. Another first step is a retroene reaction to form vinyl chloride + HSCH<sub>2</sub>CH<sub>2</sub>Cl. The initiation steps are followed by three parallel reactions: 1. a retroene reaction leading to S=C-CH<sub>3</sub> + ·CH=CCl<sub>2</sub>, 2. a reaction to C=C-S-C=C + HCl; and 3. a reaction to ClC-C· + ·S-C=C. Since the thermodynamic properties have yet to be determined for many of the unstable intermediate species produced from these initial steps, a complete mechanism for

the oxidation and pyrolysis is not yet available for use in this study. However, work on this mechanism is continuing and is expected to be completed during the course of this Phase II effort.

In the study presented here we have used the conservative approach to calculate the destruction efficiency based on just the above initial unimolecular pathways assuming pyrolysis is the only destruction path. Figure 3 shows destruction efficiency at a two second residence time as a function of temperature. The pyrolysis kinetics are compared with experimental pyrolysis data [5]. The figure shows that this approach is conservative as it predicts lower destruction efficiency for a given temperature. As an alternative, Tsang [6], also on the project advisory panel, recommended dimethyl ether, as a simulant compound for HD; a detailed chemical oxidation model is available [7].

## RESULTS

We present model results for three cases to demonstrate the models. The first consists of baseline operation of the three-zone MPF with 155-mm projectiles containing 5% residual HD. The second involves the same three-zone furnace but with 4.2-inch projectiles full of HD. In this case we have attempted to replicate conditions for which data has been taken at the Johnston Atoll Chemical Agent Disposal System (JACADS). The final case also consists of processing full 4.2-inch projectiles for a proposed four-zone furnace.

### Three-Zone Furnace With 5% HD In 155 mm Projectiles

Figure 4 shows the gas temperature, total agent release rate, fuel flow rate, and oxygen concentration model as a function of time for zone 1 of this three-zone furnace. Zone 1 is the focus for this furnace because zone 1 is the first zone into which trays are introduced and zone 1 contains the primary furnace outlet leading to the afterburner. The agent is nearly gone by the time the trays reach zone 2 and is completely gone at when they reach zone 3. The total time in Figure 4 covers three tray feeds and is therefore periodic with a tray introduced every 16 minutes. As the projectiles heat up and rapidly vaporize the HD the temperature control reduces the fuel flow rate so as to maintain the set point temperature of 1144 K (1600 F). Since the zone temperature does not reach the higher set point (1700 F for this case) the water quench remains at zero. Had the zone temperature exceeded this upper set point, the quench flow rate would have adjusted to maintain the upper set point. The oxygen concentration does not change by more than a percentage point. The oxygen time plot is not exactly periodic in the figure because initially zones 2 and 3 did not have trays, which require more fuel and hence lower oxygen. Had the calculation continued the remaining cycles would have looked identical to the last shown.

Figure 5 shows the destruction of the agent as calculated along the streamlines shown. The blue dots show the starting locations. The agent is seen to be fully destroyed by the conservative pyrolysis assumption before exiting the primary furnace. When oxidation is included in the mechanism the destruction will be much faster. It should be remembered that after the gases exit the MPF they are processed in the afterburner.

### Three-Zone Furnace With Full 4.2 Inch Projectiles

We have obtained test data taken at the JACADS site. This data was obtained for PMCD to determine how well full projectiles of HD can be processed. The projectiles are 4.2-inch mortars.

The MPF at the JACADS site is operated with fuel oil. Figure 6 shows a comparison between measured data and the model. Both zone 1 temperatures and agent vaporization rate are compared. The “measured” vaporization rates were actually estimated based on measured afterburner exit O<sub>2</sub> concentrations, and afterburner fuel and air flow rates of the primary furnace and afterburner. The model has reasonably captured the temperature control for the zone. There is reasonable agreement of the vaporization rates in terms of the shape of the profile. The onset of vaporization calculated by the transient model also occurs at about the same delay as the data of about 6 minutes after the trays are introduced.

Figure 7 shows the O<sub>2</sub> concentration in zone 1, which represents the overall excess O<sub>2</sub> in the primary furnace. With full projectiles, the overall primary furnace is predicted to approach substoichiometric with the O<sub>2</sub> dropping to a fraction of a percent. Although not shown, the JACADS data showed a temperature spike (~1450 K) in the cross-over duct at the time of peak vaporization rate probably due to the combustion of unburned intermediate pyrolysis products coming from substoichiometric regions in the primary furnace.

### **Four-Zone Furnace With Full 4.2 Inch Projectiles**

A four-zone furnace has been proposed for the Pueblo, CO site, which would process full projectiles. An additional zone is added and the outlet duct to the afterburner is moved to the second zone. Also the furnace interior is slightly taller and wider than the baseline three-zone furnace.

Figure 8 presents the calculated agent vaporization rate, natural gas flow rate, water quench rate, and O<sub>2</sub> concentration in zone 1 for three cycles of tray charging. Figure 9 shows the same parameters as Figure 8 for zone 2 and includes the zone 2 temperatures. The fuel flow rate is seen to back off to the minimum turn down as the agent vaporization rate increases. The water quench also increases to maintain temperatures at the maximum set point temperature of 1200 K. Zone 1 becomes substoichiometric (Figure 8d). However, overall there is enough air. At the peak overall vaporization rate of zone 1, there is about 4% excess O<sub>2</sub> going out the furnace from zone 2 (Figure 9c). Comparing Figure 9c with Figure 7 from the three-zone furnace with full projectiles, it can be seen that the capacity with the added zone results in more excess O<sub>2</sub> exiting the primary furnace. The four-zone furnace has greater capacity.

Some residual agent remains in the projectiles as the tray in zone 1 moves to zone 2 so there is some initial vaporization that occurs in zone 2 (Figure 9a). This initial zone 2 agent vaporization causes a brief flow of quench water. The larger peak quench that occurs in zone 2 (Figure 9d) is not from this vaporization but occurs to maintain temperatures in zone 2 from the combustion of uncombusted intermediate pyrolysis products from zone 1. Once the vaporization rate in zone 1 has dropped to a level at which there is enough oxygen to complete combustion in zone 1, the temperature in zone 2 falls to the minimum set point, the fuel flow rate in zone 2 rises to maintain temperature, and the quench falls to zero.

Figure 10 shows the destruction of the agent as calculated along the streamlines shown. Because of somewhat lower temperatures in the near vicinity of the projectiles, some delay in the destruction of the agent is noted. Nevertheless, full destruction occurs well before the streamlines reach the outlet.

## CONCLUSION

This paper has demonstrated that zonal and CFD models of the Metal Parts Furnace (MPF) can be constructed and provide useful information on the physical processes that affect furnace performance in terms of destruction efficiency and operability. A comparison has been made to available data and some deficiencies in the model have been identified and are being corrected. 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 gets to the afterburner. The four-zone furnace has been shown to have more capacity than the three-zone furnace for the processing of full projectiles. The models may also be useful in simulating incineration system upset conditions and failures that could lead to an agent release, so that appropriate design and operational modifications can be made to mitigate such occurrences.

## ACKNOWLEDGEMENT

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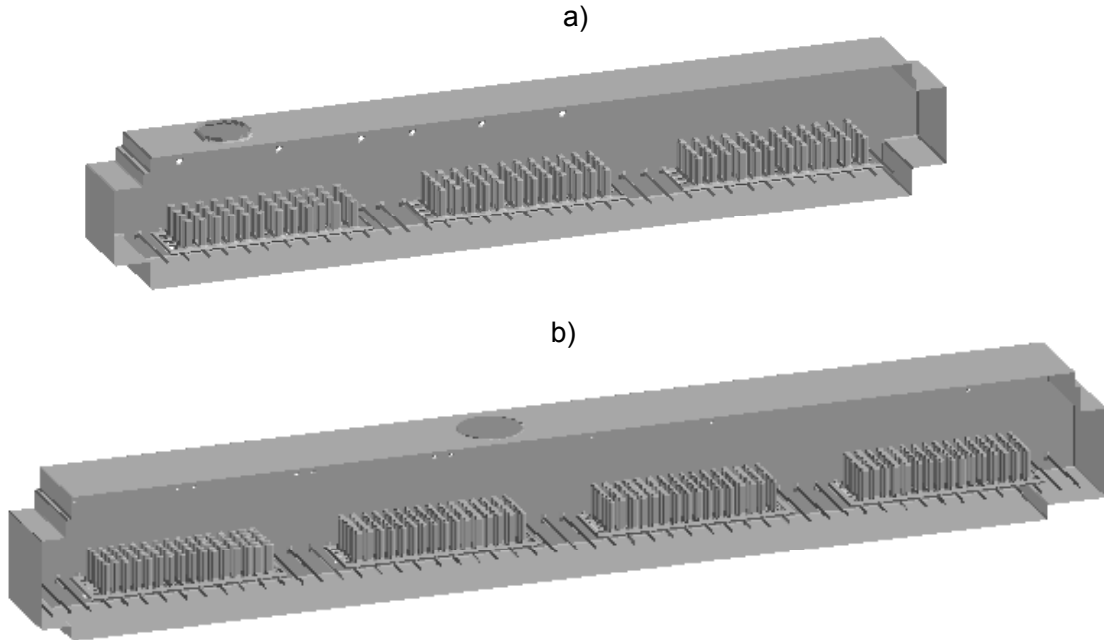


Figure 1. Three-zone (a) and four-zone (b) MPF primary furnace configurations.

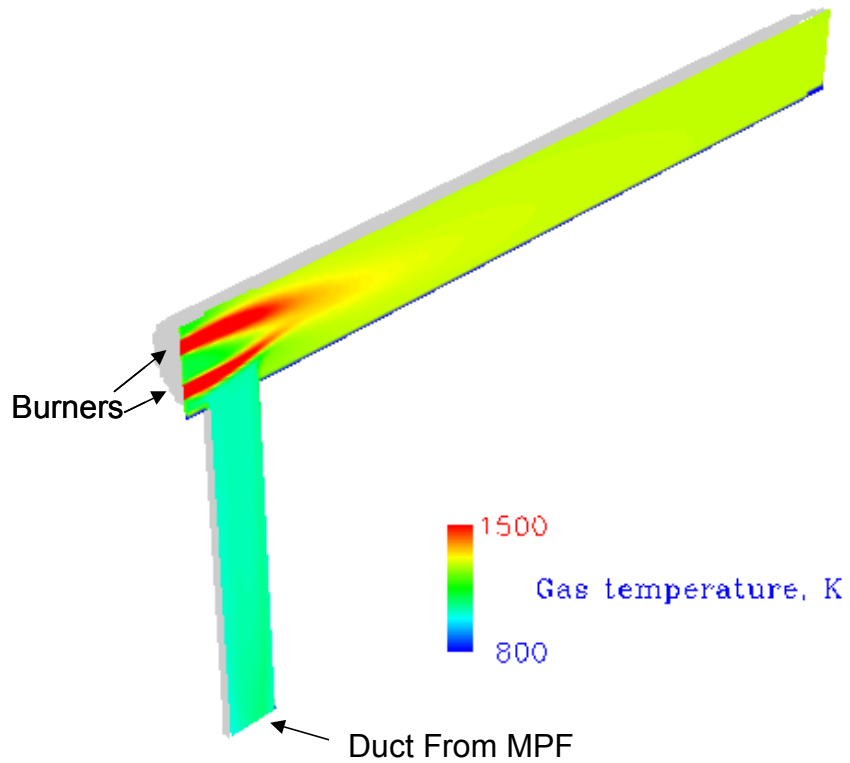


Figure 2. Gas temperature distribution in the afterburner of the three-zone MPF.

### HD pyrolysis, 2 sec residence time

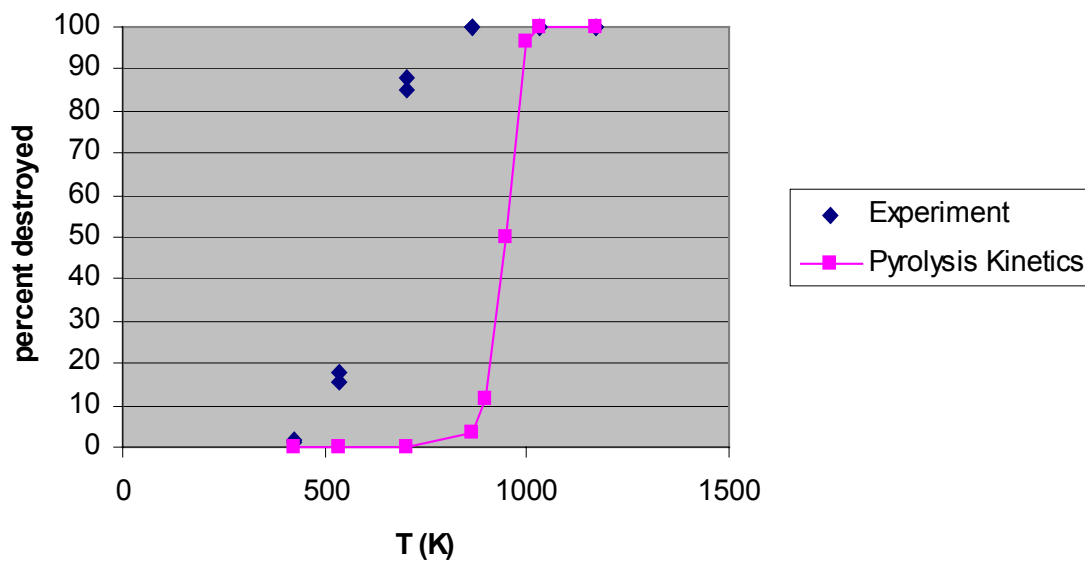


Figure 3. Comparison of unimolecular path destruction kinetics of HD with experimental pyrolysis data.

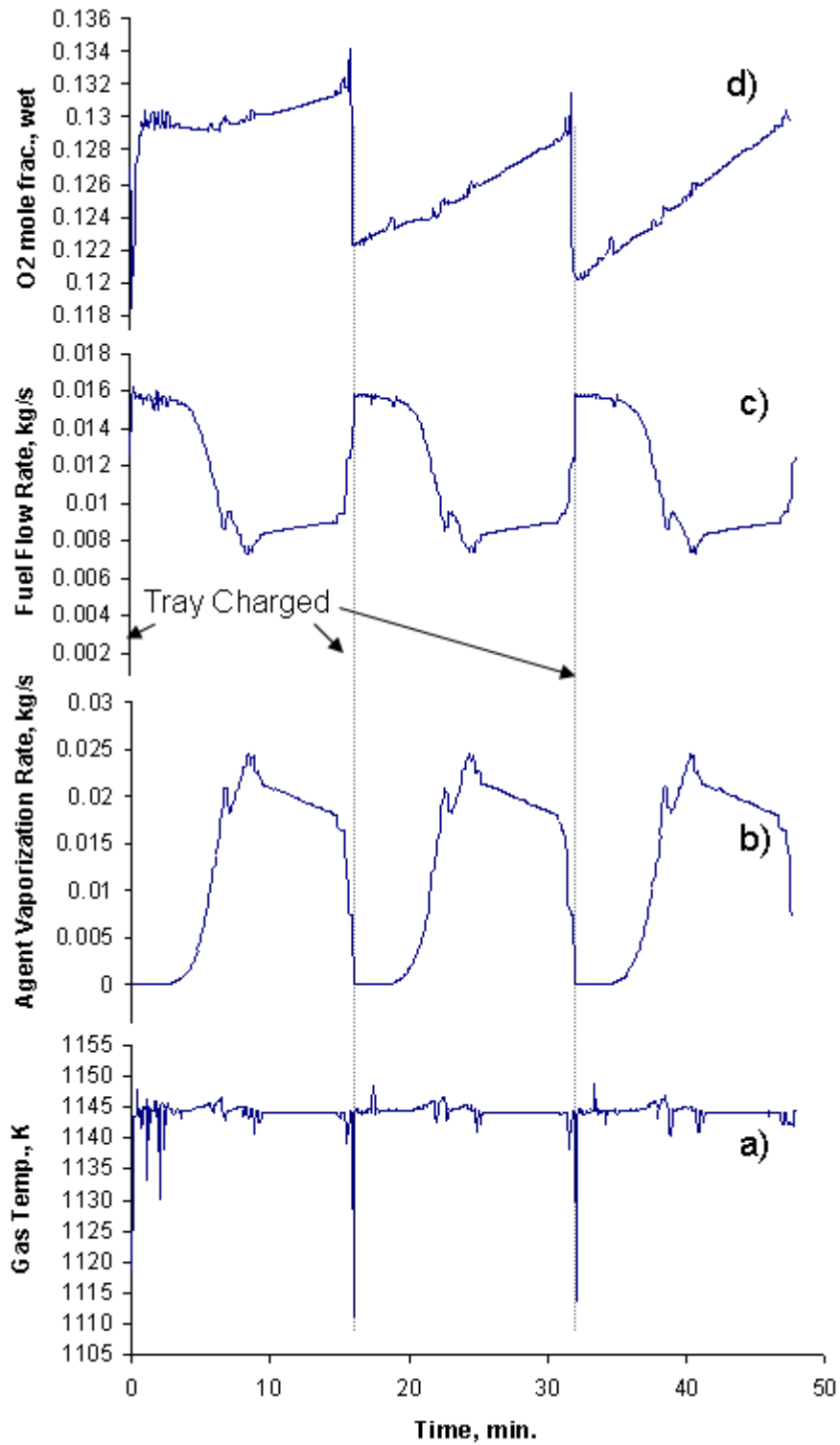


Figure 4. Calculated time profiles of zone 1 for 48 155mm projectiles with 5% residual agent introduced into three-zone furnace.

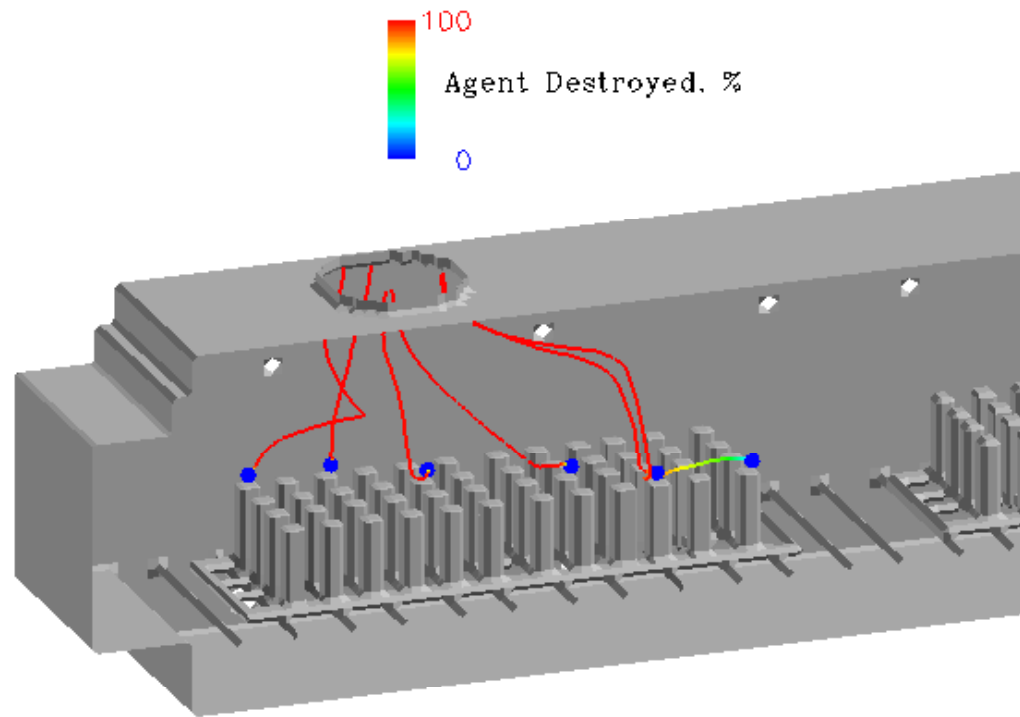


Figure 5. Agent destruction along stream lines within three-zone furnace processing 155 mm projectiles with 5% residual agent.

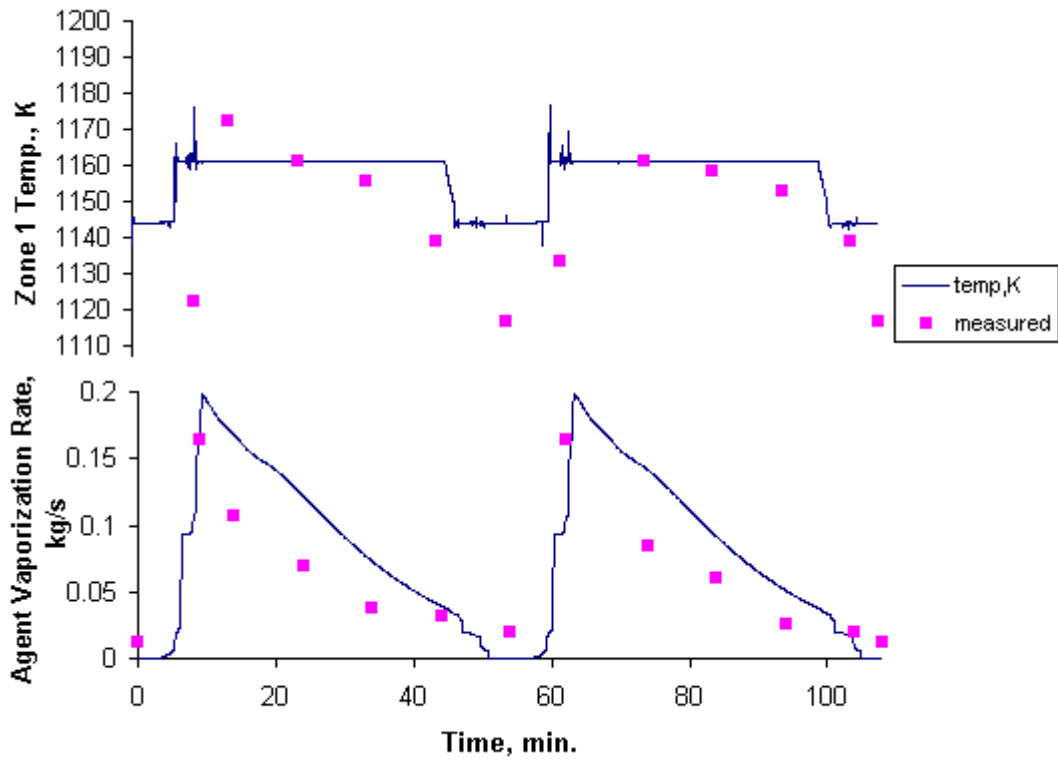


Figure 6. Comparison of model calculations with test data of full 4.2 inch projectiles in a three-zone MPF.

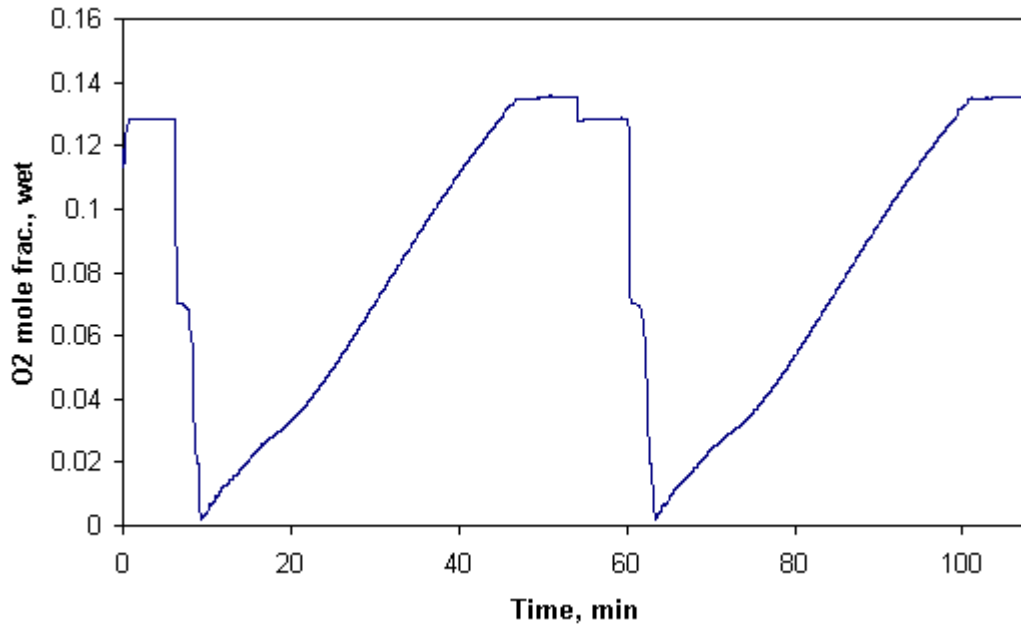


Figure 7. Calculated Oxygen concentration in zone 1 of the three-zone MPF with 96 full 4.2 inch projectiles.

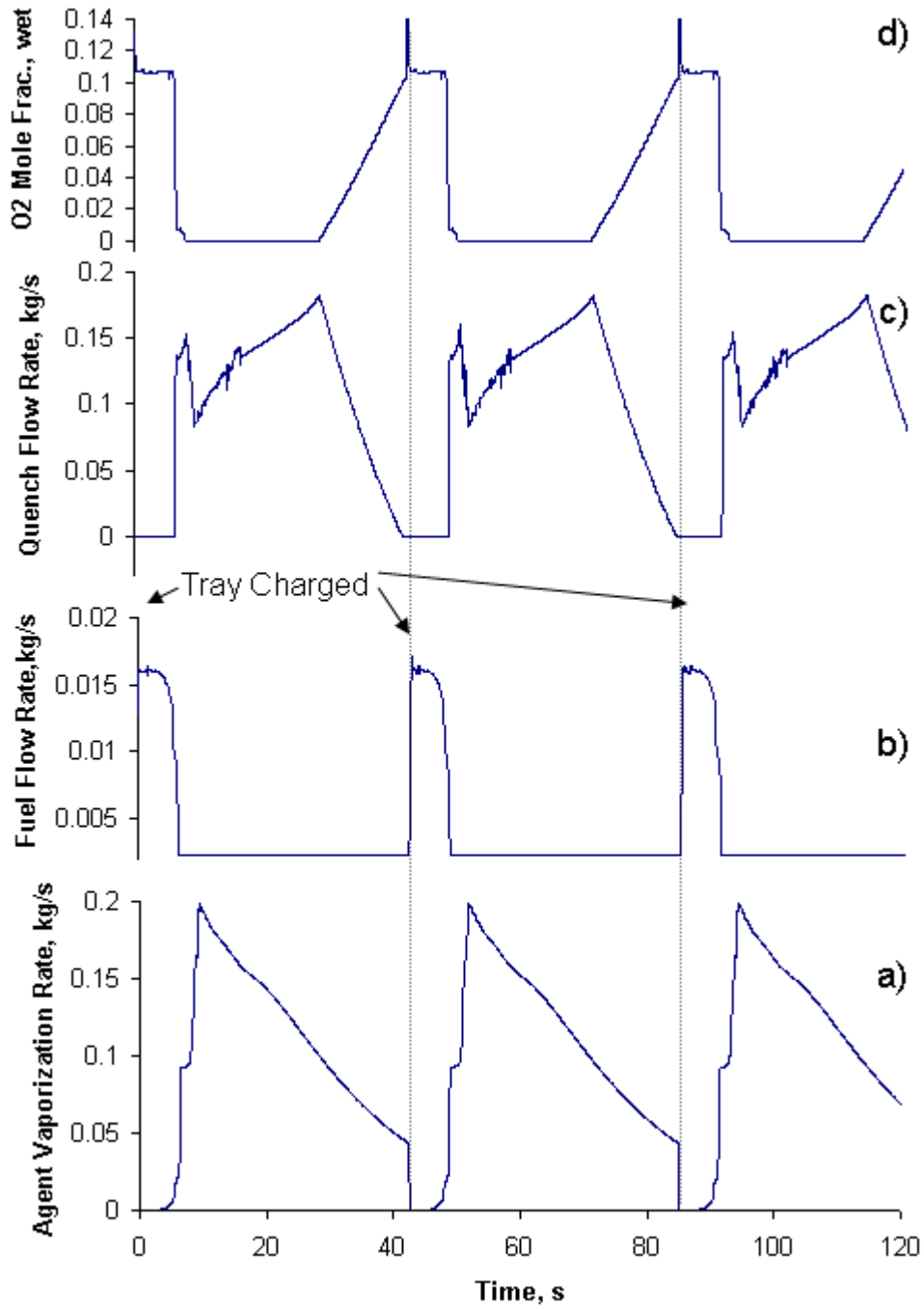


Figure 8. Calculated time profiles of zone 1 for 96 full 4.2-inch projectiles introduced into the four-zone furnace.

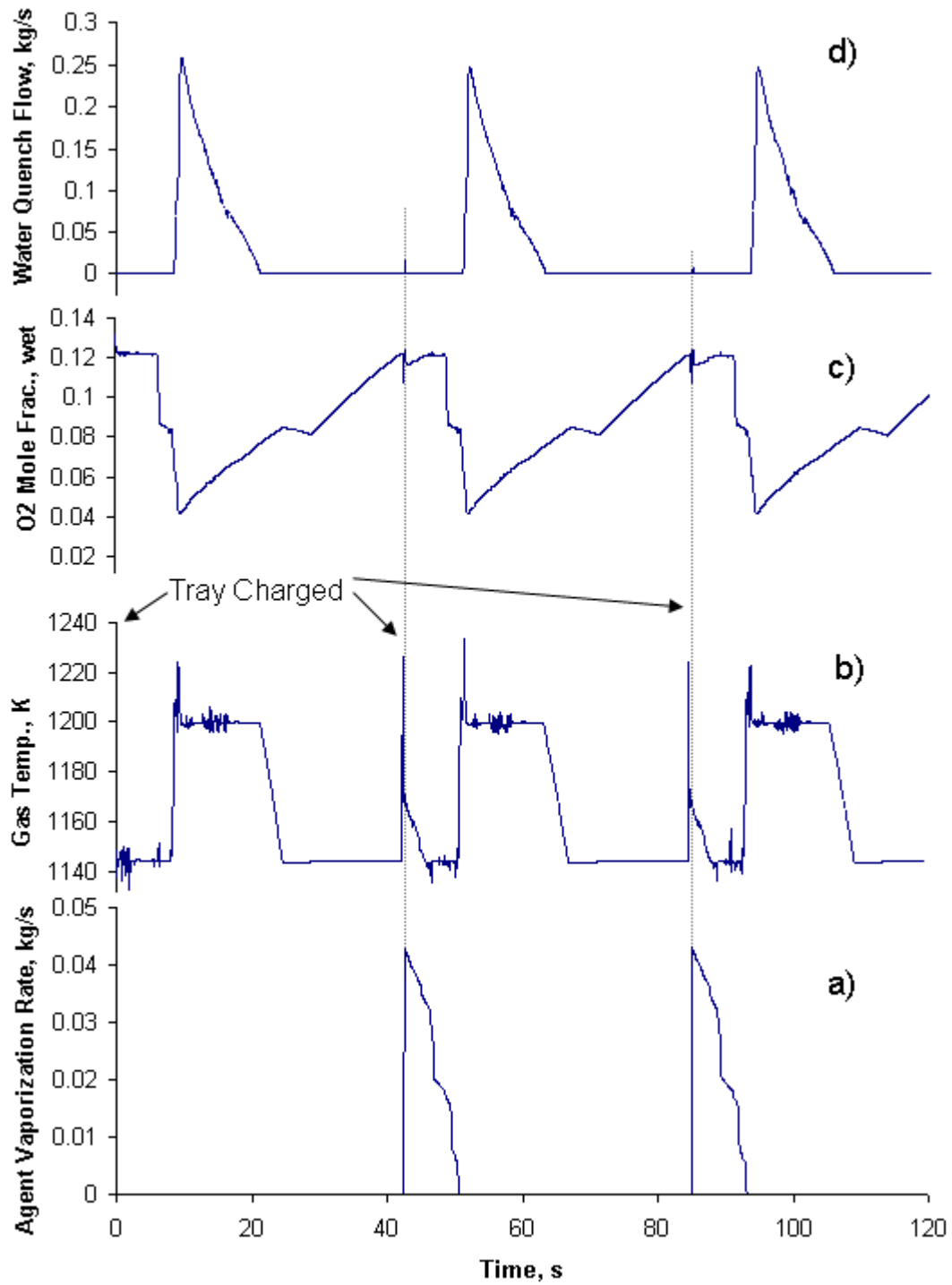


Figure 9. Calculated time profiles of zone 2 for 96 full 4.2-inch projectiles introduced into the four-zone furnace.

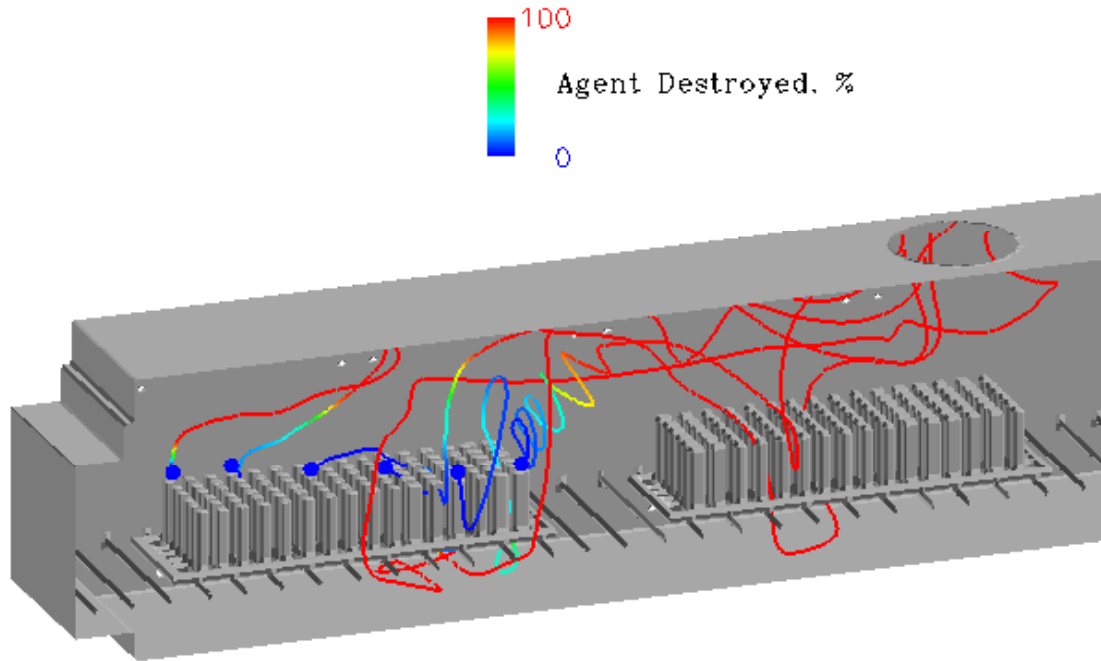


Figure 10. Agent destruction along stream lines within three-zone furnace processing full 4.2 inch projectiles.