

Computational Modeling of a Chemical Demilitarization Deactivation Furnace System

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ABSTRACT

This paper presents the development of the models for analyzing a Deactivation Furnace System (DFS) for processing rockets containing the agent GB (Sarin). The DFS is one of the US Army incinerators for destroying the highly toxic chemical agents and munitions contained within the chemical weapons stockpile. The DFS is a gas-fired counterflow rotary kiln designed to treat energetics (fuses, boosters, bursters, and solid rocket propellant). The DFS model consists of two parts: (1) an energetics/rocket piece combustion submodel coupled with a transient zonal furnace combustion model, and (2) the gas phase combustion/destruction computational fluid dynamics (CFD) model. The model exhibits good agreement with measured data taken at two incineration sites processing M55 rockets containing GB.

INTRODUCTION

Incineration has been selected by the United States as one of the methods for destroying highly toxic chemical agents and munitions contained within the chemical weapons stockpile. Advanced computer modeling tools can play an important role in reducing the time, cost and technical risk of destroying the stockpile. Incineration technology has been used at two sites, and is under construction/systemization at three additional sites.

A simulation tool for analyzing chemical demilitarization incinerators is being developed [1, 2]. Within the furnaces and afterburners, agent destruction is analyzed using recently developed detailed chemical kinetics integrated with computational fluid dynamics (CFD). Both full CFD and streamline calculations are possible. The development of models for the destruction of mustard agent (HD) in the Metal Parts Furnace (MPF) has been previously demonstrated [2].

This paper presents the development of the models for analyzing the DFS for processing rockets containing the agent GB. The modeling approach for the DFS is discussed. The current status of development of destruction chemistry for the actual agent is reviewed and results for several demonstration cases are presented.

DFS DESCRIPTION

The DFS incinerator is a gas-fired counterflow rotary kiln or retort (Figure 1) designed to treat energetics (fuses, boosters, bursters, and solid rocket propellant). Energetics are all contained in

thin-walled metallic housings that must be sheared into pieces prior to burning; otherwise confined energetics would detonate in the kiln rather than burn. Rocket pieces are dumped into the kiln at the feed end through two feed chutes. The number of rockets fed per hour can range between 1 and 40 depending on the retort operating conditions. Firing an auxiliary fuel with air provides high temperature combustion products at the discharge end. The burner fuel flow rate is controlled to maintain a set point temperature of about 1000 °F. In addition to the burner air, negative pressure draws shroud air from the surroundings, which flows over the exterior of the kiln shell for cooling and then is used for combustion air. The rocket pieces are carried through the kiln via spiral flights or helical baffles as the kiln is rotated. Upon completion of energetics combustion, the rocket pieces fall from the kiln on to a heated discharge conveyor (HDC), which brings the rocket pieces to at least 1000 °F for at least 10 minutes. .

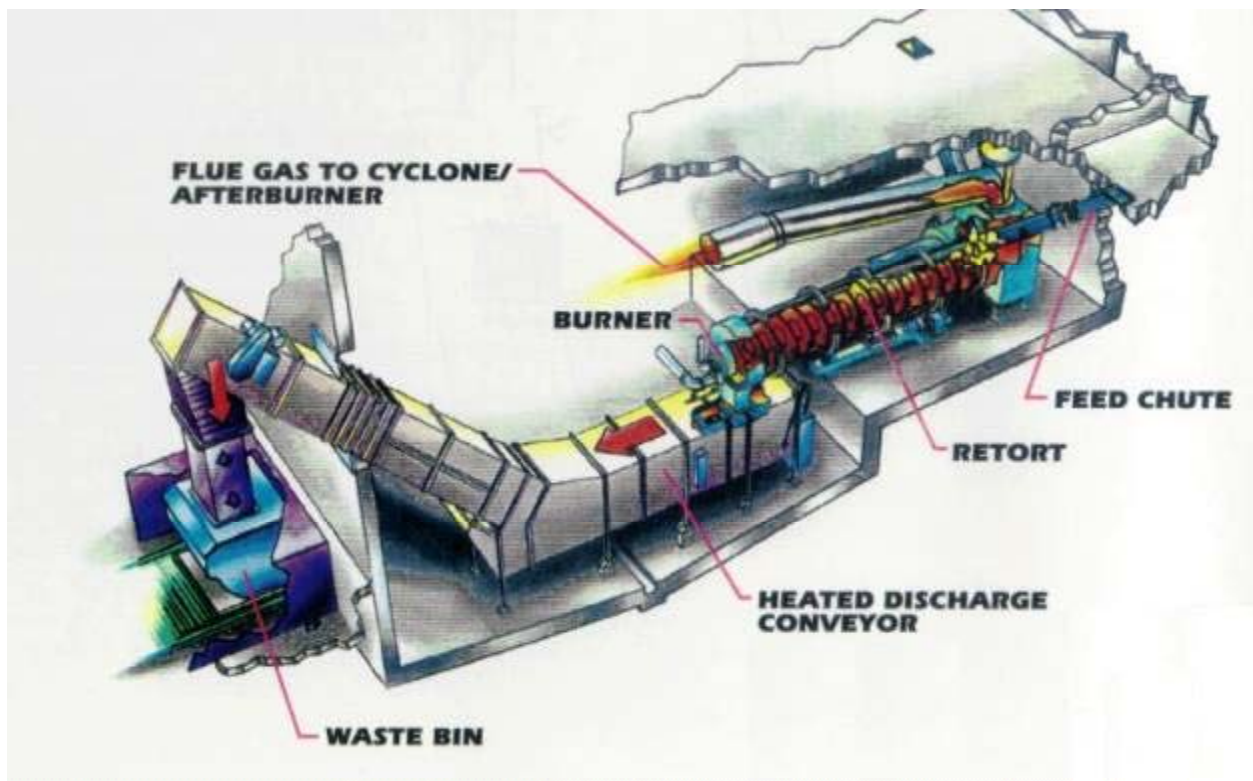


Figure 1. Deactivation Furnace System (Courtesy of the US Army, Program Manager for Chemical Demilitarization).

Downstream of the DFS kiln is a long duct that leads to a blast attenuation duct, followed by a cyclone separator and afterburner. The afterburner has two natural gas burners in a tangential firing arrangement. Following the afterburner is the Pollution Abatement System (PAS) consisting of a quench tower, venturi scrubber, a scrubbing tower, and demister. While models for these downstream equipment have been developed, this paper will focus on the kiln.

DFS MODELING APPROACH

In modeling the military chemical weapons agent (CWA) incinerators there is a need to sufficiently resolve the geometry to capture details of mixing and agent destruction. CFD can simulate the mixing and destruction with a reasonable amount of computation time on a desktop PC if steady state can be assumed. However, the DFS is inherently transient due to the periodic

loading of sheared rocket pieces containing energetics and un-drained agent, combined with the kiln burner and quench spray control that maintain the burner and chute temperatures, respectively. The DFS model must adequately capture the inherently time dependent operation.

An approach that has proved quite successful in modeling the transient behavior of the Metal Parts Furnace (MPF) [2] is used. To better represent the time dependent nature of the DFS in an efficient manner, the approach consists of a combination of a transient “zonal” model and a steady state CFD model. The transient zonal model captures the transient effect on the overall kiln/afterburner temperature and gas composition due to sudden changes in agent release rate, burner turndown and quench flows. The conditions predicted by the transient zonal model are subsequently used to define the boundary conditions for a steady state 3D CFD model that is used to compute the local mixing and destruction efficiency for a prescribed instant in time. The CFD model boundary conditions include the munitions metal temperatures, agent release rate, fuel flow rate and quench flow rate.

Transient DFS Zonal Model

The DFS model consists of two parts: an energetics/rocket piece combustion submodel coupled with a transient zonal furnace combustion model and the gas phase combustion/destruction 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 and the pitch of the spiral flights. The incident radiation field as well as convection heat transfer is used to calculate the rocket piece temperature, burn rate of the propellant, and release rate of remaining agent as a function of time and axial position. A quasi-steady-state assumption is then used in the reacting CFD model using boundary conditions at the instant of time of interest from the transient zonal model.

The approach for the gas phase combustion and heat transfer has been described previously for a metal parts furnace (MPF) transient model [2]. In summary, ordinary differential equations (ODE's) are integrated over time representing the material (elemental) and energy balances of the gas phase of each zone and the energetics and agent within each individual rocket piece. The DFS model assumes a constant linear velocity of the pieces along the bottom of kiln based on kiln rotation rate and the pitch of the spiral flights. The pieces relative position in the kiln is determined by the timing of the dumps down the feed chutes.

Output from the transient model includes the time history for the vaporization rate (i.e., flow rate of vaporized agent from the projectiles), fuel flow rate, quench flow rate, furnace gas temperature, gas composition, and wall temperature. The vaporization rate and the burner, quench and airflow rates are used as inputs (boundary conditions) to the 3D CFD model. The agent in the rocket pieces vaporizes quite rapidly due to the combined effects of heat transfer from the metal walls of the rocket pieces and from radiation from the kiln directly onto the open ends of the rocket pieces.

The kiln is divided into three zones with the gas composition and temperature assumed to be uniform within each zone. Additional zones have been included to model the feed chutes, shroud air, afterburner, cyclone and duct work between the kiln and cyclone, including the blast attenuation duct.

The energetics combustion rate and the agent release rate for each pieces is stored in a file as a function of time and position to be used by the reacting CFD model. The predicted kiln wall

temperatures, which are also governed by energy conservation equations within the transient model, are also used as boundary conditions in the CFD model.

The propellant burn rate is calculated as the product of a linear burn rate, exposed propellant area, and propellant density. The burn rate is known to be a function of pressure and propellant bulk temperature. For the simulations presented here, the propellant accounts for nearly all the energetics mass and heating value. Therefore, the burster, igniter, and explosive mass was lumped into and treated as propellant

Kiln and Afterburner CFD Models

Since the zonal model is incapable of resolving small scale mixing and destruction efficiency, the CFD furnace model is applied at an instant of time of interest. As many as 106 control volume cells are used in the CFD calculation. The technical approach used in the furnace CFD model involves the following:

1. *GLACIER*, an inhouse 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 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 possible approaches may be used to calculate the agent destruction: (1) integrate the complete detailed kinetic mechanism along streamlines, (2) applying some reduced mechanism in the solution of conservation equations for each species, and (3) solving a conservation equation for just the agent applying only the initial destruction paths in the detailed mechanism. The first and third approaches are demonstrated in this paper since the reduced mechanism is still under construction.

For the streamline calculations detailed chemical kinetics calculations are performed along streamlines originating at the location of the rocket pieces from which agent release is calculated. The streamline kinetics calculations assume that the gas at the starting locations is 100% GB. For the latter two Eulerian approaches, appropriate source terms at the location of the rocket pieces are used. If any agent survives the primary furnace, the kinetic calculations may continue as a post process calculation with the afterburner CFD model.

CWA Mechanism Development

The detailed chemical kinetic mechanism for oxidation of nerve agent GB [3] was developed at Lawrence Livermore National Laboratory by building on previous work [4] on kinetics of organophosphorus GB simulants trimethyl phosphate (TMP), dimethyl methylphosphonate (DMMP), and diisopropyl methylphosphonate (DIMP). The most important reaction for the destruction of GB was found to be a six-center unimolecular retro-ene reaction eliminating propene. This reaction is illustrated in Figure 2. Rates of destruction of organophosphorus compounds were verified by comparison to the experiments of Zegers & Fisher [5,6,7].

The rate of the dominant GB destruction pathway was estimated by Glaude et al. [3,4] “based on commonly used principles of bond additivity and hierarchical reaction mechanisms.”

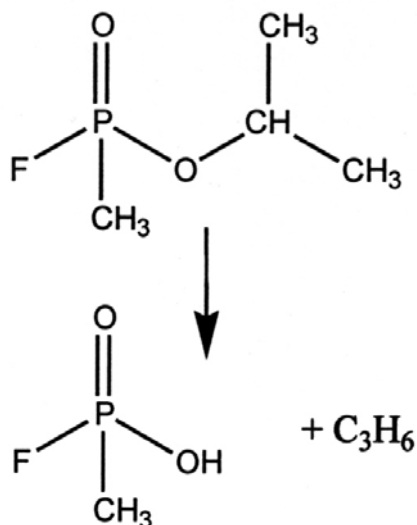


Figure 2. Dominant destruction pathway for GB (from Glaude et al. 2002).

To improve the precision of the dominant rate expression for GB destruction in the Glaude et al. mechanism, Bozzelli and Chen (unpublished) have performed calculations on the retro-ene and bond cleavage reactions using density functional computational chemistry and canonical transition state theory thermochemical kinetics techniques. The calculated rate expression for the lowest energy reaction (illustrated in Figure 2) is:

$$k = 2.03 \times 10^7 T^{1.62574} e^{(-40.69/RT)} \text{ sec}^{-1} \quad (1)$$

where R is in kcal/mol K and T is in Kelvin.

RESULTS

Model results are presented for three cases to demonstrate the models. All cases involve the processing of GB M55 rockets. The first two consist of baseline operation at Johnston Atoll Chemical Agent Disposal System (JACADS) and the trial burns at the Tooele Chemical Demilitarization Facility (TOCDF). The baseline operation of the existing unit in operation at TOCDF and under construction at the Umatilla Chemical Disposal Facility (UMCDF) requires that the rockets be drained to have no more than 5% residual agent when introduced into the DFS. Comparisons are made with measured data. The third case involves undrained rockets containing gelled agent. Gelled rockets have been identified as a processing issue because these rockets cannot be drained. The effect of gelled rockets was modeled by doubling the heat of vaporization of the agent.

Processing of Drained Rockets

As part of the validation effort we have obtained data taken at three second resolution at the JACADS site while processing drained M55 GB rockets at a rate of 35 rockets/hr. The rockets

were drained to have only 1% residual agent. Figure 3 shows a comparison of kiln exit oxygen with that calculated by the transient model over several cycles. The agreement is quite good. Model adjustments were made only to the exposed propellant area versus time profile, propellant linear burn rate, and shroud airflow to provide this agreement. The shroud airflow rate was not measured. In addition, most available propellant burn data are applicable to normal rocket motor operation at much higher pressures than atmospheric.

In the JACADS and TOCDF operation the rockets are sheared into eight pieces that are introduced into the DFS kiln in three dumps down the feed chutes. Dump #1 involves two pieces: the tail section from the previous rocket and the nose of the current rocket containing the fuse. At 66 seconds later dump #2 involves four pieces containing all the undrained agent, burster, ignitor, and nearly one third of the propellant. Finally, 19 seconds later, dump #3 consists of two pieces containing the remaining propellant.

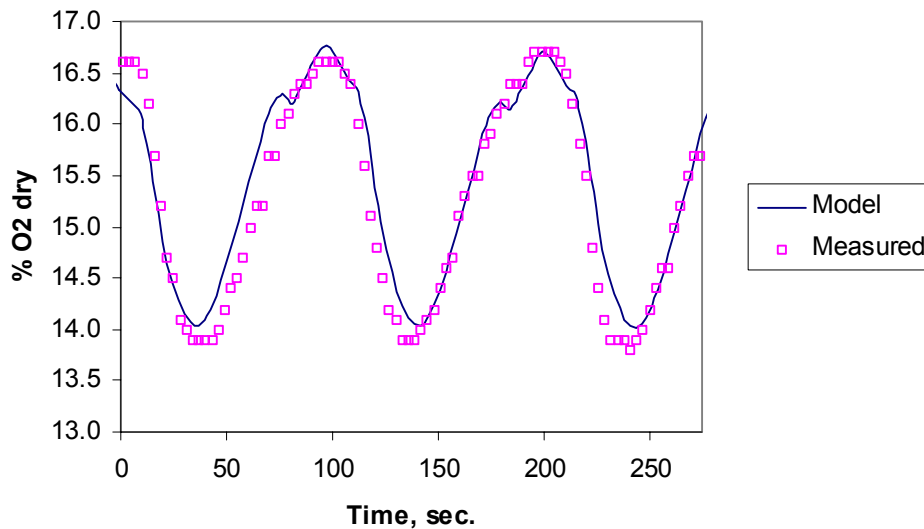


Figure 3. Comparison of kiln exit gas oxygen between the transient model and measurements.

Illustrated in Figure 4 is the calculated time history for the agent vaporization rate and energetics combustion rate in the first third of the kiln at feed end for processing 33 drained rockets/hr with 5% residual agent per rocket. In Figure 4, the colored arrows denote the relative times of the dumps #1, #2 and #3 associated with processing each rocket. Note that the material associated with the first dump is from the rocket tip and fin section of the previous rocket. There is little heating value with this dump and the energetics rate at this time is from the energetics from the previous two dumps. The peak in energetics combustion is associated with the propellant in the third dump. The entire agent is contained in the second dump of rocket pieces. The periodic behavior is noted to be consistent with the rocket-processing period of 109 seconds.

Illustrated in Figure 5 are, the calculated time history for the kiln exit gas temperature and the bulk oxygen concentration. Also shown in these figures are one-hour average data taken at TOCDF. The model does capture the average kiln exit temperature and oxygen.

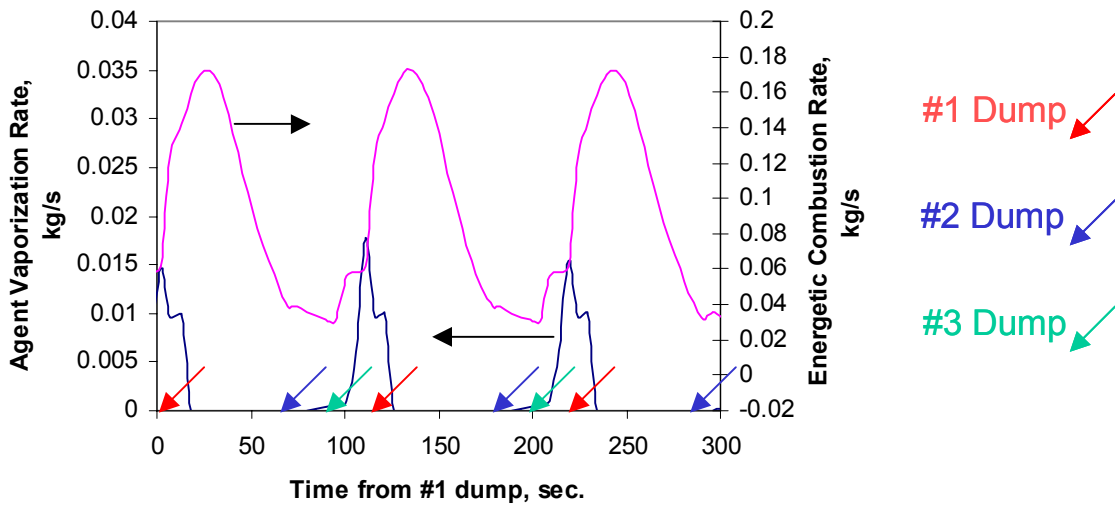


Figure 4. Agent vaporization rate and energetics combustion rate versus time for 33 rockets/hr.

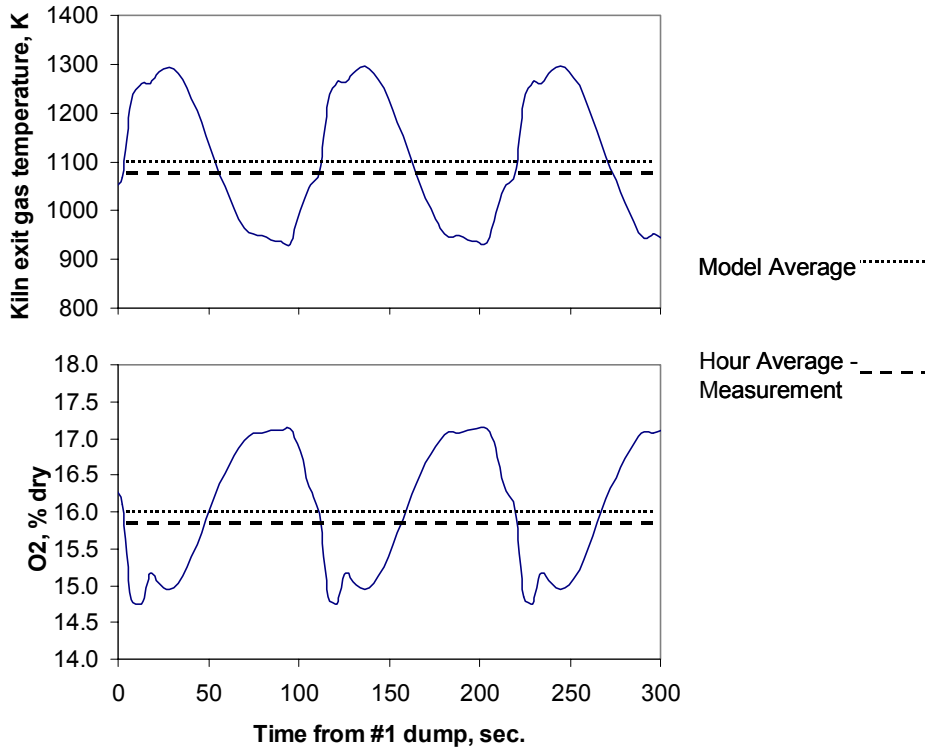


Figure 5. Calculated kiln exit gas temperature, oxygen concentration and hour average data.

Processing of Undrained Gelled Rockets

In the third simulation the processing of one undrained rocket/hr was modeled, where the rocket contains 100% gelled agent. Figure 6 shows the energetics combustion rate and agent release rate as a function of time as calculated by the model. Nearly ten minutes of time is shown in the figure, after which the combustion is complete. For the remaining fifty minutes, before the next

rocket is processed, there are no significant changes in flow rates in the kiln and the kiln is in an idle mode. The one rocket/hr feed rate was based on an equivalent hourly processing rate of agent relative to that demonstrated during trial burns with drained rockets. A significant increase in throughput looks achievable.

CFD and Destruction Results

Figure 7 shows gas temperature distributions calculated by the CFD model for the 33 rockets/hr and 1 rocket/hr cases. These calculations were performed at the instant in time of peak agent vaporization rate (at 116 seconds in Figure 4 and 148 seconds in Figure 6). The majority of the combustion occurs toward the feed end of the kiln. The temperatures at the feed end (gas exit end) are higher for the 1 rocket/hr case. This is because at the time of peak agent vaporization rate the peak energetics combustion rate is higher in the 1 rocket/hr case. The non-symmetric temperature patterns seen at the feed end of the kiln are due to swirl flow patterns produced from the helical flights along the kiln wall.

Destruction along streamlines is shown in Figure 8 for the 33 rockets/hr and 1 rocket/hr case. These streamlines were started at the location of the rocket pieces with the largest agent release rate at the time selected. An agent mass fraction of unity was used as the initial condition. The model predicts very rapid agent destruction due to the high local temperatures for three of the four streamlines shown. The high temperatures are caused by the large heat release from the energetics and burning vaporized agent. Streamline 2 of the 33 rockets/hr case initially experiences a much lower temperature so the agent survives over a longer period of time until the streamline temperature increases sufficient for rapid destruction.

The destruction was also calculated over the entire Eulerian flow field using the initial destruction kinetic steps of the detailed mechanism. The destruction calculated in this manner is consistent with the streamline approach – the agent is destroyed rapidly. In fact, since the sources of agent are at nearly the same location as the sources from propellant combustion, the maximum agent concentration calculated is near the detect limit.

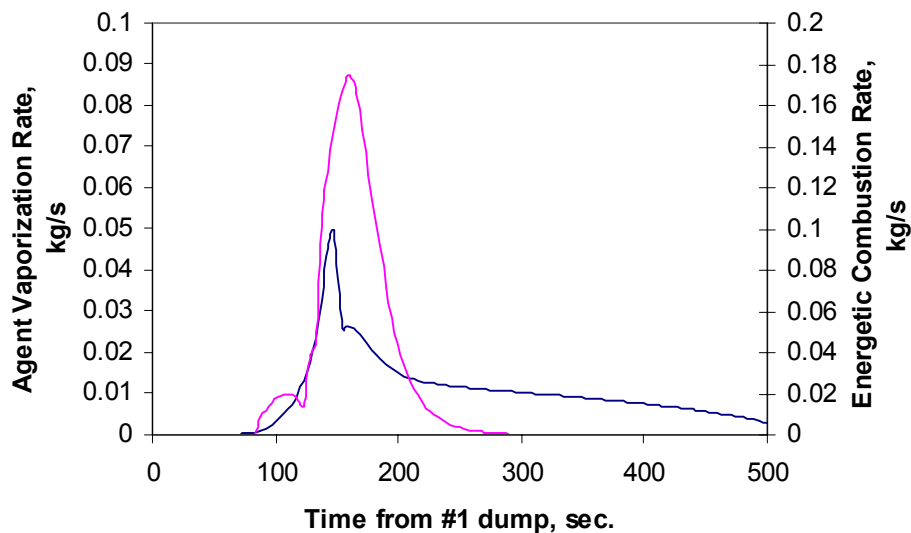


Figure 6. Agent vaporization rate and energetics combustion rate versus time for 1 rocket/hr.

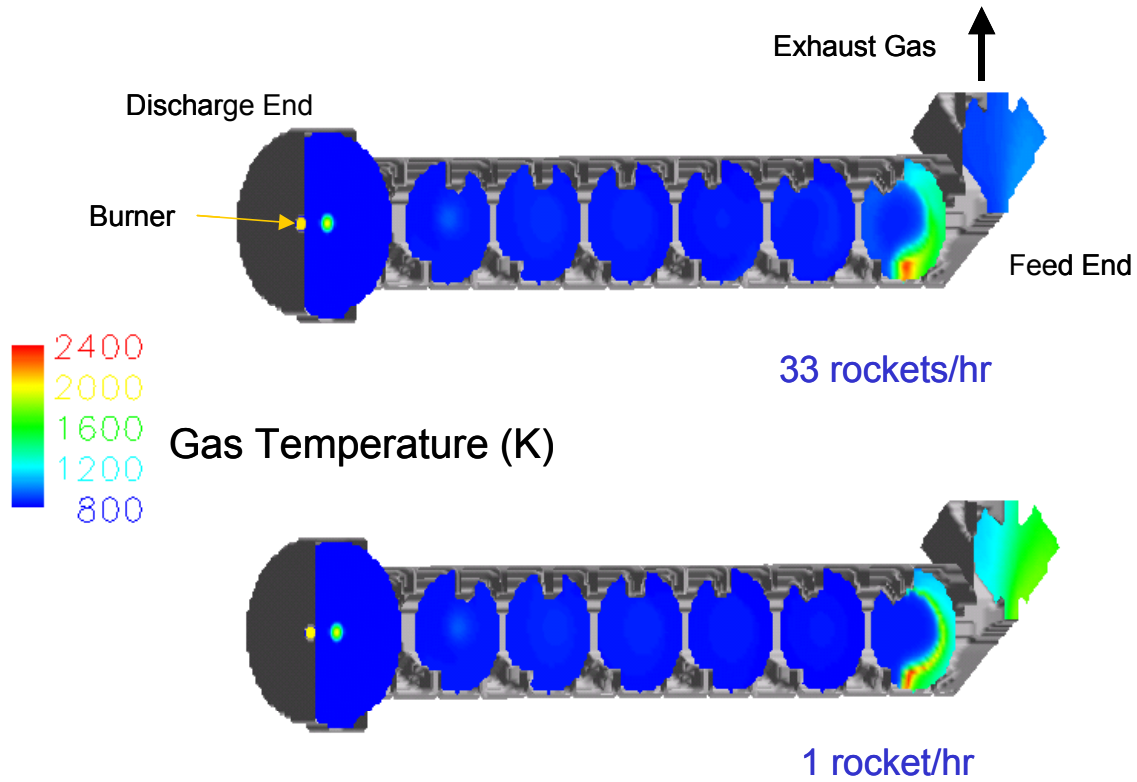


Figure 7. Gas temperature distributions calculated by the CFD model for the DFS.

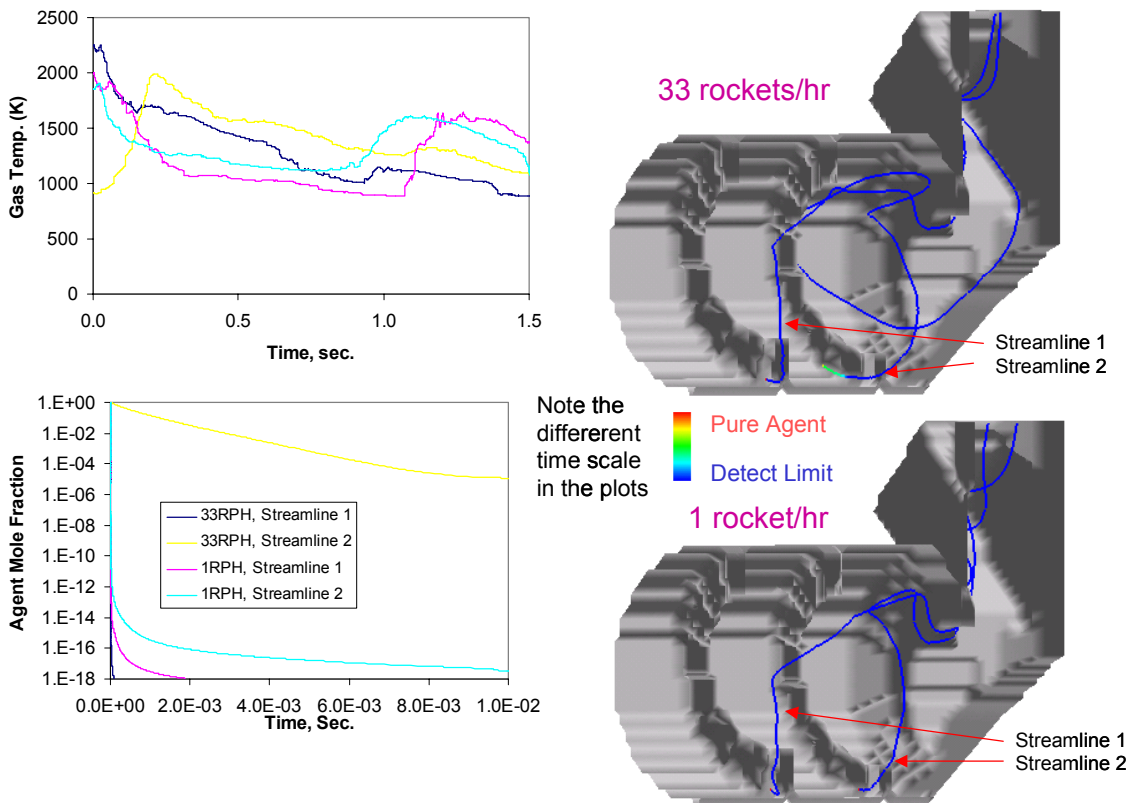


Figure 8 Agent destruction calculated along streamlines.

CONCLUSION

This paper has demonstrated that zonal and CFD models of the Deactivation Furnace System (DFS) can be constructed to provide useful information on the physical processes that affect furnace performance in terms of destruction efficiency and operability. A comparison with available measurements shows good agreement. 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 modeling has also demonstrated a potential for increased throughput for processing undrained gelled rockets. 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.

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