CHEMICAL EROSION OF GRAPHITE AND REFRACTORY METAL NOZZLES AND ITS MITIGATION IN SOLID-PROPELLANT ROCKET MOTORS

A Dissertation in
Mechanical Engineering

by

Piyush Thakre

© 2008 Piyush Thakre

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2008
The dissertation of Piyush Thakre was reviewed and approved* by the following:

Vigor Yang
John L. and Genevieve H. McCain Professor of Engineering
Dissertation Advisor
Chair of Committee

Kenneth K. Kuo
Distinguished Professor of Mechanical Engineering

Richard A. Yetter
Professor of Mechanical Engineering

Stephen Thynell
Professor of Mechanical Engineering

Michael M. Micci
Professor of Aerospace Engineering

Karen A. Thole
Professor of Aerospace Engineering
Head of the Department of Mechanical and Nuclear Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The erosion of rocket-nozzle materials during motor firings continues to be one of the major hindrances in the advancement of solid-rocket propulsion. The primary research objectives are: 1) to establish a unified theoretical/numerical framework to predict the chemical erosion of nozzle material by utilizing advances in chemical kinetics, turbulence modeling, and numerical algorithm, 2) to identify key physiochemical mechanisms and parameters that dictate nozzle erosion and 3) to investigate different ways to help minimize the nozzle material erosion with emphasis on the technique called nozzle boundary-layer control system (NBLCS).

The formulation takes into account detailed thermofluid dynamics for a multi-component reacting flow, heterogeneous reactions at the nozzle surface, condensed-phase energy transport, and nozzle material properties. Both metallized and non-metallized AP/HTPB (ammonium perchlorate/hydroxyl-terminated ploy butadiene) composite propellants are treated. Many restrictive assumptions and approximations made in the previous models have been relaxed. A two-layer $k$-$\varepsilon$ turbulence model was implemented, as it performs well for transpiration and accelerating flows. The governing equations and the associated boundary conditions are solved using a density-based, finite-volume approach and explicit time marching by means of a four-step Runge-Kutta scheme. The code is parallelized using the domain decomposition technique and message passing interface (MPI). The theoretical formulation and numerical scheme was validated with three test cases including turbulent flow over a flat plat, heat transfer in convergent-divergent nozzles, and two-dimensional oblique shock.
The different nozzle materials considered were graphite/carbon-carbon and such refractory metals as tungsten, molybdenum, and rhenium. The predicted nozzle surface recession rates compare well with different sets of available experimental data. The erosion rate follows the trend exhibited by the heat-flux distribution, and is most severe in the throat region. H₂O proved to be the most detrimental oxidizing species in dictating nozzle erosion. The erosion rate increases almost linearly with chamber pressure, mainly due to higher convective heat transfer and enhanced heterogeneous surface reactions. For non-metallized propellants, the graphite recession rate is dictated by heterogeneous chemical kinetics since the nozzle surface temperature is relatively low. For metallized propellants, however, the process is diffusion controlled due to the high surface temperature. The erosion rate decreases with increasing aluminum content, a phenomenon resulting from reduced concentrations of oxidizing species H₂O, OH, and CO₂. The tungsten nozzle erodes much slower than graphite, but at a rate comparable to that of rhenium. The molybdenum nozzle exhibits the least erosion but its low melting temperature (2896 K) is a serious limitation.

The analysis was extended to include NBLCS. The strategy involves injection of relatively low-temperature species, obtained from reactions of an ablative material SA/PVA (succinic acid/poly-vinyl acetate) and a small amount of propellant combustion gases, to a location slightly upstream of the nozzle. The effect of NBLCS injection on the near-surface physiochemistry is investigated in detail. Various fundamental mechanisms dictating the effectiveness of NBLCS are identified and quantified. The calculated erosion rates with NBLCS are negligible, even at ultra-high pressures. The mitigation of nozzle erosion is attributed primarily to the low temperature of the injected fluid, and
secondarily to the reduced concentrations of oxidizing species, H$_2$O, CO$_2$, and OH, near the nozzle surface.
TABLE OF CONTENTS

LIST OF FIGURES ..................................................................................................... viii

LIST OF TABLES ....................................................................................................... xiv

NOMENCLATURE .................................................................................................... xvi

ACKNOWLEDGEMENTS ......................................................................................... xix

Chapter 1 Introduction ............................................................................................. 1
  1.1 Background and Significance ....................................................................... 1
  1.2 Physical and Chemical Process in a Rocket Nozzle ....................................... 4
  1.3 Literature Review ........................................................................................ 13
  1.4 Research Objectives and Thesis Outline ....................................................... 18

Chapter 2 Theoretical Formulation ........................................................................... 22
  2.1 Gas-Phase Governing Equations .................................................................. 22
  2.2 Gas-Phase Chemical Kinetics ...................................................................... 26
  2.3 Heterogeneous Chemical Reactions at Nozzle Surface ................................ 30
    2.3.1 Heterogeneous Kinetics of Graphite .................................................. 32
    2.3.2 Heterogeneous Kinetics of Tungsten (W) .......................................... 39
    2.3.3 Heterogeneous Kinetics of Molybdenum (Mo) .................................... 43
    2.3.4 Heterogeneous Kinetics of Rhenium (Re) .......................................... 44
  2.4 Solid-Phase Governing Equation .................................................................. 46
  2.5 Gas-Solid Interfacial Condition ................................................................... 47
  2.6 Nozzle Recession Rate ................................................................................ 48

Chapter 3 Numerical Methods and Validations ....................................................... 51
  3.1 Favre-averaged Governing Equations .......................................................... 51
  3.2 Turbulence Closure ...................................................................................... 54
  3.3 Spatial Discretization ................................................................................... 57
    3.3.1 Finite Volume Approach .................................................................... 57
    3.3.2 Evaluation of Inviscid Fluxes ............................................................. 61
    3.3.3 Evaluation of Viscous Fluxes ............................................................. 63
    3.3.4 Evaluation of Artificial Dissipation ................................................... 65
  3.4 Temporal Integration: Runge-Kutta Scheme ............................................... 69
  3.5 Parallel Computing Strategies ...................................................................... 70
    3.5.1 Parallel Architecture ........................................................................ 70
    3.5.2 Beowulf Cluster Parallel Computers .................................................. 72
    3.5.3 Domain Decomposition ..................................................................... 74
  3.6 Verification and Validation .......................................................................... 76
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>A typical solid-propellant rocket motor</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Illustration of basic rocket-nozzle configurations and their nomenclature (a) external nozzle (b) submerged nozzle (Anon, 1975)</td>
<td>7</td>
</tr>
<tr>
<td>1.3</td>
<td>Different materials used for nozzle assemblies in (a) apogee motor, HS-303A satellite (b) pershing first stage (Anon, 1975)</td>
<td>8</td>
</tr>
<tr>
<td>1.4</td>
<td>Physical and chemical processes encountered in rocket-nozzle erosion</td>
<td>10</td>
</tr>
<tr>
<td>1.5</td>
<td>Typical heat-transfer rate at rocket-nozzle surface</td>
<td>11</td>
</tr>
<tr>
<td>2.1</td>
<td>Comparison of reaction rates for C(s) + H₂O at 1 atm</td>
<td>37</td>
</tr>
<tr>
<td>2.2</td>
<td>Kinetic rate constants for three different surface reactions of graphite</td>
<td>38</td>
</tr>
<tr>
<td>2.3</td>
<td>Energy balance at the gas-solid interface</td>
<td>48</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic of three-dimensional adjacent cells in finite-volume discretization</td>
<td>58</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic diagram of the stencil used for evaluation of inviscid flux terms in the x-y plane</td>
<td>62</td>
</tr>
<tr>
<td>3.3</td>
<td>Schematic diagram of three-dimensional auxiliary cell</td>
<td>64</td>
</tr>
<tr>
<td>3.4</td>
<td>Multiple Instruction Multiple Data (MIMD) architecture</td>
<td>72</td>
</tr>
<tr>
<td>3.5</td>
<td>Parallel computing facility at Penn State</td>
<td>74</td>
</tr>
<tr>
<td>3.6</td>
<td>Schematic of ghost cells in a two-dimensional domain with fourth-order accuracy in spatial discretization</td>
<td>75</td>
</tr>
<tr>
<td>3.7</td>
<td>An example of the data communication with an east surface in three-dimensional simulation (second-order spatial accuracy)</td>
<td>76</td>
</tr>
<tr>
<td>3.8</td>
<td>Comparison of predicted skin-friction coefficient with experimental data</td>
<td>78</td>
</tr>
<tr>
<td>3.9</td>
<td>Comparison of predicted velocity profile with experimental data (x = 1.237 m)</td>
<td>78</td>
</tr>
<tr>
<td>3.10</td>
<td>Comparison of predicted velocity profile with experimental data (x = 2.28 m)</td>
<td>79</td>
</tr>
</tbody>
</table>
Figure 3.11: Comparison of predicted turbulent kinetic energy profiles with experimental data.................................................................79

Figure 3.12: (a) Convergent-divergent nozzle configuration used by Back et al. (1964) (b) comparison of calculated and measured heat transfer coefficients ...82

Figure 3.13: Schematic diagram of two-dimensional oblique shock wave ..............83

Figure 3.14: Snapshots of flowfields of a 2D oblique shock (a) static temperature contour (b) static pressure contours........................................84

Figure 4.1: Baseline nozzle configuration .................................................................89

Figure 4.2: Computational grid at a particular azimuthal location ......................89

Figure 4.3: Distributions of temperature, pressure, axial velocity, and Mach number along the nozzle centerline (non-metallized propellant, $T_i = 3000$ K, $p_i = 6.9$ MPa, no surface reactions, adiabatic wall) .................................................92

Figure 4.4: Distributions of temperature, pressure, axial velocity, and Mach number in the nozzle interior (non-metallized propellant, $T_i = 3000$ K, $p_i = 6.9$ MPa, no surface reactions, adiabatic wall) ..................................................93

Figure 4.5: Distributions of mass fractions of H$_2$O, CO$_2$, CO, and H$_2$; effect of water-gas shift reaction in the gas phase (non-metallized propellant, $T_i = 3000$ K, $p_i = 6.9$ MPa, no surface reactions, adiabatic wall)........................................93

Figure 4.6: Distributions of temperature and mass fractions of H$_2$O, CO$_2$, OH, CO, H$_2$, H, and N$_2$ in the nozzle interior (non-metallized propellant, $T_i = 3000$ K, $p_i = 6.9$ MPa, with surface reactions, conductive wall).................................................96

Figure 4.7: Tilted view of distributions mass fractions of H$_2$O and CO$_2$ to highlight concentrations at nozzle surface (non-metallized propellant, $T_i = 3000$ K, $p_i = 6.9$ MPa, with surface reactions, conductive wall).................................97

Figure 4.8: Nozzle erosion rate with and without water-gas shift reaction in the gas phase; non-metallized propellants .........................................................98

Figure 4.9: Close-up view of throat region for baseline nozzle configuration ........98

Figure 4.10: (a) Erosion rate profile for smooth nozzle contour (b) close-up view of throat region .................................................................99

Figure 4.11: Nozzle erosion rate due to various graphite-oxidizing species; non-metallized propellants .................................................................101
Figure 4.12: Distribution of heat flux at the nozzle surface; non-metallized propellants .............................................................. 101

Figure 4.13: Radial distributions of temperature at the nozzle throat ...................... 103

Figure 4.14: Radial distributions of species at the nozzle throat; non-metallized propellant .............................................................. 103

Figure 4.15: Radial distribution of species at the nozzle throat; metallized propellant .............................................................................. 104

Figure 4.16: Nozzle erosion rates for metallized and non-metallized propellants at \( p_t = 25 \) MPa ........................................................................................................ 105

Figure 4.17: Effect of chamber pressure on graphite erosion rate at the nozzle throat .................................................................................. 106

Figure 4.18: Radial distribution of \( H_2O \) mass fraction at the throat for two different chamber pressures; non-metallized propellant .............................................................................. 107

Figure 4.19: Graphite erosion rate along the nozzle length at various chamber pressures; non-metallized propellants .............................................................................. 107

Figure 4.20: Graphite erosion rate along the nozzle length at various chamber pressures; metallized propellants .............................................................................. 108

Figure 4.21: Comparison between calculated and measured\(^{11}\) nozzle material (carbon-carbon) erosion .............................................................................. 110

Figure 4.22: Comparison between calculated and measured (Geisler, 1978) nozzle material (bulk graphite) erosion .............................................................................. 111

Figure 4.23: Radial distribution of species at the nozzle throat for metallized propellant with 18\% Al in BATES motor ................................................................. 112

Figure 4.24: Calculated erosion-rate profile for RMS nozzle ........................................ 115

Figure 5.1: Tungsten nozzle erosion rate with different chemical kinetics using \( \text{WO}_3(g) \) as the final oxidation product .............................................................................. 126

Figure 5.2: Tungsten nozzle erosion rate using different final oxidation products and chemical kinetics from Kalipatrick and Lott (1966a) ........................................ 128

Figure 5.3: Tungsten nozzle erosion rate due to individual oxidizing species \( H_2O \) and \( CO_2 \) ........................................................................................................... 128

Figure 5.4: Effect of nozzle outer boundary condition on erosion rate ........................ 130
Figure 5.5: Distributions of temperature, Mach number and mass fractions of H₂O, CO₂, CO, and H₂ in the nozzle ($T_t = 3000$ K, $p_t = 6.9$ MPa, with surface reactions and conductive wall) ......................................................................................... 130

Figure 5.6: A tilted view of the nozzle showing distributions of temperature and mass fractions of CO ($T_t = 3000$ K, $p_t = 6.9$ MPa, with surface reactions and conductive wall).................................................................................................... 133

Figure 5.7: Comparison of erosion rates of graphite and tungsten nozzles for non-metallized propellant ......................................................................................................................... 133

Figure 5.8: Radial distribution of temperature at the tungsten nozzle throat............. 134

Figure 5.9: Radial distribution of temperature at a location downstream of the nozzle throat................................................................................................................................. 135

Figure 5.10: Radial distributions of species concentrations at the nozzle throat........ 135

Figure 5.11: Distributions of tungsten erosion rates along the nozzle length at various chamber pressures.................................................................................................................. 138

Figure 5.12: Effect of chamber pressure on tungsten and rhenium erosion rates at the nozzle throat.......................................................................................................................... 138

Figure 5.13: Calculated tungsten nozzle erosion rate for the experimental study by Haugen (2007) ............................................................................................................................ 140

Figure 5.14: Calculated tungsten and molybdenum nozzle erosion rate for the experimental study by Johnston et al. (1966) .............................................................. 142

Figure 5.15: Calculated tungsten and rhenium nozzle erosion rate for the experimental study by Haugen (1998)......................................................................................... 143

Figure 6.1: Schematic of solid rocket motor with nozzle boundary-layer control system (NBLCS); concept adopted from Evans et al. (2007b; 2008) .............. 149

Figure 6.2: Close-up view of NBLCS duct and injection location; concept adopted from Acharya and Kuo (2007b) ......................................................................................... 149

Figure 6.3: Rocket nozzle with flow injection from nozzle boundary-layer control system ................................................................................................................................. 152

Figure 6.4: Two different views showing distribution of vertical velocity in nozzle interior ($T_i = 3000$ K, $p_i = 6.9$ MPa, $T_{inj} = 1200$ K, no surface reactions, adiabatic wall)................................................................................................................................. 158
Figure 6.5: Close-up view of streamlines near NBLCS injection port and nozzle throat ($T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, no surface reactions, adiabatic wall)............................................................................................................... 158

Figure 6.6: Distributions of temperature and mass fractions of H$_2$O, CO$_2$, and OH in nozzle interior ($T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, no surface reactions, adiabatic wall)............................................................................................................... 159

Figure 6.7: Radial distributions of species concentrations at nozzle throat ($x = 2.65$ cm) with NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, no surface reactions, adiabatic wall)............................................................................................................... 160

Figure 6.8: Radial distributions of temperature at nozzle throat ($x = 2.65$ cm) with NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, no surface reactions, adiabatic wall)............................................................................................................... 161

Figure 6.9: Distributions of mass fractions of H$_2$O, CO$_2$, OH, and CO in nozzle interior $T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, surface reactions, conductive wall)............................................................................................................... 162

Figure 6.10: Radial distributions of H$_2$O at nozzle throat ($x = 2.65$ cm) with and without NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, surface reactions, conductive wall)............................................................................................................... 162

Figure 6.11: Radial distributions of CO$_2$ at nozzle throat ($x = 2.65$ cm) with and without NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, surface reactions, conductive wall)............................................................................................................... 163

Figure 6.12: Distribution of temperature in nozzle interior (a) with and (b) without NBLCS ($T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, surface reactions, conductive wall)............................................................................................................... 164

Figure 6.13: Radial distributions temperature at nozzle throat with and without NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, surface reactions, conductive wall)............................................................................................................... 165

Figure 6.14: Axial distributions of nozzle surface temperature with and without NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, surface reactions, conductive wall)............................................................................................................... 165

Figure 6.15: Graphite nozzle erosion rate with and without NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, surface reactions, conductive wall)............................................................................................................... 167

Figure 6.16: Effect of chamber pressure on graphite erosion rate at nozzle throat with and without NBLCS ............................................................................................................... 168
Figure C.1: Schematic of energy balance at gas-solid interface with radiation ........ 195
Figure C.2: Effect of radiation on erosion-rate profile (non-metallized propellant) ... 197
Figure C.3: Effect of radiation on erosion-rate profile (metallized propellant) ........ 198
Figure C.4: Effect of surface roughness on erosion-rate profile (non-metallized propellant) ........................................................................................................................................................................ 199
LIST OF TABLES

Table 1.1: Typical properties of materials used for nozzle throat inserts at 300 K ..... 9
Table 1.2: Empirical Correlations for Erosion Rates................................................. 16
Table 2.1: Mass fractions of prominent combustion species in the free-stream of non-metallized AP/HTPB (88/12)........................................................................... 27
Table 2.2: Mass fractions of prominent combustion species in the free-stream of AP/HTPB/AL (75/10/15)............................................................................. 28
Table 2.3: Chemical kinetics at the gas-solid interface for non-porous graphite ......... 34
Table 2.4: Kinetic data * used in current model for heterogeneous surface reactions of graphite (Bradley et al, 1984; Chelliah et al, 1996)................................. 37
Table 2.5: Chemical equilibrium calculations for tungsten oxidation (reactants at 2800 K, 40 atm, and mass ratio of 1:1)......................................................... 42
Table 2.6: Chemical kinetics data * for heterogeneous surface reactions of tungsten .. 42
Table 2.7: Chemical equilibrium calculations for molybdenum oxidation (reactants at 2800 K, 40 atm, and mass ratio 1:1) ...................................................... 43
Table 2.8: Chemical kinetics data * for heterogeneous surface reactions of molybdenum .......................................................... 44
Table 2.9: Chemical kinetics data * for heterogeneous surface reactions of rhenium .. 45
Table 3.1: Inlet conditions for simulating experiments by Back et al. (1964)............ 80
Table 3.2: Results from theory and numerical simulations on oblique shock wave.... 84
Table 4.1: Nozzle Inlet Flow Conditions* ................................................................. 90
Table 4.2: Experimental Studies of Nozzle Erosion................................................. 91
Table 4.3: Effect of Outer Boundary Condition of Nozzle Material on Erosion Rates* ........................................................................................................... 100
Table 4.4: Inlet Conditions* for Simulating Experiments by Borie et al. (1989) ....... 109
Table 4.5: Inlet Conditions* for Simulating Experiments by Geisler (1978) .......... 109
Table 4.6: Inlet Conditions* for Simulating Rocket-Motor Tests by Evans et al. (2007a)............................................................................................................. 109
Table 4.7: Comparison between calculated and measured (Geisler, 1978) nozzle recession rates ................................................................. 111

Table 4.8: Comparison between calculated and measured (Evans et al. 2007a) nozzle recession rates ................................................................. 113

Table 4.9: Inlet Conditions* for Simulating RMS Experiments by Evans et al. (2008) ...................................................................................... 115

Table 5.1: Nozzle inlet flow conditions* ........................................................................................................ 124

Table 5.2: Experimental studies of refractory metal nozzle erosion .................. 124

Table 5.3: Effect of outer boundary condition of nozzle on tungsten erosion rate* .... 129

Table 5.4: Inlet conditions* for simulations of experiments by Haugen (2007) ........... 139

Table 5.5: Inlet conditions* for simulations of experiments by Johnston (1966) .......... 139

Table 5.6: Inlet conditions* for simulations of experiments by Haugen (1998) .......... 139

Table 5.7: Comparison between calculated and measured nozzle erosion rates ........ 143

Table 6.1: Thermodynamic properties of SA/PVA ablative material (Kuo et al., 2007) ......................................................................................... 151

Table 6.2: Rocket Nozzle Inlet Flow Conditions* ................................................... 153

Table 6.3: Flow Conditions at NBLCS Injection Port ............................................. 155

Table B.1: Changes in Gibbs free energies for different surface reactions .............. 194
NOMENCLATURE

Symbols

$A_i$ = pre-exponential factor for rate constant in reaction $i$

$b_i$ = temperature exponent for rate constant in reaction $i$

$C_p$ = constant pressure specific heat

$Da$ = Damköhler number

$D_{ij}$ = binary mass diffusivity

$D_{lm}$ = molecular mass diffusivity

$E_i$ = activation energy for reaction $i$

$E$ = specific total internal energy

$h$ = enthalpy

$k$ = turbulent kinetic energy

$Le$ = Lewis number

$Le_t$ = turbulent Lewis number

$\dot{m}$ = mass flow rate

$N$ = total species numbers

$p$ = pressure

$p_t$ = chamber pressure

$Pr$ = Prandtl number

$Pr_t$ = turbulent Prandtl number

$R$ = particular gas constant

$Re$ = Reynolds number
\[ Ru = \text{universal gas constant} \]
\[ \dot{r}_c = \text{net surface recession rate (m/s)} \]
\[ \dot{r}_{i,\text{erosion}} = \text{recession rate due to species } i \text{ (kg/m}^2\text{-s)} \]
\[ \dot{r}_{i,\text{ch}} = \text{chemical-kinetics controlled recession rate due to species } i \text{ (kg/m}^2\text{-s)} \]
\[ \dot{r}_{i,\text{diff-lim}} = \text{diffusion-controlled recession rate due to species } i \text{ (kg/m}^2\text{-s)} \]
\[ Sc = \text{Schmidt number} \]
\[ Sc_t = \text{turbulent Schmidt number} \]
\[ T = \text{temperature} \]
\[ T_t = \text{chamber temperature} \]
\[ U_k = \text{mass diffusion velocity of species } k \]
\[ u, v, w = \text{x, y, z component of velocity respectively} \]
\[ W_k = \text{molecular weight of species } k \]
\[ W_{\text{mix}} = \text{average molecular weight of the gases} \]
\[ \dot{\omega} = \text{species mass production rate} \]
\[ \omega_{i,\text{diff-lim}} = \text{maximum diffusion rate of species } i \text{ towards the surface (kg/m}^2\text{-s)} \]
\[ \dot{w} = \text{species molar production rate} \]
\[ X_k = \text{mole fraction of species } k \]
\[ Y_k = \text{mass fraction of species } k \]

**Greek Symbols**

\[ \lambda = \text{thermal conductivity} \]
\[ \mu = \text{viscosity} \]
\( \mu_t \) = turbulent viscosity

\( \rho \) = density

\( \kappa \) = von Kármán constant

\( \varepsilon \) = dissipation rate

\( \gamma \) = ratio of specific heats

\( \alpha \) = thermal diffusivity

**Subscripts**

\( c \) = solid phase

\( g \) = gas phase

\( c-g \) = gas-solid interface

\( s \) = surface

\( o \) = outer boundary of nozzle material

\( amb \) = ambient conditions

**Diacriticals**

\( - \) = time average

\( \sim \) = mass-weighted average (Favre average)
ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to my advisor, Dr. Vigor Yang, for his patience, encouragement, support, and guidance during the course of my graduate study. Working with him has been a great pleasure and a wonderful learning experience. I thank Dr. Kenneth Kuo, Dr. Richard Yetter, Dr. Stephen Thynell, and Dr. Michael Micci for serving as committee members and for providing valuable suggestions and guidance.

This work is financially supported by the U.S. Office of Naval Research as a part of multi-university research initiative (MURI) under Contract N00014-04-1-0683. The support from the contract monitors, Dr. Judah Goldwasser and Dr. Cliff Bedford, is gratefully acknowledged. Sincere thanks to Mr. Robert Geisler, Dr. Kenneth Kuo, Dr. Richard Yetter, Mr. Steinar Haugen, Mr. Brian Evans, and Mr. Justin Sabourin for experimental data and/or technical discussions.

I thank my former colleagues, Fuhua Ma, Ying Huang, Tao Liu, Shanwu Wang, Nan Zong, and Yanxing Wang for their guidance and technical discussions. Thanks to all of my current group members and friends at Penn State, especially Jian Li, Punnesh Puri, and Vivek Verma for their wonderful company and support.

I would particularly like to acknowledge Archana Iyer for her unconditional support and for always being there for me. I take this opportunity to express my deepest gratitude to my parents, Kishor Thakre and Krupali Thakre, and my brother Swapnil, for their endless love, patience, and encouragement.
Chapter 1

Introduction

1.1 Background and Significance

As flight vehicles are required to travel ever-increasing distances in ballistic, orbital, and interplanetary trajectories, there is a need for enhancing the range and performance of existing rocket motors. The chamber pressure is a key parameter influencing the range and performance of a solid-propellant rocket motor, as it directly impacts the thrust produced and the propellant burning rate. For a given chamber volume, more propulsive energy can be gained from combustion systems with higher pressures. Thus, there exists a demand for higher propulsive power and also for propellants with improved specific impulse. The current operating pressures of rocket motors are less than 3500 psi (~250 atm), but will increase to a much higher value in the future. The pressures could reach 4,500-5,000 psi in the near term and 8,000-10,000 psi in the long term.

Figure 1.1 shows a typical solid-propellant rocket motor with igniter, combustion chamber, motor casing, propellant grain, and the nozzle. The erosion of nozzle material during motor firings continues to be one of the major hindrances in the advancement of solid-rocket propulsion. The material erosion reduces the area ratio of the nozzle exit to throat, and consequently decreases the overall propulsive efficiency of the vehicle. A non-eroding nozzle throat is desired as it maintains a constant nozzle expansion ratio and optimal thrust performance. Another issue attributed to the nozzle surface recession is the
loss of ability to accurately predict the performance of a rocket motor. Over the years, the materials used for rocket nozzles include reinforced plastics, different types of graphites (e.g., pyrolytic and bulk/artificial graphites), carbon-carbon composites, refractory metals, and ceramics (Anon, 1975). Graphite and carbon-carbon composites, which have excellent thermophysical properties as well as low densities, are most widely used for rocket nozzle inserts. These materials, however, undergo significant erosion at high chamber pressures and surface temperatures (Geisler, 1978; Swope and Berard, 1964). Refractory metals such as tungsten and rhenium, although known to better resist the chemical erosion, suffer from weight and cost penalties. The use of ceramics has been limited due to poor thermal-shock characteristics (Anon, 1975).

Figure 1.1: A typical solid-propellant rocket motor
The increase in the chamber pressure will result in a substantial increase of heat-transfer rate from the propellant combustion products to the nozzle material, particularly at the throat. The nozzle throat diameter can increase rapidly due to erosion, rendering it incapable for long-duration firings. Since a throat-area increase of more than 5% is considered excessive for most solid-rocket applications (Wong, 1968), the nozzle erosion levels for ultra-high pressures and long-duration firings can become unacceptable. It is thus important to investigate the erosion phenomenon at higher pressure for different nozzle materials and devise ways to minimize the erosion.

The flame temperatures of many advanced propellants are in the range of 3000 - 3600 K. This results in enhanced thermal loading and chemical reactions at the nozzle surface. The increase the surface roughness due to erosion occurring at the nozzle surface can further reduce the motor performance. To determine performance reduction caused by nozzle erosion, test firings on full-scale or proto-type motors are generally conducted. Multiple test firings, however, require considerable time and expense. An efficient and economical approach is to couple the associated full-scale and proto-type experiments with the modeling studies, in order to predict the recession rate and device ways to minimize the erosion. It is thus vitally important to theoretically study the fundamental interactions between the propellant combustion products and nozzle materials under severe motor-operating conditions.

The development of reliable analytical and simulation tools for erosion prediction can provide designers with important information as to whether certain design changes could improve or degrade the erosion characteristics of a particular configuration. There are other examples where material erosion in a high pressure and temperature
environment are significant. The erosion of the metallic surface on the inside of the gun tube during the course of firing can have a detrimental affect on its performance and service life. One of the primary erosion mechanisms in gun tubes stems from the high heat transfer from the combustion gases to the wall and the heterogeneous chemical reactions occurring at the inner surface of the bore.

The current work focuses on the chemical erosion of rocket nozzle materials at practical rocket-motor operating conditions. The propellants considered are metallized and non-metallized AP (ammonium perchlorate)/HTPB (hydroxyl-terminated polybutadiene), which are very commonly used in solid-rocket propulsion. The nozzle materials considered are graphite, carbon-carbon composites, and refractory metals such as tungsten (W), rhenium (Re), and molybdenum (Mo). Furthermore, the mitigation of rocket-nozzle erosion is also studied in detail by employing a recently developed concept of nozzle boundary-layer control system (NBLCS).

1.2 Physical and Chemical Process in a Rocket Nozzle

Figure 1.2 presents the two frequently used rocket-nozzle configurations and illustrates the associated basic nomenclature. The external nozzle, shown in Fig. 1.2a, is the classic convergent-divergent nozzle and is entirely external to the combustion chamber. In the submerged-nozzle configuration (Fig. 1.2b), the nozzle entry, throat, and part or the entire exit are cantilevered into the combustion chamber. The phenomenon of nozzle erosion is common to both kinds of nozzles.
Figure 1.3 shows the different materials employed in the assembly typical rocket nozzles. The functions of these materials are also explained. The throat region is given due importance by placing a special erosion-resistant insert in that region, to limit the increase in the throat area. High-density graphite, carbon-carbon composites, or refractory metals are frequently employed at such locations. The entrance and the exit cone, which do not suffer from severe erosion, can be made of lower density materials such as carbon/phenolic or silica/phenolic tape. In Fig. 1.3a, tungsten is used as throat insert, whereas in Figure 1.3b, polycrystalline graphite (bulk graphite) is employed in the throat region. Table 1.1 summarizes thermophysical properties of some nozzle materials at 300 K. The densities, thermal conductivities, and specific heats of graphites and carbon-carbon are only representative values. The actual values may slightly differ depending on the manufacturing processes. Moreover, thermal conductivities and specific heats are strong functions of temperature.

The overall nozzle erosion process is extremely complex, comprising the interplay of numerous factors including the propellant composition, motor operating conditions, duration of firing, nozzle geometry and material properties, transport of reacting species, homogeneous reactions in the gas phase, and heterogeneous reactions at the nozzle surface. Figure 1.4 shows a schematic of various complex physiochemical mechanisms occurring in the rocket nozzle. During motor operation, propellant combustion gases generated in the chamber flow through the nozzle, producing the required thrust. Although the combustion products are in near-equilibrium, some gas-phase reactions may still continue to occur as the gases flow through the rocket nozzle. The nozzle surface is rapidly heated due to the high heat-transfer rate from the
combustion gases. Figure 1.5 shows the typical heat-transfer rate profile in MW/m$^2$, which attains a maximum value near the throat region. The surface temperature rises very rapidly and reaches a high value. The surface may melt either by the surface temperature exceeding the melting point of the nozzle material or the lowering of melting point by formation of eutectics via phase transformations or heterogeneous reactions. The melted material could be swept away by the shear flow of the gases. The nozzle material could also erode by evaporation and pyrolysis which will depend on the vapor pressure of the material and the rate constant. Normally to avoid evaporation a material with a low vapor pressure at the operating temperature is used.
Figure 1.2: Illustration of basic rocket-nozzle configurations and their nomenclature (a) external nozzle (b) submerged nozzle (Anon, 1975)
Figure 1.3: Different materials used for nozzle assemblies in (a) apogee motor, HS-303A satellite (b) Pershing first stage (Anon, 1975)
Table 1.1: Typical properties of materials used for nozzle throat inserts at 300 K

<table>
<thead>
<tr>
<th></th>
<th>pyrolytic graphite</th>
<th>bulk graphite</th>
<th>carbon-carbon</th>
<th>tungsten</th>
<th>rhenium</th>
<th>molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol. wt. (g/mol)</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>183.84</td>
<td>186.21</td>
<td>95.94</td>
</tr>
<tr>
<td>ρ (gm/cm³)</td>
<td>~2.0-2.2</td>
<td>~1.8-2.0</td>
<td>~1.6-2.0</td>
<td>19.25</td>
<td>21.02</td>
<td>10.28</td>
</tr>
<tr>
<td>melting pt. (K)</td>
<td>~4000ᵃ</td>
<td>~4000ᵃ</td>
<td>~4000ᵃ</td>
<td>3695</td>
<td>3459</td>
<td>2896</td>
</tr>
<tr>
<td>boiling pt. (K)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5828</td>
<td>5869</td>
<td>4912</td>
</tr>
<tr>
<td>C_p (J/kg-K)</td>
<td>~710-900</td>
<td>~1050</td>
<td>~1300</td>
<td>132</td>
<td>136.8</td>
<td>250.8</td>
</tr>
<tr>
<td>λ (W/m-K)</td>
<td>~300-350 (in plane)</td>
<td>~120-170 (in plane)</td>
<td>~30</td>
<td>173</td>
<td>47.9</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>~3-5 (perp.)</td>
<td>~70-90 (perp.)</td>
<td>~13</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃ sublimates
Figure 1.4: Physical and chemical processes encountered in rocket-nozzle erosion
At sufficiently high surface temperatures, the nozzle material is prone to react with such oxidizing species as $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{OH}$, $\text{O}_2$, and $\text{O}$. Chemical reactions could also take place in the nozzle boundary layer due to the change in the concentrations of the oxidizing species. In addition, some gas molecules may also be adsorbed at the nozzle material. Intense thermal stresses caused by steep temperature gradients in the nozzle material can lead to the formation of subsurface cracks. When these cracks propagate to the surface, pieces of the surface material can spall-off. The spallation of partially damaged nozzle material is another factor that could be associated with the erosion process. Micro-structural changes can also occur rapidly in materials when subjected to
sufficiently elevated temperatures. These changes can be caused by a number of processes including phase transformations, grain growth, coarsening, and creep. Rapid changes in temperature can also damage inhomogeneous materials such as composites, due to internal variations in thermal expansion coefficients that lead to high residual stresses. The design strategy to avoid the thermal stresses is to use high-conductivity nozzle materials.

The most important factor influencing the nozzle erosion is perhaps the heterogeneous chemical reactions of the nozzle material with the combustion species that diffuse to the nozzle surface. The consumption of oxidizing species that react with the nozzle surface causes the species to diffuse across the boundary layer and changes its concentration in the gas phase. If the nozzle material melts at its surface, the melted material can be swept away by the shear flow of gases, which could further enhance nozzle erosion. In addition to chemical erosion, there could be contributions from mechanical processes associated with the impingement of metal oxide particles (e.g., Al₂O₃) on to the nozzle surface and from the thermal-stress induced structural failure. The mechanical erosion caused by the impingement of Al₂O₃ particles is negligible in the throat region as the particles travel almost parallel to the surface. The effect may be crucial in the converging part of the nozzle. The changes in the area of the converging part due to the erosion, however, are not as crucial as the increase in the throat diameter.

Analytical and experimental understating of the erosion rates of a wide variety of metals and ceramics in high-pressure rocket environments and low pressure scramjet environments are critical to design advanced nozzle materials for future propulsion
systems. High-temperature carbon-carbon composite materials and tungsten-rhenium alloys can provide high performance for rocket and scramjet propulsion components. For aluminized propellant environments, the flame temperatures could reach about 3770 K. In terms of the melting temperature, graphite/carbon-carbon (~ 4000 K), tungsten (3695 K), and rhenium (3459 K) are attractive. But we need to consider not only the melting point of these materials, but also the melting point of their oxides, carbides, and nitrides, since these compounds can be formed near the surface due to the thermochemical attack of gas-phase species in the combustion products of rocket propellants.

The purpose of the current research is to present a comprehensive theoretical/numerical framework that can accurately predict the nozzle erosion rate by utilizing recent advances in chemical kinetics, turbulence modeling, and numerical algorithm. Many approximations and assumptions employed in the previous studies have been relaxed. The overall formulation should take into account detailed thermofluid dynamics for a multi-component chemically reacting flow, heterogeneous reactions at the nozzle surface, and condensed-phase energy transport.

1.3 Literature Review

In the 1960s and 1970s, with limited computational resources and a lack of in-depth understanding, many investigators (Delaney et al., 1964; McDonald and Hedman, 1965; McCuen et al., 1965; Gowariker, 1966) developed simplistic models to predict the nozzle-throat recession rates. The models mostly used one-dimensional approach, along with the empirical correlations for turbulent flows. Attempts were made to obtain the
dependence of erosion rates as a function of propellant composition, chamber pressure, and motor firing time. Other variables included were density, chemical reactivity, thermal conductivity, porosity, and roughness of the nozzle material. It was pointed out that the erosion rate depends on the heterogeneous chemical kinetics at the surface as well as the diffusion of the oxidizing species towards the surface (Delaney et al., 1964; McDonald and Hedman, 1965). Although previous studies have been simplistic, they do offer valuable qualitative understanding of the recession process and its dependence on some variables. Majority of the earlier modeling studies have been confined to graphite as nozzle material, while only a few have considered carbon-carbon composites. No modeling studies, however, were conducted for evaluating the erosion of refractory nozzle inserts.

Many experimental studies to characterize the erosion rates of different nozzle materials have also been carried out. Johnston et al. (1966) experimentally investigated the performance of a variety of rocket-nozzle materials including refractory metals (W, Mo), metal carbides (ZrC, TaC, HfC), graphite, and fiber-reinforced plastics. The effect of three propellants with different flame temperatures was studied. McDonald and Hedman (1965) conducted short-duration firings (~ 3 sec) with high-density bulk graphite nozzles and propellants with aluminum content varying from 16% to 24%. Geisler (1978) used BATES (Ballistic Test and Evaluation System) motor firings (~ 5 sec) and determined the recession rates of bulk graphite in the case of metallized propellants with 15% to 30% of aluminum content. Klager (1977) conducted a similar study for measuring the recession rates of ZTA and ATJ graphites using Material Evaluation Research Motor (MERM) with long-duration burning time (~ 60 sec). All the
researchers found that recession rates decreased with increasing aluminum content even though the flame temperature increased.

Previous investigations suggest that the nozzle surface recession is strongly influenced by the concentrations of oxidizing species and the chamber pressure. It is also clear that the loss of nozzle material by mechanical erosion by the condensed phase Al₂O₃ particles is not a significant portion of the total mass loss. Particulate mass loss, caused by preferential attack of the binder, is of some importance for such materials as bulk graphite, and probably of much less importance for other materials. A good summary of the experimental and numerical work on nozzle erosion till 1980 has been elaborated by Keswani (1984).

A more detailed model was developed by Kuo and Keswani (1985; 1986). This work represents a significant improvement over the earlier approaches and predicts the nozzle throat recession rates reasonably well. One of the major assumptions includes the calculation of the recession rate empirically as the harmonic mean of the kinetics- and diffusion-limited rates. This approach is valid when the heterogeneous reactions are first order, the effective Schmidt numbers for all reactants are nearly equal, and the surface mass blowing is not too strong (Keswani and Kuo, 1986). The assumption of first-order reactions strongly restricts the kind of surface kinetics that can be adopted. The model employs the boundary-layer approximation for solving the gas-phase conservation equations and neglects the effect of surface-reaction products on the nozzle erosion in the downstream region. Other approximations include the unity Lewis number, a single binary diffusion coefficient applied to all the species, a constant Prandtl number, and the
use of infinitely fast heterogeneous kinetics (infinite Damköhler number) in obtaining the solution to the gas-phase species equations.

Another nozzle erosion model subsequently developed by Borie et al. (1989) for carbon-carbon composites bears a close resemblance to that of Kuo and Keswani (1985). Keswani et al. (1985) also obtained an empirical correlation to relate total recession with the mole fractions of H₂O and CO₂, density of nozzle, chamber pressure, axial distance from the stagnation point to the throat location, radius of nozzle throat, and duration of the firing. More recently, Acharya and Kuo (2007a; 2007b) updated the model of Kuo and Keswani (1985) by adopting improved heterogeneous kinetics at the nozzle surface. The underlying assumptions and approximations, however, remain identical to their previous model. Table 1.2 summarizes different empirical correlations suggested by various researchers over the years.

Table 1.2: Empirical Correlations for Erosion Rates

<table>
<thead>
<tr>
<th>Researcher (Year)</th>
<th>Formula</th>
<th>Assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>McDonald &amp; Hedman (1965)</td>
<td>( \dot{r}_c = \frac{1}{\rho_c} \sum k_j p_j^{0.5} )</td>
<td>Kinetically limited case with half order surface reactions.</td>
</tr>
<tr>
<td></td>
<td>( \dot{r}_c = \frac{1}{\rho_c} \left[ \beta \rho_c U c S t \right] C_H \beta )</td>
<td>Diffusion-limited case, where ( \beta ) is the blowing rate, ( C_H ) is the coefficient of heat transfer obtained from Bartz correlation, and ( S t ) is the Stanton number for mass transfer.</td>
</tr>
<tr>
<td></td>
<td>( \beta = \frac{W_c}{W_g (1 - X_{AL_2O_3}) - X_{AL_2O_3} W_{AL_2O_3}} \sum \frac{v_j - X_j}{v_j} )</td>
<td></td>
</tr>
<tr>
<td>Mayberry et al. (1968)</td>
<td>( \frac{\dot{r}<em>c}{D</em>{m,CO}} = 0.0188 \left( \frac{D U_{avg} \rho_g}{\mu} \right)^{0.8} \left( \frac{\rho_c}{\rho_g} \right)^{1.4} \left( \frac{tD_{m,CO}}{D_t^2} \right)^{0.09} \times Pr^{0.60} \left( \frac{\mu}{D_{m,CO} \rho_g} \right)^{0.08} \left( \frac{x}{D_t} \right)^{-0.47} \beta^{0.11} e^{0.89} )</td>
<td>( D_{m,CO} ) is the diffusion coefficient for CO. ( D_t ) is the throat diameter. ( \rho_g ) is the density of gas-particle mixture. The correlation attempts to take into account all parameters.</td>
</tr>
<tr>
<td>Author(s)</td>
<td>Equation</td>
<td>Notes</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>-------</td>
</tr>
<tr>
<td>Boyarintsev &amp; Zvyagin (1974)</td>
<td>( \dot{r}<em>c = \frac{1}{\rho_c \left( \frac{c_p}{c_p}</em>{\text{wall}} \right)} B_c )</td>
<td>Kinetically limited case. The value of ( B_c ) asymptotically reaches a value of the oxidizing potential of the combustion gases ( B_m ) as the temperature increases and diffusion-limited rate is achieved.</td>
</tr>
<tr>
<td></td>
<td>( B_c = \left[ \left( \frac{W_c}{W_{\text{mix}}} \right) \Omega + 1 \right]^2 + 4B_m \left( \frac{W_c}{W_{\text{mix}}} \right) \Omega - \left( \frac{W_c}{W_{\text{mix}}} \right) \Omega + 1 \right] \frac{2(W_c/W_{\text{mix}})}{\Omega} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( B_m = \frac{W_c}{W_{\text{mix}}} (X_{H_2O} + X_{CO_2}) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Omega = \left( \frac{hT}{c_p p} \right) \frac{1}{(c_p p)_{\text{wall}}} \exp \left( \frac{E_0}{R_T T_w} \right) )</td>
<td></td>
</tr>
<tr>
<td>Boyarintsev &amp; Zvyagin (1974)</td>
<td>( \dot{r}<em>c = \frac{1}{\rho_c \left( \frac{c_p}{c_p}</em>{\text{wall}} \right)} B_m )</td>
<td>Diffusion-limited case.</td>
</tr>
<tr>
<td>Anon (1975)</td>
<td>( \dot{r}<em>c = \dot{r}</em>{c,m} \left( \frac{P_{c,m}}{P_{c,m}} \right)^{0.8} \left( \frac{D_{t,m}}{D_t} \right)^{0.2} )</td>
<td>( \dot{r}<em>{c,m}, P</em>{c,m}, ) and ( D_{t,m} ) are the measured erosion rate, chamber pressure and throat diameter for a particular case. Based on Bartz relation.</td>
</tr>
<tr>
<td>Geisler (1981)</td>
<td>( \dot{r}<em>c (\text{cm/s}) = 0.0318 X</em>{H_2O} p^{0.8} )</td>
<td>Correlation derived from the experiments</td>
</tr>
<tr>
<td>Keswani et al. (1985)</td>
<td>( \dot{r}<em>c (\text{mm/s}) = \frac{0.5946}{\rho_c} (X</em>{H_2O} + X_{CO_2})^{1.02} p^{0.876} x^{0.343} R_{0.076} )</td>
<td>( x_i ) is the subsonic entry length up to the throat. ( R_i ) is the throat radius. Correlation applied to data from Geisler (1981) and Swope and Berard (1964)</td>
</tr>
<tr>
<td>Kuo and Keswani (1985)</td>
<td>( \frac{1}{\dot{r}<em>c} = \frac{1}{\dot{r}</em>{\text{diff}}} + \frac{1}{\dot{r}_{\text{chem}}} )</td>
<td>Assumes 1st order surface reactions, equal Schmidt numbers for all reactant species, and low surface blowing.</td>
</tr>
<tr>
<td>Evans et al. (2008)</td>
<td>( \frac{\dot{r}<em>c \rho_c}{G</em>{\text{tot}}} = 8.583 \frac{\rho_{\text{th}}}{0.905} \frac{Re_{D_{th}}}{0.287} (X_{O_{\text{th},d}} + 0.413 X_{H_2O})^{2.322} )</td>
<td>Based on the measured erosion rates of RMS (Rocket Motor Simulator)</td>
</tr>
</tbody>
</table>

Most studies (Klager, 1977; McDonald and Hedman, 1965; McCuen et al., 1965; Kuo and Keswani, 1985) have concluded that chemical erosion is the primary cause for the nozzle throat recession. Moreover, mechanical erosion caused by the impingement of Al₂O₃ particles is negligible in the throat region as the particles travel almost parallel to
the surface (Sutton, 2001). Experimental studies on graphite nozzle erosion with aluminized composite solid-propellants have indicated that the graphite removal depended primarily on the chemical attack by the oxidizing species of H₂O and CO₂ (Klager, 1977; Geisler, 1978; Swope and Berard, 1964). A strong correlation was noted between the recession rate at the throat and the mass fractions of H₂O and CO₂. The nozzle erosion decreased with increasing aluminum content in the propellant. If mechanical processes were significant, then the throat erosion would have increased with the increase of condensed-phase Al₂O₃ particles in the combustion stream, but on the contrary the erosion decreased. So the chemical erosion of rocket nozzles is the major focus of this study. There is still lack of clarity in the literature about which oxidizing species is most detrimental. The relative importance between mass diffusion and chemical kinetics in dictating nozzle erosion is also not known accurately. One of the goals of the present study is to resolve these issues not only in qualitative but also in a quantitative manner.

1.4 Research Objectives and Thesis Outline

It will be highly beneficial to develop a comprehensive theoretical model and numerical code for accurate prediction of nozzle erosion rate under various practical rocket-motor operating conditions. The model must encompass the fundamental interactions between the propellant combustion products and nozzle materials. The framework should be able to treat any nozzle configuration and material and propellant composition. In addition, the model should have the capability to predict the erosion rate
along the entire axial length of the nozzle, as a part of complete flow solution. In the past, researchers have only studied the erosion rate at the throat without obtaining the erosion-rate profile along the entire nozzle length.

In order to simulate realistic conditions, detailed understanding of the reaction mechanisms and thermal and mass transport mechanisms for both the gas phase and condensed phase must be acquired. Furthermore, kinetic rates for homogeneous and heterogeneous reactions and mass diffusion rates of all the species involved must be known. With an in-depth understanding of the physiochemical processes obtained from the modeling studies, the means to mitigate throat erosion can then be devised.

The research objectives of the present work are three fold. First, to establish a unified theoretical/numerical framework to predict the chemical erosion of nozzle material by treating nozzle interior flow development, near-surface physiochemistry, gas-phase chemistry, and processes occurring in the nozzle material and at the gas-solid interface. Second, to identify key physiochemical mechanisms and parameters that dictate nozzle erosion, after validating the erosion model. Third, to investigate different techniques to help minimize erosion, in particular, to implement the concept of nozzle boundary-layer control system (NBLCS). The work involves following tasks and stages:

- Study of propellant combustion products obtained from the burning of metallized and non-metallized AP/HTPB, as functions of pressure and composition. This will enable us to obtain the species involved in the nozzle flow, as well as their thermal properties and transport data.
- Development of comprehensive theoretical formulation for:
• gas phase with multi-component system
• condensed phase (nozzle material)
• interface between the gas and condensed phases
• chemical kinetics in the gas phase and at the gas-solid interface
• turbulence closure

• Development of numerical methods to solve the theoretical formulation
• Application of the model to different nozzle geometries to obtain the chemical erosion rates and compare them with available experimental data. Different nozzle materials including graphite, carbon-carbon, and refractory metals will be considered.
• Various physiochemical mechanisms that dictate nozzle erosion under different circumstances will be identified and quantified.
• The effectiveness of the so-called nozzle boundary-layer control system (NBLCS) to minimize nozzle erosion will be investigated.

The thesis is structured as follows. Chapter 2 describes the theoretical formulation used in the current framework. The analysis is based on the complete conservation equations of mass, momentum, energy, and species concentration, with appropriate interfacial boundary conditions. The chemical kinetics employed in the gas phase as well as at the surface is also described in detail.

In Chapter 3, the governing systems are discretized using a density-based finite volume methodology. Turbulent closure is achieved using the two-layered $k$-$\varepsilon$ model. The spatial discretization employs a second-order, central-differencing scheme in generalized
coordinates. A fourth-order matrix dissipation model with a total-variation-diminishing (TVD) switch is employed to ensure computational stability and to prevent numerical oscillations in regions with steep gradients. Temporal discretization is obtained using a four-step Runge-Kutta scheme. A multi-block domain decomposition technique along is used to facilitate the implementation of parallel computation with message passing interface (MPI).

In Chapters 4 and 5, the theoretical/numerical framework is applied to predict the chemical erosion rates of graphite and refractory metals, respectively. Many different nozzle geometries under various motor-operating conditions are treated. The predicted erosion rates are validated against the available experimental data. The key mechanisms dictating nozzle erosion phenomenon in each case are described. In chapter 6, the concept of NBLCS is implemented to investigate its effect on reducing chemical erosion. Chapter 7 summarizes all the results and discusses future work.
Chapter 2
Theoretical Formulation

The theoretical formulation involves the general conservation laws for the gas phase, the energy equation for the solid phase (nozzle material), and the boundary conditions at the gas-solid interface and the outer surface of the nozzle material. The gas phase comprises of the multi-component mixture arising from the combustion products of the solid propellants. The nozzle surface temperature rises rapidly because of high convective heat transfer from the combustion products. Heterogeneous reactions occur between the oxidizing species such as H2O, CO2, and OH and the heated nozzle material, causing the surface to regress. These oxidizing species then diffuse across the boundary layer towards the surface forming a concentration boundary layer. The nozzle recession rate can be influenced by both chemical kinetics of the heterogeneous reactions at the surface and diffusion of the oxidizing species across the boundary layer.

2.1 Gas-Phase Governing Equations

The gas-phase dynamics is based on full conservation equations of mass, momentum, energy, and species concentration in axisymmetric coordinates.
where \( i, j, \) and \( k \) are the spatial coordinate index, the dummy index for the spatial coordinate, and the species index, respectively. \( N \) is the total number of species. \( Y_k \) and \( U_{k,j} \) represent mass fraction and diffusion velocities of species \( k \), respectively. The viscous stress tensor \( \tau_{ij} \) for a Newtonian fluid (with Stokes assumption) and the heat-flux vector \( q_j \) are defined as

\[
\tau_{ij} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_i}{\partial x} \right) \tag{2.5}
\]

\[
q_j = -\lambda \frac{\partial T}{\partial x_j} + \rho \sum_{k=1}^{N} \hat{h}_k Y_k U_{k,j} \tag{2.6}
\]

where \( \mu \) and \( \lambda \) are the coefficient of viscosity and thermal conductivity, respectively. Fick’s law is used to approximate the species diffusion in a multi-component mixture,

\[
Y_k U_{k,j} = -D_{km} \frac{\partial Y_k}{\partial x_i} \tag{2.7}
\]

The specific total energy \( E \) is given by
The governing equations are supplemented with the equation of state for an ideal gas. Then the specific internal energy, $e$, is obtained as

$$ e = h - \frac{p}{\rho} \quad (2.9) $$

The specific enthalpy of mixture, $h$, which contains contributions from its component species, is given by

$$ h = \sum_{k=1}^{N} Y_k h_k = \sum_{k=1}^{N} Y_k \left( \Delta h_{f,k} + \int_{T_{ref}}^{T} C_{p,k}(T') dT' \right) \quad (2.10) $$

where $C_{p,k}$ is the specific heat at constant pressure for a species $k$. It is approximated by a fourth-order polynomial function of temperature as

$$ C_{p,k} = \sum_{p=1}^{M} a_{k,p} T^{p-1} \quad (2.11) $$

The formulation is closed by an equation of state for a perfect gas mixture

$$ p = \rho R_u \sum_{k=1}^{N} \frac{Y_k}{W_k} = \rho RT \quad (2.12) $$

where $R_u$ is the universal gas constant and $W_k$ is the molecular weight of species $k$.

Full account is taken of variable transport and thermodynamic properties. Within the thermodynamic regime of concern in practical rocket-motor environments, the viscosity and thermal conductivity for individual species are approximated by fourth-order polynomials of temperature. The coefficients of these polynomials for individual
species are obtained from McBride et al. (1993; 2002). The coefficients are valid in the
temperature range of 300 - 6000 K. The viscosity and thermal conductivity of the mixture
is obtained through Wilke’s method and Wassiljewa’s approach, respectively, as follows
(Poling et al., 2000).

\[ \eta_{\text{mix}} = \sum_{i=1}^{N} X_i \eta_i \]

where \( X_i \) represents mole fraction of species \( i \) and the inter-collision parameter \( \phi_{ij} \) is
given by,

\[ \phi_{ij} = \left[ \frac{1 + (\eta_i / \eta_j)^{1/2} (W_j / W_i)^{1/4}}{8(1 + W_i / W_j)^{1/2}} \right]^2 \]

The binary mass diffusivity \( D_{ij} \) between species \( i \) and \( j \) is obtained using the Chapman-
Enskog theory in conjunction with the Lennard-Jones intermolecular potential energy
function (Poling et al., 2000) as,

\[ D_{ij} = 0.0018583 \frac{T^3(1/W_i + 1/W_j)^{1/2}}{p\sigma_{ij}^3\Omega_{ij}} \]

where the units of \( T \) and \( p \) are in K and atm, respectively. The Lennard-Jones mixture
length scale, \( \sigma_{ij} \), and the collision integral for diffusion, \( \Omega_{ij} \), are obtained from (Reid and
Sherwood, 1966),

\[ \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \]

\[ \Omega_{ij} = \frac{1}{T_0^{0.145}} + \frac{1}{(T_0 + 0.5)^2} \]
where \( T_D \) is given by,

\[
T_D = \frac{kT}{\sqrt{\varepsilon_i \varepsilon_j}} \tag{2.18}
\]

\( k \) is the Boltzmann constant. The constants \( \sigma_i \) and \( \varepsilon_i \) are obtained from McBride et al. (1993; 2002). The effective diffusion coefficient \( D_{im} \) in a multi-component mixture is then related to the binary diffusion coefficient \( D_{ij} \) through the following equation

\[
D_{im} = (1 - X_i) / \sum_{i \neq j} X_i / D_{ij} \tag{2.19}
\]

2.2 Gas-Phase Chemical Kinetics

In the current study, the flowfield in the rocket nozzle consists of combustion products of either metallized or non-metallized AP/HTPB composite propellants. Tables 2.1 and 2.2 summarize the composition of the combustion products of the non-metallized and metallized AP/HTPB propellant, respectively. The species compositions in the chamber and at the throat are obtained from the chemical equilibrium calculations by using the CEC code (Gordon and McBride, 1994). The main species in the combustion stream of a non-metallized propellant are \( H_2O, CO_2, CO, HCl, N_2, \) and \( H_2 \), along with small amounts of \( OH \) and \( Cl \), and negligible concentrations of \( NO, O_2, H, \) and \( O \). In the case of a metallized propellant, condensed-phase species of \( Al_2O_3 \) is also present in addition to the aforementioned gaseous species. Tables 2.1 and 2.2 show the fact that a large change in the chamber pressure causes a very small change in the composition of free stream. It is thus a good approximation to assume that the free-stream species
composition entering the nozzle are unaffected by the changes in the operating pressure. At a given operating pressure, the equilibrium composition at the nozzle throat \((M = 1)\) changes slightly from that at the chamber \((M = 0)\). It is also clear that in the case of the metallized propellant the concentrations of oxidizing species, H\(_2\)O and CO\(_2\), are much lower as compared to their counterparts for non-metallized propellant, due to the formation of Al\(_2\)O\(_3\).

Table 2.1: Mass fractions of prominent combustion species in the free-stream of non-metallized AP/HTPB (88/12)

<table>
<thead>
<tr>
<th>species</th>
<th>(p_t = 68) atm</th>
<th>(p_t = 250) atm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>chamber (p = 68) atm (T = 3023) K (M = 0)</td>
<td>throat (p = 39.2) atm (T = 2826) K (M = 1)</td>
</tr>
<tr>
<td>CO</td>
<td>0.10662</td>
<td>0.09998</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.21025</td>
<td>0.22070</td>
</tr>
<tr>
<td>HCl</td>
<td>0.25586</td>
<td>0.26048</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>0.28654</td>
<td>0.28907</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.10488</td>
<td>0.10540</td>
</tr>
<tr>
<td>Cl</td>
<td>0.01635</td>
<td>0.01202</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0.00343</td>
<td>0.00328</td>
</tr>
<tr>
<td>OH</td>
<td>0.00887</td>
<td>0.00543</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.00365</td>
<td>0.00175</td>
</tr>
<tr>
<td>NO</td>
<td>0.00237</td>
<td>0.00128</td>
</tr>
<tr>
<td>O</td>
<td>0.00049</td>
<td>0.00022</td>
</tr>
<tr>
<td>H</td>
<td>0.00017</td>
<td>0.00011</td>
</tr>
</tbody>
</table>
Even though near-equilibrium conditions exit in the rocket-motor chamber, some gas-phase reactions may still occur as the combustion products flow through the nozzle. This is true more so because species concentrations are perturbed in the boundary layer, due to the heterogeneous chemical reactions taking place at the nozzle surface. The concentrations of highly reactive species such as O, O₂, and OH at the nozzle surface are likely to be even lower than their counterparts at the free stream because the temperature...
decreases from the free-stream to the surface. Since the concentrations of O\textsubscript{2} and O are negligible, the oxidation of H\textsubscript{2} and CO to form H\textsubscript{2}O and CO\textsubscript{2}, respectively, is ignored. It is also reasonable to assume that HCl, Cl, N\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3} are not involved in the gas-phase chemical reactions.

The most probable reaction mechanism occurring in the gas phase is the so-called Bradford mechanism (Bradford, 1933) represented by a set of reversible reactions (R1-R4).

\begin{align*}
\text{H}_2 + \text{M} & \leftrightarrow 2\text{H} + \text{M} \quad \text{(R1)} \\
\text{H} + \text{CO}_2 & \leftrightarrow \text{CO} + \text{OH} \quad \text{(R2)} \\
\text{OH} + \text{H}_2 & \leftrightarrow \text{H}_2\text{O} + \text{H} \quad \text{(R3)} \\
\text{H}_2\text{O} + \text{M} & \leftrightarrow \text{H} + \text{OH} + \text{M} \quad \text{(R4)}
\end{align*}

The overall process is represented by a one-step reaction, the so-called reversible water-gas shift reaction, given by

\[ \text{CO} + \text{H}_2\text{O} \underset{k_b}{\overset{k_f}{\leftrightarrow}} \text{CO}_2 + \text{H}_2 \quad \text{(R5)} \]

Based on the experimental data of Bustamante et al. (2004; 2005), the rates of the forward and reverse reactions take the following forms:

\[ \tilde{w}_{\text{CO}_2} = k_f [\text{CO}]^{0.5} [\text{H}_2\text{O}] \quad \text{(2.20)} \]

\[ \tilde{w}_{\text{CO}} = k_b [\text{H}_2]^{0.5} [\text{CO}_2] \quad \text{(2.21)} \]
These expressions represent the chemical source terms in Eq. (2.4). The rate constants are obtained from the Arrhenius form as

\[ k = A \exp\left(-\frac{E_A}{R_a T}\right) \quad (2.22) \]

The chemical kinetics data are obtained by extrapolating the experimental data (Bustamante et al., 2004; Bustamante et al., 2005) for the temperature and pressure ranges encountered in the current problem. The pre-exponential factor and the activation energy for the backward rate constant are \(5.99 \times 10^8\) (m\(^3\)/kmol\(-s^2\))\(^{0.5}\) and 213.3 kJ/mol, respectively (Bustamante et al., 2004). The corresponding values for the forward rate constant are \(2.34 \times 10^{10}\) (m\(^3\)/kmol\(-s^2\))\(^{0.5}\) and 288.3 kJ/mol, respectively (Bustamante et al., 2005). Recently, Culbertson et al. (2008) conducted experiments to investigate the forward water-gas shift reaction at elevated pressures. In the present analysis, the kinetics data for either \(k_f\) or \(k_b\) was first chosen, and the other rate constant was estimated from the equilibrium constant, \(K_{eq}\). In a manner similar to the approach of Bustamante et al. (2004), \(K_{eq}\) was estimated with the following temperature-dependent correlation (Moe, 1962):

\[ K_{eq} = \exp\left(-4.33 + \frac{4577.8}{T}\right) \quad (2.23) \]

### 2.3 Heterogeneous Chemical Reactions at Nozzle Surface

The rocket-nozzle materials considered in the present study are graphite, carbon-carbon, and refractory metals including tungsten, rhenium, and molybdenum. Since
chemical erosion is the primary mechanism for nozzle erosion, it is essential to know the reactions taking place at the surface of the chosen nozzle materials, along with the associated mechanisms and kinetics data. The rate of consumption of the nozzle material by a surface reaction with an oxidizing species, \( i \), is expressed as

\[
\dot{r}_{i,\text{ch}} = k_i \ p_i^{\nu_i} \quad (\text{kg} / \text{m}^2 \text{s})
\]

where

\[
p_i_{i,s} = p_s Y_{i,s} \frac{W_{\text{mix},s}}{W_i}
\]

\[
k_i = A_i T_s^b \exp(-E_i / R_n T_s)
\]

\( Y_{i,s} \) and \( p_{i,s} \) represent the mass fraction and partial pressure of species \( i \) at the surface, respectively, \( W_{\text{mix},s} \), \( p_s \), and \( T_s \) the molecular weight of the gas mixture, pressure, and temperature at the surface, respectively, and \( n \) the overall order of the heterogeneous reaction. The mass rate of consumption of an oxidizing species, \( i \), at the gas-solid interface is given by

\[
\dot{\omega}_i = \dot{r}_{i,\text{ch}} \frac{\nu_i W_i}{\nu_s W_s}
\]

where \( \nu_i \) and \( \nu_s \) are the stoichiometric coefficients for the oxidizing species and the nozzle material, respectively, in the surface reaction under consideration. \( W_s \) is the molecular weight of the nozzle material.
2.3.1 Heterogeneous Kinetics of Graphite

It is important to know which among the species present in the combustion stream are likely to react with the graphite surface. The chemical equilibrium calculations using the CEC code (Gordon and McBride, 1994) at the rocket motor conditions indicate that the major oxidation product is CO, with very small amounts of hydrocarbons such as C$_2$H$_2$ and CH$_4$. Thus, the most probable surface reactions are the ones which yield CO. To identify thermodynamically favored surface reactions, Keswani (1984) tabulated the change in Gibbs free energy associated with the heterogeneous reactions between graphite and each of the combustion species. The reactions of carbon with the species of O, OH, O$_2$, NO, CO$_2$, and H$_2$O were found to be favorable. The reactions with H$_2$, Cl, HCl, and N$_2$ were not found favorable. Even though the reaction of carbon with condensed-phase Al$_2$O$_3$ appears thermodynamically feasible, it is almost certainly limited by the kinetics of the reactions, because it requires atoms and molecules to diffuse from one condensed-phase to another. Also, previous experimental studies (Klager, 1977; Geisler, 1978) have found that the graphite recession rate decreases with increasing aluminum content. Thus, Al$_2$O$_3$ is treated as inert species.

Extensive literature review was conducted to investigate the heterogeneous reactions of graphite with various gaseous species present in the combustion stream. At high temperatures and pressures, the graphite surface is prone to chemical attack by such oxidizing species as H$_2$O, CO$_2$, OH, H$_2$, O$_2$, and O, to form primarily CO (Klager, 1977; Delaney et al., 1964; McDonald and Hedman, 1965; Swope and Berard; 1964; Keswani 1984). Bradley et al. (1984) compiled a list of kinetics data for heterogeneous reactions of
nonporous graphite with different species, as shown in Table 2.3. Although the reactivity of graphite with O and O\textsubscript{2} is significant (Bradley et al., 1984; Chelliah et al., 1996; Chelliah, 1996), this effect can be ignored due to the fuel-rich nature of AP/HTPB propellants, which produces negligible amounts of O and O\textsubscript{2} in the gas phase. There is a disagreement between Tong et al. (1976) and other investigators (Klager, 1977; McDonald and Hedman, 1965) concerning the importance of the reaction between C\textsubscript{(s)} and H\textsubscript{2}. In the present work, this reaction was excluded based on the kinetic data from Chi and Landahl (1968) and the modeling studies on graphite recession by Borie et al. (1989) and Kuo and Keswani (1985; 1986). Moreover, the mass fraction of H\textsubscript{2} is much lesser than H\textsubscript{2}O and CO\textsubscript{2}. The assumption is further supported by the experimentally observed decrease in the nozzle recession rate with increasing concentration of H\textsubscript{2} (Klager, 1977; McDonald and Hedman, 1965; Geisler 1978). Thus, the three heterogeneous chemical reactions considered at the nozzle surface are

\begin{align*}
\text{C}_{(s)} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 \quad (R6) \\
\text{C}_{(s)} + \text{CO}_2 & \rightarrow 2\text{CO} \quad (R7) \\
\text{C}_{(s)} + \text{OH} & \rightarrow \text{CO} + \text{H} \quad (R8)
\end{align*}
The reactions of C(s) with H2O and CO2 have been extensively investigated at high temperature (Lewis et al., 1970; King, 1971; Tong et al. 1976; Golovina, 1980; Borie et al., 1989). The types of graphite samples, however, were different. Lewis et al. (1970) studied the carbon-steam reaction at pressures of 1-3 atm and surface temperatures of 1500-3000 K, by employing an impingement reactor to minimize boundary layer diffusion effects. King (1971) used graphite material as extended throats for a rocket
simulator and studied a carbon-steam reaction at surface temperatures from 2000-2500 K, and H₂O partial pressures of 6 to 20 psi. He accounted for diffusion effects, by measuring Stanton number for heat transfer and using it to estimate the diffusional resistance. Tong et al. (1976) used an Arc Plasma Generator and extended nozzle throat inserts to study the reactions of carbon with various gases in the pressure and temperature range of 3-5 atm and 2000-3000 K, respectively, and obtained a rate expression for the carbon-steam reaction. The reaction rates for PO3 and CFZ graphites measured by King (1971) are close to the reaction rates measured by Lewis et al. (1970) for 5890 graphite. The rate expression of Tong et al. (1976) is in reasonable agreement with the data of Lewis et al. (1970).

Considering a large scatter in the experimentally available data for the reaction of steam with different types of graphites, the kinetic expression complied by Libby and Blake (1979; 1981) seems to be in good agreement with the majority of data (King 1971; Lewis et al. 1970; Libby and Blake 1979; 1981). However, they considered the specific rates of both reactions (C(s) + H₂O and C(s) + CO₂) to be equal, with a pre-exponential factor of 41.9 kcal/mole and an activation energy of 2470 kg/(m²-atm-s). Golovina (1980) provided the kinetic data for the reaction between C(s) and CO₂ with the pre-exponential factor and activation energy as 40 kcal/mol and 158 kg/(m²-atm-s), respectively. It has been suggested in previous studies (Swope and Berard, 1964; Lewis et al., 1970; Klager 1977) that at high temperatures, H₂O could be the more detrimental oxidizing species responsible for nozzle erosion. Consequently, the rate constants for the reactions of C(s) with H₂O and CO₂ should not be treated identical, as employed by Libby and Blake (1979; 1981) and others. In the current study, the kinetic parameters $A_i$ and $E_i$, are
adopted from the experimental data compiled by Bradley et al. (1984). These parameters were used with success by Chelliah et al. (1996) and Lee et al. (1995) in their studies of carbon ignition and oxidation at high temperatures.

Table 2.4 lists the kinetic data for the three heterogeneous reactions used in the current study. Figure 2.1 shows a comparison of the reaction rates of C\(_{(s)}\) with H\(_2\)O at 1 atm obtained from the kinetic data compiled by Bradley et al. (1984) and Libby and Blake (1981). The corresponding orders of reaction are 0.5 and 1.0, respectively. The agreement in the reaction rates at 1 atm appears to be reasonably close. According to Bradley et al. (1984), the reaction rates of C\(_{(s)}\) with CO\(_2\) at 1 atm and high temperatures obtained from Golovina (1980) are in good agreement with the kinetic data listed in Table 2.4., for the corresponding surface reaction. The melting and sublimation/pyrolysis of the graphite/carbon-carbon material are not considered because these phenomena (Savvatimskiy, 2005) are significant only at a surface temperature greater than 4000 K, which is never attained in practical rocket-motor environments.
The earlier nozzle erosion models from 1980s did not include the reaction of graphite with the oxidizing species OH. The reason to exclude the reaction (R8) was based on the fact that the OH mass fractions in the combustion stream of AP/HTPB composite propellants is very small as compared to the mass fractions of other oxidizing species.
species of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) (see Table 2.1 and 2.2 in Chapter 2). But it was noted that the kinetic rate of reaction (R8) was much higher than the reactions rates of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) with graphite in the temperature range of concern. Figure 2.2 shows the plot of rate constants of reactions (R6), (R7), and (R8), based on the kinetic data used by Bradley et al. (1984) and Chelliah et al. (1996). It is clear that in the concerned temperature range of 2000-3500 K, the rate constant for (R8) is order of magnitudes greater than the rate constants of (R6) and (R7). Hence, even though the mass fraction of OH may be very small, the reaction (R8) could prove important in determining the erosion rates.

A literature survey was conducted by Acharya and Kuo (2007a) to find the possible reactions and the reaction kinetics of halogens (particularly chlorine) with graphite. Freedman (1995) exposed the basal plane of graphite to beams of atomic and molecular fluorine and chlorine in an ultrahigh vacuum environment. X-ray
photoelectron spectroscopy (XPS) and low-energy electron diffraction techniques were then used to elucidate the chemistry involved. It was found that the exposure of the HOPG substrates to molecular chlorine produced no evidence of any uptake of chlorine. In the work conducted by Gonzalez et al. (1999), the oxidation reaction of carbon black, sucrose carbon, and graphite in the presence of chlorine was studied by thermal analysis (thermogravimetric analysis and differential thermal analysis). Heating the three carbons in a chlorine atmosphere showed that graphite exhibited the smallest mass gain (0.5%) of all three carbons. It was also shown that the oxygen uptake by graphite does not change in the presence of chlorine and vice versa. Oxidation in the absence of chlorine started at 933 K for graphite. When gaseous chlorine was present, oxidation started at 1043 K. However, because the temperatures at the nozzle surface are much higher, such difference in the oxidation temperatures is not important (Acharya and Kuo, 2007a). In a study by Henning (1952), it was suggested that chlorine reacts with graphite only at low temperatures. Based on all these studies, it was concluded that the reaction of graphite with Cl is negligible and the presence of Cl atoms in the vicinity of the nozzle surface does not affect graphite reactions with other oxidizing species. Accordingly the graphite reaction with chlorine is not considered in the present model.

2.3.2 Heterogeneous Kinetics of Tungsten (W)

For aluminized propellants, the flame temperatures could reach as high as 3700 K. Tungsten, on account of its high melting temperature of 3695 K, is an attractive material for rocket-nozzle insert. It can be used at the throat location, as shown in Fig 1.3a.
Copper-infiltrated tungsten has been often used as either a monolithic insert or a thin liner encased by a graphite body (Wong, 1968). This type of tungsten consists of a porous, pressed, and sintered matrix, which is infiltrated with a metal coolant. Because of the cooling effect by transpiration of the metallic coolant, the material can withstand a higher exhaust gas temperature than the un-infiltrated tungsten. The high cost and difficulties encountered in the fabrication of infiltrated tungsten components, however, have limited their use to small nozzles.

Similar to situation with graphite, tungsten is also prone to chemical attack by the oxidizing species of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) present in the combustion stream of the AP/HTPB composite propellant. The effect of \( \text{HCl} \) is negligible, according to the experimental study by Farber (1959). Chemical equilibrium calculations (Gordon and McBride, 1994) also suggest that the species of \( \text{HCl}, \text{H}_2, \text{N}_2, \) and \( \text{CO} \) do not react with \( \text{W} \), while \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) show significant reactions. Olcott and Batchelor (1964), however, observed that the presence of \( \text{H}_2 \) and \( \text{CO} \), respectively, reduces the reaction rates of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) with \( \text{W} \). Similar reduction of \( \text{CO}_2 \) reaction with \( \text{W} \) due to the presence of \( \text{CO} \) was observed by Walsh et al. (1967).

Several experimental studies have been devoted to the oxidation of tungsten with steam (Olcott and Batchelor, 1964; Belton and McCarron, 1965; Kalipatrick and Lott, 1966a; Smolik et al., 1998; Unal et al., 2000; Greene and Finfork, 2001) and \( \text{CO}_2 \) (Olcott and Batchelor, 1964; Walsh et al., 1967) at high temperatures. There seems to be a fair bit of disagreement about the form of the final oxidation product. Some consider \( \text{WO}_3(g) \) as the major oxidation product (Olcott and Batchelor, 1964; Smolik et al., 1998), while others have suggested \( \text{WO}_2(g) \) as the major product (Walsh, 1967; Harvey, 1974). Greene
and Finfork (2001) found that the oxide formed has a stoichiometry of WO$_{2.7}$, which indicates that both WO$_3$ and WO$_2$ may be present. Kalipatrick and Lott (1966a) performed experiments over a temperature range of 1273–1973 K and atmospheric pressure to determine the mechanism of the tungsten reaction with steam. The measured activation energies were 48.9 kcal/mol and 22.7 kcal/mol in the temperature ranges of 1273–1723 K and 1723–1973 K, respectively. At temperatures greater than 1723 K, it was suggested that the final oxidation products could be either the vapor-phase WO$_3$ and its polymers or the volatile WO$_3$H$_2$O$_{(g)}$. The rate-determining step was proposed to be the oxidation of WO$_2(s)$ to WO$_3$H$_2$O$_{(g)}$ and WO$_3(g)$ and its polymers.

Based on the observations of Belton and McCarron (1965), the major species could be WO$_3$H$_2$O$_{(g)}$, which is formed due the reaction of WO$_3$ and H$_2$O in the gas phase. Such a reaction, if it occurs, could be effective in reducing the amount of H$_2$O attacking the surface, and hence the erosion rate. The chemical equilibrium calculations (Gordon and McBride, 1994) also show that WO$_3(l,g)$ and its polymers are the major products at high temperature, as described in Table 2.5. For temperatures above 1700 K, a thermodynamic analysis based on the Gibbs free energy indicates that formation of WO$_3(g)$ is favored (Appendix B). In the current study, both WO$_3(g)$ and WO$_2(g)$ are considered individually as the final oxidation product. The chemical pathways and associated kinetics data are summarized in Table 2.6. The decrease in the reaction rate of CO$_2$ and W due the presence of CO is accounted as a function of the ratio of the mole fractions of CO and CO$_2$ (Walsh et al., 1967). Wherever the reaction order with respect to H$_2$O is not mentioned explicitly in the literature, a first order reaction is assumed.
Table 2.5: Chemical equilibrium calculations for tungsten oxidation (reactants at 2800 K, 40 atm, and mass ratio of 1:1)

<table>
<thead>
<tr>
<th></th>
<th>H(_2)O</th>
<th>WO(_3)(l)</th>
<th>WO(_3) and its polymers</th>
<th>H(_2)</th>
<th>WO(_2)</th>
<th>(\Delta H_R) (kJ/kg)</th>
<th>(\Delta G_R) (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/H(_2)O</td>
<td>0.35</td>
<td>0.12</td>
<td>0.51</td>
<td>0.02</td>
<td>~0</td>
<td>-2910.20</td>
<td>-23939.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>CO(_2)</th>
<th>WO(_3)(l)</th>
<th>WO(_3) and its polymers</th>
<th>CO</th>
<th>WO(_2)</th>
<th>(\Delta H_R) (kJ/kg)</th>
<th>(\Delta G_R) (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/CO(_2)</td>
<td>0.14</td>
<td>0.42</td>
<td>0.21</td>
<td>0.23</td>
<td>~0</td>
<td>-2285.98</td>
<td>-13354.6</td>
</tr>
</tbody>
</table>

Table 2.6: Chemical kinetics data* for heterogeneous surface reactions of tungsten

<table>
<thead>
<tr>
<th>surface reaction</th>
<th>(A_i)</th>
<th>(E_i) (kcal/mol)</th>
<th>(\dot{\omega}_i) (kg/m(^2)-s)</th>
<th>temperature range (K)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>W + 3H(_2)O(_g) (\rightarrow) WO(_3)(g) + 3H(_2)(_g)</td>
<td>8.64 (kg/m(^2)-s-atm)</td>
<td>22.70</td>
<td>(k_i p_{H_2O})</td>
<td>1723 – 1973</td>
<td>Kalipatrick and Lott (1966a)</td>
</tr>
<tr>
<td>or W + 2H(_2)O(_g) (\rightarrow) WO(_2)(g) + 2H(_2)(_g)</td>
<td>5.722 x 10(^4) (kg/m(^2)-s-atm)</td>
<td>48.13</td>
<td>(k_i p_{H_2O})</td>
<td>1073 – 1973</td>
<td>Unal et al. (2000)</td>
</tr>
<tr>
<td>W + 3CO(_2)(g) (\rightarrow) WO(_3)(g) + 3CO(_g)</td>
<td>1.433 x 10(^4) (kg/m(^2)-s-atm)</td>
<td>47.23</td>
<td>(k_i p_{H_2O})</td>
<td>1073 – 1623</td>
<td>Greene and Finfork (2001)</td>
</tr>
<tr>
<td>or W + 2CO(_2)(g) (\rightarrow) WO(_2)(g) + 2CO(_g)</td>
<td>4.026 x 10(^3) (kg/m(^2)-s-torr(^{0.88}))</td>
<td>79.00</td>
<td>(k_i p_{CO_2}^{0.88})</td>
<td>2200 – 3200</td>
<td>Walsh et al. (1967)</td>
</tr>
</tbody>
</table>

*\(k_i = A_i \exp(-E_i / R_T)\), the rate of tungsten consumption is obtained in kg/m\(^2\)/s
2.3.3 Heterogeneous Kinetics of Molybdenum (Mo)

Although molybdenum has performed satisfactorily as a nozzle throat insert and a structural support material, its usefulness is limited by its relatively high ductile-to-brittle transition temperature (Wong, 1968) and low melting point of 2896 K. The use of molybdenum inserts is thus usually restricted to propellants with lower flame temperatures. Gulbransen et al. (1963) and Kalipatrick and Lott (1965) studied the oxidation of molybdenum at high temperatures in steam and oxygen environments, respectively. The studied suggested that oxidation of molybdenum at high temperature yields \( \text{H}_2(g) \) and volatile \( \text{MoO}_3 \) along with its polymers. The chemical equilibrium calculations (Gordon and McBride, 1994) at high temperature and pressure also indicate that \( \text{H}_2(g) \) and \( \text{MoO}_3(g) \) and its polymers are the major products at high temperatures, as listed in Table 2.7.

Table 2.7: Chemical equilibrium calculations for molybdenum oxidation (reactants at 2800 K, 40 atm, and mass ratio 1:1)

<table>
<thead>
<tr>
<th></th>
<th>( \text{H}_2\text{O} )</th>
<th>( \text{Mo}(_c) )</th>
<th>( \text{MoO}_3 ) and its polymers</th>
<th>( \text{H}_2 )</th>
<th>( \Delta H_R ) (kJ/kg)</th>
<th>( \Delta G_R ) (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mo}/\text{H}_2\text{O} )</td>
<td>0.36</td>
<td>0.26</td>
<td>0.36</td>
<td>0.015</td>
<td>-2497.07</td>
<td>-24292.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( \text{CO}_2 )</th>
<th>( \text{Mo}(_c) )</th>
<th>( \text{MoO}_3 ) and its polymers</th>
<th>( \text{CO} )</th>
<th>( \Delta H_R ) (kJ/kg)</th>
<th>( \Delta G_R ) (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mo}/\text{CO}_2 )</td>
<td>0.15</td>
<td>0.25</td>
<td>0.38</td>
<td>0.22</td>
<td>-1828.15</td>
<td>-13692.9</td>
</tr>
</tbody>
</table>

Kalipatrick and Lott (1965) experimentally investigated the oxidation of Mo under different mass-flow rates of steam. They suggested that along with the vapor of \( \text{MoO}_3 \), volatile \( \text{MoO}_2(\text{OH})_2 \) can also be formed. Based on the chemical equilibrium study
(Table 2.7), H$_2$(g) and MoO$_3$(g) are considered as the final product of molybdenum oxidation by steam. In the current study, the experimentally obtained kinetics data corresponding to the maximum mass-flow rate are adopted, as they represent the condition closest to the kinetically-limited reaction rates. Table 2.8 gives the stoichiometry of the employed surface reaction and the chemical kinetics data for the oxidation of Mo by steam at high temperatures. First-order kinetics with respect to H$_2$O is assumed, as it was not explicitly mentioned in the literature. The reaction of CO$_2$ with Mo is not included in the present work due to the lack of relevant kinetics data in the literature. The thermodynamic analysis based on the Gibbs free energy (Appendix B), however, indicates that the reaction of Mo with CO$_2$ may be as significant as that of W with CO$_2$.

Table 2.8: Chemical kinetics data* for heterogeneous surface reactions of molybdenum

<table>
<thead>
<tr>
<th>surface reaction</th>
<th>$A_i$ (kg/m$^2$-s-atm)</th>
<th>$E_i$ (kcal/mol)</th>
<th>$\dot{\omega}_i$ (kg/m$^2$-s)</th>
<th>temperature range (K)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo + 3H$_2$O(g) $\rightarrow$ MoO$_3$(g) + 3H$_2$(g)</td>
<td>4.48</td>
<td>57.5</td>
<td>$k_i p_{H_2O}$</td>
<td>1373 –1973</td>
<td>Kalipatrick and Lott (1965)</td>
</tr>
</tbody>
</table>

$k_i = A_i \exp(-E_i / R T_i)$, the rate of molybdenum consumption is obtained in kg/m$^2$/s

2.3.4 Heterogeneous Kinetics of Rhenium (Re)

Rhenium-based nozzle inserts can be used for propellants with high flame temperatures due to the high melting point of rhenium (3459 K). They have been used in small liquid rocket engines (Schoenman, 1995). The oxidation of rhenium by steam at
high temperatures has been experimentally studied by Kalipatrick and Lott (1966b) and Duriez (2003). Kalipatrick and Lott (1966b) suggested that the oxide formed is Re$_2$O$_7$, which is volatile at high temperatures. Table 2.9 lists the stoichiometry of the surface reaction and the chemical kinetics data for the oxidation of Re by steam. Duriez (2003) concluded that the reaction is first order with respect to H$_2$O. The reaction rate was found to be highly dependent on the mass-flow rate of the steam and the gas velocity, indicating that the experimental conditions were not close to the kinetically-limited case.

Table 2.9: Chemical kinetics data* for heterogeneous surface reactions of rhenium

<table>
<thead>
<tr>
<th>Surface reaction</th>
<th>$A_i$</th>
<th>$E_i$</th>
<th>$\dot{\omega}_i$</th>
<th>Temperature range (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{Re} + 7\text{H}_2\text{O} \rightarrow \text{Re}_2\text{O}_7 + 7\text{H}_2$</td>
<td>29.85</td>
<td>29.80</td>
<td>$k_i p_{H_2O}$</td>
<td>1123–1973</td>
<td>Kalipatrick and Lott (1966b)</td>
</tr>
<tr>
<td></td>
<td>57.97</td>
<td>34.90</td>
<td>$k_i p_{H_2O}$</td>
<td>1873–2473</td>
<td>Duriez (2003)</td>
</tr>
</tbody>
</table>

* $k_i = A_i \exp(-E_i / RT_i)$, the rate of molybdenum consumption is obtained in kg/m$^2$/s

In the current study, the kinetics data of Kalipatrick and Lott (1966b) are chosen since the data fit well for all the steam flow rates considered, indicating the situation closest to the kinetically-limited reaction rates. The reaction of CO$_2$ with Re is not included, as no kinetics data relevant to this reaction is found in the literature. Unlike the reaction of CO$_2$ and W, the reaction of CO$_2$ and Re is not likely to be significant, due to the higher oxidation resistance of Re. No thermodynamic analysis of the oxidation
reaction based on the Gibbs free energy was performed because of the lack of thermodynamic properties for rhenium oxides.

2.4 Solid-Phase Governing Equation

With the neglect of thermal decomposition and chemical reactions in the solid phase, the heat conduction in the radial direction is governed by the following equation:

\[
\rho_c \frac{\partial h_c}{\partial t} + \frac{\rho_c}{r} \frac{\partial}{\partial r} \left( r h_c \dot{r} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( \lambda_c r \frac{\partial T_c}{\partial r} \right)
\]  \hspace{1cm} (2.28)

This equation takes into account the effect of surface recession and variable thermophysical properties of the considered nozzle material. Integration of Eq. (2.28) at steady-state across the nozzle thickness gives:

\[
r_i \left[ \lambda_c \frac{\partial T_c}{\partial r} \right]_{r_i} = \dot{r} \rho_c (h_{c-g} r_i - h_o r_o) + r_o \left[ \lambda_c \frac{\partial T_c}{\partial r} \right]_{r_o}
\]  \hspace{1cm} (2.29)

where \( r_i \) and \( r_o \) are the inner and outer radii of the nozzle material at any axial location, respectively, and \( h_{c-g} \) and \( h_o \) the corresponding specific enthalpies, respectively.

In most existing studies, the outer boundary of the nozzle material is modeled to be adiabatic. Such a treatment is valid when the nozzle material is sufficiently thick or well insulated and the thermal conductivity of the material is low. Calculations with typical thermophysical properties of graphite indicated that the thermal penetration depth \((\sim \alpha_c / \dot{r}_c)\) in graphite under a typical nozzle operating condition is on the order of 1 cm, which could be on the order of the thickness of the material. Considering the high thermal conductivity of refractory metals, the thermal penetration depth in the nozzle material
under typical motor-operating conditions could be of the same order as the thickness of the insert. Thus, the enforcement of the adiabatic condition needs to be carefully examined. An adequate sensitivity study on the effect of the outer boundary condition on the nozzle material erosion is required, and will be elaborated later.

2.5 Gas-Solid Interfacial Condition

The processes in the gas and solid phases are matched at the nozzle surface by enforcing the continuities of mass, species, and energy fluxes. The procedure eventually gives the erosion rate of nozzle material. The conservation laws at the gas-solid interface can be written as

**Mass:**

\[ \rho_g u_r = \rho_c r_c \]

(2.30)

**Species:**

\[ \left( -\rho_g D_{km} \frac{dY_k}{dr} + \rho_g Y_k u_r \right) = \omega_k \]

(2.31)

**Energy:**

\[ \left[ \lambda_c \frac{\partial T_c}{\partial r} \right]_r + \dot{\varepsilon}_c \rho_c h_{c-g} = \left[ \lambda_g \frac{\partial T_g}{\partial r} \right]_r + \sum_{k=1}^{N} \omega_k h_{g,k} \]

(2.32)

where \( u_r \) stands for the radial velocity in the gas phase due to material erosion. The rate of production of gas-phase species \( k \) at the nozzle surface on account of heterogeneous reactions (e.g., R6-R8) is denoted by \( \omega_k \). Figure 2.3 shows the energy balance at the nozzle surface. The first term in Eq. (2.32) can be obtained by considering the overall energy balance in the solid phase represented by Eq. (2.29). Radiation is neglected in Eq. (2.32), due to the prevalence of convective heat transfer (Borie et al., 1989; Kuo and
Keswani, 1985). The axial velocity and the turbulent kinetic energy and dissipation rate (encountered in the turbulence model described in Chapter 3) at the gas-solid interface are

\[
u_x = 0, \quad k = 0, \quad \frac{\partial \varepsilon}{\partial r} = 0 \quad (2.33)
\]

Finally, flow symmetry is enforced along the nozzle centerline by implementing

\[
\nu = 0, \quad \frac{\partial u}{\partial r} = 0, \quad \frac{\partial T}{\partial r} = 0, \quad \frac{\partial p}{\partial r} = 0, \quad \frac{\partial Y_i}{\partial r} = 0 \quad (2.34)
\]

### 2.6 Nozzle Recession Rate

The heterogeneous reactions consume the oxidizing species such as H₂O, OH, and CO₂ at the nozzle surface. Concentration gradients then form in the nozzle flowfield, and cause the diffusion of those species towards the surface. At a high surface temperature, the heterogeneous chemical reactions proceed so rapidly that the graphite erosion rate is dictated by the species diffusion process. The diffusion-controlled recession rate (\( \dot{r}_{i, \text{diff-lim}} \))
due to an oxidizing species \( i \) can be determined by first calculating \( \dot{\omega}_{i,\text{diff-lim}} \) from Eq. (2.31) with \( Y_i = 0 \), and then applying the following equation:

\[
\dot{r}_{i,\text{diff-lim}} = \dot{\omega}_{i,\text{diff-lim}} \frac{v_i W_x}{v_i W_i} \tag{2.35}
\]

At a low surface temperature the heterogeneous reactions become the rate-controlling process for nozzle erosion due to reduced chemical activity, and the recession rate is obtained purely from the chemical kinetics (\( \dot{r}_{i,\text{ch}} \)).

In the graphite recession model of Kuo and coworkers (1985; 1986; 2007a) and Borie et al. (1989), the species equations were not solved for the mass fractions of the oxidizing species at the surface. The graphite recession rate was calculated empirically as the harmonic mean of the kinetics- and diffusion-limited rates. The former was obtained based on the species concentrations in the core flow. The use of the harmonic mean may not be accurate for non first-order surface reactions. No such assumption is employed in the current model. The graphite recession rate (kg/m²-s) due to an oxidizing species, \( i \), is obtained appropriately as

\[
\dot{r}_{i,\text{erosion}} = \min (\dot{r}_{i,\text{diff-lim}}, \dot{r}_{i,\text{ch}}) \tag{2.36}
\]

The contributions of \( \dot{r}_{i,\text{ch}} \) and \( \dot{r}_{i,\text{diff-lim}} \) from each of the oxidizing species are calculated along the entire nozzle length by means of Eqs. (2.24) and (2.35), respectively, for each time step, until the steady-state condition is achieved. The net recession rate (m/s) of the nozzle surface is determined by

\[
\dot{r} (x) = \frac{1}{\rho_c} \sum_i \dot{r}_{i,\text{erosion}} \tag{2.37}
\]
The non-metallized propellants do not lead to mechanical erosion. Such erosion which is associated with the impingement of alumina particles is not considered for metallized propellants, since the collision of these particles with the nozzle surface is minimal at the throat and its downstream region.
Chapter 3

Numerical Methods and Validations

An accurate numerical scheme is essential for resolving a high-speed turbulent multi-component flow, such as the one encountered in rocket nozzles. This chapter addresses the numerical methods used for solving the theoretical model elaborated in the previous chapter. In Section 3.1, the Favre-averaged conservation equations are first presented in a vector form. The turbulence model used is described in Section 3.2. Section 3.3 presents the details of spatial-discretization employed in the density-based finite-volume method. A fourth-order artificial dissipation is used in the discretization scheme, in order to prevent numerical oscillation and to improve convergence. In Section 3.4, the four-step Runge-Kutta method employed for temporal integration is discussed. The concepts of parallel processing and its implementation are described in Section 3.5. Three validation cases are presented in Section 3.6.

3.1 Favre-averaged Governing Equations

The governing equations are first Favre averaged by employing

\[ f = \bar{f} + f'' \]; \quad \bar{f} = \frac{\rho f}{\bar{\rho}} \]  \hspace{1cm} (3.1)
The Favre-averaged mass, momentum, energy, and species conservation equations (excluding body forces) in the Cartesian coordinates can be expressed in a general vector form as follows:

\[
\frac{\partial \mathbf{Q}}{\partial t} + \frac{\partial (\mathbf{E} - \mathbf{E}_v)}{\partial x} + \frac{\partial (\mathbf{F} - \mathbf{F}_v)}{\partial y} + \frac{\partial (\mathbf{G} - \mathbf{G}_v)}{\partial z} = \mathbf{H}
\]  
(3.2)

where the vector \( \mathbf{Q} \) contains dependent variables and is defined as:

\[
\mathbf{Q} = [\rho, \bar{\rho}u, \bar{\rho}v, \bar{\rho}w, \bar{\rho}E, \bar{\rho}Y_i, \ldots, \bar{\rho}Y_{N-1}]^T
\]  
(3.3)

The superscript \( T \) stands for the transpose of a vector. The convective flux vectors \( \mathbf{E}, \mathbf{F}, \) and \( \mathbf{G} \) in the \( x, y, \) and \( z \) directions, respectively, take the form

\[
\mathbf{E} = 
\begin{bmatrix}
\bar{\rho}u \\
\bar{\rho}u^2 + \bar{\rho} \\
\bar{\rho}uv \\
\bar{\rho}uw \\
(\bar{\rho}E + \bar{p})\bar{u} \\
\vdots \\
\bar{u}\bar{\rho}Y_i \\
\vdots \\
\bar{u}\bar{\rho}Y_{N-1}
\end{bmatrix},
\mathbf{F} = 
\begin{bmatrix}
\bar{\rho}v \\
\bar{\rho}uv \\
\bar{\rho}v^2 + \bar{\rho} \\
\bar{\rho}vw \\
(\bar{\rho}E + \bar{p})\bar{v} \\
\vdots \\
\bar{v}\bar{\rho}Y_i \\
\vdots \\
\bar{v}\bar{\rho}Y_{N-1}
\end{bmatrix},
\mathbf{G} = 
\begin{bmatrix}
\bar{\rho}w \\
\bar{\rho}uw \\
\bar{\rho}vw \\
\bar{\rho}w^2 + \bar{\rho} \\
(\bar{\rho}E + \bar{p})\bar{w} \\
\vdots \\
\bar{w}\bar{\rho}Y_i \\
\vdots \\
\bar{w}\bar{\rho}Y_{N-1}
\end{bmatrix}
\]  
(3.4)
The diffusive flux vectors $\mathbf{E}_v$, $\mathbf{F}_v$, and $\mathbf{G}_v$ in the $x$, $y$, and $z$ directions, respectively, are

\[
\mathbf{E}_v = \begin{bmatrix}
0 \\
\bar{\tau}_{xx} - \rho u^s u^s \\
\bar{\tau}_{xy} - \rho u^s v^s \\
\bar{\tau}_{xz} - \rho u^s w^s \\
\rho D_{tm} \frac{\partial \bar{Y}_i}{\partial x} - \rho Y_i u^s \\
\vdots \\
\rho D_{N-1,m} \frac{\partial \bar{Y}_{N-1}}{\partial x} - \rho Y_{N-1} u^s
\end{bmatrix},
\]

\[
\mathbf{F}_v = \begin{bmatrix}
0 \\
\bar{\tau}_{yx} - \rho v^s u^s \\
\bar{\tau}_{yy} - \rho v^s v^s \\
\bar{\tau}_{yz} - \rho v^s w^s \\
\rho D_{tm} \frac{\partial \bar{Y}_i}{\partial y} - \rho Y_i v^s \\
\vdots \\
\rho D_{N-1,m} \frac{\partial \bar{Y}_{N-1}}{\partial y} - \rho Y_{N-1} v^s
\end{bmatrix},
\]

\[
\mathbf{G}_v = \begin{bmatrix}
0 \\
\bar{\tau}_{zx} - \rho w^s u^s \\
\bar{\tau}_{zy} - \rho w^s v^s \\
\bar{\tau}_{zz} - \rho w^s w^s \\
\rho D_{tm} \frac{\partial \bar{Y}_i}{\partial z} - \rho Y_i w^s \\
\vdots \\
\rho D_{N-1,m} \frac{\partial \bar{Y}_{N-1}}{\partial z} - \rho Y_{N-1} w^s
\end{bmatrix},
\]

(3.5)

The source term $\mathbf{H}$ is given by,

\[
\mathbf{H} = (0, 0, 0, 0, 0, \hat{\omega}, \ldots, \hat{\omega}_{N-1})^T
\]

(3.6)

The unclosed terms such as $\bar{\rho} u^s u^s$, $\bar{\rho} E^s u^s$, $\bar{\rho} Y_i u^s$, etc., which will not be explicitly solved for, require a turbulence model.
3.2 Turbulence Closure

The unclosed terms, \( \rho u_i^* u_i^*, \rho E^* u_i^*, \rho Y_i^* u_i^* \), in Eqs. (3.5) are treated using a two-layer turbulence model well-calibrated for transpiration and accelerating flows (Rodi, 1991; Tseng and Yang, 1994). Since the flow through a convergent-divergent nozzle is relatively smooth and well defined, the more computationally demanding and time-consuming techniques employing Large Eddy Simulation (LES) are not needed. In comparison to the conventional low-Reynolds-number \( k-\varepsilon \) schemes, the two-layer model shows superior performance in terms of numerical accuracy and convergence. The model employs the standard \( k-\varepsilon \) two-equation approach for the bulk flow away from the wall (i.e., the outer layer). The equations representing the transport of turbulent kinetic energy and its dissipation rate are:

\[
\frac{\partial \bar{k}}{\partial t} + \frac{\partial (\bar{\rho} \bar{u}_i \bar{k})}{\partial x_j} = \nabla \cdot \left[ \left( \mu + \frac{\mu_t}{\sigma_k} \right) \nabla k \right] + \mu_t G - \rho \varepsilon \tag{3.7}
\]

\[
\frac{\partial \bar{\varepsilon}}{\partial t} + \frac{\partial (\bar{\rho} \bar{u}_i \bar{\varepsilon})}{\partial x_j} = \nabla \cdot \left[ \left( \mu + \frac{\mu_t}{\sigma_\varepsilon} \right) \nabla \varepsilon \right] + C_{\varepsilon 1} \frac{\varepsilon}{k} \mu_t G - C_{\varepsilon 2} \frac{\varepsilon}{k} \rho \varepsilon \tag{3.8}
\]

where

\[
G = 2 \left[ \left( \frac{\partial \bar{u}}{\partial x} \right)^2 + \left( \frac{\partial \bar{v}}{\partial y} \right)^2 + \left( \frac{\partial \bar{w}}{\partial z} \right)^2 \right] + \left( \frac{\partial \bar{u}}{\partial y} + \frac{\partial \bar{v}}{\partial x} \right)^2 + \left( \frac{\partial \bar{v}}{\partial z} + \frac{\partial \bar{w}}{\partial y} \right)^2 + \left( \frac{\partial \bar{w}}{\partial x} + \frac{\partial \bar{u}}{\partial z} \right)^2 \tag{3.9}
\]

The turbulent eddy viscosity is obtained from the Prandtl-Kolmogorov relation,

\[
\mu_t = C_{\mu} \left( \frac{\rho k^2}{\varepsilon} \right) \tag{3.10}
\]
The standard and well-tested values used for the empirical constants are \( \sigma_k = 1.0, \sigma_\varepsilon = 1.3, \) 
\( C_{\varepsilon_1} = 1.44, C_{\varepsilon_2} = 1.92, \) and \( C_\mu = 0.09. \)

Unlike the low-Reynolds-number treatment, which solves the two turbulent transport equations all the way to the surface, the two-layer approach (Tseng and Yang, 1994) solves only the turbulent kinetic energy equation in the near-surface region (i.e. the inner layer) and greatly reduces the complexities associated with the stiff distributions of turbulent transport properties. The dissipation rate of the turbulent kinetic energy is determined by,

\[
\varepsilon = \frac{k^{3/2}}{l_\varepsilon}
\]  
(3.11)

The turbulent eddy viscosity is obtained as,

\[
\mu_t = C_\mu \rho \sqrt{k l_\mu}
\]  
(3.12)

The near-wall damping is modeled through specification of the length scales \( l_\mu \) and \( l_\varepsilon \):

\[
l_\mu = C_\mu r_n \left[ 1 - \exp \left( - \frac{Re_y}{A_\mu} \frac{25}{A^+} \right) \right]
\]  
(3.13)

\[
l_\mu = C_\mu r_n \left[ 1 - \exp \left( - \frac{Re_y}{A_\mu} \frac{25}{A^+} \right) \right]
\]  
(3.14)

where the turbulent Reynolds number is defined as \( Re_y = \sqrt{k r_n / \nu} \), with \( r_n \) representing the distance from the surface. The coefficient \( C_l \) is given by

\[
C_l = \kappa C_\mu^{-3/4}
\]  
(3.15)
where $\kappa$ is the von Kármán constant. The effect of pressure gradient and surface transpiration is included in $A^+$. For an accelerating flow with wall transpiration, it is given by the empirical correlation (Andersen et al., 1975) as

$$A^+ = \frac{24}{7.1\left\{v_w^* + \left[ 4.25P^*/(1+10v_w^*) \right] \right\} + 1.0} \tag{3.16}$$

The dimensionless wall blowing velocity ($v_w^*$) and pressure gradient ($P^*$) are given respectively by

$$v_w^* = \frac{u_r}{u_f}; \quad P^* = \frac{v}{\rho u_f^3} \frac{dp}{dx} \tag{3.17}$$

where $u_r$ is the velocity at the nozzle surface due to the material erosion and $u_f$ the friction velocity. Other constants applied here are $A_\mu = 70.0$ and $A_c = 2C_l$.

The inner and outer layers are matched at locations where viscous effects are negligible, according to the following criteria. First, the minimum $y^+$ running along these matching points must be between 80 and 120. Second, the local turbulent Reynolds number $Re_y$ must be larger than 200 in strong turbulent regions. These critical numbers of $y^+$ and $Re_y$ are taken from the analysis conducted by Chen and Patel. In the present study, the matching of the two layers occurs in the region of $y^+ = 80$-120 for all the grids employed for various nozzle geometries. After the turbulent eddy viscosity is obtained, the effective viscosity, conductivity, and diffusivity are calculated as follows:

$$\mu_{eff} = \mu + \mu_t, \quad \lambda_{eff} = \lambda + \frac{\mu C_p}{Pr_t}, \quad D_{eff} = D + \frac{\mu_t}{\rho Sc_t} \tag{3.18}$$
A standard value of 0.9 is used for the turbulent Prandtl number $Pr_t$, and the turbulent Lewis number $Le_t$ is unity.

3.3 Spatial Discretization

3.3.1 Finite Volume Approach

The governing equations listed in Section 3.1 are solved through a density-based finite volume methodology. The scheme exhibits excellent parallel efficiency and scalability attributes. This method allows for the treatment of arbitrary geometry, and avoids problems of metric singularities, usually associated with the finite-difference methods. To utilize the finite-volume approach, the governing equation is integrated over a small control volume, enclosed by the volume integral in the physical domain as:

$$
\int_V \left( \frac{\partial Q}{\partial t} + \frac{\partial (E - E_v)}{\partial x} + \frac{\partial (F - F_v)}{\partial y} + \frac{\partial (G - G_v)}{\partial z} - H \right) dV = 0
$$

(3.19)

The volume integral is then converted to a surface integral by using Gauss divergence theorem. The resultant integral equation takes the form

$$
\int_V \frac{\partial Q}{\partial t} dV + \oint_S W \cdot n dS = \int_V H dV
$$

(3.20)

where $n$ is the outward unit vector normal to each surface and the flux tensor, $W$, is given by:

$$
W = (E - E_v) i + (F - F_v) j + (G - G_v) k
$$

(3.21)
For a three-dimensional cell with six surfaces, as shown in Figure 3.1, the governing equation can be written as follows:

\[
\int_V \frac{\partial Q}{\partial t} \, dV + \int_{S_\xi} W \cdot n_\xi \, dS_\xi + \int_{S_\eta} W \cdot n_\eta \, dS_\eta + \int_{S_\zeta} W \cdot n_\zeta \, dS_\zeta = \int_V H \, dV \tag{3.22}
\]

Figure 3.1: Schematic of three-dimensional adjacent cells in finite-volume discretization

The subscripts \( \xi \), \( \eta \), and \( \zeta \) represent quantities aligned with the axial, radial, and azimuthal directions, respectively, and \( n_\xi \), \( n_\eta \), and \( n_\zeta \) represent the corresponding unit vectors normal to the surface. The unit vectors are related to the cell surface areas \( S_\xi \), \( S_\eta \), and \( S_\zeta \) as:

\[
\begin{align*}
    n_\xi &= \left( S_\xi i + S_{\xi j} j + S_{\xi k} k \right) / \left| S_\xi \right| \\
    n_\eta &= \left( S_\eta i + S_{\eta j} j + S_{\eta k} k \right) / \left| S_\eta \right| \\
    n_\zeta &= \left( S_\zeta i + S_{\zeta j} j + S_{\zeta k} k \right) / \left| S_\zeta \right|
\end{align*}
\tag{3.23}
\]

The cell surface areas are defined as:
The magnitude of each surface vector represents the cell interface area and can be obtained with the following formulas.

\[ S_x = \frac{1}{2} (r_{ij} \times r_{k}) = \frac{1}{2} \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x_2 - x_1 & y_2 - y_1 & z_2 - z_1 \\ x_3 - x_1 & y_3 - y_1 & z_3 - z_1 \end{vmatrix} = S_{\xi x} \vec{i} + S_{\xi j} \vec{j} + S_{\xi z} \vec{k} \]

\[ S_y = \frac{1}{2} (r_{ij} \times r_{k}) = \frac{1}{2} \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x_2 - x_1 & y_2 - y_1 & z_2 - z_1 \\ x_4 - x_1 & y_4 - y_1 & z_4 - z_1 \end{vmatrix} = S_{\eta x} \vec{i} + S_{\eta j} \vec{j} + S_{\eta z} \vec{k} \] (3.24)

\[ S_z = \frac{1}{2} (r_{ij} \times r_{k}) = \frac{1}{2} \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x_2 - x_1 & y_2 - y_1 & z_2 - z_1 \\ x_5 - x_1 & y_5 - y_1 & z_5 - z_1 \end{vmatrix} = S_{\zeta x} \vec{i} + S_{\zeta j} \vec{j} + S_{\zeta z} \vec{k} \]

The volume \( \Delta V \) associated with each cell can be evaluated using the formula of Kordulla and Vinokur (1983)

\[ \Delta V = \frac{1}{3} r_{ij} \cdot (S_x + S_y + S_z) \] (3.26)

We also define cell surface areas per cell volume as:

\[ \tilde{S}_\xi = \frac{S_x}{\Delta V}, \tilde{S}_\eta = \frac{S_y}{\Delta V}, \tilde{S}_\zeta = \frac{S_z}{\Delta V} \] (3.27)

Substitution of Eqs. (3.21) and (3.23) in Eq. (3.22) gives,
\[
\frac{\partial Q}{\partial t} + \int_V \left[ S_{\xi \xi} (E - E_v) + S_{\xi \eta} (F - F_v) + S_{\xi \zeta} (G - G_v) \right] / |S_\xi| dS_\xi \\
+ \int_S \left[ S_{\eta \eta} (E - E_v) + S_{\eta \zeta} (F - F_v) + S_{\eta \xi} (G - G_v) \right] / |S_\eta| dS_\eta \\
+ \int_S \left[ S_{\zeta \zeta} (E - E_v) + S_{\zeta \xi} (F - F_v) + S_{\zeta \eta} (G - G_v) \right] / |S_\zeta| dS_\zeta \\
- \int_V H dV = 0
\]  \tag{3.28}

By assuming the increments in body-fitted coordinates as unity, i.e., \( \Delta \xi = \Delta \eta = \Delta \zeta = 1 \), the Eq. (3.28) yields:

\[
\frac{\Delta Q}{\Delta t} + \left( E_\xi - E_{\xi v} \right)_{i+1/2,j,k} + \left( F_\eta - F_{\eta v} \right)_{i,j+1/2,k} + \left( G_\zeta - G_{\zeta v} \right)_{i,j,k+1/2} = H \tag{3.29}
\]

where the vectors \( E_{\xi}, F_\eta, G_\zeta, E_{\xi v}, F_{\eta v}, G_{\zeta v} \) and \( \Delta Q \) are defined as:

\[
\Delta Q = Q^{n+1} - Q^n \tag{3.30}
\]

\[
E_{\xi} = \left( \tilde{S}_{\xi \xi} E + \tilde{S}_{\xi \eta} F + \tilde{S}_{\xi \zeta} G \right) \quad E_{\xi v} = \left( \tilde{S}_{\xi \xi} E_v + \tilde{S}_{\xi \eta} F_v + \tilde{S}_{\xi \zeta} G_v \right)
\]

\[
F_\eta = \left( \tilde{S}_{\eta \xi} E + \tilde{S}_{\eta \eta} F + \tilde{S}_{\eta \zeta} G \right) \quad F_{\eta v} = \left( \tilde{S}_{\eta \xi} E_v + \tilde{S}_{\eta \eta} F_v + \tilde{S}_{\eta \zeta} G_v \right)
\]

\[
G_\zeta = \left( \tilde{S}_{\zeta \xi} E + \tilde{S}_{\zeta \eta} F + \tilde{S}_{\zeta \zeta} G \right) \quad G_{\zeta v} = \left( \tilde{S}_{\zeta \xi} E_v + \tilde{S}_{\zeta \eta} F_v + \tilde{S}_{\zeta \zeta} G_v \right)
\]  \tag{3.31}

The quantities \( E_{\xi,i,j,z+1/2}, F_{\eta,i,j,z+1/2}, G_{\zeta,i,j,k+1/2} \) and \( G_{\zeta v,i,j,k+1/2} \) represent the numerical fluxes associated with each cell interface (see Fig. 3.1). \( \tilde{S} \) represents cell surface areas per cell volume. In fact, the above analysis describes the transformation of a quadrilateral cell with a volume \( \Delta V \) in \( x-y-z \) coordinates to a cubic cell with unit volume in the general coordinates (i.e., \( \xi-\eta-\zeta \) coordinates).

The maximum time increment \( \Delta t \) of each cell can be evaluated by:
\[
\Delta t = \frac{\Delta t_\xi \Delta t_\eta \Delta t_\zeta}{\Delta t_\xi \Delta t_\eta + \Delta t_\eta \Delta t_\zeta + \Delta t_\zeta \Delta t_\xi}
\] (3.32)

where

\[
\begin{align*}
\Delta t_\xi & = \frac{CFL \cdot \Delta V}{|\vec{u} S_{\xi} + \vec{v} S_{\eta} + \vec{w} S_{\zeta} + |\vec{S}_\xi| + c|\vec{S}_\xi|} \\
\Delta t_\eta & = \frac{CFL \cdot \Delta V}{|\vec{u} S_{\eta} + \vec{v} S_{\xi} + \vec{w} S_{\zeta} + |\vec{S}_\eta| + c|\vec{S}_\eta|} \\
\Delta t_\zeta & = \frac{CFL \cdot \Delta V}{|\vec{u} S_{\zeta} + \vec{v} S_{\eta} + \vec{w} S_{\xi} + |\vec{S}_\zeta| + c|\vec{S}_\zeta|}
\end{align*}
\] (3.33)

CFL is the Courant number and \(c = \sqrt{\gamma RT}\) is the local speed of sound.

### 3.3.2 Evaluation of Inviscid Fluxes

Different approaches used for evaluating the numerical fluxes lead to different schemes with disparate numerical characteristics. For central difference scheme, the convective flux at any cell face in the axial direction can be written as:

\[
\dot{E}_{\xi,i+1/2,j} = \frac{1}{2} \left[ E_{\xi}(Q^L) + E_{\xi}(Q^R) \right]
\] (3.34)

where the left and right stencils are used to obtain desired accuracy. The above equation corresponds to the stencil illustrated in Fig. 3.2. The superscripts L and R represent the left and right cells. Depending on the manner in which these terms are evaluated, a wide variety of central and upwind schemes can be obtained. In the present work, the methodology proposed by Rai and Chakravarthy (1993) is used. Accordingly, the numerical flux is computed as:
where $\phi^{(4)}$ is the flux limiter. This term switches the truncation error associated with the flux-difference from fourth-order accuracy when $\phi^{(4)} = 1$, to second-order accuracy when $\phi^{(4)} = 0$. To evaluate Eq. (3.34) to the desired accuracy, the left and right state terms in Eq. (3.35) must be computed using the same or higher-order accuracy. These terms are written as follows to facilitate easy switching and to make the scheme TVD (total variation diminishing).
These stencils can be used to get fifth-order accuracy \( (\phi^{(4)}=1, \phi^{(2)}=1) \), third-order accuracy \( (\phi^{(4)}=0, \phi^{(2)}=1) \), and first-order accuracy \( (\phi^{(4)}=0, \phi^{(2)}=0) \), respectively. The present work utilizes second-order overall accuracy for the spatial discretization except the cells close to the physical boundaries. At the near boundary region, the third-order accurate evaluation of the left and right states is thus employed. The fluxes in \( y \) and \( z \) directions can be computed in a similar fashion as above.

### 3.3.3 Evaluation of Viscous Fluxes

A central difference scheme is employed to evaluate the viscous terms. The procedure requires the calculations of the gradients of \( u, v, w, \) and \( T \) at the cell interfaces. Figure 3.3 shows the schematic of a three-dimensional auxiliary cell with dash-dotted lines. There centers are located at the midpoints of the interfaces of the primary cells.

\[
\begin{align*}
Q_{i+1/2,j,k}^L &= Q_{i,j,k} + \phi^{(2)}_{i-1/2,j,k} \left( \frac{3\nabla Q_{i+1,j,k} + \nabla Q_{i,j,k}}{8} \right) \\
&\quad + \phi^{(4)}_{i+1/2,j,k} \left( -\frac{5\nabla Q_{i+2,j,k} + 7\nabla Q_{i+1,j,k} + \nabla Q_{i,j,k} - 3\nabla Q_{i-1,j,k}}{128} \right) \quad (3.36) \\
Q_{i+1/2,j,k}^R &= Q_{i,j,k} + \phi^{(2)}_{i+1/2,j,k} \left( \frac{3\nabla Q_{i-1,j,k} + \nabla Q_{i,j,k}}{8} \right) \\
&\quad + \phi^{(4)}_{i+1/2,j,k} \left( -\frac{5\nabla Q_{i+2,j,k} + 7\nabla Q_{i+1,j,k} + \nabla Q_{i,j,k} - 3\nabla Q_{i-1,j,k}}{128} \right) \quad (3.37)
\end{align*}
\]

where

\[
\nabla Q_{i,j} = Q_{i,j} - Q_{i-1,j} \quad (3.38)
\]
(solid line). The viscous fluxes need to be evaluated at the center of the primary cell faces, for e.g., at \( i+1/2, j, k \) for the viscous flux in the axial direction. By applying the Gauss divergence theorem to a small control volume \( \Delta V \), the viscous fluxes can be approximated as:

\[
\nabla \cdot \tilde{f} = \frac{1}{\Delta V} \oint_S \tilde{f} \cdot \hat{n} dS
\]

Application of the above formula to the auxiliary cell centered at \( (i+1/2, j, k) \) gives:

\[
\left( \frac{\partial f}{\partial x} \right)_{i+1/2, j, k} = \frac{1}{\Delta V_{i+1/2, j, k}} \left[ fS_{x\xi} \bigg|_{i+1/2, j, k} - fS_{x\xi} \bigg|_{i, j, k} + fS_{\eta\xi} \bigg|_{i+1/2, j+1/2, k} - fS_{\eta\xi} \bigg|_{i-1/2, j+1/2, k} + fS_{\zeta\xi} \bigg|_{i+1/2, j, k+1/2} - fS_{\zeta\xi} \bigg|_{i+1/2, j, k-1/2} \right]
\]

Similarly,

Figure 3.3: Schematic diagram of three-dimensional auxiliary cell
Note that $f$ in the above equations are elements of the viscous flux vectors $E_{\xi}, F_{\eta},$ or $G_{\zeta}$. Physical variables with one-half indices need to be interpolated from the quantities at the neighboring cell centers and are given as,

\[
\left( \frac{\partial f}{\partial y} \right)_{i+1/2,j,k} = \frac{1}{\Delta V_{i+1/2,j,k}} \left[ f_{i+1,j,k} - f_{i,j,k} + f_{i+1,j+1/2,k} + f_{i+1,j,k+1/2,k} - f_{i+1,j-1/2,k} - f_{i+1,j,k-1/2,k} \right]
\]  \hspace{1cm} \text{(3.41)}

\[
\left( \frac{\partial f}{\partial z} \right)_{i+1/2,j,k} = \frac{1}{\Delta V_{i+1/2,j,k}} \left[ f_{i+1,j,k} - f_{i,j,k} + f_{i+1,j+1/2,k} + f_{i+1,j,k+1/2,k} - f_{i+1,j-1/2,k} - f_{i+1,j,k-1/2,k} \right]
\]  \hspace{1cm} \text{(3.42)}

The evaluation of SGS fluxes follows a procedure similar to those for the viscous and diffusive fluxes

\[ f_{i+1/2,j\pm1/2,k} = \frac{1}{4} \left( f_{i,j,k} + f_{i+1,j,k} + f_{i+1,j \pm 1,k} + f_{i,j \pm 1,k} \right) \]  \hspace{1cm} \text{(3.43)}

The 3.3.4 Evaluation of Artificial Dissipation

Numerical dissipation is required in central difference schemes to avoid artificial oscillations in regions with steep gradients and to improve overall numerical stability and convergence. The form of these artificial dissipation terms depends on the order of accuracy of the numerical scheme, and must be higher-order accurate to keep its magnitude minimal. For the present case, the numerical differentiation of the flux vectors is second-order accurate in the core region of the computational domain. Accordingly, the artificial dissipation is fourth-order
accurate. The order of accuracy of the numerical scheme decreases near the physical boundary, and accordingly the artificial dissipation used is also of a lower order. The form of numerical dissipation employed in the present schemes is often a blend of second- and fourth-order dissipation terms. The second-order terms are used to prevent spurious oscillations near shock waves and in the flame zones, while the fourth-order terms are important for stability and convergence. The standard dissipation model can be written as:

$$\mathbf{AD}(\text{artificial dissipation}) = \mathbf{d}_{i+1/2,j,k} - \mathbf{d}_{i-1/2,j,k} \quad (3.44)$$

where

$$\mathbf{d}_{i\pm1/2,j,k} = \frac{\epsilon_2}{8} \frac{1}{\Delta t} \frac{\partial \mathbf{Q}}{\partial \xi} |_{i\pm1/2,j,k} - \frac{\epsilon_4}{8} \frac{1}{\Delta t} \frac{\partial^3 \mathbf{Q}}{\partial \xi^3} |_{i\pm1/2,j,k} + \frac{\epsilon_6}{8} \frac{1}{\Delta t} \frac{\partial^5 \mathbf{Q}}{\partial \xi^5} |_{i\pm1/2,j,k} \quad (3.45)$$

and $\epsilon_2, \epsilon_4, \epsilon_6$ correspond to the coefficients of the second-, fourth- and sixth-order accurate artificial dissipation terms and in the present formulation, $\Delta \xi = 1$.

Even though the standard dissipation model has been proven to be reasonably effective in many cases, there are strong motivations for reducing the numerical dissipation being produced. Also, the standard model has difficulties in hypersonic flows and reactive flows with steep discontinuities. A matrix dissipation model was constructed by Swanson and Turkel (1992) and by Jorgenson and Turkel (1993) to overcome the above difficulties. In their model,

$$\mathbf{d}_{i+1/2,j,k} = \mathcal{E}_{i+1/2,j,k} \left[ \mathbf{A} \left|_{i+1/2,j,k} \frac{\partial \mathbf{Q}}{\partial \xi} \right|_{i+1/2,j,k} - \mathcal{E}_{i+1/2,j,k} \left| \mathbf{A} \left|_{i+1/2,j,k} \frac{\partial^3 \mathbf{Q}}{\partial \xi^3} \right|_{i+1/2,j,k} \right] \quad (3.46)$$

with
\[
|\hat{\Lambda}| = M_\xi |\hat{\Lambda}_\xi| M_\xi^{-1}
\]  
(3.47)

\[
\varepsilon_{i+1/2,j,k}^{(2)} = \kappa^{(2)} \max(v_{i-1,j,k}, v_{i,j,k}, v_{i+1,j,k}, v_{i+2,j,k})
\]  
(3.48)

\[
v_{i,j,k} = \left| \frac{p_{i-1,j,k} - 2p_{i,j,k} + p_{i+2,j,k}}{p_{i-1,j,k} + 2p_{i,j,k} + p_{i+1,j,k}} \right|
\]  
(3.49)

\[
\varepsilon_{i+1/2,j,k}^{(4)} = \max\left(0, \left(\kappa^{(4)} - \varepsilon_{i+1/2,j,k}^{(2)}\right)\right)
\]  
(3.50)

\[
\kappa^{(2)} = \frac{1}{4} - \frac{1}{2}, \quad \kappa^{(4)} = \frac{1}{64} - \frac{1}{32}
\]  
(3.51)

The matrix dissipation model causes the central-difference scheme to closely resemble an upwind scheme near flow discontinuities and have the total variation diminishing (TVD) property, which prevents the occurrence of spurious oscillations. The terms \( M_\xi \) and \( M_\xi^{-1} \) are the right and left eigenvectors matrices, which diagonalize \( A \), where \( A = \partial E_\xi / \partial Q \).

The eigenvalues of the flux Jacobian matrix \( A \) are:

\[
\lambda_1 = \lambda_2 = \lambda_3 = \lambda_6 = U; \quad \lambda_{4,5} = U \pm C
\]  
(3.52)

where \( U = \tilde{S}_\xi u + \tilde{S}_\xi v + \tilde{S}_\xi w \) and \( C = \frac{\tilde{S}_\xi}{\tilde{\xi}} \). The term \( \hat{\Lambda}_\xi \) in Eq. (3.47) represents the modified diagonal matrix of eigenvalues \( \hat{\Lambda}_\xi = \text{diag}(\tilde{\lambda}_1, \tilde{\lambda}_2, \tilde{\lambda}_3, \tilde{\lambda}_4, \tilde{\lambda}_5, \tilde{\lambda}_6) \) to avoid zero eigenvalues. The modified eigenvalues are:

\[
\tilde{\lambda}_1 = \tilde{\lambda}_2 = \tilde{\lambda}_3 = \tilde{\lambda}_6 = \max(|\lambda_i|V_\sigma); \quad \tilde{\lambda}_{4,5} = \max(|\lambda_{4,5}|V_\sigma)
\]  
(3.53)
where $\sigma$ is the spectral radius of the flux Jacobian matrix $A$. We use $V_f = 0.025$ and $V_n = 0.25$ (Zingg et al., 2000) for the present study. In evaluating $|\hat{A}| = M_s \hat{A}_s M_s^{-1}$, Roe Average is used to deal with large density-gradients.

The scalar dissipation model first developed by Jameson et al. (1981) is a simpler version of the matrix dissipation model. In the scalar dissipation model, the modified eigenvalues are given as:

$$\tilde{\lambda}_1 = \tilde{\lambda}_2 = \tilde{\lambda}_3 = \tilde{\lambda}_4 = \tilde{\lambda}_5 = \tilde{\lambda}_6 = \sigma \quad (3.54)$$

Then Eq. 3.46 can be written as:

$$d_{i+1/2,j,k} = \epsilon_{i+1/2,j,k}^{(2)} \sigma_{i+1/2,j,k} \frac{\partial Q}{\partial \xi} - \epsilon_{i+1/2,j,k}^{(4)} \sigma_{i+1/2,j,k} \frac{\partial^3 Q}{\partial \xi^3} \quad (3.55)$$

The matrix dissipation model is more generalized and accurate, although the computation of these matrices at every grid-cell requires more computational time and memory.

The second-difference dissipation term given in Eq. 3.46 and Eq. 3.55 is nonlinear. Its purpose is to introduce an entropy-like condition and to suppress oscillations in the neighborhood of shock discontinuities. This term is small in the smooth portion of the flow field. The switch $\nu_{i,j,k}$ is important near discontinuities, since there are large pressure-gradients across them. For resolving flames, however, this switch is changed to include temperature- or density-gradients, as pressure may still be uniform across the flame. The fourth-order term is basically linear and is included to damp high-frequency modes and allow the scheme to approach a steady state. Only this term affects the linear stability of the scheme. Near discontinuities it is reduced to zero.
3.4 Temporal Integration: Runge-Kutta Scheme

A fourth-order Runge-Kutta (RK4) explicit scheme is used to solve the governing equations, due to its higher temporal accuracy and relatively larger CFL number. This scheme has been widely used in the simulation of turbulent flows (Hsieh and Yang, 1997; Apte and Yang, 2001), on account of its low memory requirement, low dissipation, and high order accuracy. The governing conservation equation (Eq. 3.29) in the general coordinates can be rewritten as:

\[
\Delta \mathbf{Q} = \mathbf{H} \cdot \Delta t - \Delta t \left[ (\mathbf{E}_x^j - \mathbf{E}_x^{j+1/2})_{i,j-1/2,k} + (\mathbf{F}_y^j - \mathbf{F}_y^{j+1/2})_{i,j-1/2,k} + (\mathbf{G}_z^j - \mathbf{G}_z^{j+1/2})_{i,j,k-1/2} \right] (3.56)
\]

Using the four-stage Runge-Kutta scheme, each temporal-integration is completed through four consecutive intermediate steps as given below.

\[
Q_0 = Q^n
\]
\[
Q_1 = Q_0 + \alpha_1 \Delta t \cdot R(Q_0)
\]
\[
Q_2 = Q_0 + \alpha_2 \Delta t \cdot R(Q_1)
\]
\[
Q_3 = Q_0 + \alpha_3 \Delta t \cdot R(Q_2)
\]
\[
Q^{n+1} = Q_0 + \Delta t \cdot R(Q_3)
\]

where

\[
R(Q) = \mathbf{H} - \left[ (\mathbf{E}_x^j - \mathbf{E}_x^{j+1/2})_{i,j-1/2,k} + (\mathbf{F}_y^j - \mathbf{F}_y^{j+1/2})_{i,j-1/2,k} + (\mathbf{G}_z^j - \mathbf{G}_z^{j+1/2})_{i,j,k-1/2} \right] (3.57)
\]

Superscripts ‘n’ and ‘n+1’ stand for the solution at the ‘nth’ and ‘n+1 th’ time steps, respectively. Evaluation of the \( \Delta \mathbf{Q} = Q^{n+1} - Q^n \) term in Eq. (3.29) is performed as explained above. The coefficients \( \alpha_1, \alpha_2, \text{ and } \alpha_3 \) can be varied to obtain a variety of
schemes with different stability properties. The standard four-stage scheme has the following values (Jameson, 1983):

\[ \alpha_1 = \frac{1}{4}, \ \alpha_2 = \frac{1}{3}, \ \alpha_3 = \frac{1}{2} \]  (3.59)

In order to ensure stability and convergence of the explicit scheme for reacting flows, the stiff source terms arising from chemical reactions in the gas phase are treated in a semi-implicit manner. The details of the source-term treatment appear in Appendix A. In order to enhance numerical efficiency and minimize the complexity arising from the irregular shape of the computational mesh, a curvilinear coordinate transformation of the governing equations is employed so that the grid spacing in the transformed domain is unity.

3.5 Parallel Computing Strategies

3.5.1 Parallel Architecture

The parallel computing architecture can be classified as four categories depending on whether there is one or several of instruction streams and data streams: Single Instruction Single Data (SISD), Multiple Instructions Single Data (MISD), Single Instruction Multiple Data (SIMD), and Multiple Instruction Multiple Data (MIMD). The most widely used computing architecture is the Multiple Instruction Multiple Data (MIMD) system as indicated schematically in Fig. 3.4. In this configuration, each processor has its own data set and also a set of instructions to follow. The processors
work independent of each other on these data sets. They only communicate at some point
during the computation where the data set and the results obtained are shared by two or
more processors. MIMD-type computers include IBM SP-2, Cray T3E, CM5 and
Beowulf Clustered computers.

For the SIMD or MIMD systems, it is usually necessary to exchange data between
processors. This can be done in two ways: 1) Shared Memory systems and 2) Distributed
memory systems or Message Passing Interconnection (MPI) Network. The shared
memory system consists of global address space, which is accessible by all processors
and thus memory is shared among the processors. One processor can communicate with
other processors by writing into or reading from the global memory. This architecture
inherently solves the inter-processor communication problem, but introduces bottleneck
problems created from simultaneous access to the memory by more than one processor.
In the distributed memory systems, each processor has its own local (or private) memory
and the global/shared memory is absent. The processors are connected externally to
switches and a network of wires to allow communications among them. The efficiency of
these systems is based on the communication time required among the processors. The
architecture has several advantages such as hardware compatibility, functionality, and
performance. The only drawback, however, is the enormous responsibility placed on
software programmers. The programmers must provide an efficient scheme to distribute
the data and set of instructions, and also explicitly provide the instruction set for
communications among the various CPUs. This requires reconstruction of the numerical
algorithm and synchronization of the processors for efficient parallel computing.
3.5.2 Beowulf Cluster Parallel Computers

A Beowulf system is a multi-computer high-performance architecture used for parallel computations. In a Beowulf system, one server computer and many other client computers are connected together via high-speed networks. It is a distributed memory MIMD system, built primarily using commodity hardware components such as any PC capable of running the free operating system Linux, standard Ethernet adapters, and switches. The primary advantage of a Beowulf system is its high performance/price ratio in comparison with other dedicated MPP systems.

The first Beowulf system was built by Donald Becker in 1994 (Beowulf, 2002) and it consisted of 16 486DX4-100MHz machines, each with 16 MB of memory. An
important characteristic of the Beowulf clusters is compatibility. The changes in hardware, including the node and network system, will not affect the programming model. A Beowulf system also takes the advantage of commodity software such as the Linux operating system, Message Passing Interface (MPI), and other available open-source software. With the maturity and robustness of Linux, GNU software and the standardization of message passing via PVM or MPI, users have a guarantee that the programs they write will run on future Beowulf clusters.

The Beowulf system operated at Dr. Vigor Yang’s group consists of three Intel-based and one AMD-based Linux clusters. The parallel computing system presently includes 510 Pentium II/III/IV and 160 AMD Opteron processors, as shown in Fig. 3.5. These computers are connected with nine 100M Fast Ethernet switches and four gigabit switches in a tree topology to facilitate parallel processing. The cumulative internal memory is 210 GB, and the total disc storage is 5 TB. This system can sustain 1200 gigaflops total peak performance, providing substantial number-crunching capabilities for large-scale computations. Parallel operation is accomplished by implementing the MPI (Message Passing Interface) library. Representative parallel performance of CFD algorithms on 120 Pentium processors with Fast Ethernet interconnection is about 80-85% efficient. In addition to those high-performance computing systems, two Pentium workstations with high-speed graphics cards are used to provide 3D visualization capabilities. This allows researchers to explore 3D flow structures obtained from numerical calculations in real time.
3.5.3 Domain Decomposition

Explicit time stepping numerical scheme (RK4) is applied in the current study and only the neighboring data instead of the whole computational domain data are required during the calculation of a variable in each cell. This implies weak data dependence. This application is best suited for domain-decomposition technique, which is also a common implementation for a distributed-memory computer system. In the field of computational fluid dynamics (CFD), it is generally referred to as mesh partitioning and is based on the geometric substructure of the computational domain.

In a domain-decomposition technique, the physical domain is divided into several sub-domains. Variables in each cell are updated to next time step simultaneously. In order to calculate the spatial derivatives near the processors’ domain boundaries, ghost cells are introduced. These cells are located in the overlap regions of sub-domains.

Figure 3.5: Parallel computing facility at Penn State
Figure 3.6 shows an example of two-dimensional ghost cells with a fourth-order spatial accuracy. Because the variables in the ghost cell are updated in another sub-domain, message passing is required to synchronize data between different sub-domains. Figure 3.7 shows an example of the inter-processor communication. Overlapped regions, where information must be obtained from neighboring processors, exist on each side of the local domain. Likewise, these processors would also need to send some data to their neighbors. To evaluate viscous fluxes at that corner, the data at the eight corners of the overlapped regions are exchanged with those at the diagonally opposite corners. The communication overhead is directly proportional to the volume-to-surface ratio of that sub-domain. Maximizing the computation-to-communication ratio, i.e. increasing the thickness of each nodes, leads to higher parallel execution efficiency.

Figure 3.6: Schematic of ghost cells in a two-dimensional domain with fourth-order accuracy in spatial discretization
For the acceptance and successful use of CFD simulations, it is essential to achieve sufficient level of reliability. The theoretical formulation and numerical scheme described in the preceding sections were first validated with several model problems. Various aspects of the analysis were examined carefully and compared with existing experimental data. In the current study, three cases including turbulent flow over a flat plat, heat transfer in convergent-divergent nozzle, and a two-dimensional oblique shock

![Diagram of data communication with corner and side communication between face neighbors and diagonally opposite corners.](image)

**Figure 3.7:** An example of the data communication with an east surface in three-dimensional simulation (second-order spatial accuracy)

### 3.6 Verification and Validation

For the acceptance and successful use of CFD simulations, it is essential to achieve sufficient level of reliability. The theoretical formulation and numerical scheme described in the preceding sections were first validated with several model problems. Various aspects of the analysis were examined carefully and compared with existing experimental data. In the current study, three cases including turbulent flow over a flat plat, heat transfer in convergent-divergent nozzle, and a two-dimensional oblique shock
wave are presented to test various aspects of the numerical methods. These validation cases are chosen because of their relevance to the present topic of investigation.

3.6.1 Turbulent Flow over a Flat Plate

Since the nozzle erosion phenomenon is prominently dictated by the near-surface processes, the accuracy of the turbulence model close to the surface should be carefully assessed. To establish confidence in the turbulence modeling, the two-layer model was first used to calculate near-wall flow properties for a flat-plate boundary layer. The calculations are validated against the available experimental data (Wieghardt and Tillman, 1951; Coles and Hirst, 1969; Patel et al., 1985). The physical domain is 2.47 m in length. The computational grid is 136 x 51 in the x and y directions, respectively. The grid is clustered near the surface ($y^+ \sim 1$), to capture the turbulent boundary-layer flow characteristics. To accelerate the convergence rate of the compressible flow solver, the free stream Mach number was set to 0.20 ($u = 68.9$ m/s). The inlet flow temperature and pressure are 298 K and 1 atm, respectively.

Figure 3.8 shows the predicted skin friction coefficient ($C_f$) in comparison with experimental data. Figures 3.9 and 3.10 show the variation of $y^+$ (= $yu_c/v$) with $u^+$ (= $u/u_c$) at different axial locations. The predicted and measured profiles of turbulent kinetic energy ($k^+ = k/u_c^2$) are shown in Fig. 3.11. The corresponding data was compiled by Patel et al. (1985). The calculations exhibit an excellent agreement with the available experimental data, indicating the high fidelity of the current numerical model, even very close to the surface.
Figure 3.8: Comparison of predicted skin-friction coefficient with experimental data

Figure 3.9: Comparison of predicted velocity profile with experimental data (x = 1.237 m)
Figure 3.10: Comparison of predicted velocity profile with experimental data (x = 2.28 m)

Figure 3.11: Comparison of predicted turbulent kinetic energy profiles with experimental data
3.6.2 Heat transfer in convergent-divergent nozzle

To accurately simulate the material erosion of a convergent-divergent nozzle, it is essential to predict the correct variation of the heat flux at the nozzle surface. An extensive numerical study was conducted for various nozzle geometries to benchmark the predicted heat-transfer coefficients. In particular, the nozzle configuration of Back et al. (1964) was considered, and the calculated heat-transfer coefficients were compared with the measurements. Figure 3.12a shows the nozzle configuration used by Back et al. (1964) for their experiments. The axisymmetric computational grid used is 151 x 71 in the \( x \) and \( r \) directions, respectively. The grid was clustered at the surface (\( y^+ \sim 1 \)) to resolve the near-wall flow properties.

The nozzle flow inlet conditions are summarized in Table 3.1. An isothermal temperature boundary was employed, since the nozzle surface was cooled in the experiments. The nozzle wall temperatures were available from the measurements (Back et al., 1963). A standard value of 0.89 was considered for the recovery factor (\( R \)). The chamber pressure (\( p_i \)) and temperature (\( T_i \)) are specified at the nozzle inlet and the velocity at the exit is supersonic.

Table 3.1: Inlet conditions for simulating experiments by Back et al. (1964)

<table>
<thead>
<tr>
<th>No.</th>
<th>( p_i )</th>
<th>( T_i )</th>
<th>( \gamma )</th>
<th>( T_{wall} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.517 MPa (75 psi)</td>
<td>840 K</td>
<td>1.38</td>
<td>415 K</td>
</tr>
<tr>
<td>2</td>
<td>1.752 MPa (254 psi)</td>
<td>840 K</td>
<td>1.38</td>
<td>600 K</td>
</tr>
</tbody>
</table>
Figure 3.12b shows the comparison between calculated and measured values of the wall heat-transfer coefficients. The calculations are much better than the prediction obtained from the Bartz correlation (1957), which is widely used for estimating the convective heat transfer in rocket-nozzle flows. The model predictions match better at the nozzle throat, than at the entrance. This is attributed to the use of isothermal temperature boundary. In reality, even if the nozzle wall is cooled, the surface temperature varies slightly along the axial length and peaks at the nozzle throat due to the maximum heat transfer in the throat region. Since a constant wall temperature was used throughout the axial length, the heat transfer coefficient agreement at some axial locations is only reasonable. Another thing that affects calculation results is the assumption of constant recovery factor. It is speculated that in the region of high acceleration, recovery factor may decrease and reach a minimum of about 0.75 in the throat region (Keswani, 1984). A recovery factor lower than 0.89 in the throat region will improve the predictions, since the heat transfer coefficient will slightly increase based on the following equations,

\[
T_{aw} = T + R \frac{u^2}{2c_p};
\]

\[
h_g = q^a / (T_{aw} - T_{wall})
\]

where \(T_{aw}\), the adiabatic wall temperature, decreases with the recovery factor. This in turn increases the heat-transfer coefficient.
Figure 3.12: (a) Convergent-divergent nozzle configuration used by Back et al. (1964) (b) comparison of calculated and measured heat transfer coefficients
3.6.3 Oblique Shock Wave

The purpose of this simulation was to test the ability of the numerical scheme to capture steep gradients in a supersonic flow domain. The nozzle erosion process may encounter steep concentration gradients at the surface. The artificial dissipation implemented using the TVD feature enables the numerical scheme to capture such gradients or shock waves accurately. Figure 3.13 shows the schematic of a two-dimensional oblique shock wave under investigation. The supersonic inflow Mach number is 2.0 and the turn angle is $10^\circ$. An ideal gas is considered, with the ratio of heat capacity $\gamma$ as 1.4.

The snapshots of temperature and pressure fields are shown in Fig. 3.14. The present scheme clearly shows its capability of capturing a thin oblique-shock wave, without much numerical dissipation. The results based on theoretical oblique-shock relations and the numerical predictions are summarized in Table 3.2. The agreement with the predictions from the oblique-shock relations is excellent, with a relative error of less than 1%.

![Figure 3.13: Schematic diagram of two-dimensional oblique shock wave](image)
Table 3.2: Results from theory and numerical simulations on oblique shock wave

<table>
<thead>
<tr>
<th></th>
<th>$M_2$</th>
<th>$p_2/p_1$</th>
<th>$T_2/T_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>theoretical</td>
<td>1.64</td>
<td>1.70</td>
<td>1.170</td>
</tr>
<tr>
<td>numerical</td>
<td>1.65</td>
<td>1.71</td>
<td>1.172</td>
</tr>
</tbody>
</table>

$M_1 = 2.0$, turn angle = $10^\circ$, shock angle = $39.31^\circ$

Figure 3.14: Snapshots of flowfields of a 2D oblique shock (a) static temperature contour (b) static pressure contours
Chapter 4

Chemical Erosion of Graphite/Carbon-Carbon Nozzle Materials

4.1 Introduction

Graphite and carbon-carbon composites, which have excellent thermophysical properties as well as low densities, are widely used as materials for rocket-nozzle inserts. These materials are relatively low cost and possess the unique characteristic of strengthening as temperature rises (Anon, 1975). The hostile thermochemical environment imposed by the combustion products of solid propellants, however, causes undesirable erosion of these materials. The chemical erosion is caused due to the heterogeneous chemical reactions that occur between the nozzle material and oxidizing species of H₂O, OH, and CO₂.

Different types of graphite such as polycrystalline graphite (also known as bulk or artificial graphite) and pyrolytic graphite have been employed over the years. The former is relatively a low strength and brittle material, susceptible to thermally-induced cracks. It is often used in some sections of small test nozzles (Anon, 1975). The latter is high-density (1.9-2.2 g/cm³) anisotropic material, formed by layer-by-layer deposition. The thermophysical properties of nozzle materials are summarized in Table 1.1 of Chapter 1. Pyrolytic graphite coatings on a polycrystalline-graphite substrate have been successfully test fired in solid rocket motors with high-performance propellants (Payne, 1974). The carbon-carbon composites are a class of high strength and low density (1.6-2.0 g/cm³)
materials. In their nomenclature, the first carbon represents the reinforcement material and the second carbon identifies the matrix that binds the reinforcement. For composites, the orientation of fibers can be two-, three-, or even four-dimensional called as 2D, 3D, and 4D carbon-carbon, respectively. Some of the advantages of using the pyrolytic graphite and carbon-carbon materials result from the facts that the erosion causes less change from the initial contour, less surface roughness in the eroded condition, and no char layer.

This chapter presents and discusses the results obtained from comprehensive theoretical/numerical framework which utilizes the recent advances in chemical kinetics, turbulence modeling, and numerical algorithm. The formulation takes into account detailed thermofluid dynamics for a multi-component chemically reacting flow, heterogeneous reactions at the nozzle surface, and condensed-phase energy transport, as described in the previous chapters. Many approximations and assumptions employed in the previous studies have been relaxed. The model has been validated by comparing the calculated erosion rates with four different sets of experimental data. In addition, a systematic study of the dependence of nozzle erosion on motor operating conditions, chemical kinetics, propellant compositions, and nozzle material properties has been carried out.

### 4.2 Modeling Inputs

The gas-phase and heterogeneous chemical kinetics are detailed in Sections 2.2 and 2.3.1, respectively, of Chapter 2. The multi-component flow consists of species of
H₂O, CO₂, CO, HCl, N₂, H₂, OH and H. In the case of a metallized propellant, Al₂O₃ is also present in addition to the aforementioned gaseous species. The gas-phase treatment includes a water-gas shift reaction represented by a one-step global reversible reaction,

\[
\frac{k_f}{k_r} \quad \text{CO} + \text{H}_2\text{O} \quad \leftrightarrow \quad \text{CO}_2 + \text{H}_2
\]  

(R5)

The rates of the forward and reverse reactions are obtained from Bustamante et al. (2004, 2005). To simulate the chemical erosion three heterogeneous chemical reactions considered at the nozzle surface are,

\[
\text{C}(s) + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]  

(R6)

\[
\text{C}(s) + \text{CO}_2 \rightarrow 2\text{CO} \]  

(R7)

\[
\text{C}(s) + \text{OH} \rightarrow \text{CO} + \text{H} \]  

(R8)

The kinetics data associated with these surface reactions appears in Table 2.4. The kinetics data were chosen carefully by considering various sources and is the best available at this stage. The kinetics schemes assembled by Bradley et al. (1984), Libby and Blake (1981), and King (1971), respectively meant for graphite power, carbon, and bulk graphite were compared and the mass burning rates did not differ much in the temperature range of 2000-3000 K. In practice, the chemical kinetics will depend on the type of graphite and associated manufacturing processes. In the current work, the chemical kinetics rates for C-C and graphite are assumed to be same. However, different material densities and thermophysical properties were used. The thermophysical
properties for carbon-carbon as a function of temperature were adopted from Taylor et al.

4.3 Nozzle Configurations and Boundary Conditions

Figure 4.1 shows the baseline nozzle configuration considered here, similar to the experiments detailed by Evans et al. (2007a) for the study of the erosion of graphite (G-90) nozzle material. Only the upper half is simulated due to the flow symmetry. Figure 4.2 shows the computational grid at a particular azimuthal location of the axisymmetric configuration. The computational domain of the rocket nozzle is divided into 141 x 80 grid points in the $x$ and $r$ directions, respectively. The grid is stretched in the radial direction and is very fine close the surface for resolving the near-surface phenomena with high fidelity. The centers of the computational cells adjacent to the nozzle surface are located at $y^+ < 1$ in order to capture accurately the near-wall turbulence. Numerically, $Y_{ls}$ in Eq. (2.25) amounts to the species concentration at the center of the first computational cell from the surface. Grid independence studies were carried out for all the nozzle geometries to ensure the independence of the results on the chosen grid. For parallel processing the computational domain was divided in to 28 sub-domains along the axial length, with each sub-domain calculations on a different processor.
The incoming flow consists of the combustion products of either metallized or non-metallized AP/HTPB composite propellants. The chamber pressure \( (p_t) \) and temperature \( (T_t) \) are specified at the nozzle inlet. The velocity at the exit is supersonic, and no physical boundary condition needs to be prescribed at that location. Table 4.1 lists the species mass fractions at the inlet obtained from chemical equilibrium calculations (Gordon and McBride, 1994) at \( p_t = 6.9 \) MPa. Six different chamber pressures and their
corresponding temperatures are used to study the effect of motor operating conditions on the nozzle erosion rate. The species mass fractions remain nearly constant in the pressure range of 6.9 - 45 MPa, except for a noticeable drop in OH at high pressures. Accordingly, OH species was not considered for the chamber pressures above 10 MPa because of its negligible concentration. At a given pressure, the metallized propellant leads to a higher chamber temperature and lower mass fractions of oxidizing species as compared to its non-metallized counterpart. Since a single-phase formulation was used, Al$_2$O$_3$ was treated as part of the homogeneous mixture. The ambient temperature was taken as 300 K. Table 4.2 summarizes the experimental studies used for validating the current model.

Table 4.1: Nozzle Inlet Flow Conditions*

<table>
<thead>
<tr>
<th></th>
<th>non metallized AP/HTPB</th>
<th>metallized AP/HTPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{H,O}$</td>
<td>0.29</td>
<td>0.09</td>
</tr>
<tr>
<td>$Y_{CO_2}$</td>
<td>0.22</td>
<td>0.02</td>
</tr>
<tr>
<td>$Y_{CO}$</td>
<td>0.11</td>
<td>0.23</td>
</tr>
<tr>
<td>$Y_{H_2}$</td>
<td>0.003</td>
<td>0.01</td>
</tr>
<tr>
<td>$Y_{OH}$</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>$Y_{H}$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$Y_{N_2}$</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>$Y_{Al_2O_3}$</td>
<td>0.00</td>
<td>0.34</td>
</tr>
<tr>
<td>$Y_{HCl}$</td>
<td>0.267</td>
<td>0.20</td>
</tr>
<tr>
<td>$p_i$ (MPa)</td>
<td>6.9, 10, 15, 25, 35, 45</td>
<td>6.9, 10, 15, 25, 35, 45</td>
</tr>
<tr>
<td>$T_i$ (K)</td>
<td>3000, 3020, 3040, 3050, 3060, 3065</td>
<td>3500, 3530, 3550, 3560, 3570, 3575</td>
</tr>
<tr>
<td>$T_{amb}$ (K)</td>
<td>300</td>
<td>300</td>
</tr>
</tbody>
</table>

*graphite density = 1.92 g/cc, average nozzle material thickness = 4.8 cm, throat radius = 0.5715 cm
### Table 4.2: Experimental Studies of Nozzle Erosion

<table>
<thead>
<tr>
<th>experimental study</th>
<th>nozzle material</th>
<th>density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geisler (1978)</td>
<td>bulk graphite</td>
<td>1.83</td>
</tr>
<tr>
<td>Borie et al. (1989)</td>
<td>carbon-carbon</td>
<td>1.90</td>
</tr>
<tr>
<td>Evans et al. (2007a; 2008)</td>
<td>G-90</td>
<td>1.92</td>
</tr>
</tbody>
</table>

### 4.4 Results and Discussions

The theoretical/numerical framework described in the preceding chapter was implemented to simulate the chemical erosion of nozzle material in practical rocket-motor environments. The turbulent flow development in the nozzle is studied first at the steady-state condition. Figure 4.3 shows the distributions of the temperature, pressure, axial velocity, and Mach number along the centerline for inlet conditions of \( T_i = 3000 \text{ K} \) and \( p_i = 6.9 \text{ MPa} \). The nozzle surface is treated as an adiabatic wall without including heterogeneous chemical reactions. The calculations exhibit good agreement with the corresponding one-dimensional results for an isentropic flow with \( \gamma = 1.2 \). The Mach number increases from 0.28 at the inlet to 2.3 at the exit, but the pressure and temperature decrease monotonically from values slightly less than the chamber conditions to 0.49 MPa and 1890 K, respectively. Figure 4.4 shows the entire flowfield in terms of temperature, pressure, Mach number, and axial velocity. The flowfield is predominantly one-dimensional except in the thin layer near the surface.

The effect of the water-gas shift reaction (R5) in the gas phase is also studied. Figure 4.5 shows the species-concentration fields including only this reaction, with all other conditions unchanged. The mass fractions of \( \text{H}_2\text{O} \) and CO increase marginally near
the nozzle entrance, and those of CO$_2$ and H$_2$ decrease accordingly. The concentrations are almost unchanged downstream of the throat. This may be attributed to the high activation energy associated with the water-gas shift reaction, which necessitates high temperature. In the downstream region, the relatively lower temperature restricts the reaction. The most probable gas-phase reactions thus do not modify the chemical equilibrium significantly. Furthermore, since the water-gas shift reaction is nearly thermally neutral, the temperature field is almost unaffected.

Figure 4.3: Distributions of temperature, pressure, axial velocity, and Mach number along the nozzle centerline (non-metallized propellant, $T_i = 3000$ K, $p_i = 6.9$ MPa, no surface reactions, adiabatic wall)
Figure 4.4: Distributions of temperature, pressure, axial velocity, and Mach number in the nozzle interior (non-metallized propellant, $T_t = 3000$ K, $p_t = 6.9$ MPa, no surface reactions, adiabatic wall)

Figure 4.5: Distributions of mass fractions of $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{CO}$, and $\text{H}_2$; effect of water-gas shift reaction in the gas phase (non-metallized propellant, $T_t = 3000$ K, $p_t = 6.9$ MPa, no surface reactions, adiabatic wall)
To simulate the erosion of nozzle material, the three heterogeneous reactions, (R6-R8), along with the energy balance, Eq. (2.32), are implemented at the nozzle surface. Figure 4.6 shows the calculated temperature and species-concentration fields for the case of non-metallized AP/HTPB propellants. The incoming flow temperature and pressure are \( T_i = 3000 \) K and \( p_i = 6.9 \) MPa, respectively, and the outer boundary of the nozzle material is assumed to be adiabatic. As a consequence of surface reactions, the oxidizing species CO\(_2\), H\(_2\)O, and OH are consumed to form CO, H\(_2\), and H. Concentration gradients then form near the wall. The slight decrease in the N\(_2\) concentration near the surface is attributed to the wall blowing effect associated with the material erosion. Compared with the non-reactive case with an adiabatic wall (Fig 4.4), the surface temperature is considerably reduced due to the conductive heat transfer to the nozzle material. The endothermicity of surface reactions also helps lower the surface temperature. The thickness of the species-concentration boundary layer (\( \delta_c \)) is greater than its velocity counterpart, and can be estimated using a simple order-of-magnitude analysis as follows:

\[
\delta_c \sim \sqrt{D_{\text{eff}} \tau_f}
\]  

(4.1)

where \( D_{\text{eff}} \) is the effective mass diffusivity on the order of \( 10^{-2} \) m\(^2\)/s. The flow residence time \( \tau_f \) is approximated as the ratio of the nozzle length to the average axial velocity, and has a value of about 0.1 ms. Based on Eq. (4.1), the concentration boundary layer thickness thus becomes 1 mm, close to that observed in Fig. 4.6. A tilted view of distributions of mass fractions of H\(_2\)O and CO\(_2\) is shown in Fig. 4.7, in order to highlight the concentrations at nozzle surface.
Figure 4.8 shows the distribution of the erosion rate along the entire length of the nozzle for non-metallized AP/HTPB with $T_i = 3000$ K and $p_i = 6.9$ MPa. Two points should be noted. First, the erosion rate reaches its maximum (0.124 mm/s) near the throat, mainly due to the enhanced heat transfer in that region. Second, the inclusion of the water-gas shift reaction has a negligible effect on the calculated erosion rate. Part of the reason, as explained earlier, is attributed to high activation energy of the water-gas shift reaction. The other reason may be linked to the fact that flow residence time ($\sim 0.1$ ms) in the nozzle may not be sufficient for gas-phase reactions to occur. It has been recently reported that the residence time required by the reactants to undergo the water-gas shift reaction is about 0.09 s (Chen et al., 2008).

As such, the remaining computations in the present study were performed by assuming a frozen flow in the gas phase. Although the high temperature prevails in the upstream region of the nozzle throat, the convective heat transfer is relatively small because of low flow velocity. In the downstream region, however, the heat transfer is reduced due to the low temperature condition resulting from the flow expansion. In Fig. 4.8, the small wiggle in the erosion-rate profile arises from the sharp change in the nozzle contour at the beginning of the throat. A close-up view of throat region, as shown in Fig. 4.9, makes this point clear. Such small irregularities in erosion-rate profiles were not observed in other cases with smooth nozzle contours, as seen in Fig. 4.10.
Figure 4.6: Distributions of temperature and mass fractions of H$_2$O, CO$_2$, OH, CO, H$_2$, H, and N$_2$ in the nozzle interior (non-metallized propellant, $T_i = 3000$ K, $p_i = 6.9$ MPa, with surface reactions, conductive wall)
The dependence of the erosion rate on the outer boundary condition of the nozzle material was also examined, since this condition affects the nozzle surface temperature and associated chemical reaction rates. Table 4.3 lists three different outer boundary conditions considered herein. The baseline adiabatic condition was relaxed by allowing convective heat transfer at the outer boundary. The heat transfer coefficient $h_{amb}$, estimated from standard correlations for turbulent flows over a flat plate, falls in the range of 100-500 W/m-K² depending on the specific configuration of the nozzle assembly and the vehicle speed. The calculated erosion rate decreases slightly with enhanced heat transfer at the outer boundary. All the results presented subsequently were obtained based on the adiabatic outer boundary of the nozzle material, following the approach employed by most existing models.

Figure 4.7: Tilted view of distributions mass fractions of H₂O and CO₂ to highlight concentrations at nozzle surface (non-metallized propellant, $T = 3000$ K, $p = 6.9$ MPa, with surface reactions, conductive wall)
Figure 4.8: Nozzle erosion rate with and without water-gas shift reaction in the gas phase; non-metallized propellants

Figure 4.9: Close-up view of throat region for baseline nozzle configuration
Figure 4.10: (a) Erosion rate profile for smooth nozzle contour (b) close-up view of throat region
Table 4.3: Effect of Outer Boundary Condition of Nozzle Material on Erosion Rates

<table>
<thead>
<tr>
<th>outer boundary condition</th>
<th>erosion rate at throat (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>adiabatic</td>
<td>0.124</td>
</tr>
<tr>
<td>$h_{amb} = 300 \text{ W/m}^2$, $T_{c,o} = 600 \text{ K}$</td>
<td>0.116</td>
</tr>
<tr>
<td>$h_{amb} = 500 \text{ W/m}^2$, $T_{c,o} = 600 \text{ K}$</td>
<td>0.098</td>
</tr>
</tbody>
</table>

* $T_{amb} = 300 \text{ K}$, $T_i = 3000 \text{ K}$, $p_i = 6.9 \text{ MPa}$, non-metallized propellant

Figure 4.11 shows the nozzle erosion rate caused by each of the three oxidizing species H$_2$O, OH, and CO$_2$ for non-metallized case. Based on the kinetic data employed in the current work, the most detrimental species is H$_2$O, followed by much lesser contributions from OH and CO$_2$, in that order. At higher chamber pressures and temperatures, the OH concentration reduces to a very small value and its contribution can be neglected in comparison with H$_2$O. Figure 4.12 shows the distribution of heat flux along the nozzle surface for two different chamber pressures, 6.9 MPa and 10 MPa. As expected, the heat-transfer rate rises with increasing pressure and attains a maximum value in the throat region. The distribution of the erosion rate mimics that of the surface heat flux along the entire nozzle length, indicating a direct correlation between the two quantities.
Figure 4.11: Nozzle erosion rate due to various graphite-oxidizing species; non-metallized propellants

Figure 4.12: Distribution of heat flux at the nozzle surface; non-metallized propellants
The radial distributions of the temperature and oxidizing-species concentrations are instrumental in identifying the mechanisms of nozzle material erosion. Figure 4.13 shows the radial distributions of temperature at the nozzle throat for non-metallized and metallized propellants. The temperature varies from 2710 K at the centerline to 2285 K at the surface for the former case, and the corresponding temperatures for the latter case are 3170 K and 2820 K. Figures 4.14 and 4.15 show the radial distributions of the species mass fractions at the nozzle throat for the two propellants. The finite amounts of H₂O and CO₂ and the relatively low temperature (~2285 K) at the surface for the non-metallized case indicate that the recession is kinetically controlled for these species. The situation for the metallized propellant is quite different. The concentrations of the three oxidizing species are nearly zero at the nozzle surface because of the relatively high temperature (~2820 K). Thus, the erosion rate is governed by the diffusion-controlled process. Since the OH mass fraction reduces to zero at the surface for both the propellants, nozzle erosion is diffusion controlled with respect to OH, a phenomenon that can be attributed to the fast reaction between C₆(s) and OH. The transition from the kinetics- to diffusion-controlled mechanism occurs at a surface temperature of around 2800 K. Above this temperature, the reaction rates become sufficiently high to rapidly consume all the oxidizing species diffusing towards the surface. The transition temperature is highly dependent on the chemical kinetics involved and the species concentrations considered at the nozzle inlet, and is applicable only to the current problem scenario.
Figure 4.13: Radial distributions of temperature at the nozzle throat

Figure 4.14: Radial distributions of species at the nozzle throat; non-metallized propellant
The effect of the chamber pressure on nozzle erosion was studied. Figure 4.16 shows the erosion-rate profiles for metallized and non-metallized propellants at a chamber pressure of 25.0 MPa. The corresponding chamber temperatures were 3560 K and 3050 K, respectively. The significant difference between the two cases results from different mechanisms that control the recession rate, i.e., chemical kinetics for the non-metallized case vs. species diffusion for the metallized case. Even though the flame temperature of the metallized propellant is much higher than its non-metallized counterpart, the erosion rate for the former is lower. This can be attributed to the lower concentrations of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) (see Table 4.1) in the metallized case due to the formation of alumina, which consumes the majority of the free molecular oxygen.

Figure 4.17 shows the linear variation of the graphite erosion rate at the nozzle throat with the chamber pressure. Since the convective heat-transfer rate increases with pressure, there is a corresponding rise in the erosion rate. At a chamber pressure greater...
than ~10 MPa, the erosion rate for the non-metallized case is higher than that for the metallized one. Thus, at high chamber pressures, the erosion rate shows a stronger correlation with the concentrations of the oxidizing species than with the flame temperatures.

Figure 4.16: Nozzle erosion rates for metallized and non-metallized propellants at $p_t = 25$ MPa
The increased densities of the oxidizing species at high pressures also contribute to the severity of the nozzle erosion through their influence on rates of the heterogeneous surface reactions. Figure 4.18 indicates that the mass fractions of H$_2$O at the surface of the nozzle throat are 0.134 and 0.099 for two different chamber pressures of 6.9 and 15 MPa, respectively. The high pressure condition indeed facilitates the reaction of H$_2$O and graphite, leading to a higher erosion rate. Figures 4.19 and 4.20 show the graphite erosion rates along the entire length of the nozzle at various chamber pressures for non-metallized and metallized AP/HTPB propellants, respectively. The erosion rates attain a maximum value in the throat region in all the cases.
Figure 4.18: Radial distribution of H$_2$O mass fraction at the throat for two different chamber pressures; non-metallized propellant

Figure 4.19: Graphite erosion rate along the nozzle length at various chamber pressures; non-metallized propellants
To validate the current analysis, calculations were performed to simulate the nozzle-erosion experiments by Borie et al. (1989), Geisler (1978), and Evans et al. (2007a; 2008). Exact nozzle configurations and propellant compositions used in the experiments were treated. Tables 4.4, 4.5, and 4.6 summarize the nozzle inlet conditions. The oxidizing species OH was not considered because its small concentration resulted in a negligible difference in the calculated erosion rates. Borie et al. (1989) reported the nozzle recession data obtained by the SEP (Société Européene de Propulsion) based on the measured evolution of the nozzle contour during the motor operation and the post-firing analysis. The onset of erosion was detected only after the first ten seconds of motor operation. Figure 4.21 shows the calculated and measured time histories of carbon-carbon

Figure 4.20: Graphite erosion rate along the nozzle length at various chamber pressures; metallized propellants

![Graph showing erosion rate along nozzle length at various chamber pressures](image)
nozzle erosion. The calculated erosion rate of 0.130 mm/s at the steady-state condition matches closely with the measured value of 0.139 mm/s.

Table 4.4: Inlet Conditions* for Simulating Experiments by Borie et al. (1989)

<table>
<thead>
<tr>
<th>Y_{CO_2}</th>
<th>Y_{H_2O}</th>
<th>Y_{H_2}</th>
<th>Y_{CO}</th>
<th>Y_{HCL}</th>
<th>Y_{Al,O_i}</th>
<th>Y_{N_2}</th>
<th>p_t (MPa)</th>
<th>T_t (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.035</td>
<td>0.075</td>
<td>0.02</td>
<td>0.20</td>
<td>0.17</td>
<td>0.40</td>
<td>0.1</td>
<td>4.9</td>
<td>3390</td>
</tr>
</tbody>
</table>

*nozzle (carbon-carbon) density = 1.9 g/cc, throat radius = 2.54 cm, assumed nozzle material thickness = 8-10 cm

Table 4.5: Inlet Conditions* for Simulating Experiments by Geisler (1978)

<table>
<thead>
<tr>
<th>Y_{CO_2}</th>
<th>Y_{H_2O}</th>
<th>Y_{H_2}</th>
<th>Y_{CO}</th>
<th>Y_{HCL}</th>
<th>Y_{Al,O_i}</th>
<th>Y_{N_2}</th>
<th>p_t (MPa)</th>
<th>T_t (K)</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.145</td>
<td>0.02</td>
<td>0.175</td>
<td>0.24</td>
<td>0.28</td>
<td>0.1</td>
<td>.9</td>
<td>3580</td>
<td>15 %</td>
</tr>
<tr>
<td>0.025</td>
<td>0.105</td>
<td>0.02</td>
<td>0.18</td>
<td>0.23</td>
<td>0.34</td>
<td>0.1</td>
<td>6.9</td>
<td>3655</td>
<td>18 %</td>
</tr>
<tr>
<td>0.015</td>
<td>0.07</td>
<td>0.02</td>
<td>0.20</td>
<td>0.195</td>
<td>0.40</td>
<td>0.1</td>
<td>6.9</td>
<td>3715</td>
<td>21 %</td>
</tr>
<tr>
<td>0.005</td>
<td>0.045</td>
<td>0.02</td>
<td>0.20</td>
<td>0.190</td>
<td>0.44</td>
<td>0.1</td>
<td>6.9</td>
<td>3750</td>
<td>24 %</td>
</tr>
<tr>
<td>0.0015</td>
<td>0.025</td>
<td>0.02</td>
<td>0.20</td>
<td>0.190</td>
<td>0.47</td>
<td>0.1</td>
<td>6.9</td>
<td>3745</td>
<td>27 %</td>
</tr>
</tbody>
</table>

*nozzle (bulk graphite) density = 1.83 g/cc, throat radius = 2.54 cm, average nozzle material thickness = 8 cm

Table 4.6: Inlet Conditions* for Simulating Rocket-Motor Tests by Evans et al. (2007a)

<table>
<thead>
<tr>
<th>case</th>
<th>Y_{CO_2}</th>
<th>Y_{H_2O}</th>
<th>Y_{H_2}</th>
<th>Y_{CO}</th>
<th>Y_{HCL}</th>
<th>Y_{Al,O_i}</th>
<th>Y_{N_2}</th>
<th>Y_{OH}</th>
<th>T_t (K)</th>
<th>p_t (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>metallized AP/HTPB</td>
<td>0.02</td>
<td>0.06</td>
<td>0.03</td>
<td>0.25</td>
<td>0.20</td>
<td>0.34</td>
<td>0.1</td>
<td>0.0</td>
<td>3500</td>
<td>8.13</td>
</tr>
<tr>
<td>non-metallized AP/HTPB</td>
<td>0.21</td>
<td>0.27</td>
<td>0.01</td>
<td>0.11</td>
<td>0.28</td>
<td>0.0</td>
<td>0.11</td>
<td>0.01</td>
<td>3000</td>
<td>8.27</td>
</tr>
</tbody>
</table>

*nozzle (G-90) density = 1.92 g/cc, throat radius = 0.508 cm, average nozzle material thickness = 1.5 cm
Geisler (1978) employed a BATES (Ballistic Test and Evaluation System) motor to study nozzle material erosion. The instantaneous throat radius was obtained from the measurements of thrust and chamber pressure. Figure 4.22 shows excellent agreement between the predictions and measurements. In practice, since it takes about a second to attain the steady-state operating condition, there exists a corresponding time delay in the commencement of the nozzle surface recession. Geisler detected this onset of erosion between one to two seconds for all the firings. Accordingly, Fig. 4.22 includes the time delay at which the erosion was first detected. Table 4.7 shows the comparison between the calculated and measured bulk-graphite erosion rates at steady-state conditions. Even though the chamber temperature rises with increasing Al content, the erosion rate decreases. This phenomenon can be attributed to the reduced mass fractions of the oxidizing species H₂O and CO₂ with increasing Al content. Figure 4.23 shows the radial
distribution of the oxidizing species at the nozzle throat for the case with 18% Al. Since 
the surface temperature is very high (~ 3000 K), the erosion rate is diffusion controlled. 
Consequently, the dependency of the calculated erosion rate on the chemical kinetics data 
is eliminated. The good agreement between predictions and measurements for metallized 
propellants corroborates the model accuracy. This is also attributed to the fact that no 
Al$_2$O$_3$ deposited in the throat region as the flow direction is parallel to the surface.

Figure 4.22: Comparison between calculated and measured (Geisler, 1978) nozzle 
material (bulk graphite) erosion

Table 4.7: Comparison between calculated and measured (Geisler, 1978) nozzle 
recession rates

<table>
<thead>
<tr>
<th>$Al$</th>
<th>$\dot{r}_{\text{exp}}$ (mm/sec)</th>
<th>$\dot{r}_{\text{model}}$ (mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15%</td>
<td>0.353</td>
<td>0.337</td>
</tr>
<tr>
<td>18%</td>
<td>0.284</td>
<td>0.275</td>
</tr>
<tr>
<td>21%</td>
<td>0.200</td>
<td>0.207</td>
</tr>
<tr>
<td>24%</td>
<td>0.124</td>
<td>0.131</td>
</tr>
<tr>
<td>27%</td>
<td>0.069</td>
<td>0.076</td>
</tr>
</tbody>
</table>
In the experimental work by Geisler (1978), a significant increase in the nozzle throat erosion rate was observed when the surface temperature rose above 2600 K. It was postulated that the phenomenon could be attributed to the phase transformation of graphite to a more reactive species called carbyne (Whittaker, 1978), which exists as a polyyne $\left[-C \equiv C - C \equiv C -\right]_n$. For metallized propellants, the graphite-to-carbyne transformation may occur because the surface temperature exceeds 2800 K. But with the current chemical kinetics for graphite, the erosion rate for the metallized case is already diffusion limited with respect to $H_2O$, OH, and CO$_2$. Even if the reaction rates are higher for carbyne, it is unlikely to have much effect on the erosion rates as the diffusion limit
has already been attained. The nozzle erosion, however, may increase if carbyne starts reacting with other species such as HCl, CO, or N₂.

The third validation study was based on the rocket-motor experiments of Evans et al. (2007a). The nozzle surface recession rate was obtained from the pressure and thrust measurements during the motor firings and post-firing analyses. Table 4.8 lists the calculated and measured graphite erosion rates for the two propellants considered. The agreement is good for the metallized propellant and reasonable for the non-metallized propellant. In the latter case, the relatively low surface temperature at the throat (~ 2300 K) renders the material erosion a kinetically-controlled process. The discrepancy between the measurement and prediction may arise from the uncertainties in the kinetics data employed for the heterogeneous surface reactions, as well as the uncertainties in experiments. There exists a need to develop a more accurate kinetic mechanism for the specific nozzle material under consideration and for the temperature and pressure ranges in rocket-motor environments.

Table 4.8: Comparison between calculated and measured (Evans et al. 2007a) nozzle recession rates

<table>
<thead>
<tr>
<th>case</th>
<th>( \dot{r}_{\text{exp}} ) (mm/sec)</th>
<th>( \dot{r}_{\text{model}} ) (mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>metallized AP/HTPB</td>
<td>0.084</td>
<td>0.094</td>
</tr>
<tr>
<td>non-metallized AP/HTPB</td>
<td>0.099</td>
<td>0.125</td>
</tr>
</tbody>
</table>

The fourth validation study was based on the rocket-motor simulator (RMS) experiments of Evans et al. (2008). RMS is a bidirectional vortex combustor based on the vortex injection of oxidizers (O₂ and N₂ combination) and fuel (CH₄ and H₂ combination)
streams. The instantaneous erosion rate is measured by using X-ray radiography, wherein an X-ray beam is passed through an X-ray translucent nozzle throat section. A CCD camera is used to capture the instantaneous nozzle throat contour. All the tests used G-90 graphite material for nozzles, with 1.27 cm initial throat diameter. A nozzle configuration identical to the RMS nozzle was used in the simulation. Table 4.9 summarizes the input conditions at the chamber as well as the comparison between the calculated and measured values. The mole fractions of H$_2$O and OH employed in the model were very close to the equilibrium concentrations mentioned by Evans et al. (2008).

Figure 4.24 shows the erosion-rate profile along the nozzle length of RMS at 3.35 MPa. Evans et al. (2008) found that CO$_2$ was the least detrimental oxidizing species, as predicted by the current model for non-metallized propellants (Thakre and Yang, 2008a). Table 4.9 shows the estimated values of free-stream gas temperature and the erosion rate at throat, along with the mass-flow rate. The agreement between the calculated and measured values of mass-flow rates is excellent. The agreement between the computed and measured erosion rates is good at the chamber pressure of 3.35 MPa, but only reasonable at 4.71 MPa. As such, there was a considerable scatter in the measured erosion data obtained from the RMS. For instance, in the pressure range of 3.23 - 3.35 MPa the measured erosion rate varied between 0.15 (RMS test No.03) and 0.192 (RMS test No.12) mm/s. In the pressure range of 4.24 - 4.71 MPa the corresponding values ranged from 0.224 (RMS test No.20) to 0.284 mm/s (RMS test No.06). It is speculated that at higher pressures (i.e., at higher mass flow rates), the swirl component of the vortex combustor might contribute towards the more-than-expected increase in the erosion rate.
There is also a possibility that at higher pressures a small fraction of pure O₂ oxidizer may leak to the nozzle throat causing the rise in erosion rate.

Table 4.9: Inlet Conditions* for Simulating RMS Experiments by Evans et al. (2008)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>$p_i$ (MPa)</th>
<th>$T_i$ (K)</th>
<th>$\dot{m}_{\text{expt}}$ (g/s)</th>
<th>$\dot{r}_{\text{expt}}$ (mm/s)</th>
<th>$X_{H,O}$</th>
<th>$X_{OH}$</th>
<th>$T_{g,th}$ (K)</th>
<th>$\dot{m}_{\text{model}}$ (g/s)</th>
<th>$\dot{r}_{\text{model}}$ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS-03</td>
<td>3.35</td>
<td>3170</td>
<td>244.8</td>
<td>0.150</td>
<td>0.42</td>
<td>0.017</td>
<td>2872.8</td>
<td>241.2</td>
<td>0.160</td>
</tr>
<tr>
<td>RMS-06</td>
<td>4.71</td>
<td>3250</td>
<td>355.3</td>
<td>0.284</td>
<td>0.42</td>
<td>0.017</td>
<td>3004.8</td>
<td>356.4</td>
<td>0.194</td>
</tr>
</tbody>
</table>

*nozzle (G-90) density = 1.92 g/cc, throat radius = 0.635 cm, average nozzle material thickness = 1.5 cm

Figure 4.24: Calculated erosion-rate profile for RMS nozzle
4.5 Conclusions

A comprehensive analysis has been established to predict the chemical erosion of graphite/carbon-carbon nozzle materials in solid-propellant rocket motors. Both non-metallized and metallized AP/HTPB propellants were considered over a wide range of chamber pressures. Good agreement was achieved with four different sets of experimental data. The key factors dictating the erosion process are motor operating conditions, concentrations of the oxidizing species in the core flow, heterogeneous chemical kinetics at the surface, and nozzle geometry and material properties. The erosion rate is found to be most severe in the throat area due to the maximum heat-transfer rate in that region. H$_2$O is the most detrimental oxidizing species in dictating the graphite/carbon-carbon nozzle erosion, followed by much lesser contributions from OH and CO$_2$ in that order. The erosion rate increases linearly with the chamber pressure. At high pressures, the elevated convective heat transfer and enhanced heterogeneous surface reactions contribute to the severity of the material erosion. The chamber temperature is instrumental in determining the nozzle surface temperature, which in turn dictates the rate of heterogeneous surface reactions.

The erosion rate is dictated by heterogeneous chemical kinetics for non-metallized propellants for which the surface temperatures are low, and by diffusion-controlled process for metallized propellants for which the surface temperatures are high. The transition from the kinetics- to diffusion-controlled mechanism occurs at a surface temperature of around 2800 K. This transition temperature, however, is dependent the chemical kinetics employed and the species concentrations considered at the nozzle inlet,
and should be considered specific to the current problem scenario. If the throat surface temperature is above 2800 K, then further increase in the propellant flame temperature will not affect the erosion rate. In such a scenario, chamber pressure is the only crucial parameter affecting nozzle erosion rate.

For the non-metallized propellant, the calculated erosion rates are sensitive to the chemical kinetics data employed for the heterogeneous surface reactions. A more accurate kinetic mechanism is needed for the specific nozzle material and propellant formulation under consideration. For metallized propellants, the erosion rate decreases with increasing aluminum content, in spite of the associated increase in the flame temperature. The phenomenon can be attributed to the reduction in mass fractions of the oxidizing species H₂O and CO₂ with increasing aluminum content.

It is speculated that surface roughness can play some role in determining nozzle surface erosion rates. Surface roughness can enhance the near-wall turbulence leading to an increase in species diffusivities and thermal conductivities. Radiation can also affect the erosion rates because of the difference in the temperatures of the bulk flow and the nozzle surface. The effects of surface roughness and radiation have been treated in Appendix C.
Chapter 5

Chemical Erosion of Refractory Metal Nozzle Materials

5.1 Introduction

The erosion levels of graphite and carbon-carbon rocket nozzles can become unacceptable for ultra-high pressures and long-duration firings. Different types of erosion-resistant nozzle materials are thus required to further the development of rocket technology. In terms of high melting temperature, refractory metals such as tungsten (W at 3695 K), rhenium (Re at 3459 K), tantalum (Ta at 3290 K), molybdenum (Mo at 2896 K), and niobium (Nb at 2750 K) are very attractive. The flame temperatures for aluminized AP/HTPB propellants may reach 3700 K, making tungsten and rhenium as promising candidates. One needs to consider, however, not only the melting points of these pure metals, but also their oxides, carbides, and nitrides, since such compounds/eutectics can be formed at the nozzle surface, and may modify the chemical behavior of the nozzle material. In general, tungsten nitrides are unstable and dissociate below 1100 K (Toth, 1971). Consequently, oxidation is likely to dominate, with nitrogen serving as a diluent.

Refractory metals (W, Mo, and Re) and their alloys and carbides (e.g., zirconium carbide ZrC, tantalum carbide TaC, and hafnium carbide HfC) have exhibited a potential to provide zero-erosion performance (Olcott and Batchelor, 1964; Opeka et al., 1999), due to their resistance to chemical attack at high temperatures. Copper/Silver infiltrated
tungsten has been used for some tactical nozzles (Anon, 1975). At high temperatures the technique provides cooling as the infiltrant vaporizes (Cannon, 1969). The infiltrant also reduce thermal-shock sensitivity by increasing thermal conductivity. Despite of some advantages of using refractory metal nozzles, the material and processing costs associated with them are relatively high. In addition, the high material density increases the inert mass of the vehicle. Metal carbides even suffer from poor thermal shock resistance, leading to the formation of cracks (Olcott and Batchelor, 1964; Johnston et al., 1966). Refractory metals may also form interstitial solutions with the interdiffusion of O, N, or C, which will make the materials more brittle and susceptible to cracking and spalling.

A fundamental understanding of the physiochemical processes dictating the erosion of nozzle material is critical to the development of new materials which can resist erosion more effectively. Experimental data with different materials are scarce, not only because of high costs involved in conducting measurements at practical rocket-motor conditions, but also because of the proprietary nature of the data. Only a limited amount of information is available in the open literature (Olcott and Batchelor, 1964; Johnston et al., 1966; Haugen, 1998). Olcott and Batchelor (1964) studied tungsten nozzle inserts and attributed the two principal failure mechanisms to the chemical attack of the propellant combustion gases, H₂O and CO₂, and cracking due to thermal stresses. Results from their subscale motor firings indicated a higher level of erosion with propellants possessing a higher oxidation potential. The addition of 2% thorium dioxide (ThO₂) helped reduce the erosion rate. Arc-cast tungsten with coarse grain was found to be more resistant to the thermal-stress induced fracture than fine-grain tungsten
Johnston et al. (1966) experimentally investigated the performance of a variety of rocket nozzle materials, including refractory metals (W, Mo), metal carbides (ZrC, TaC, HfC), graphite, and fiber-reinforced plastics. Three different propellants with flame temperatures of 2865 K, 3365 K, and 3810 K were used. Some of the metal-carbide nozzles showed outstanding erosion resistance, comparable to that of the best refractory-metal nozzles. However, all of the metal-carbide nozzles cracked as a result of thermal stresses. Haugen (1998; 2007) tested different nozzle materials, including W, Mo, Mo/Re, and W coated with Re, with non-metallized AP/HTPB propellants.

It is imperative to develop a comprehensive model to accurately explore the erosion process under various rocket-motor operating conditions, and to identify materials with effective resistance to erosion. While a few models (Acharya and Kuo, 2007a; Shimada et al., 2007; Thakre and Yang, 2008a) have been established for treating graphite nozzle erosion, until now there have been no efforts to develop such models for refractory metals. This chapter presents the first comprehensive analysis for studying the chemical erosion of refractory metal nozzle inserts under a broad range of practical rocket-motor environments. Various key mechanisms dictating the nozzle erosion rate for AP/HTPB composite propellants are identified and quantified.

5.2 Theoretical /Numerical Model

The present work follows the general approach detailed in the model for graphite erosion (Thakre and Yang, 2008a), and incorporates the physiochemical properties of refractory metals in the combustion streams of AP/HTPB propellants. The formulation
involves general conservation equations for the gas phase, energy transport in the solid phase, interfacial conditions between the gas and solid phases, and the outer boundary condition of the nozzle material. The gas-phase dynamics are modeled using the Favre-averaged conservation equations of mass, momentum, energy, and species concentration in axisymmetric coordinates. Turbulence closure is achieved by means of a well-calibrated two-layer turbulence model suitable for transpiration and accelerating flows (Rodi, 1991; Tseng and Yang, 1994). Full account is taken of variable transport and thermodynamic properties.

The current work aims to study the erosion of three refractory metals, W, Re, and Mo, with primary focus on tungsten. Most existing studies have concluded that chemical erosion is the principal cause for the surface recession in non-metallized propellant environments. In the case of aluminized propellants, mechanical erosion caused by the impingement of metal oxide particles could also be significant. In addition, there is the possibility of thermite reactions between unoxidized aluminum and metal oxides (e.g., $2\text{Al} + \text{WO}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{W}$ or $2\text{Al} + \text{MoO}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{Mo}$) (Sanders et al., 2007). Such highly exothermic reactions may increase the temperature to a level sufficient to melt the metal nozzle surface (Wang et al., 1993). The wetting of metal surface by $\text{Al}_2\text{O}_3(l)$ droplets, on the other hand, may provide a liquid coating that can help resist further oxidation and erosion. The deposition of $\text{Al}_2\text{O}_3(l)$ may also increase the heat transfer rate to the nozzle wall. All these phenomena related to aluminized propellants are still relatively poorly understood and require further investigation. In order to avoid such complications, only chemical erosion associated with non-metallized AP/HTPB solid propellants is considered.
At sufficiently high temperatures, the metal surface is prone to chemical attack by such oxidizing species as H₂O, CO₂, O₂, and O. Although the reactivity of metals with oxygen is significant (Walsh et al., 1967; Gulbransen et al. 1963), this effect can be ignored due to the fuel-rich nature of AP/HTPB propellants, which produce negligible amounts of O₂ and O in the gas phase. The main species considered in the combustion stream are thus H₂O, CO₂, CO, HCl, N₂, and H₂. Minor species with negligible concentrations, such as NO, OH, Cl, H, O₂ and O, are ignored. The present study further neglects changes in the physiochemical properties of nozzle materials and variations of their melting temperatures due to the possibility of the formation of any eutectics. The heterogeneous chemical kinetics of the refractory metals has been detailed in Sections 2.3.2, 2.3.4, and 2.3.5 of Chapter 2. The corresponding kinetics data for the chemical reaction of tungsten, molybdenum, and rhenium with oxidizing species is summarized in Tables 2.6, 2.8, and 2.9, respectively.

The governing equations and associated boundary conditions are solved numerically by means of a density-based finite-volume approach with body-fitted coordinates. A four-stage Runge-Kutta scheme is used for the time integration. The convective fluxes are treated explicitly with a second-order central-difference scheme. The chemical reaction source terms are handled in a semi-implicit manner. To ensure numerical stability and convergence, a fourth-order artificial dissipation based on the scalar dissipation is employed. The grid is stretched in the radial direction and clustered near the surface. The centers of the computational cells adjacent to the nozzle surface are located at \( y^+ < 1 \) in order to capture accurately the near-wall phenomena.
5.3 Nozzle Configurations and Boundary Conditions

The baseline nozzle configuration considered here is shown in Fig. 4.1 of Chapter 4. The geometry is identical to that employed in our study on graphite material, so that a direct comparison of the erosion rates of different materials can be made. The incoming flow consists of the combustion products of non-metallized AP/HTPB composite propellants. The chamber pressure \( p_t \) and temperature \( T_t \) are specified at the nozzle inlet. The velocity at the exit is supersonic. Table 5.1 summarizes the species mass fractions at the inlet obtained from the chemical equilibrium code (Gordon and McBride, 1994) at \( p_t = 6.9 \) MPa. Six different chamber pressures and their corresponding temperatures are used to study the effect of motor operating conditions on nozzle erosion. The species mass fractions remain nearly constant in the pressure range of 6.9-45 MPa. The ambient temperature is taken as 300 K. The thermophysical properties of W, Mo, and Re are adopted as fourth-order polynomial functions of temperature (McBride et al., 2002).

The discussion of results is organized as follows. First, tungsten erosion for the baseline nozzle configuration is studied by employing the different surface chemical kinetic schemes outlined in Section 2.3.2 (see Table 2.6) of Chapter 2. Based on the results, appropriate kinetics data and reaction products are chosen for further parametric studies. The chemical erosion model is then validated against experimental data for W, Mo, and Re, as summarized in Table 5.2. The nozzle geometry and inlet flow conditions simulate exactly those in the corresponding experimental studies used for model validation.
combustion product species (non-metallized AP/HTPB)

<table>
<thead>
<tr>
<th>Species</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.29</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.22</td>
</tr>
<tr>
<td>CO</td>
<td>0.11</td>
</tr>
<tr>
<td>H₂</td>
<td>0.01</td>
</tr>
<tr>
<td>N₂</td>
<td>0.10</td>
</tr>
<tr>
<td>HCl</td>
<td>0.27</td>
</tr>
</tbody>
</table>

motor operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pₗ (MPa)</td>
<td>6.9, 10, 15, 25, 35, 45</td>
</tr>
<tr>
<td>Tₗ (K)</td>
<td>3000, 3020, 3040, 3050, 3060, 3065</td>
</tr>
<tr>
<td>Tamb (K)</td>
<td>300</td>
</tr>
</tbody>
</table>

* tungsten nozzle density = 19.25 g/cc, throat radius = 0.57 cm, average thickness = 4.8 cm

Table 5.2: Experimental studies of refractory metal nozzle erosion

<table>
<thead>
<tr>
<th>ref.</th>
<th>nozzle material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnston et al.(1966)</td>
<td>W, Mo, refractory compounds</td>
</tr>
</tbody>
</table>

5.4 Results and Discussions

The theoretical/numerical framework described in the preceding sections was implemented to explore the chemical erosion of refractory metal (W, Mo, and Re) nozzles in practical rocket-motor environments. The axisymmetric computational domain of the rocket nozzle, shown in Fig. 4.1, is divided into 141 x 80 grid points in the x and r directions, respectively. The turbulent flow development in the same nozzle configuration
was detailed earlier. To simulate the erosion of the tungsten nozzle, two heterogeneous reactions of W with H$_2$O and CO$_2$, along with the energy balance given by Eq. (2.32), are implemented at the surface. The oxidizing species CO$_2$ and H$_2$O are consumed to form CO, H$_2$, and gaseous tungsten oxides (WO$_3$ or WO$_2$). Concentration gradients are then established near the wall. The gas-phase reactions among the AP/HTPB combustion product species were not included because of their negligible effect on nozzle erosion. (Thakre and Yang, 2007a) It should be noted that for tungsten and other refractory metals, volatile oxides (e.g., WO$_3$ and WO$_2$) formed at the nozzle surface may react with HCl(g) to generate compounds such as WO$_2$Cl$_2$(g). Such gas-phase reactions, however, do not have any significant impact on the nozzle erosion rate as they will not affect either the concentrations of H$_2$O and CO$_2$ species or the rate of heat transfer to the nozzle wall.

As shown in Table 2.3.2, three different sets of kinetics data are available for the reaction between W and H$_2$O at high temperatures. It is important to make a judicious selection of the data that yields the most accurate erosion rate. Figure 5.1 shows a comparison of the predicted tungsten nozzle erosion rates based on different chemical kinetics data. The incoming flow temperature and pressure are $T_i = 3000$ K and $p_i = 6.9$ MPa, respectively, and the outer boundary of the nozzle material is assumed to be adiabatic. The maximum erosion rates obtained from the three sets of kinetics data (Unal et al., 2000; Kalipatrick and Lott, 1966a; Greene and Finfork, 2001) are 0.078, 0.069, and 0.047 mm/s, respectively. The most severe erosion occurs near the throat, due to the enhanced heat transfer in that region. The measured erosion rates of tungsten nozzle inserts obtained from various experimental studies (Johnston et al., 1966; Haugen, 1998; 2007) with similar nozzle throat diameters consistently lie in the range of 0.02 – 0.05
mm/s. On this basis, the kinetics data of Kalipatrick and Lott (1966a), which lead to the lowest erosion rate, appear to be most appropriate for the present application. The small wiggle in the erosion-rate profile arises from the discontinuity in the slope of nozzle contour at the entrance of the throat region. Such small irregularities were not observed in other cases with smooth nozzle profiles shown later.

The stoichiometry of surface reactions and the overall heat of reaction depend strongly on the final product species, which in turn affect the calculated surface temperature and erosion rate. Existing experimental studies on tungsten oxidation (Olcott and Batchelor, 1964; Walsh et al., 1967; Smolik et al., 1998; Harvey, 1974), have suggested either $\text{WO}_2(g)$ or $\text{WO}_3(g)$ as the final oxidation product. To clarify the effect of this choice on the predicted erosion rates, calculations were performed for both $\text{WO}_2(g)$ or $\text{WO}_3(g)$. Figure 5.2 shows a comparison of the predicted tungsten nozzle erosion rates.

Figure 5.1: Tungsten nozzle erosion rate with different chemical kinetics using $\text{WO}_3(g)$ as the final oxidation product

The stoichiometry of surface reactions and the overall heat of reaction depend strongly on the final product species, which in turn affect the calculated surface temperature and erosion rate. Existing experimental studies on tungsten oxidation (Olcott and Batchelor, 1964; Walsh et al., 1967; Smolik et al., 1998; Harvey, 1974), have suggested either $\text{WO}_2(g)$ or $\text{WO}_3(g)$ as the final oxidation product. To clarify the effect of this choice on the predicted erosion rates, calculations were performed for both $\text{WO}_2(g)$ or $\text{WO}_3(g)$. Figure 5.2 shows a comparison of the predicted tungsten nozzle erosion rates.
obtained by considering either WO$_3$(g) ($\Delta h_f^\circ = -319.725$ kJ/mol) or WO$_2$(g) ($\Delta h_f^\circ = 29.062$ kJ/mol) as the final oxidation product of surface reactions. The chemical kinetics data from Kalipatrick and Lott (1966a) are utilized. The use of WO$_3$(g) gives rise to an erosion rate that is $0.005$ mm/s lower. It is possible that if the oxidation product emerging from the surface is WO$_2$, then it may further react with H$_2$O to form either WO$_3$(g) or WO$_2$(OH)$_2$(g) (Kalipatrick and Lott, 1966a). This process reduces the oxidation potential of combustion products by depleting the concentration of H$_2$O, thereby causing a reduced erosion rate. A similar situation occurs if the oxidation product WO$_3$(g) reacts with water to form WO$_3$H$_2$O$_{(g)}$. Although such reactions can take place in the gas phase, the lack of associated kinetics data renders their inclusion in the analysis futile. In the present study, all the further calculations for tungsten nozzles are performed by considering the kinetics data of Kalipatrick and Lott (1966a) with the following surface reactions,

$$W + 3H_2O \rightarrow WO_3 + 3H_2 \quad (R9)$$
$$W + 3CO_2 \rightarrow WO_3 + 3CO \quad (R10)$$

Figure 5.3 shows the nozzle erosion rates caused by each of the oxidizing species, H$_2$O and CO$_2$. The former proves to be much more detrimental (about three times) than the latter. The situation is similar to graphite-nozzle erosion, where H$_2$O proved much more detrimental that CO$_2$ for non-metallized propellants (Thakre and Yang, 2008a).
Figure 5.2: Tungsten nozzle erosion rate using different final oxidation products and chemical kinetics from Kalipatrick and Lott (1966a)

Figure 5.3: Tungsten nozzle erosion rate due to individual oxidizing species H₂O and CO₂
The dependence of the erosion rate on the outer boundary condition of the nozzle material was examined, since this condition affects the nozzle surface temperature and associated chemical reaction rates. Table 5.3 lists three different outer boundary conditions considered herein. The baseline adiabatic condition was relaxed by allowing convective heat transfer at the outer boundary. The outer heat-transfer coefficient $h_{amb}$, estimated from standard correlations for turbulent flows over a flat plate, falls in the range of 100-500 W/m²-K, depending on the specific configuration of the nozzle assembly and vehicle speed. Figure 5.4 shows that the calculated erosion rate decreases slightly with enhanced heat transfer at the outer boundary, due to the decrease in the nozzle inner surface temperature. The erosion rate calculated by employing the adiabatic outer nozzle boundary thus represents the upper limit. Table 5.3 summarizes the results. All the calculations presented subsequently are based on the adiabatic outer boundary of the nozzle material unless mentioned otherwise.

Table 5.3: Effect of outer boundary condition of nozzle on tungsten erosion rate*

<table>
<thead>
<tr>
<th>outer boundary condition</th>
<th>erosion rate at throat (mm/s)</th>
<th>inner surface temperature at the throat (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>adiabatic</td>
<td>0.047</td>
<td>2450</td>
</tr>
<tr>
<td>$h_{amb} = 300$ W/m², $T_{c,o} = 600$ K</td>
<td>0.042</td>
<td>2390</td>
</tr>
<tr>
<td>$h_{amb} = 500$ W/m², $T_{c,o} = 600$ K</td>
<td>0.036</td>
<td>2320</td>
</tr>
</tbody>
</table>

* $T_{amb} = 300$ K, $T_i = 3000$ K, $p_i = 6.9$ MPa
Figure 5.4: Effect of nozzle outer boundary condition on erosion rate

Figure 5.5: Distributions of temperature, Mach number and mass fractions of H₂O, CO₂, CO, and H₂ in the nozzle ($T_\text{i} = 3000$ K, $p_\text{i} = 6.9$ MPa, with surface reactions and conductive wall)
Figure 5.5 shows the entire nozzle flowfield in terms of the temperature, Mach number, and mass fractions of H$_2$O, CO$_2$, CO, and H$_2$. The Mach number increases from 0.28 at the inlet to 2.3 at the exit, but the temperature decreases monotonically from a value slightly less than that of the chamber condition to about 1900 K. The endothermic surface reactions and conductive heat transfer through the nozzle material help lower the surface temperature. The thickness of the species-concentration boundary layer ($\delta_c$) is greater than its velocity counterpart, and can be estimated using a simple order-of-magnitude analysis as follows:

$$\delta_c \sim \sqrt{D_{\text{eff}} \tau_f}$$  \hspace{1cm} (5.1)

where $D_{\text{eff}}$ is the effective mass diffusivity on the order of $10^{-2}$ m$^2$/s. The flow residence time $\tau_f$ is approximated as the ratio of the nozzle length to the average axial velocity, and has a value of about 0.1 ms. Based on Eq. (5.1), the concentration boundary layer thickness is about 1 mm, which is close to that observed in Fig. 5.5.

At a quasi steady-state condition, whether the species diffuse towards or away from the surface depends on the sign of the species gradient ($dY_k/dr$) at the surface as governed by the following equation, which is a rearranged form of Eq. (2.31).

$$\left(\frac{d\bar{Y}_k}{dr}\right) = \frac{(-\bar{\omega}_k + \bar{p}_g \bar{Y}_k \bar{u}_r)}{\bar{p}_g D_{\text{km}}^c}$$  \hspace{1cm} (5.2)

The species gradient in turn depends on two factors: the rate of production/consumption of species ($\bar{\omega}_k$) and surface blowing velocity ($u_r$). Since H$_2$O and CO$_2$ are consumed at the surface, their gradients are always positive, with diffusion towards the surface. The direction of CO and H$_2$ diffusion, however, is affected by the relative magnitudes of
\( \dot{\omega}_k \) and \( u_r \). As a result of the dominance of reaction (R9) in dictating the erosion rate, a large amount of \( \text{H}_2 \) is produced and diffuses away from the surface. In the case of graphite nozzle erosion (Thakre and Yang, 2008a), since both the surface reactions of \( \text{C(s)} \) with \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) yield \( \text{CO} \), the higher value of \( \dot{\omega}_{\text{CO}} \) dominates the effect of \( u_r \). Consequently, the mass fraction of \( \text{CO} \) at the surface becomes much higher than that in the core flow, causing it to diffuse away from the surface throughout the nozzle length. For a tungsten nozzle, however, only a limited amount of \( \text{CO} \) emerges from the surface through reaction (R10), leading to a low value of \( \dot{\omega}_{\text{CO}} \). In the upstream converging section of the nozzle, as a consequence of high surface blowing (higher erosion rate) the mass fraction of \( \text{CO} \) is lower than in the core flow and \( \text{CO} \) diffuses towards the surface. In the downstream region, however, the low surface blowing (lower erosion rate) reverses the situation. Figure 5.6 clearly shows the distributions of mass fraction of \( \text{CO} \) and temperature at the nozzle surface.

Figure 5.7 compares tungsten and graphite nozzle erosion rates for the same operating condition and nozzle configuration. The erosion rate at the graphite nozzle throat (0.124 mm/s) is about 2.6 times that of tungsten (0.047 mm/s). This suggests that tungsten (19.25 g/cm\(^3\)), which is approximately 10 times denser than graphite (1.9 g/cm\(^3\)), actually exhibits a higher mass consumption rate (g/cm\(^2\)-s). The lower erosion rate of tungsten is thus attributed to its higher density. It is clear from Eq. (2.37) that the net nozzle erosion rate is inversely proportional to its material density.
Figure 5.6: A tilted view of the nozzle showing distributions of temperature and mass fractions of CO ($T_i = 3000$ K, $p_f = 6.9$ MPa, with surface reactions and conductive wall)

Figure 5.7: Comparison of erosion rates of graphite and tungsten nozzles for non-metallized propellant
The radial distributions of temperature and oxidizing-species concentrations are instrumental in identifying the mechanisms of nozzle material erosion. Figures 5.8 and 5.9 show the radial distributions of temperature at the throat and a downstream location, respectively. The temperature at the throat decreases monotonically from 2785 K at the centerline to 2450 K at the surface. The corresponding values at the downstream location are 2280 K and 2550 K, respectively, but the radial profile does not decrease monotonically. The temperature rise near the surface in Fig. 5.9 results from the dissipation of the flow kinetic energy into thermal energy. The lower surface temperature at the throat as compared with its counterpart at the downstream location is attributed to the higher rate of endothermic heterogeneous reactions at the throat. Figure 5.10 shows the radial distributions of species mass fractions at the nozzle throat. The finite concentrations of H₂O and CO₂ at the surface indicate that erosion is kinetically controlled.

Figure 5.8: Radial distribution of temperature at the tungsten nozzle throat
Figure 5.9: Radial distribution of temperature at a location downstream of the nozzle throat

Figure 5.10: Radial distributions of species concentrations at the nozzle throat
The effect of chamber pressure on nozzle erosion rate was also studied. Figure 5.11 shows the distribution along the entire length of the tungsten nozzle at various chamber pressures. The maximum value is attained in the throat region for all cases. It is worth noting from Fig. 5.1 that for surface reactions with lower activation energies, the peak in the erosion-rate profile spreads more widely in the upstream region than the cases with higher activation energies. As the pressure increases, the peak becomes more prominent at the throat, as evidenced in Fig. 5.11. The surface temperature, pressure, and activation energies of surface reactions are thus the three factors most instrumental in determining the characteristics of the erosion-rate profile. Figure 5.12 shows the linear variations of the tungsten and rhenium erosion rates at the throat with the chamber pressure. Since the convective heat-transfer rate increases with pressure, there is a corresponding rise in the erosion rate. The lower value of the rhenium erosion rate, as compared to that of tungsten, can be attributed to the lack of including CO₂ reaction in the former case. The observations based solely on the effect of the H₂O reaction show that the erosion rates of tungsten and rhenium are comparable, especially taking into account the scatter in the kinetics data from the experimental studies.

To validate the current analysis, calculations were performed to simulate the nozzle-erosion experiments by Johnston et al. (1966) and Haugen (1998; 2007). The nozzle geometries and inlet flow conditions simulate exactly those in the corresponding experimental studies. Tables 5.4, 5.5, and 5.6 summarize the inlet conditions in terms of mass fractions of the species and motor operating conditions. Haugen (2007) reported the tungsten nozzle recession data from an earlier subscale motor firing of the Penguin Mk3 missile. The erosion rate was deduced from measurements of the thrust and chamber
pressure over the firing duration. The nozzle material was tungsten with 2% La2O3, and the propellant used was non-metallized AP/HTPB (88:11) with 1% additives. The nozzle surface showed some deposition of silica released from the upstream thermal insulation. Figure 5.13 shows the calculated nozzle erosion rate along with the nozzle contour for the inlet conditions listed in Table 5.4. The erosion-rate profile peaks in the nozzle throat region. Since the nozzle contour is very smooth, the erosion profile does not exhibit any irregularity, unlike the situation with the nozzle contour in Fig. 5.1. The calculated erosion rate of 0.047 mm/s matches closely the measured value of 0.040 mm/s. The slight over-prediction may be attributed to two facts: the assumption of an adiabatic outer boundary and the neglect of gas-phase reactions of tungsten oxide with H2O. Silica deposition, detected in the post-firing analysis (Haugen, 2007), may also contribute to the decrease in the measured throat diameter. If heat transfer is allowed at the outer boundary, the predicted erosion rate is lowered marginally to 0.042 mm/s, as shown in Fig. 5.13. The uncertainty of the kinetics data employed for heterogeneous reactions also affects the calculated erosion rate.
Figure 5.11: Distributions of tungsten erosion rates along the nozzle length at various chamber pressures

Figure 5.12: Effect of chamber pressure on tungsten and rhenium erosion rates at the nozzle throat
Table 5.4: Inlet conditions* for simulations of experiments by Haugen (2007)

<table>
<thead>
<tr>
<th>(Y_{CO_2})</th>
<th>(Y_{H_2O})</th>
<th>(Y_{H_2})</th>
<th>(Y_{CO})</th>
<th>(Y_{HCl})</th>
<th>(Y_{N_2})</th>
<th>(p_i) (MPa)</th>
<th>(T_i) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>0.28</td>
<td>0.01</td>
<td>0.10</td>
<td>0.29</td>
<td>0.11</td>
<td>5.6</td>
<td>3000</td>
</tr>
</tbody>
</table>

* Tungsten density = 19.25 g/cc, throat radius = 0.4 cm, average thickness = 3 cm

Table 5.5: Inlet conditions* for simulations of experiments by Johnston (1966)

<table>
<thead>
<tr>
<th>(Y_{CO_2})</th>
<th>(Y_{H_2O})</th>
<th>(Y_{H_2})</th>
<th>(Y_{CO})</th>
<th>(Y_{HCl})</th>
<th>(Y_{N_2})</th>
<th>(p_i) (MPa)</th>
<th>(T_i) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.27</td>
<td>0.01</td>
<td>0.12</td>
<td>0.30</td>
<td>0.10</td>
<td>6.9</td>
<td>2860</td>
</tr>
</tbody>
</table>

*Tungsten density = 19.25 g/cc, Molybdenum density = 10.28 g/cc, throat radius = 0.39 cm, average thickness = 1 cm

Table 5.6: Inlet conditions* for simulations of experiments by Haugen (1998)

<table>
<thead>
<tr>
<th>(Y_{CO_2})</th>
<th>(Y_{H_2O})</th>
<th>(Y_{H_2})</th>
<th>(Y_{CO})</th>
<th>(Y_{HCl})</th>
<th>(Y_{N_2})</th>
<th>(p_i) (MPa)</th>
<th>(T_i) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.16</td>
<td>0.26</td>
<td>0.01</td>
<td>0.20</td>
<td>0.27</td>
<td>0.10</td>
<td>6.9</td>
<td>2810</td>
</tr>
</tbody>
</table>

*Tungsten density = 19.25 g/cc, Rhenium density = 21.20 g/cc, throat radius = 0.53 cm, average thickness = 2 cm
The second validation was performed, based on the extensive experimental work of Johnston et al. (1966) to evaluate the performance of several rocket nozzle materials including W, Mo, refractory metal carbides, and graphite. The instantaneous throat radius was obtained from measurements of the thrust and chamber pressure, as well as post firing analyses. The high-density tungsten nozzles performed well with only slight to moderate erosion. One of the propellants used was Arcite 368 (polyvinyl chloride and ammonium perchlorate). The inlet conditions based on this non-metallized propellant are summarized in Table 5.5. While the arc-cast tungsten nozzle obtained from the commercial supplier showed an erosion rate of 0.028 mm/s, the molybdenum nozzle insert did not erode at all. Figure 5.14 shows calculated erosion-rate profiles for the tungsten and molybdenum nozzle inserts, along with the nozzle contour. The maximum convective heat transfer and erosion rate occurred slightly upstream of the throat. For a
curved nozzle with a large angle of convergence, the wall heat transfer usually reaches its maximum just before the throat. Such a phenomenon has been observed both experimentally (Back et al., 1964) as well as computationally (Shimada et al., 2007) for curved nozzles. The calculated erosion rate with an adiabatic outer nozzle boundary is 0.041 mm/s for tungsten and nearly zero for molybdenum, as shown in Fig. 5.14. If this adiabatic condition is relaxed, then the predicted erosion rate decreases. The measured erosion rate could, in fact, be lower due to the fact that gas-phase reactions between volatile tungsten oxides and H₂O may reduce the oxidation potential of the propellant.

The third validation study was based on experiments by Haugen (1998). The nozzle materials tested on the sub-scale motor were W, Mo, Mo/Re, and W coated with Re. A reduced smoke AP/HTPB propellant was employed with varying composition. Table 5.6 summarizes the nozzle geometry and inlet conditions. The validity of erosion-rate measurements remains to be clarified (Haugen, 1998) as heavy silica deposition from the upstream region protected the nozzle surface from exposure to the combustion species for a major part of the firing duration. The erosion rate for the tungsten nozzle was reported to be in the range of 0.02-0.03 mm/s, while the values for other materials were not mentioned. It was concluded, however, that the best insert material was rhenium-coated tungsten. The molybdenum insert showed negligible erosion, with the propellant having a lower flame temperature (2476 K), but the erosion increased drastically at a higher flame temperature (2810 K). This is in contrast to the negligible erosion for the Mo insert observed by Johnston et al. (1966) for a similar flame temperature (2860 K). Figure 5.15 shows the calculated erosion rates for tungsten and rhenium along with the nozzle contour. The erosion rates at the nozzle throat are 0.040 mm/s and 0.032 mm/s, for
W and Re, respectively. Table 5.7 summarizes the comparison of all the calculated and measured erosion rates at the throat. The slight discrepancies may be attributed to the uncertainties of the chemical kinetics data for surface reactions and the adiabatic outer boundary condition employed.

Figure 5.14: Calculated tungsten and molybdenum nozzle erosion rate for the experimental study by Johnston et al. (1966)
Table 5.7: Comparison between calculated and measured nozzle erosion rates

<table>
<thead>
<tr>
<th>Ref. (propellant)</th>
<th>nozzle material</th>
<th>( \dot{r}_{\text{exp}} ) (mm/s)</th>
<th>( \dot{r}_{\text{model}} ) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haugen (2007) (AP/HTPB)</td>
<td>W with 2% La(_2)O(_3)</td>
<td>0.040</td>
<td>0.047 (adiabatic outer boundary) 0.042 ((h_{\text{amb}} = 300) W/m(^2)-K)</td>
</tr>
<tr>
<td>Johnston et al. (1966) (Arcite 368)</td>
<td>arc-cast W</td>
<td>0.028</td>
<td>0.041 (adiabatic outer boundary) 0.037 ((h_{\text{amb}} = 500) W/m(^2)-K)</td>
</tr>
<tr>
<td>Haugen (1998) (AP/HTPB)</td>
<td>molybdenum</td>
<td>negligible</td>
<td>negligible</td>
</tr>
<tr>
<td></td>
<td>W with 2% La(_2)O(_3)</td>
<td>0.020 - 0.030</td>
<td>0.040 (adiabatic outer boundary) 0.035 ((h_{\text{amb}} = 500) W/m(^2)-K)</td>
</tr>
<tr>
<td></td>
<td>Re-coated W</td>
<td>not mentioned</td>
<td>0.032 (adiabatic outer boundary)</td>
</tr>
</tbody>
</table>

Figure 5.15: Calculated tungsten and rhenium nozzle erosion rate for the experimental study by Haugen (1998).
5.5 Conclusions

A comprehensive analysis has been established to predict the chemical erosion of refractory metal (tungsten, molybdenum, rhenium) nozzle materials in rocket motors with non-metallized AP/HTPB solid propellants. The primary focus was on the tungsten nozzle. The predicted erosion rates matched reasonably well with three different sets of measurements. H₂O proved to be the more detrimental oxidizing species than CO₂ in dictating tungsten nozzle erosion, similar to the situation with graphite nozzles. The material recession rate is controlled by heterogeneous chemical kinetics and increases linearly with the chamber pressure.

In order to improve the model predictivity, more accurate chemical properties for heterogeneous reactions of refractory metals with oxidizing species at realistic rocket-motor operating conditions are needed. The gas-phase kinetics of volatile tungsten oxides and steam also needs to be studied further and incorporated into the analysis to account for the fact that a reduction in H₂O concentration may reduce the erosion rate. The erosion rate for tungsten was found to be much lower than for graphite, but comparable to that of rhenium. The least erosion was exhibited by molybdenum, whose implementation, however, is restricted to propellants with lower flame temperatures (less than 3000 K) due to its low melting point. It should be noted that the effect of CO₂ reaction with Mo and Re was not considered due to lack of the corresponding chemical kinetics data. Table 5.8 shows the comparison of erosion rates for different nozzle materials for same inlet conditions and baseline nozzle configuration.
Table 5.8: Erosion rates of different nozzle materials for baseline configuration

<table>
<thead>
<tr>
<th>material</th>
<th>density (gm/cm$^3$)</th>
<th>melting point (K)</th>
<th>erosion rate (mm/s) (6.9 MPa, 3000K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1.90</td>
<td>3950</td>
<td>0.124</td>
</tr>
<tr>
<td>Tungsten</td>
<td>19.25</td>
<td>3695</td>
<td>0.047</td>
</tr>
<tr>
<td>Rhenium</td>
<td>21.20</td>
<td>3459</td>
<td>0.039</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>10.28</td>
<td>2896</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Chapter 6

Mitigation of Chemical Erosion by Nozzle Boundary-Layer Control Mechanism

6.1 Introduction

The surface recession in graphite and carbon-carbon nozzles is primarily due to the chemical erosion caused by heterogeneous reactions between the nozzle material and oxygen-containing species in the propellant combustion products (Thakre and Yang, 2008a). The erosion rate is found to increase linearly with the chamber pressure. Since a throat-area increase of more than 5% is considered alarming for most propulsion applications, the erosion level for ultra-high pressures (~ 50 MPa) and long-duration firings can become unacceptable. It is thus crucial to devise methods to mitigate nozzle throat erosion over a wide range of operating conditions, especially at high pressures.

Some of the approaches that can be used to reduce nozzle erosion rate are: 1) to modify the composition of solid propellant, 2) to improve the thermochemical resistance of the nozzle materials, 3) to modify nozzle configuration and/or 4) to control the nozzle boundary-layer flow. Any combination of the above techniques can also be applied. The approach to alter the solid-propellant formulation would aim to develop a composition that yields minimal concentrations of undesirable oxidizing species (H₂O, OH, and CO₂). This may, however, not be practical from the perspective of system-level implementation in the near term. It is known that the chemical erosion of a nozzle can be lowered by increasing the aluminum (Al) content in a metallized AP/HTPB propellant (Klager, 1977;
Geisler, 1978). Such an increase is limited by the possibility of clogging due to alumina slag and the mechanical erosion due to impingement of condensed-phase Al₂O₃ particulates on the converging section of the nozzle surface.

Refractory metals such as tungsten, rhenium, molybdenum, and their alloys can been used as materials for nozzle inserts, since they can resist chemical erosion more effectively than carbon-based materials (Thakre and Yang, 2008b; Johnston et al., 1966). Unfortunately, the cost and weight penalties associated with these metals may sometimes render their use uneconomical. Refractory ceramic materials have also been employed because of their remarkable erosion resistance. Although ceramics present lesser weight penalties than refractory metals, they are known to frequently suffer from cracking caused by thermal shocks (Johnston et al., 1966). Much effort has been made recently to address this issue by developing new materials. A notable example is composites of zirconium carbide (ZrC) and tungsten, which exhibit a strong resistance to both chemical erosion and thermal shocks (Dickerson et al., 2004).

Certain changes in the nozzle configuration can possibly reduce erosion. The level of reduction, however, may be too small to dedicate efforts in this direction. Bartz (1957) correlation suggests that the heat-transfer rate to the nozzle wall is inversely proportional to the diameter. Since erosion rate is directly correlated to the rate of heat-transfer, reduction in the throat diameter may possibly decrease the erosion rate. The throat diameter, however, depends heavily on other crucial motor-operating parameters and it may not be a desirable to change the diameter. It has also been reported that relatively long cylindrical throat sections help reduce erosion rate (Anon, 1975). Long cylindrical
sections, however, will increase the weight penalty and may nullify the advantage of reducing the erosion rate.

In addition to the implementation of better thermochemical resistant materials, the erosion problem can be circumvented by exercising some sort of control on the nozzle boundary layer. Since the temperature and oxidizing-species concentrations near the surface are the two key parameters dictating chemical erosion (Thakre and Yang, 2008a), any effective scheme for minimizing erosion must be executed through these parameters. Wolt and Webber (2004) appear to have been the first to employ the so-called nozzle boundary-layer control system (NBLCS), as shown schematically in Fig. 6.1. The system diverts a small portion ($\dot{m}_{\text{div}}$) of hot combustion product gases from the chamber, and allows it to pass over grains of such ablative materials as succinic acid (SA) and polyvinyl acetate (PVA). The species generated from the interaction between the diverted propellant combustion products and the ablative material are injected slightly upstream of the nozzle throat, as shown in a close-up view in Fig. 6.2. The injection temperature is much lower than the flame temperature of the solid propellant. Furthermore, the mass fractions of oxidizing species H$_2$O, CO$_2$, and OH near the nozzle surface are substantially reduced as compared to those in the propellant combustion product stream.
The rate of pyrolysis of SA/PVA grain has been experimentally investigated by Kuo et al. (2007). A companion numerical study of the reduction of nozzle throat erosion by NBLCS has been carried out by Acharya and Kuo (2007b). The purpose of the chapter is to further the previously described comprehensive theoretical/numerical model to study the mitigation of nozzle throat erosion by employing the NBLCS. The analysis simulates
the experimental configuration reported in Evans et al. (2007b; 2008), by extending our model on graphite erosion (Thakre and Yang, 2008a). Special attention is given to the effect of the injected flow on the physiochemical processes near the nozzle surface. In addition, a systematic study of the dependence of the nozzle erosion rate on the NBLCS injection temperature is carried out.

6.2 Nozzle Configuration with NBLCS and Boundary Conditions

Figure 6.3a shows the physical domain of concern, including a graphite nozzle and a NBLCS injection for erosion mitigation. The flow entering the nozzle consists of the combustion products of a non-metallized AP/HTPB propellant. The main species considered are H₂O, CO₂, CO, HCl, N₂, H₂, OH, and H. Minor species, NO, O₂, and O, are ignored, as they are present in negligible concentrations due to the fuel rich nature of the propellant. The basis of the present analysis is the general framework developed and validated for graphite-nozzle erosion (Thakre and Yang, 2008a). The formulation involves general conservation equations for the gas phase, energy transport in the solid phase, interfacial conditions between the gas and solid phases, and the outer boundary condition of the nozzle material. Table 2.4 summarizes the kinetics data employed for the heterogeneous reactions at the graphite nozzle surface. Table 6.1 summarizes the thermodynamic properties of SA and PVA.
Table 6.1: Thermodynamic properties of SA/PVA ablative material (Kuo et al., 2007)

<table>
<thead>
<tr>
<th></th>
<th>SA</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical name/formula</td>
<td>Butanedioic acid (C₄H₆O₄)</td>
<td>Poly-vinyl acetate [-CH₂CH(OOCCH₃)-]n</td>
</tr>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>118.09</td>
<td>86 x n</td>
</tr>
<tr>
<td>λ (W/m-K)</td>
<td>0.137</td>
<td>~0.16</td>
</tr>
<tr>
<td>ρ (kg/m³)</td>
<td>1,560</td>
<td>1,190 @ 15°C</td>
</tr>
<tr>
<td>C (J/kg-K)</td>
<td>1,360</td>
<td>1294.24 @ 25°C</td>
</tr>
<tr>
<td>Tₘ₀ (K)</td>
<td>493</td>
<td>503</td>
</tr>
<tr>
<td>Tₜ₀ (K)</td>
<td>508</td>
<td>-</td>
</tr>
<tr>
<td>Lₘ (J/kg)</td>
<td>274,367</td>
<td>-</td>
</tr>
<tr>
<td>Lₜ (J/kg)</td>
<td>~374,000</td>
<td>-</td>
</tr>
</tbody>
</table>
The computational domain of the nozzle and the injection location are shown in Fig. 6.3b. The injection is axisymmetric, with the port width being 0.15 cm. The pressure ($p_t$) and temperature ($T_t$) at the nozzle inlet are specified according to the chamber conditions. The velocity at the exit is supersonic. Table 6.2 lists the species mass fractions at the nozzle inlet obtained from the chemical equilibrium calculation (Gordon and McBride, 1994) for a non-metallized AP/HTPB propellant at $p_t = 6.9$ MPa. Three different chamber pressures and their corresponding flame temperatures are used to study the effect of motor operating conditions and the NBLCS on the nozzle erosion. The species mass fractions remain nearly constant in the pressure range of 6.9-45 MPa. The ambient temperature is taken as 300 K.

Figure 6.3: Rocket nozzle with flow injection from nozzle boundary-layer control system

(a)

(b)
In the experimental study conducted by Evans et al. (2007b; 2008) to implement the NBLCS in a rocket motor simulator (RMS), a small portion of propellant combustion gases from the combustion chamber is diverted and passed over multiple centre-perforated grains of the ablative material made of SA/PVA (90/10 by mass). This material has a relatively low pyrolysis temperature. The energy transfer from the diverted combustion gases ($\dot{m}_{\text{div}}$) pyrolyzes the SA/PVA grain. The value of $\dot{m}_{\text{div}}$ is about 1% of the total mass-flow rate. The species resulting from the reactions between the diverted propellant combustion gases and pyrolyzed SA/PVA ($\dot{m}_{\text{pyro}}$) are introduced slightly upstream of the nozzle throat through four injection ports. The fuel-rich species so

<table>
<thead>
<tr>
<th>combustion product species</th>
<th>(non-metallized AP/HTPB propellant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{H_2O}$</td>
<td>0.29</td>
</tr>
<tr>
<td>$Y_{CO_2}$</td>
<td>0.22</td>
</tr>
<tr>
<td>$Y_{CO}$</td>
<td>0.11</td>
</tr>
<tr>
<td>$Y_{H_2}$</td>
<td>0.003</td>
</tr>
<tr>
<td>$Y_{OH}$</td>
<td>0.01</td>
</tr>
<tr>
<td>$Y_{H}$</td>
<td>0.00</td>
</tr>
<tr>
<td>$Y_{N_2}$</td>
<td>0.10</td>
</tr>
<tr>
<td>$Y_{HCL}$</td>
<td>0.267</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>motor operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_t$ (MPa)</td>
</tr>
<tr>
<td>$T_t$ (K)</td>
</tr>
<tr>
<td>$T_{\text{amb}}$ (K)</td>
</tr>
</tbody>
</table>

* nozzle material density = 1.92 g/cc, throat radius = 0.57 cm, average thickness = 4.8 cm
formed can serve as scavengers for oxidizing species in the boundary layer. The injection mass flux \( \dot{m}_{inj} \) through each of the four injection ports is given by,

\[
\dot{m}_{inj} = \dot{m}_{div} + \dot{m}_{pyro}
\]  

(6.1)

Kuo et al. (2007) experimentally characterized the pyrolysis of SA/PVA grains in the temperature range of 543 - 1163 K, by employing a confined rapid thermolysis technique as well as a conduction-driven heat transfer. It was found that the SA/PVA grain, when subject to rapid heating, melts and/or evaporates without undergoing any decomposition. A linear regression rate of the grain was established as a function of heat flux. A companion study of the flow through the NBLCS injection port was conducted by Kuo and coworkers (2007; 2007b). Their calculations suggest that the ratio of \( \dot{m}_{div} \) to \( \dot{m}_{pyro} \) falls in the range of 0.2 - 0.3, after a steady-state motor operating condition is attained. In practice, however, the value of \( \dot{m}_{pyro} \) continues to increase with time, due to increasing surface area of the cylindrical SA/PVA grain during pyrolysis. Since the high heat flux from the diverted propellant combustion gases leads to rapid pyrolysis of SA/PVA, it is reasonable to assume an equilibrium composition at the NBLCS exit (Acharya and Kuo, 2007b; Evans et al., 2007a; Thakre and Yang, 2008c). The local temperature varies between 1000 and 1500 K (Gordon and McBride, 1994), depending on the value of \( \dot{m}_{div} / \dot{m}_{pyro} \).

In the current analysis, the value of \( \dot{m}_{div} / \dot{m}_{pyro} \) was taken to be constant at 0.3. Two different injection temperatures \( T_{inj} \) of 1200 and 1500 K were considered. The injection velocity \( u_{r-inj} \) was estimated to be in the range of 100 - 120 m/s, according to
mass conservation. It should be noted that the values of $\dot{m}_{\text{div}}/\dot{m}_{\text{pyro}}$, $T_{\text{inj}}$, and $u_{r-\text{inj}}$ used here are only representative values that are likely to exist at the injection location. The estimates are believed to be sufficiently accurate for the purpose of evaluating the ability of the NBLCS to reduce nozzle throat erosion. The actual values may be somewhat different and may vary marginally with time during the course of motor operation. The species mass fractions at the injection port were calculated through the chemical equilibrium analysis (Gordon and McBride, 1994). Table 6.3 lists the inlet conditions at the NBLCS injection port. The concentrations of the oxidizing species of H$_2$O and CO$_2$ are reduced significantly, as compared to their counterparts at the nozzle entrance. OH radical was not considered at the injection port, due to its negligible concentration.

Table 6.3: Flow Conditions at NBLCS Injection Port

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{H_2O}$</td>
<td>0.06</td>
</tr>
<tr>
<td>$Y_{CO_2}$</td>
<td>0.03</td>
</tr>
<tr>
<td>$Y_{CO}$</td>
<td>0.76</td>
</tr>
<tr>
<td>$Y_{H_2}$</td>
<td>0.05</td>
</tr>
<tr>
<td>$Y_{N_2}$</td>
<td>0.03</td>
</tr>
<tr>
<td>$Y_{HCL}$</td>
<td>0.07</td>
</tr>
<tr>
<td>$T_{\text{inj}}$</td>
<td>1500 K, 1200 K</td>
</tr>
<tr>
<td>$u_{r-\text{inj}}$</td>
<td>100 m/s</td>
</tr>
</tbody>
</table>
6.3 Results and Discussions

The theoretical/numerical framework described in the preceding sections was implemented to explore the effect of NBLCS on the chemical erosion of graphite nozzles in practical rocket-motor environments. Only the upper half of the nozzle is simulated due to flow symmetry. The axisymmetric computational domain in Fig. 6.3 is divided into 141 x 80 grid points in the $x$ and $r$ directions, respectively. The NBLCS injection temperature is 1200 K unless mentioned otherwise. The turbulent flow development in the same nozzle configuration was detailed earlier in Chapter 4. The gas-phase reactions were not considered in our previous studies because of their negligible effect on nozzle erosion (Thakre and Yang, 2008a). In the present case, chemical reactions among the AP/HTPB combustion products and the injected species may occur in the boundary layer. It is a reasonable assumption that such reactions will not have any significant impact on either the concentrations of H$_2$O, OH, and CO$_2$ or the rate of heat transfer to the nozzle wall.

Calculations were first conducted without including any heterogeneous surface reaction along the nozzle wall. The adiabatic wall condition was also enforced. The purpose was to examine the effect of NBLCS injection on the development of the flow and concentration fields, especially in the near-surface region. The results also provided a basis for clearly identifying the impact of surface reactions on the nozzle flow evolution. Figure 6.4a shows the distribution of the vertical velocity component in the nozzle interior. As expected, the vertical velocity is quite high at the injection location, reaching
a local maximum value of about 120 m/s. The velocity increases downstream of the throat, due to the flow expansion caused by the divergent geometry.

Figure 6.4b shows a tilted view of the vertical velocity distribution, highlighting the strategy of axisymmetric injection for mitigating erosion in a circumferentially uniform manner. Figure 6.5 presents a close-up view of the flowfield and associated streamlines near the injection port. The incoming flow from the combustion chamber is pushed slightly downwards. The influence of the NBLCS injection remains close to the nozzle surface and the core flow is not perturbed much. Consequently, the nozzle efficiency and overall vehicle thrust will almost be unaffected. Figure 6.6 shows the distributions of temperature and mass fractions of H₂O, CO₂, and OH. The injection of fuel-rich species gives rise to a concentration boundary layer above the nozzle surface. The effect is present even slightly upstream of the injection port because of species diffusion. Both the temperature and oxidizing species concentrations decrease substantially in the near-surface region.
Figure 6.4: Two different views showing distribution of vertical velocity in nozzle interior
($T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, no surface reactions, adiabatic wall)

Figure 6.5: Close-up view of streamlines near NBLCS injection port and nozzle throat
($T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, no surface reactions, adiabatic wall)
The effect of the NBLCS injection on the radial distributions of the oxidizing-species concentrations and temperature was studied. Figure 6.7 shows the result at the nozzle throat ($x = 2.65$ cm). The mass fraction of H$_2$O drops from 0.29 at the centerline to 0.114 at the surface. The corresponding values for CO$_2$ are 0.22 and 0.0074, respectively. The OH mass fraction at the throat is negligible. On the other hand, the mass fraction of H$_2$ at the throat increases from 0.003 at the centerline to 0.039 at the surface. Figure 6.8 shows the radial distributions of temperature at the throat for two different injection temperatures of 1200 K and 1500 K. The temperature drops from about 2600 K at the centerline to 1670 K at the surface for the former case and to 2150 K for the latter case. The temperature profiles do not decrease monotonically from the centerline. The rise near the surface results from the dissipation of the flow kinetic energy into its thermal energy. The reduction in the near-surface temperature and oxidizing species concentrations, as compared to their counterparts in the non-injection case, augurs well for minimizing the nozzle erosion.

Figure 6.6: Distributions of temperature and mass fractions of H$_2$O, CO$_2$, and OH in nozzle interior ($T_i = 3000$ K, $p_i = 6.9$ MPa, $T_{inj} = 1200$ K, no surface reactions, adiabatic wall)
To study the chemical erosion of graphite nozzle material, the three heterogeneous surface reactions summarized in Table 2.4 were implemented. The oxidizing species of CO$_2$, H$_2$O, and OH are consumed at the surface to form CO, H$_2$, and H. The temperature boundary condition at the nozzle surface is made conductive by considering the energy transport in the solid phase (Thakre and Yang, 2008a). Figure 6.9 shows the distributions of mass fractions of H$_2$O, CO$_2$, OH, and CO for the case with surface reactions and a conductive nozzle wall. Unlike the situation shown in Fig. 6.6 without surface reactions, the species concentration gradients exist from the nozzle entrance, due to the combined effect of surface reactions and the NBLCS injection. Figures 6.10 and 6.11 show, respectively, the radial distributions of mass fractions of H$_2$O and CO$_2$ at the nozzle throat. Both cases with and without the NBLCS are included.
As expected, the injection of boundary-layer control gases reduces the H$_2$O and CO$_2$ concentrations at the surface. The value of H$_2$O mass fraction at the surface (~0.107) is very close to that (~0.114) shown in Fig. 6.7, where surface reactions were turned off. A limited quantity of H$_2$O is consumed at the surface, which indicates that minimal chemical erosion takes place when the NBLCS is activated. A similar comparison of CO$_2$ mass fractions was made between Figs. 6.7 and 6.11. Almost no CO$_2$ is consumed in the NBLCS case. The rate of graphite consumption by CO$_2$ is rendered negligible because of the drop in the nozzle surface temperature.

Figure 6.8: Radial distributions of temperature at nozzle throat ($x = 2.65$ cm) with NBLCS injection ($T_i = 3000$ K, $p_i = 6.9$ MPa, no surface reactions, adiabatic wall)
Figure 6.9: Distributions of mass fractions of H$_2$O, CO$_2$, OH, and CO in nozzle interior $T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, surface reactions, conductive wall)

Figure 6.10: Radial distributions of H$_2$O at nozzle throat ($x = 2.65$ cm) with and without NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, $T_{inj} = 1200$ K, surface reactions, conductive wall)
Figure 6.12 shows the distributions of temperature in the nozzle interior under conditions with and without the NBLCS injection. The NBLCS proves very effective in lowering the nozzle surface temperature downstream of the injection port. Figure 6.13 shows the radial distributions of temperature at the throat for injection temperatures of 1200 and 1500 K. The surface temperatures reduce to 1640 K and 2015 K, respectively, as compared to 2285 K for the non-injection case. The value of 1640 K is slightly lower than its counterpart of 1670 K in Fig. 6.8, on account of the endothermicity of the surface reactions and wall heat transfer. The small difference in the surface temperature, however, indicates very nominal rates of surface reactions in the NBLCS case. Figure 6.14 shows the axial distribution of the surface temperature along the entire length of the nozzle. The surface temperatures are identical for all of the three cases upstream of

Figure 6.11: Radial distributions of CO$_2$ at nozzle throat ($x = 2.65$ cm) with and without NBLCS injection ($T_i = 3000$ K, $p_i = 6.9$ MPa, $T_{inj} = 1200$ K, surface reactions, conductive wall)
the injection port. The NBLCS injection results in a sharp decrease near the injection port and in its downstream region.

Figure 6.12: Distribution of temperature in nozzle interior (a) with and (b) without NBLCS ($T_i = 3000$ K, $p_i = 6.9$ MPa, $T_{inj} = 1200$ K, surface reactions, conductive wall)
Figure 6.13: Radial distributions temperature at nozzle throat with and without NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, surface reactions, conductive wall)

Figure 6.14: Axial distributions of nozzle surface temperature with and without NBLCS injection ($T_t = 3000$ K, $p_t = 6.9$ MPa, surface reactions, conductive wall)
Figure 6.15 shows the distribution of the graphite erosion rate along the entire length of the nozzle, for the cases with and without the NBLCS injection. The erosion rates at the nozzle inlet start at nearly the same level for all cases, but the rate drops significantly for the NBLCS cases in the region downstream of the injection port. The calculated erosion rate at the throat with NBLCS injection is much lower (0.027 mm/sec for $T_{inj} = 1500$ K and 0.0033 mm/sec for $T_{inj} = 1200$ K) than for the non-injection case (0.124 mm/sec). The erosion is found to be negligible when the injection temperature falls below 1200 K. Figure 6.16 shows a comparison of graphite erosion rates at the nozzle throat at various chamber pressures under conditions with and without NBLCS. Even at high pressures, the erosion rates are negligible with the NBLCS injection. Although the species concentrations employed at the NBLCS injection port were identical for the two injection cases, the erosion rate for $T_{inj} = 1200$ K was much lower than that for $T_{inj} = 1500$ K. The reduction in the erosion rate is thus attributed primarily to the low injection temperature and secondarily to the reduced concentrations of oxidizing species, H$_2$O, CO$_2$, and OH, in the near-surface region. Near-zero throat erosion was also observed experimentally by Evans et al. (2008) when NBLCS injection was activated.
Although the strategy of NBLCS injection shows potential to mitigate nozzle erosion, there may still be some outstanding issues with respect to its implementation on a practical rocket motor. The influence of NBLCS injection on the nozzle efficiency and overall vehicle specific impulse has to be studied in detail. The injection flow parameters must be known precisely to enable accurate predictions of the nozzle erosion rate. The high-velocity vertical injection may possibly interfere with the nozzle core flow. Further studies are needed to find an optimum injection angle to limit the impact of NBLCS to the near-surface region, so that the nozzle core flow is not perturbed much. It is also necessary to ensure that the injection port does not clog during the course of motor operation. This aspect is crucial in the case of metallized propellants, where the molten alumina can condense and cover the port, thus rendering the strategy of NBLCS ineffective. The possibility of flow reversal from the nozzle interior towards the injection

![Graphite nozzle erosion rate with and without NBLCS injection](image)

Figure 6.15: Graphite nozzle erosion rate with and without NBLCS injection ($T_i = 3000$ K, $p_i = 6.9$ MPa, surface reactions, conductive wall)
port must be completely eliminated. A detailed parametric numerical investigation with respect to the injection angle and port diameter can help determine optimal conditions so that throat erosion is mitigated with minimal perturbation of the primary nozzle flow.

![Graph showing effect of chamber pressure on graphite erosion rate at nozzle throat with and without NBLCS](image)

Figure 6.16: Effect of chamber pressure on graphite erosion rate at nozzle throat with and without NBLCS

6.4 Conclusions

A comprehensive theoretical/numerical analysis was performed to study the mitigation of graphite nozzle erosion in solid-propellant rocket motors by employing a nozzle boundary-layer control system (NBLCS). The strategy was based on the injection of relatively low-temperature species slightly upstream of the nozzle throat, which were obtained from chemical reactions between pyrolyzed ablative material (succinic acid/poly-vinyl acetate) and a small diverted portion of propellant combustion gases. The
thermofluid dynamics in the nozzle were investigated in detail. Special attention was given to the flow evolution, species transport, and chemical reactions near the nozzle surface.

A systematic study was performed to determine the dependence of nozzle erosion on the NBLCS operating parameters. The calculated erosion rates with NBLCS are negligible, even at ultra-high pressures. The mitigation of nozzle erosion is attributed primarily to the low temperature of the injected fluid, and secondarily to the reduced concentrations of oxidizing species, H$_2$O, CO$_2$, and OH, near the nozzle surface. The implementation of NBLCS shows the potential to substantially reduce the chemical erosion of a rocket nozzle throat over a wide range of pressures.
Chapter 7
Summary and Future Work

7.1 Summary and Conclusions

The objective of this thesis was to study the chemical erosion of rocket nozzle material and to investigate ways for minimizing the erosion. A comprehensive theoretical/numerical model was developed to accurately predict nozzle surface erosion rates at practical operating conditions in solid-propellant rocket motors. The formulation takes into account detailed thermofluid dynamics for a multi-component reacting flow, heterogeneous reactions at the nozzle surface, condensed-phase energy transport, and nozzle material properties. Both metallized and non-metallized AP/HTPB solid propellants were considered. Many restrictive assumptions and approximations made in previous models were relaxed. The model has the capability to predict the erosion rate along the entire axial length of the nozzle, as part of the complete flow solution. The nozzle materials considered were graphite, carbon-carbon, and such refractory metals as tungsten, molybdenum, and rhenium.

A two-layer turbulence model was implemented, as it performed well for transpiration and accelerating flows. The numerical scheme developed is a density-based finite-volume approach with low-dissipation and explicit marching in time. The chemical source terms in the gas phase were treated in a semi-implicit manner. The program has been parallelized using a domain-decomposition method, in conjunction with the
message-passing interface (MPI) library. The theoretical formulation and numerical scheme were first verified and validated with several model problems. Three cases, including turbulent flows over a flat plat, heat transfer in a convergent-divergent nozzle, and two-dimensional oblique shock waves, were examined to test various aspects of the numerical methods.

The chemical erosion of graphite/carbon-carbon nozzles was modeled by considering the oxidation of carbon to CO by H₂O, OH, and CO₂. The surface kinetics data were chosen after a careful literature survey. Good agreement was achieved with four different sets of measure erosion rates obtained from Geisler (1978), Borie et al. (1989), and Evans et al. (2007a; 2008). The key factors dictating the erosion process are motor operating conditions, concentrations of the oxidizing species in the core flow, heterogeneous chemical kinetics at the surface, and nozzle geometry and material properties. The erosion rate increases almost linearly with the chamber pressure. At high pressures, the elevated convective heat transfer and enhanced heterogeneous surface reactions both contribute to the severity of the material erosion. The core-flow temperature is instrumental in determining the nozzle surface temperature, which in turn dictates the rate of heterogeneous surface reactions.

The graphite erosion rate was found to be most severe in the throat area due to the maximum heat-transfer rate in that region. H₂O was the most detrimental oxidizing species in dictating the graphite/carbon-carbon nozzle erosion, followed by much lesser contributions from OH and CO₂, in that order. The inclusion of the water-gas shift reaction had a negligible effect on the calculated erosion rate. The limited influence of gas-phase reactions on the concentrations of dominant oxidizing species is attributed to
the high activation energy required for the water-gas shift reaction as well as the low flow residence time in the nozzle. The reactions occurring in the boundary layer do not affect the recession rates, since they do not impact the heat-transfer rate to the nozzle surface.

One of the important features of the model developed in this thesis research is its ability to predict the concentrations of oxidizing species at the nozzle surface. This makes it possible to determine with certainty, whether the erosion process is chemical kinetics or diffusion controlled. It was found that the graphite nozzle erosion rate is dictated by heterogeneous chemical kinetics for non-metallized propellants for which the surface temperatures are low (~2300 K), and by diffusion-controlled process for metallized propellants for which the surface temperatures (~2800 K) are high. The transition from the kinetics- to diffusion-controlled mechanism occurs at a surface temperature of around 2800 K. This transition temperature is highly dependent on the chemical kinetics employed and the species concentrations considered at the nozzle inlet, and should be considered specific to the current problem scenario. If the surface temperature at the nozzle throat is above 2800 K, then further increase in the propellant flame temperature does not affect the erosion rate. In such a scenario, the chamber pressure is the only crucial parameter affecting the nozzle erosion rate.

For non-metallized propellants, calculated erosion rates are sensitive to the chemical kinetics data employed for surface reactions. For metallized propellants, since the process is diffusion controlled, the errors in kinetics parameters show up as relatively small errors in the recession predictions. It should also be noted that the effect of nozzle geometry is more prominently seen on the erosion rates of metallized propellants. This is attributed to the fact that diffusion-limited processes will be impacted more by the nature
of the boundary layer flow as compared to the kinetics-limited processes. The chemical erosion rate decreases with increasing aluminum content, in spite of the associated increase in the flame temperature. The phenomenon can be attributed to the reduction in mass fractions of the oxidizing species H$_2$O and CO$_2$ with increasing aluminum content. The effect of radiation and surface roughness on the nozzle erosion rates has also been studied.

The theoretical/numerical model was extended to predict the chemical erosion of refractory metals including tungsten, molybdenum, and rhenium nozzle materials in rocket motors with non-metallized AP/HTPB solid propellants. The primary focus was on the tungsten nozzle. The predicted erosion rates matched reasonably well with three different sets of measurements. H$_2$O proved more detrimental than CO$_2$ in dictating the tungsten nozzle erosion, similar to the situation with graphite nozzles. The material recession rate was dictated by heterogeneous chemical kinetics and increased linearly with the chamber pressure. The erosion rate for tungsten was found to be much lower (about 2.6 times) than that for graphite, but comparable to that of rhenium. This implies that tungsten, which is approximately 10 times denser than graphite, actually exhibits a higher mass consumption rate. The lower erosion rate of tungsten is thus attributed to its higher density. This also confirmed that the erosion rate is inversely proportional to the density of the nozzle material. The least erosion was exhibited by molybdenum, whose implementation, however, is restricted to propellants with lower flame temperatures (less than 3000 K) due to its low melting point of 2896 K.

The dependence of the erosion rate on the outer boundary condition of the nozzle material was examined, since this condition affects the nozzle surface temperature and
associated chemical reaction rates. A slight decrease in the erosion rate was noted when
the adiabatic condition at the outer boundary was relaxed by allowing some heat transfer
to the surrounding. This further indicates that a nozzle material with a higher thermal
conductivity decreases the chemical erosion.

The analysis was further extended to study the mitigation of graphite nozzle
erosion in solid-propellant rocket motors by employing a nozzle boundary-layer control
system. The strategy was based on the injection of relatively low-temperature species
slightly upstream of the nozzle throat. The injection species were obtained from chemical
reactions between pyrolyzed ablative material (succinic acid/poly-vinyl acetate) and a
small diverted portion of propellant combustion gases. The thermofluid dynamics in the
nozzle were investigated in detail. Special attention was given to the flow evolution,
species transport, and chemical reactions near the nozzle surface.

A systematic study was performed to determine the dependence of nozzle erosion
on the NBLCS (nozzle boundary layer control system) operating parameters. The
calculated erosion rates with NBLCS are negligible, even at ultra-high pressures. The
mitigation of nozzle erosion is attributed primarily to the low temperature of the injected
fluid, and secondarily to the reduced concentrations of oxidizing species, H₂O, CO₂, and
OH, near the nozzle surface. Results also indicated that the NBLCS injection had a
limited influence on the bulk of the nozzle flow. The implementation of NBLCS shows
the potential to substantially reduce the chemical erosion of a rocket nozzle throat over a
wide range of pressures.
7.2 Future Work

The current study lays a solid foundation that can be extended for further detailed investigation of rocket nozzle erosion and its mitigation. In order to improve the model predictivity, more accurate surface kinetics mechanisms and data are needed for the specific nozzle material and oxidizing species under consideration at rocket-motor operating conditions. The currently employed kinetics data are obtained from the studies conducted in 1980s and earlier. More accurate reaction rates between the specific type of graphite/carbon-carbon and H$_2$O, CO$_2$, and OH will be helpful. Since H$_2$ and NO are present in non-negligible amounts (slightly lesser in quantity than OH) for metallized propellants, it may be important to include their contribution to the erosion rates. At present no data exists for the reaction of CO$_2$ with molybdenum and rhenium. The influence of these reactions could be important. In addition, more accurate chemical properties for heterogeneous reactions of refractory metals with oxidizing species (H$_2$O, CO$_2$, H$_2$, OH, and NO) are needed. The gas-phase kinetics of volatile tungsten oxides and steam also needs to be studied and incorporated into the current analysis to account for the fact that such a reduction in H$_2$O concentration may reduce the erosion rate.

Another major step would be to incorporate the effect of active-site coverage by species such as HCl, Cl, CO, N$_2$, and H$_2$. The surface site coverage will affect the rate of heterogeneous reactions. This is a formidable task, as it may require changing the treatment of surface reactions from global to elementary kinetics. The elementary mechanism will involve the rates of adsorption and desorption along with the formation of intermediate complexes. Such a detailed approach will necessitate the treatment of
more than double the current number of species, leading to a substantial increase in the required computational time and memory. A careful analysis should be conducted to know the tradeoff between the improvement in accuracy by treating elementary surface mechanisms and the required computational resources. The fact that reliable elementary surface mechanisms and associated kinetics rates are still not available makes this task even more challenging.

A significant increase in the measured nozzle throat erosion rate was observed when the surface temperature rose above 2600 K (Geisler, 1978). It was postulated that the phenomenon could be attributed to the phase transformation of graphite to a more reactive species called carbyne, which exists as a polyyne $[-C≡C−C≡C]$.

In the case of aluminized propellant, mechanical erosion caused by the impingement of metal-oxide particles could be significant. The deposition of Al$_2$O$_3$ may increase the heat transfer rate to the nozzle wall. The wetting of metal nozzle surface by Al$_2$O$_3$ droplets, on the other hand, may provide a liquid coating that can help resist further oxidation and erosion. A two-phase treatment is required for considering all these phenomena. For refractory metals, there is also a possibility of thermite reactions.
between unoxidized aluminum and metal oxides (e.g., \(2\text{Al} + \text{WO}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{W}\) or \(2\text{Al} + \text{MoO}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{Mo}\)). Such highly exothermic reactions may increase the temperature to a level sufficient to melt the metal nozzle surface. All these phenomena related to aluminized propellants are still relatively poorly understood and require further investigation.

The chemical erosion model can be extended for treating copper-infiltrated tungsten or graphite nozzles. The melting and boiling points of Cu are 1357 K and 2835 K, respectively. At high temperatures, such nozzles can provide cooling due to the vaporization of the infiltrant. The infiltrant also reduces thermal-shock sensitivity by increasing thermal conductivity. The phase transformation of Cu is likely to dominate over its oxidation. The following phase transformations and chemical reactions will have to be added to the current framework:

\[
\begin{align*}
2 \text{Cu}_\text{s} & \rightarrow \text{Cu}_\text{2(g)} \\
\text{Cu}_\text{s} & \rightarrow \text{Cu}_\text{l} \\
\text{Cu}_\text{s} + \text{H}_2\text{O} & \rightarrow \text{CuO}_\text{g} + \text{H}_2 \\
\text{Cu}_\text{s} + \text{CO}_2 & \rightarrow \text{CuO}_\text{g} + \text{CO}
\end{align*}
\]

The model for refractory metal nozzle erosion can also be extended for predicting the erosion/corrosion in common encountered situations where metal pipes carry corrosive gases or liquids.

There may still be some outstanding issues with respect to the implementation of NBLCS on a practical rocket motor. The influence of NBLCS injection on the nozzle efficiency and overall vehicle specific impulse has to be studied in detail. The high-velocity vertical injection may possibly interfere with the nozzle core flow. Further
studies are needed to find an optimum injection angle to limit the impact of NBLCS to the near-surface region. It is also necessary to ensure that the injection port does not clog during the course of motor operation. This aspect is crucial in the case of metallized propellants, where the molten alumina can condense and cover the port, thus rendering the strategy of NBLCS ineffective. The possibility of flow reversal from the nozzle interior towards the injection port must be completely eliminated. A detailed parametric numerical investigation with respect to the injection angle and port diameter can help determine optimal conditions so that throat erosion is mitigated with minimal perturbation of the primary nozzle flow.
Bibliography


Thakre, P. and Yang, V. (2008c) “Mitigation of Graphite Nozzle Erosion by Boundary Layer Control in Solid-Propellant Rocket Motors,” submitted to *Combustion and Flame*.


Appendix A

Treatment of Chemical Source Terms

A.1 Semi-Implicit Scheme

The vector form of the gas-phase conservation equations is expressed as

\[
\begin{align*}
\frac{\partial\mathbf{Q}}{\partial t} + \frac{\partial (\mathbf{E} - \mathbf{E}_v)}{\partial x} + \frac{\partial (\mathbf{F} - \mathbf{F}_v)}{\partial y} + \frac{\partial (\mathbf{G} - \mathbf{G}_v)}{\partial z} &= \mathbf{H} \\
\end{align*}
\]

(A.1)

where \( \mathbf{Q} = [\rho, \rho u, \rho v, \rho w, \rho E, \rho Y_1, \cdots, \rho Y_{N-1}]^T \) and \( \mathbf{H} = [0, 0, 0, 0, \dot{\omega}_i, \dot{\omega}_s, \cdots, \dot{\omega}_{N-1}]^T \).

The marching in time for chemical source terms in \( \mathbf{H} \) can be either explicit or semi-implicit. For stiff source terms, a semi-implicit treatment renders the numerical scheme more stable. Consequently, a semi-implicit treatment is used in the current formulation.

For this purpose, a jacobian matrix \( \mathbf{D}(\mathbf{Q}) \) needs to be computed and it is defined as

\[
\mathbf{D}(\mathbf{Q}) = \frac{\partial \mathbf{H}}{\partial \mathbf{Q}}
\]

(A.2)

The discretization of Eq. (A.1) yields

\[
\mathbf{Q}^{n+1} - \mathbf{Q}^n = \mathbf{R}^n + \mathbf{H}^{n+1} \cdot \Delta t
\]

(A.3)

where \( \mathbf{R}^n \) represents all the inviscid and viscous fluxes. The Eq. (A.3) can be rewritten as

\[
(\mathbf{I} - \mathbf{D}^n \cdot \Delta t)(\mathbf{Q}^{n+1} - \mathbf{Q}^n) = \mathbf{R}^n + \mathbf{H}^n \cdot \Delta t
\]

(A.4)

The above equation requires the calculation of the jacobian matrix \( \mathbf{D} \).
A.2 Jacobian Matrix for Chemical Source Terms

The approach to calculate the jacobian matrix for chemical source terms is elaborated here. In the present case, the number of species treated are \( N = 8 \) for non-metallized and and \( N = 9 \) for metallized propellants. Out of all the species considered, only \( \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{and} \text{H}_2 \) participate in the reversible water-gas shift reaction in the gas phase. Consider the forward water-gas shift reaction represented by

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \tag{A.5}
\]

According to the kinetics rate law, the rate of production of \( \text{CO}_2 \) (\( \dot{\omega}_{\text{CO}_2} \)) is given by

\[
\dot{\omega}_{\text{CO}_2} = W_{\text{CO}_2} A \left( \frac{\rho Y_{\text{CO}}}{W_{\text{CO}}} \right)^{0.5} \left( \frac{\rho Y_{\text{H}_2\text{O}}}{W_{\text{H}_2\text{O}}} \right)^{1} \exp \left( \frac{-E_a}{R \cdot T} \right) \tag{A.6}
\]

The other chemical source terms are obtained as follows.

\[
\dot{\omega}_{\text{H}_2} = \left( \frac{\dot{\omega}_{\text{CO}_2}}{W_{\text{CO}_2}} \right) W_{\text{H}_2} \\
\dot{\omega}_{\text{H}_2\text{O}} = - \left( \frac{\dot{\omega}_{\text{CO}_2}}{W_{\text{CO}_2}} \right) W_{\text{H}_2\text{O}} \tag{A.7}
\]

\[
\dot{\omega}_{\text{CO}} = - \left( \frac{\dot{\omega}_{\text{CO}_2}}{W_{\text{CO}_2}} \right) W_{\text{CO}}
\]

The jacobian matrix is represented by
A given derivative in the above matrix, with respect to any particular primary variable of \( Q \), is obtained by assuming all other primary variables as constants. For instance, 

\[
\frac{\partial \omega_{CO_2}}{\partial \rho} \] 

is obtained by assuming \( \rho u, \rho v, \rho w, \rho E, \rho Y_1, \cdots, \) and \( \rho Y_{N-1} \) as constants. The approach to derive the elements of the above matrix is shown below. Equation (A.6) can be rewritten as

\[
\log \omega_{CO_2} = \log(W_{CO_2} \cdot A) + \frac{1}{2} \log\left(\frac{\rho Y_{CO_2}}{W_{CO_2}}\right) + \log\left(\frac{\rho Y_{H_2,0}}{W_{H_2,0}}\right) - \left(\frac{E_A}{R_u T}\right) \tag{A.9}
\]

Then,

\[
\frac{\partial \log \omega_{CO_2}}{\partial \rho} = \frac{\partial}{\partial \rho} \left(\frac{-E_A}{R_u T}\right) \tag{A.10}
\]

since \( \rho u, \rho v, \rho w, \rho E, \rho Y_{CO_2}, \rho Y_{H_2}, \cdots, \) and \( \rho Y_{N-1} \) are constants.

Further simplification yields,

\[
\frac{\partial \omega_{CO_2}}{\partial \rho} = \omega_{CO_2} \left(\frac{E_A}{R_u T^2}\right) \frac{\partial T}{\partial \rho} \tag{A.11}
\]
Similarly, other derivatives can be written as

\[
\frac{\partial \omega_{CO_2}}{\partial (\rho u)} = \omega_{CO_2} \left( \frac{E_A}{R_n T^2} \right) \frac{\partial T}{\partial (\rho u)}
\]

\[
\frac{\partial \omega_{CO_2}}{\partial (\rho v)} = \omega_{CO_2} \left( \frac{E_A}{R_n T^2} \right) \frac{\partial T}{\partial (\rho v)}
\]

\[
\frac{\partial \omega_{CO_2}}{\partial (\rho w)} = \omega_{CO_2} \left( \frac{E_A}{R_n T^2} \right) \frac{\partial T}{\partial (\rho w)}
\]

\[
\frac{\partial \omega_{CO_2}}{\partial (\rho E)} = \omega_{CO_2} \left( \frac{E_A}{R_n T^2} \right) \frac{\partial T}{\partial (\rho E)}
\]

\[
\frac{\partial \omega_{CO_2}}{\partial (\rho Y_{CO_2})} = \omega_{CO_2} \left( \frac{E_A}{R_n T^2} \right) \frac{\partial T}{\partial (\rho Y_{CO_2})}
\]

\[
\frac{\partial \omega_{CO_2}}{\partial (\rho Y_{H_2})} = \omega_{CO_2} \left( \frac{E_A}{R_n T^2} \right) \frac{\partial T}{\partial (\rho Y_{H_2})}
\]

\[
\frac{\partial \omega_{CO_2}}{\partial (\rho Y_{H_2,O})} = \omega_{CO_2} \left[ \frac{1}{2} \frac{E_A}{\rho Y_{CO}} \right] \frac{\partial T}{\partial (\rho Y_{CO})}
\]

\[
\frac{\partial \omega_{CO_2}}{\partial (\rho Y_{H_2,O})} = \omega_{CO_2} \left[ \frac{1}{\rho Y_{H_2,O}} + \left( \frac{E_A}{R_n T^2} \right) \right] \frac{\partial T}{\partial (\rho Y_{H_2,O})}
\]

To obtain the derivatives on the RHS of Eq. (A.12), two basic thermodynamic relations are used. One of them is given by,

\[
E = \sum_{i=1}^{N} Y_i h_i - \frac{P}{\rho} + \left[ \frac{u^2 + v^2 + w^2}{2} \right]
\]

(A.13)

which can also be expressed as
\[
\rho E = \sum_{i=1}^{N-1} \rho Y_i \left[ (h_i - h_N) - (R_i - R_N)T \right] + \rho h_N - \rho R_N T + \frac{1}{\rho} \left[ \left( \rho u \right)^2 + \left( \rho v \right)^2 + \left( \rho w \right)^2 \right] \tag{A.14}
\]

The other thermodynamic relation comes from the definition of specific heat at constant volume given by,

\[
\frac{\partial T}{\partial (\rho E)} = \frac{1}{\rho \rho_{v,mix}} \left[ \frac{\partial (\rho E)}{\partial T} \right] = \frac{1}{\rho \rho_{v,mix}} \tag{A.15}
\]

The following derivatives, which appear on the RHS of Eq. (A.12), are obtained by using Eqs. (A.14) and (A.15)

\[
\frac{\partial T}{\partial \rho} = \frac{1}{\rho \rho_{v,mix}} \left[ \frac{u^2 + v^2 + w^2}{2} - (h_N - R_N T) \right]
\]

\[
\frac{\partial T}{\partial (\rho u)} = \frac{-u}{\rho \rho_{v,mix}}
\]

\[
\frac{\partial T}{\partial (\rho v)} = \frac{-v}{\rho \rho_{v,mix}}
\]

\[
\frac{\partial T}{\partial (\rho w)} = \frac{-w}{\rho \rho_{v,mix}}
\]

\[
\frac{\partial T}{\partial (\rho Y_i)} = -\frac{1}{\rho \rho_{v,mix}} \left[ h_i - h_N - (R_i - R_N)T \right]
\]

All the elements of jacobian matrix \( \mathbf{D} \) can thus be computed.
Appendix B

Thermodynamic Analysis of Surface Chemical Reactions for Refractory Metals

The spontaneity and favorability of a chemical reaction depend on the change in the Gibbs free energy associated with the reaction. The Gibbs free energy is defined as:

\[ G = H - TS \]  \hspace{1cm} (B.1)

The change in the Gibbs free energy at a constant temperature and pressure is given by

\[ \Delta G = \Delta H - T \Delta S \]  \hspace{1cm} (B.2)

A chemical reaction is spontaneous if \( \Delta G < 0 \). Eq. (B.2) indicates that even for endothermic reactions (\( \Delta H < 0 \)), a situation similar to the present surface reactions, the process can be spontaneous if \( \Delta G < 0 \), that is, if \( T \Delta S > \Delta H \). Clearly, high temperature favors the progress of an endothermic reaction. In addition, the more negative the value of \( \Delta G \) is, the more favorable the reaction becomes.

When chemical kinetics data for a given surface reaction are not available, the related change in the Gibbs free energy can help identify whether the reaction will take place. It can further assist in the characterization of final oxidation products when there is an uncertainty and/or difference of opinion associated with it. Table B.1 lists the Gibbs free energies for different surface reactions at 1 atm and 2800 K. The latter is typical of the nozzle surface temperature in a rocket-motor environment. Since the pressure dependence of surface reactions is not known to be significant, the analysis should be
reasonably valid at higher pressures. All the thermodynamic properties are from McBride et al. (2002). No calculation for the rhenium-oxidation reaction was performed due to the lack of thermodynamic data for rhenium oxides. In the case of tungsten oxidation, when different final products are considered the change in the Gibbs free energy is negative for WO$_3$(g) but positive for WO$_2$(g), indicating the spontaneity and prevalence of the former product. The change in the Gibbs free energy of Mo oxidation by CO$_2$ has a more negative value than its counterpart for W. The former reaction is thus spontaneous and likely to occur at 2800 K.

<table>
<thead>
<tr>
<th>reaction</th>
<th>T (K)</th>
<th>$\Delta H_R$ (kJ)</th>
<th>$\Delta S_R$ (J/K)</th>
<th>$\Delta G_R = \Delta H_R - T\Delta S_R$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W+3CO$_2$(g) → WO$_3$(g)+3CO(g)</td>
<td>2800</td>
<td>489.250</td>
<td>180.866</td>
<td>-17.174</td>
</tr>
<tr>
<td>W+2CO$_2$(g) → WO$_2$(g)+2CO(g)</td>
<td>2800</td>
<td>564.023</td>
<td>184.158</td>
<td>48.380</td>
</tr>
<tr>
<td>Mo+3CO$_2$ (g) → MoO$_3$(g)+3CO(g)</td>
<td>2800</td>
<td>435.629</td>
<td>174.674</td>
<td>-52.425</td>
</tr>
</tbody>
</table>

Table B.1: Changes in Gibbs free energies for different surface reactions
Appendix C

Effect of Radiation and Surface Roughness on Nozzle Erosion Rate

Radiation can play a role in determining the surface temperature of the nozzle and hence can affect the erosion rate. Figure C.1 shows the energy balance at the nozzle surface by including the heat-transfer due to radiation. The energy balance at the gas-solid interface with radiation is given by,

\[
\left[ \lambda_c \frac{\partial T_c}{\partial r} \right]_{r_i} + \dot{r}_c \rho_c h_{c-g} + q_{rad}' = \left[ \lambda_g \frac{\partial T_g}{\partial r} \right]_{r_i} + \sum_{k=1}^{N} \dot{\omega}_k h_{g,k} \quad (C.1)
\]

The equation is further simplified as

\[
\left[ \lambda_c \frac{\partial T_c}{\partial r} \right]_{r_i} + \dot{r}_c \rho_c h_{c-g} + (\alpha G - E) = \left[ \lambda_g \frac{\partial T_g}{\partial r} \right]_{r_i} + \sum_{k=1}^{N} \dot{\omega}_k h_{g,k} \quad (C.2)
\]

![Figure C.1: Schematic of energy balance at gas-solid interface with radiation](image)

The heat-transfer rate due to radiation is estimated by,

\[
q_{rad}' = (\alpha G - E) = \sigma \alpha_s (e_g T_g^4 - T_s^4) \quad (C.3)
\]
where the subscripts $s$ and $g$ stand for surface and gas, respectively. $T_g$ is the bulk gas temperature. $G$ is the incident radiation and $E$ the emitted radiation at the graphite surface. The value of $\sigma$, the Stefan-Boltzmann constant, is $5.67 \times 10^{-8}$ W/m$^2$-K$^4$.

Based on the mole fractions of species present, H$_2$O and CO$_2$ are assumed to be the dominant radiating species for non-metallized propellants. Similarly, Al$_2$O$_3$ and CO are the dominant radiating species for metallized propellants. Reflectivity or transmittivity from graphite surface is ignored and irradiation ($G$) is considered as diffuse (i.e. independent of angle). This may be reasonable for axisymmetric flows. To simplify calculations further, graphite is assumed to be a gray surface. This implies that coefficients of absorptivity and emmisivity have the same value ($\alpha_s = \varepsilon_s$). The coefficients for graphite emmisivity and absorptivity were taken as 0.8 (an average value obtained from several references). The emmisivity of gas ($\varepsilon_g$) was estimated as 0.4 for non-metallized propellants. This value was chosen to study the worst-case scenario and the actual value is most likely to be much less that 0.4. The formula used is: $\varepsilon_g = \varepsilon_a + \varepsilon_b - \varepsilon_a \varepsilon_b$ (for non-metallized propellants, $a$ and $b$ refer to H$_2$O and CO$_2$, respectively). The emmisivity of gas ($\varepsilon_g$) was calculated as 0.9 for metallized propellants (for metallized propellants, $a$ and $b$ are Al$_2$O$_3$ and CO, respectively). The emmisivities of the individual species at a given temperature and pressure were obtained from Modest (2003). Since alumina has high emmisivity, the value of $\varepsilon_g$ is higher for metallized case.

Figure C.2 shows the erosion-rate profiles for non-metallized propellant, with and without including the heat transfer due to radiation. At the throat, the difference in the erosion rates between the cases with (0.15 mm/s) and without (0.145 mm/s) radiation is small. A slightly higher value is obtained when radiation is taken into account. In the
upstream region, the bulk gas temperature is around 2800 K (higher than the surface temperature ~2300 K), and hence the effective radiation is towards the surface. Consequently, there is an increase in the erosion rate. In the downstream region, however, the bulk gas temperature is around 2000 K (lower than surface temperature), and hence the effective radiation is towards the gas. Consequently, the erosion rate decreases. Figure C.3 shows the erosion rate profiles for metallized propellant, with and without including radiation. The trend is similar to the one observed in the non-metallized case.

Figure C.2: Effect of radiation on erosion-rate profile (non-metallized propellant)
It is speculated that surface roughness can also play a role in determining nozzle surface erosion rates. Surface roughness may enhance the near-wall turbulence, leading to the increase in the diffusivity and thermal conductivity. The two-layer turbulence model was modified to include the effect of surface roughness. Following the approach of Patel and Yoon (1985), the modified equations for the inner layer are as follows:

\[
\begin{align*}
l_\mu &= C_\mu (r_n + \Delta r_n) \left[1 - \exp\left(-\frac{(Re_y + \Delta Re_y)}{A_\mu} \frac{25}{A^+}\right)\right] \\
l_\varepsilon &= C_\varepsilon (r_n + \Delta r_n) \left[1 - \exp\left(-\frac{Re_y + \Delta Re_y}{A_\varepsilon}\right)\right]
\end{align*}
\]

(C.4)

where
\[ \Delta r_n = 0.9 \frac{\mu}{\rho u_x} \left[ \sqrt{k_s^+ - k_s^+ \exp\left(\frac{-k_s^+}{6}\right)} \right] \]

\[ k_s^+ = R_h \frac{\rho u_x}{\mu} \]

\[ \Delta Re_y = \frac{\sqrt{k_s^+(\Delta r_n)}}{\nu} \]  \hspace{1cm} (C.5)

\( R_h \) represents the equivalent sand-grain surface roughness.

Figure C.4 shows the effect of roughness \((R_h = 10 \text{ µm})\) on the nozzle erosion rate for non-metallized propellant. As expected, the erosion rate at the throat increases slightly when surface roughness is taken into account. This is attributed to enhanced near-wall turbulence, leading to the increase in mass and thermal diffusivities.

Figure C.4: Effect of surface roughness on erosion-rate profile (non-metallized propellant)
VITA

Piyush Thakre

Piyush Thakre was born in Chandrapur, India in Oct. 1980. He graduated from the Indian Institute of Technology, Madras, in 2003 with a Bachelors and a Masters degree in Aerospace Engineering. He started his Ph.D. study in the department of Mechanical Engineering at the Pennsylvania State University from August 2003. His research focused on the theoretical/numerical study of nozzle erosion in solid-rocket motors and on the combustion modeling of solid-propellant ingredients.